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STUDIES IN THE ADSORPTION OF HYDROCARBONS IN SOIL BY GAS CHROMATOGRAPHY

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ABSTRACT

A "Zero Soil" (a reference soil which no extractable organic or inorganic compounds) was used for the study of adsorption of various hydrocarbons, i.e., n-alkanes (C₆-C₁₇), 1-alkenes (C₅-C₁₀) and aromatics (benzene and monosubstituted n-alkyl (C₁-C₁₀) benzenes). Four soil samples, i.e., "Zero Soil", Villanova University campus soil (Villanova, PA), Sugartown News Apartment soil (Devon, PA), and Bryn Mawr Railroad ground soil behind the Skeleton Oil Company (Bryn Mawr, PA), and a sludge sample were used in this study. All the filtrates and methylene chloride extracts from the soil were analyzed by the gas chromatographic technique with a 20% SE-30 on Chromosorb P AW-DMCS, 60-80 mesh column at the optimum conditions. A F&M Model 402 dual column dual flame ionization detectors was used throughout the investigation. Data was handled with a H-P Model 3380A Integrator. The percent recovery of n-alkanes (C₆-C₁₇), 1-alkenes (C₅-C₁₀) and aromatics (benzene, and monosubstituted n-alkyl (C₁-C₁₀) benzenes) ranged from 35% to 99%. The percent adsorption of n-alkanes (C₆-C₁₇) were in the range of 0-13%, 0-4% for the 1-alkenes (C₅-C₁₀) and 0.1-10% for the aromatics (benzene and monosubstituted n-alkyl (C₁-C₁₀) benzenes). Peak verification was performed using the IR spectrum of each collected component. The adsorption phenomena of these hydrocarbons on the soil samples and sludge sample have a general pattern:

- The adsorption increased as the molecular weight of the homologous hydrocarbon series increased.
- The hydrocarbon adsorbed on the soil was physical adsorption rather than chemical adsorption.
- The order of the adsorption among the three series of hydrocarbon on the soil was Aromatic 1-Alkene n-Alkane when compared to the same carbon atom number within a group.

INTRODUCTION

Gas chromatography (GC) has been used as a meaningful tool for soil adsorption studies. The SE-30 and the Dexsil-300 columns had been used for analysis of aliphatic hydrocarbons and polynuclear aromatic hydrocarbons after extracted from sediments and biota (1). Cotterill (2) determined dalapon (2,2-dichloropropionic acid) residues in soil via the dalapon ester McKone (3) was determined of same substituted urea herbicide residues in soil by GC with electron capture detection.

The possibility of utilizing gas chromatographic "fingerprints" of hydrocarbon samples from the sea and natural water to correlated them with suspected source oils or petroleum products (4-8) Blumer and co-workers (6,9,10) have followed the fate of smalloil spill by hydrocarbon analyses of sediments and organisms. High-efficiency packed columns have been shown to be suitable for the rapid identification of trace quantities of common petroleum products. Petroleum hydrocarbon contaminations in soil-have been reviewed by Ellis and Adams (12)

EXPERIMENTAL

Equipment

All gas-liquid chromatographic analyses were performed on a Hewlett Packard, F and M, High Efficiency Gas Chromatograph, Model 402, equipped with dual columns and dual flame ionization detector (FID). Collected the data by a H-P 3380A integrator.

Gas soil columns was laboratory made, 80 mm long and 28 mm in diameter, connected with 6 x 45 mm glass tubing were employed for all soil sample tests (FIGURE I).

Vials (17 x 60 mm) with screw caps and Teflon^(R) silicone septa were used for collection of filtrate of the standard hydrocarbon mixtures and methylene chloride extracts.

Chemicals

All the standard hydrocarbons, i.e., n-alkanes (C₆-C₁₇), 1-alkenes (C₅-C₁₀) and aromatic (benzene and n-alkyl (C₁-C₁₀) benzenes) were obtained from Poly Science Corp., Niles, Illinois.

The methylene chloride solvent used was UV-spectrophotometric grade supplied by J.T. Baker Chemical Co., Phillipsburg, New Jersey.

The SE-30 liquid phase and Chromosorb P-AW-DMCS (60/80 mesh) support was purchased from Supelco Inc., Bellefonte, Pennsylvania.

Procedure

The soil Column set-up. Ten soil columns were set-up and each soil column had a plug of glass wool at the bottom and filled with 10.0 grams of the the soil and sludge sample. The filled column was then covered with a piece of aluminium foil to prevent contamination from the laboratory atmosphere.

Study of the hydrocarbon Adsorption Phenomena on Soils. Ten milliliters of 800 ppm standard hydrocarbon mixtures, i.e., n-alkanes (C₆-C₁₇) mixture, 1-alkenes (C₅-C₁₀) mixture and benzene and n-alkyl (C₁-C₁₀) benzenes mixture was transferred to corresponding sets of soil columns. The filtrates were collected in 17 x 60 mm vials with screw cap and Teflon^R silicone septa. After the standard hydrocarbon mixture passed through the column, the soil column was then washed three times with 5.0 ml distilled water. These aqueous washings were collected in the same size of vial as before. The aqueous washings were extracted with equal volumes of methylene chloride and the methylene chloride layers were saved for subsequent gas chromatographic analysis.

The soil sample was then removed from the glass column and transferred to a 6 oz capped bottle and extracted with 10.0 ml of methylene chloride using a mechanical shaker for 6 hours. The methylene chloride extract was filtered off and saved for analysis.

A 6 ft x 0.25 in, O.D. glass column packed with 20% SE-30 on 60/80 mesh Chromosorb P-AW-DMCS was used for this study. The gas

chromatographic conditions were: helium carrier gas flowrate 65 ml/min and the ratio of H₂:He:Air was 1:2:7. Column oven was temperature programmed from 60° to 300°C at programmed rate of 7.5°C/min.

RESULTS AND DISCUSSION

The typical separation of the methylene chloride extracts from the soil after the standard hydrocarbon mixture and three volumes of wash water had passed through one representative soil are shown in FIGURE 2.

The percent of hydrocarbons, i.e., n-alkanes (C₆-C₁₇), 1-alkenes (C₅-C₁₀), benzene and n-alkyl (C₁-C₁₀) benzenes and n-alkyl (C₁-C₁₀) benzenes adsorbed by four different soils, i.e., "Zero" soil (reference soil), Villanova University Campus soil (Villanova, Pennsylvania), Sugartown News Apartment soil (Devon, Pennsylvania), BrynMawr railroad ground soil (BrynMawr, Pennsylvania), and a sludge sample are calculated by the following equation:

$$\% \text{ Hydrocarbon Adsorbed by Soil} = (A_{SE}/A_S) \times 100 \quad (1)$$

where A_{SE} = Peak areas of methylene chloride extracts from soil after passage of standard mixture and three volumes of wash water.
 A_S = Peak area of the standard hydrocarbon solution.

FIGURE 3 shown one representative methylene chloride extract from soil after passage standard mixture and three water washings.

The percent adsorption of n-alkanes, 1-alkenes, benzene and n-alkyl benzenes are shown in TABLE I, II, and III. FIGURES 4, 5, and 6 were the adsorption curves that obtained by plotting the percent adsorption of various hydrocarbons on soil versus the number of carbon atoms in the series.

The adsorption of these series of hydrocarbons increased as the carbon atom number increased and the order of hydrocarbons adsorbed on the soil were in the order of aromatic 1-alkenes n-alkanes (when compared to the same number of carbon atoms).

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TABLE 1 THE ADSORPTION PERCENTAGE OF N-ALKANE (C_6-C_{17}) SOIL AND SLUDGE SAMPLES

Compound	% Adsorption*			
	Soil Sample I (a)	Soil Sample II (b)	Soil Sample III (c)	Sludge Sample
n-Hexane	0	0	0	0
n-Heptane	0	0	2.03±0.10	2.20±0.10
n-Octane	0.27±0.00	0.26±0.00	0.57±0.00	1.02±0.00
n-Nonane	0.53±0.00	0.51±0.00	1.10±0.10	1.92±0.10
n-Decane	0.57±0.00	0.78±0.10	1.44±0.10	1.77±0.10
n-Undecane	0.86±0.00	1.58±0.10	1.66±0.10	1.41±0.10
n-Dodecane	1.88±0.10	2.28±0.10	1.97±0.10	2.39±0.10
n-Tridecane	3.17±0.10	3.48±0.10	2.56±0.10	2.69±0.10
n-Tetradecane	5.92±0.10	5.98±0.10	2.22±0.10	2.64±0.10
n-Pentadecane	8.72±0.20	7.62±0.10	2.77±0.10	3.31±0.10
n-Hexadecane	9.94±0.20	10.71±0.20	2.51±0.10	3.26±0.10
n-Heptadecane	12.04±0.20	12.15±0.20	2.46±0.10	3.44±0.10

* % Adsorption obtained from Equation (J) :

Triplicate injections on to gas chromatographic column for each of the six soil columns, i.e., eighteen measurements total.

(a) Villanova University Campus Soil

(b) Sugartown Mews Apartment Soil

(c) Bryn Mawr Railroad Soil

TABLE 2 THE ADSORPTION PERCENTAGE OF 1-ALKENE (C_5-C_{10}) ON SOIL AND SLUDGE SAMPLES

Compound	% Adsorption*			
	Soil Sample I (a)	Soil Sample II (b)	Soil Sample III (c)	Sludge Sample
1-Pentene	0.16±0.00	0	0	0
1-Hexene	0.67±0.00	0.70±0.00	1.38±0.00	0
1-Heptene	1.12±0.00	1.33±0.00	2.46±0.05	0.17±0.00
1-Octene	1.11±0.00	1.96±0.05	2.81±0.05	0.21±0.00
1-Nonene	1.95±0.00	2.03±0.05	3.46±0.05	0.25±0.05
1-Decene	2.19±0.05	2.58±0.05	3.84±0.05	0.29±0.05

* % Adsorption obtained from Equation (J'); Triplicate injections on to gas chromatographic column for each of the six soil columns, i.e., eighteen measurements total.

(a) Villanova University Soil

(b) Sugartown Mews Apartment Soil

(c) Bryn Mawr Railroad Grounds Soil

TABLE 3 THE ADSORPTION PERCENTAGE OF BENZENE AND N-ALKYL (C_1-C_{10}) BENZENES ON SOIL AND SLUDGE SAMPLES

Compound	% Adsorption*			
	Soil Sample I (a)	Soil Sample II (b)	Soil Sample III (c)	Sludge Sample
Benzene	0.83±0.00	1.41±0.00	1.30±0.00	0.16±0.00
Toluene	0.82±0.00	1.40±0.00	2.80±0.00	0.17±0.00
Ethylbenzene	1.45±0.00	1.42±0.00	4.45±0.00	0.17±0.00
Propylbenzene	2.03±0.05	1.97±0.05	5.58±0.05	0.16±0.00
Butylbenzene	2.42±0.05	2.80±0.05	5.56±0.05	0.16±0.00
Amylbenzene	4.55±0.10	5.67±0.10	7.59±0.10	0.18±0.00
Hexylbenzene	6.00±0.10	8.26±0.15	7.64±0.10	0.20±0.00
Heptylbenzene	7.00±0.15	8.26±0.15	8.63±0.15	0.32±0.00
Octylbenzene	8.16±0.15	8.87±0.15	8.27±0.15	0.39±0.00
Nonylbenzene	9.62±0.15	10.17±0.15	9.37±0.15	0.42±0.00
Decylbenzene	9.92±0.15	10.69±0.15	8.63±0.15	0.62±0.05

* % Adsorption obtained from Equation (I); Triplicate injections on to gas chromatographic column for each of the six soil columns, i.e., eighteen measurements total.

(a) Villanova University Campus Soil

(b) Sugartown Mews Apartment Soil

(c) Bryn Mawr Railroad Grounds Soil

FIGURE 1 GLASS SOIL SAMPLE COLUMN

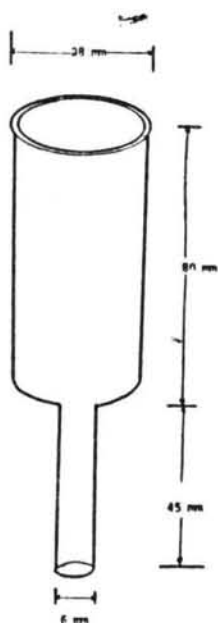
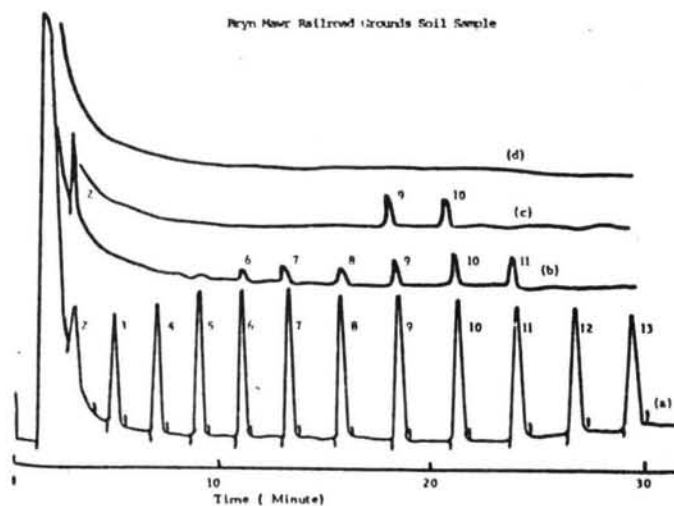


FIGURE 2 CHROMATOGRAM OF STANDARD N-ALKANE MIXTURE PASSED THROUGH SOIL COLUMN AND METHYLENE CHLORIDE EXTRACTS OF 1st, 2nd, 3rd WATER WASHINGS

- (a) Standard n-Alkane Mixture Passed Through Soil Column
 (b) Methylene Chloride Extract of 1st Water Washing
 (c) Methylene Chloride Extract of 2nd Water Washing
 (d) Methylene Chloride Extract of 3rd Water Washing



- | | |
|---------------------------------|-------------------|
| 1. Methylene Chloride (Solvent) | 7. n-Undecane |
| 2. n-Hexane | 8. n-Dodecane |
| 3. n-Heptane | 9. n-Tridecane |
| 4. n-Octane | 10. n-Tetradecane |
| 5. n-Nonane | 11. n-Pentadecane |
| 6. n-Decane | 12. n-Hexadecane |
| | 13. n-Heptadecane |

FIGURE 3 CHROMATOGRAM OF METHYLENE CHLORIDE EXTRACT FROM BRYN MAWR RAILROAD SOIL AFTER PASSAGE N-ALKANE STANDARD MIXTURE AND THREE WATER WASHINGS.

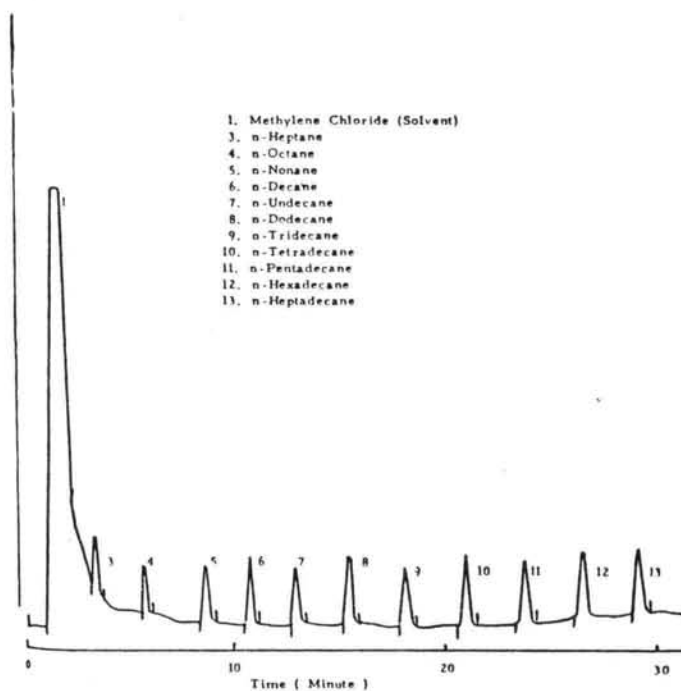


FIGURE 4 ADSORPTION CURVE OF N-ALKANE(C₆-C₁₇) SERIES ON SOIL AND SLUDGE SAMPLES.

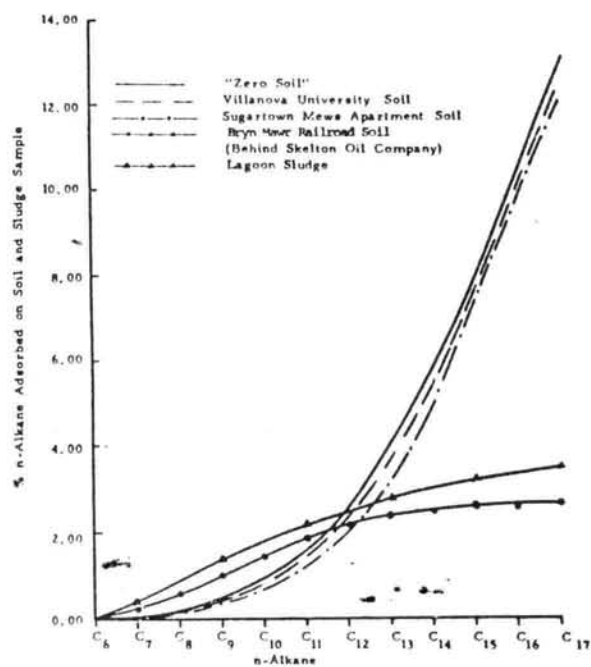


FIGURE 5 ADSORPTION CURVE OF 1-ALKENE (C_5-C_{10}) SERIES ON SOIL AND SLUDGE SAMPLES.

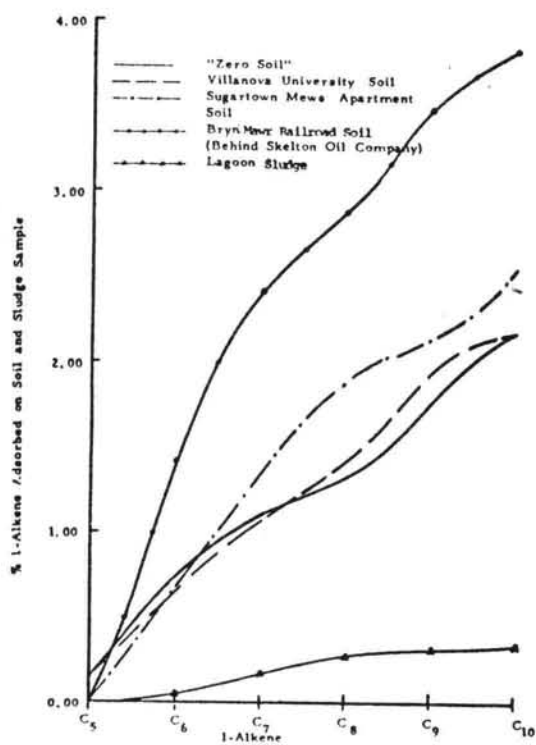
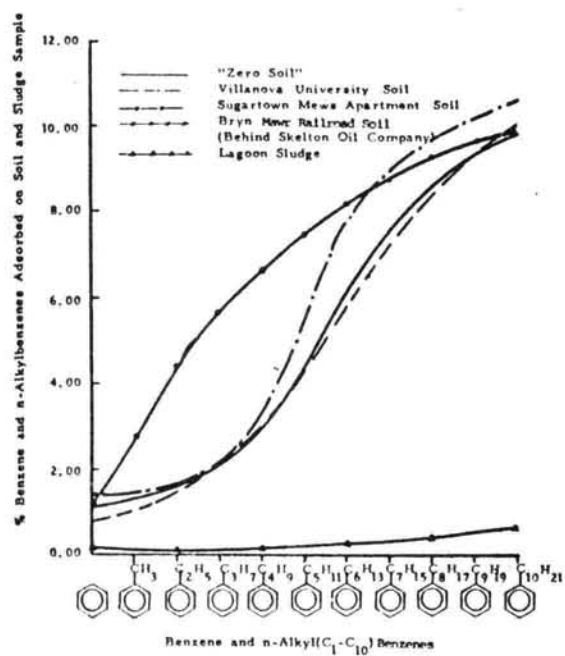


FIGURE 6 ADSORPTION CURVE OF BENZENE AND N-ALKYL (C_1-C_{10}) BENZENES ON SOIL AND SLUDGE SAMPLES.



ASBESTOS, ALPHA QUARTZ & OTHER WORKPLACE ENVIRONMENTAL CONTAMINANTS
IN NORTHERN AUSTRALIA

HOW USEFUL IS X-RAY DIFFRACTION AS AN ANALYTICAL TOOL??

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A Rigaku Geigerflex X-Ray Diffractometer was commissioned in Darwin in 1981 for Occupational Hygiene monitoring, principally for the analysis of alpha quartz in respirable dusts. Sample transportation problems from remote sites and analytical interferences from associated minerals have been overcome. Results have supported installation of dust suppression measures in quarries and mines and have shown the need for frequent routine monitoring. X-Ray diffraction is a fast and effective method for identifying asbestos in building and insulation materials. Most samples require grinding as the only pretreatment but for others interfering substances must be removed or converted to non-interfering crystal forms. Limited use for X-Ray diffraction has been found in monitoring other contaminants.

INTRODUCTION

The Northern Territory is the last major area of Australia still in the early stages of development. Formerly under the direct control of the Australian Federal Government in Canberra, it was granted self-government (with most of the powers and responsibilities of state government) in 1978. The newly formed government in its quest for development through mining realised that priority had to be given to protection of employees in their workplace environment. Accordingly an Occupational Hygiene Branch was established within the Department of Mines and Energy early in 1981.

The mining and quarrying industries are the largest employment group in the Northern Territory. The major health hazard, common to most branches of these industries, is dust, particularly dust containing significant amounts of free silica.

There are 6 major mines and 8 permanent quarries in the Northern Territory where the workforce is monitored for exposure to respirable free silica on a regular basis. Smaller mines and mobile quarries are also monitored intermittently. The National Health and Medical Research Council (NHMRC) threshold limiting value (TLV) for an 8 hour shift is currently 200 μg and will soon be reduced to 100 μg . Analysis of samples requires a method of detection limit well below this and even lower for shorter term sampling. The method must be mineral specific, distinguish between crystalline and amorphous phases and be either free of interference or able to overcome interference. Because of the large number of samples involved, it is highly desirable that the method require minimum sample pretreatment. In nearly every case, X-Ray diffraction satisfies all of these requirements.

The isomers of free silica are cristabolite, fused silica, alpha and other quartz and tridymite. By far the most common and to date the only isomer found in samples taken in the NT is alpha quartz.

An X-Ray diffractometer was commissioned towards the end of 1981 as the analytical support for extensive programs to monitor worker exposure to alpha quartz.

Asbestos has been recognised for some years as being extremely toxic and its usage is restricted in modern materials. In the past, however, asbestos was a common constituent of construction and insulating materials. Age is now causing deterioration of these materials and they become potentially hazardous to those working with or near them. Recent television programs and other media publicity on the dangers of inhalation of asbestos fibres have created an acute awareness amongst the populace of the Northern Territory. One program, in particular, showed the results of inhalation starkly and dramatically and had such impact that any material suspected of containing asbestos is now quickly brought to the attention of employers and/or government authorities. Trade unions have been quick to register concern for the well being of their members. Fast identification is required to protect health if asbestos is present and to minimise work hold-ups if the material is asbestos free. X-Ray diffraction offers a rapid means of identifying the presence and type of asbestos mineral (1). X-Ray diffraction is now routinely used as a fast, reliable means of determining whether or not asbestos is present and to characterise its mineral form.

Copper, bismuth, aluminium, manganese, uranium and lead bearing minerals are produced by major mines of the Northern Territory. X-Ray diffraction may be used to assist evaluation of the degree to which these minerals and those crystalline materials used in their treatment endanger the workforce.

INSTRUMENTATION

All measurements are carried out on a Rigaku model "Geigerflex" microprocessor controlled semi-automated X-Ray powder diffractometer with 3 KW X-Ray generator, wide range vertical goniometer, diffracted beam curved crystal monochromator with graphite crystal, forty-three place automatic sample changer and sample spinner. X-Ray source is a 2.7 KW Cu broad focus X-Ray tube and detection is by scintillation counter.

The instrument configuration allows 20 combinations of 20 different parameter programs for 43 samples. However, all scan annotation and interpretation and count data manipulation must be done manually.

In over two years operation, the only serious fault has been a gradual deterioration of the scintillation crystal due to moisture absorption. The original crystal has now been replaced.

RESPIRABLE FREE SILICA

A number of X-Ray diffraction methods have been proposed for the analysis of alpha quartz in respirable dust (eg 2-7). The method of Altree - Williams et al (7) where the sample is analysed on a collection medium which provides reasonable adhesion during transportation has the advantage of virtually no sample pretreatment. The filter on which the sample is collected is laid over a silver membrane filter. The attenuation of a diffracted Ag line by the deposited sample is used as a measurement of the sample mass absorption coefficient. The weight of alpha quartz on the filter is then calculated from the equation

$$M_Q = \frac{I_{iQ} \sin \theta_{Ag} \ln \frac{I^{\circ}Ag}{I_{Ag}}}{K_{iQ} [1 - \exp \{- \ln \frac{I^{\circ}Ag}{I_{Ag}} \sin \theta_{Ag} \operatorname{cosec} \theta_{iQ}\}]}$$

where K_{iQ} is a constant dependent on analysis conditions, area of sample deposition and the quartz diffraction line used

I_{iQ} = intensity of quartz diffraction line i

θ_{Ag} = angle of incidence of the X-Ray beam to the filter at the Ag diffraction line

$I^{\circ}Ag$ = intensity of diffracted Ag line with a blank sample filter overlay

I_{Ag} = intensity of diffracted Ag line attenuated by the sample

θ_{iQ} = angle of incidence of the X-Ray beam to the filter for quartz diffraction line i

K_{iQ} is determined from standards of pure quartz on filters

Sample Collection and Transportation

Dust monitoring programs are carried out both by Government Authorities and by the larger mining companies. The ultimate objective is to have all active mine and quarry operators responsible for their own routine sampling with the Government running periodic parallel check programs. All analyses, however, are carried out at the Occupational Hygiene Branch Laboratory in Darwin. At present this service is free of charge. Fortunately, because nearly all of this monitoring has been initiated since the establishment of the Laboratory, sampling techniques and apparatus have a high degree of uniformity throughout the Northern Territory.

Collection Filters. To utilise the above method to fullest advantage, the collection medium must:

- (1) have low and uniform mass absorption;
- (2) give low diffraction background in the region of the analyte lines; and
- (3) retain the sample intact during transportation.

Separate calibration is required for each type of filter used for collection. Several filter types were tested and calibrations established for 0.8 μ nuclepore polycarbonate and 0.8 μ millipore mixed cellulose acetate and nitrate filters. Nuclepore filters offer significant advantages for criteria (1) and (2) above and are now used exclusively. The sample chamber of the X-Ray diffractometer requires that 25 mm diameter filters be used.

Although sample weight is not needed for the diffraction calculation of alpha quartz, it is often desirable to monitor total respirable dust exposure. The filters are therefore pre-weighed and re-weighed with their sample load using a Mettler M3 microbalance with a Cahn Instruments model 1269 electrostatic charge dispeller in the weighing chamber.

Sampling Apparatus. A number of suitable sampling pumps are commercially available. The most commonly used in the NT are the American Mine Safety Appliance Co. model G with pulsation dampener (MSA part no. 456058). These are now being superseded by an MSA electronic pump offering much improved load-flow compensation. A 10 position battery charger rack with its full complement of pumps is taken on extended field trips by Government staff. Pumps are calibrated pre and post sampling by the soap bubble technique using an inverted one litre burette (Haluglass, Melbourne). Flow rates are maintained in the range 1.90 to 2.10 litres per minute.

All filter cyclone heads for respirable dust sampling show preferred deposition areas on the filter and the position of these preferred areas varies with cyclone type. It is therefore necessary to prepare calibration standards with the same cyclone model used for sampling and desirable that the one cyclone type be used in all monitoring. This uniformity has been achieved in the Northern Territory, the model chosen being the Casella T13026/2 (Casella London Ltd). These cyclones tend to concentrate sample at the centre of the filter.

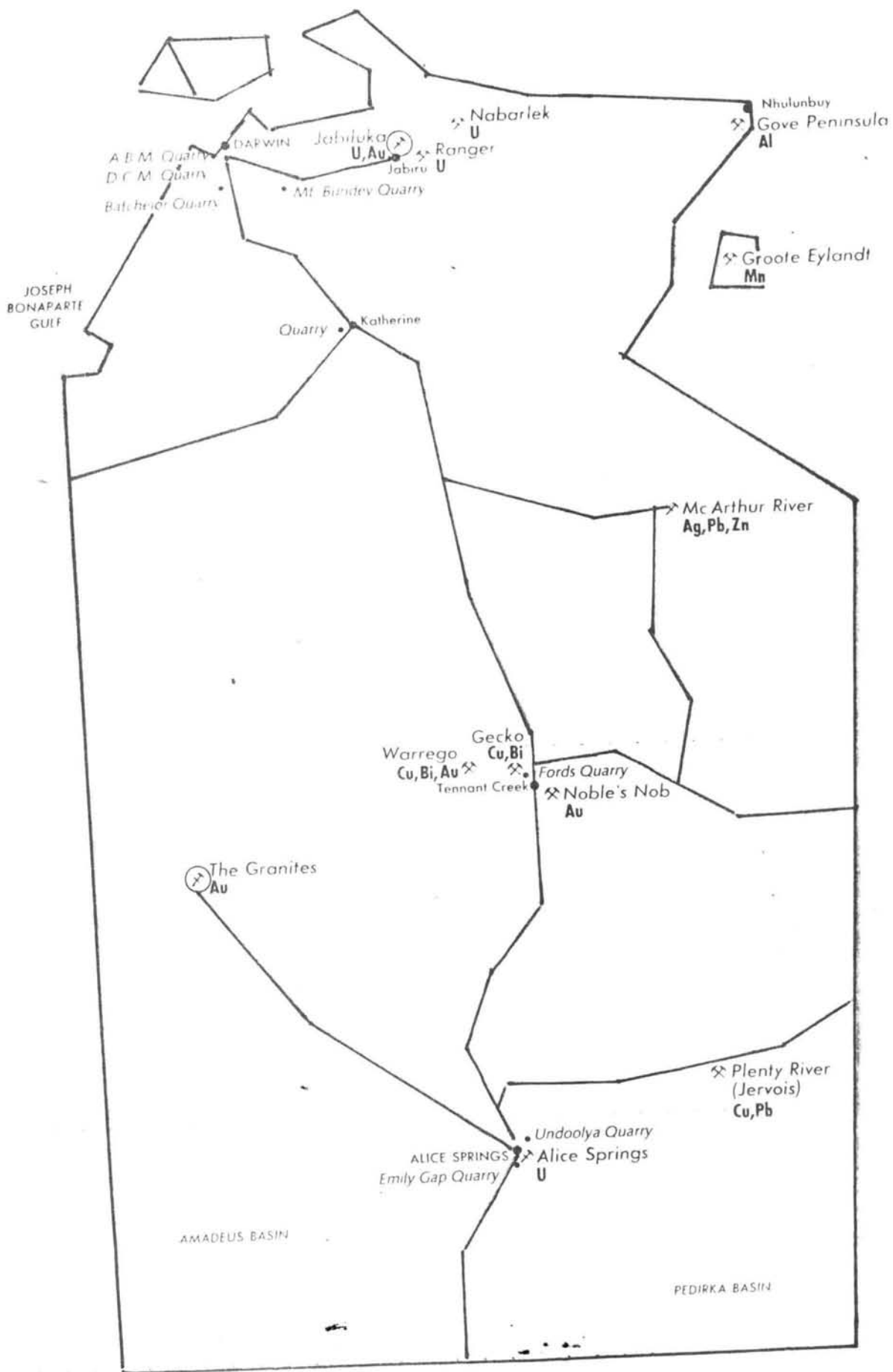
The success of any personal sampling program is wholly dependent on the co-operation of the person being sampled. This co-operation is partly achieved by communication but a major consideration is comfort. Working conditions in Northern Australia, as in many Asian countries, are harsh climatically. For the greater part of the year, the far north is hot and humid and further south, towards the centre of the continent, extremely hot and dry. Workmen wear the minimum acceptable light clothing and resent added incumbrance and any impediment to the ease of carrying out their duties. To reduce these difficulties, Sam Brown belts were purchased from an army surplus disposal store and converted to carry sampling equipment. The cyclone is attached to the shoulder sash near the breathing zone and the pump suspended from the waist band at a position suited to the duties of the wearer.

Transportation. The Northern Territory is sparsely populated - 130 000 people over 1.25 million square kilometers - and the population centres and mine and quarry sites are widespread (see Figure 1). Samples may have to be transported up to 400 km by dirt road and up to 1 500 km by air. Retention of samples on membrane filters during such transportation is a major problem. The following procedure has proved successful:

All samples are retained in the aluminium cassettes in which they are placed into the cyclone head. After sampling, the cassettes are placed in re-usable transit boxes (Casella T 13810) clearly marked to indicate the position which maintains filters with sample side uppermost. Each box holds six samples. The samples are then held on-site until they can be brought to Darwin by personal carriage. Because Department of Mines and Energy staff regularly visit all mine and quarry sites this does not result in unacceptably long delays. By ensuring that the samples are only handled by personnel who understand their delicacy, it is rare that samples are damaged to the extent that they require re-filtration or have to be discarded.

Before the establishment of X-Ray diffraction facilities in Darwin, samples had to be transported to interstate capital cities for analysis. Personal carriage to these centres was impractical.

FIGURE 1. MAP OF THE NORTHERN TERRITORY SHOWING MAJOR CENTRES AND MINE AND QUARRY SITES



Diffractometry

No suitable specimen holders for filters were available for the Rigaku X-Ray diffractometer with multi sample changer at the time of establishment of the analytical method. Aluminium holders were designed and machined in Darwin, but these were found to have an electrolytic reaction with the silver filters. Finally, inert plastic holders were manufactured by Analytron, Sydney. Samples are held in place with a circular brass clip.

All measurements are carried out using a 2.7 kW broad focus copper anode tube at 50 kV, 40 mA with pulse height selection and sample spinning.

Divergence slits of 1° ($<40^\circ 2\theta$) and 2° ($>40^\circ 2\theta$) and receiving slit of 0.3 mm are used. Each sample is scanned over Ag (111), Ag (200), alpha quartz (112), alpha Quartz (101) and alpha quartz (100) diffraction lines, the line peak being centred in a scan of $1^\circ 2\theta$. Step scanning with 10 second counts at $0.05^\circ 2\theta$ intervals is used. Background is measured at the start and finishing points of the scan and net peak area counts print out automatically. A corundum standard monitors instrument drift.

Calibration Standards

Selection of a suitable calibration standard is no less important than for any other analytical procedure. It is, however, more difficult than usual because, as well as the possibility of contamination from impurities, alpha quartz develops a surface amorphous phase. Naturally occurring quartz varies in the degree of this amorphous character (8) which also increases with increased grind time.

A large, high purity, single quartz crystal from Mt Isa, Queensland was selected as suitable standard material. A 20 g aliquot of this was ground for 30 seconds in a Rocklabs ring grinder.

Standard filters are prepared with the same type of sampling apparatus used in the field. The cyclone head is suspended in a dust chamber and samples a dust cloud generated from the standard alpha quartz at a flow rate of approximately 2 litres per minute. In this way particle size distribution, preferred orientation effects and filter impact velocity are similar to those in monitoring samples.

K_{10} values calculated from standards prepared from this material compare favourably with those from standard alpha quartz from the United Kingdom which other Australian laboratories confirm as $93 \pm 2\%$ crystalline alpha quartz (table 1). Results are the mean of four samples prepared from each standard material.

TABLE 1. COMPARISON OF K_{iQ} VALUES FROM ALPHA QUARTZ USED AS A STANDARD IN THE NT NORTHERN TERRITORY WITH THOSE FROM A $93 \pm 2\%$ CRYSTALLINE ALPHA QUARTZ STANDARD

Quartz Line (hkl)	Ag Line (hkl)	K_{iQ} NT Standard (net counts μg^{-1})	K_{iQ} $93 \pm 1\%$ Standard (net counts μg^{-1})
112	200	9.2 ($\pm 3.2\%$)	8.4 ($\pm 2.0\%$)
112	111	9.2 ($\pm 3.3\%$)	8.4 ($\pm 2.3\%$)
101	200	46.0 ($\pm 2.6\%$)	42.3 ($\pm 3.1\%$)
101	111	45.2 ($\pm 2.0\%$)	42.1 ($\pm 2.9\%$)
100	200	7.0 ($\pm 2.2\%$)	6.2 ($\pm 2.8\%$)
100	111	7.1 ($\pm 1.6\%$)	6.5 ($\pm 3.5\%$)

Interferences

If other minerals in the sample have diffraction lines overlapping the analyte line, the apparent result is enhanced. If overlap occurs at the angle of background measurement, the apparent result is reduced. Interference may also occur in the region of the Ag diffracted lines. For lightly loaded filters this is not likely to be of significance because of the high relative intensity of the diffracted silver line.

When the mineralogy of the sample site is not known, the filter sample is scanned at $1^\circ 20$ per minute and all phases identified. A bulk dust sample is taken from the site and also scanned to assist in identifying phases where diffraction from the sample is of low intensity. Concentration of minerals in the bulk sample is rarely the same as on the filter mainly due to variations in particle size distribution from the crushing process and density separation during air transportation. Interference free quartz and Ag measurements are then selected.

For follow up sampling in areas where knowledge of mineralogy indicates interference to be unlikely, alpha quartz (112), (101) and (100) and Ag (111) and (200) lines are all measured. Using combinations of these measurements, six values of quartz loading are obtained and comparison indicates whether or not interference has occurred. The laboratory instrumentation allows automation of counting and calculation but not scan identification and in this way chemist manhours are conserved.

Rock types mined or quarried in the Northern Territory range from near pure quartz at Emily Gap (near Alice Springs) and Tennant Creek quarries to very low quartz bearing bauxite at Gove, manganese oxides at Groote Eylandt and chloritic and micaceous schists at Ranger Uranium mine. Significant interference is encountered in samples from five of the fourteen sites regularly monitored.

Katherine Quarry. Rock is mainly dolomite with minor calcite, mica, microcline and quartz. The dolomite (018) line overlaps Quartz (112) and this line is therefore not used. Microcline (100) overlaps the normal high angle background measuring position for quartz (101). Baseline is steady at these angles and a useful compromise is to background correct from the low angle measurement only. Similarly, low angle background measurement is used for Ag (200) where dolomite (202) interferes at the high angle background position. Quartz (100) and Ag (111) are free of interference.

Undoolya Quarry, Alice Springs. Quartz and plagioclase are the major components here with minor hornblende and orthoclase. Quartz (112) is unreliable due to plagioclase interference. Careful selection of background count position is necessary if the Quartz (101) line is to be used. Both silver lines and the quartz (100) line are free of interference.

North Quarry, Alice Springs. The rock is dolerite, mainly hornblende with minor oligoclase and trace quartz. Hastingsite (041), (150) and (240) lines interfere with normal background measurement of the quartz (101) line. Careful selection of count position can overcome this. Quartz (100) and (112) lines are of low intensity and have hornblende line overlap.

Mount Bundy Quarry. Rock is feldspathic with minor quartz. Quartz (100) and (101) lines are overlapped by feldspar lines. Quartz (112) is free of interference. Feldspar lines interfere with positions of normal background measurement for Ag (111). Quartz (112) and Ag (200) are used for calculations. Although total respirable dust loadings are often high, quartz concentration is low.

Batchelor Quarry. Quartz is the major component with minor mica, feldspar and clays. Minor enhancement to Q (101) from mica is experienced. All other quartz and Ag lines are free of significant interference.

Although care is necessary in selection of analyte lines and background measurement positions, this X-Ray diffraction method has been applicable to all samples received to date.

Results

Tables 2 and 3 show the range of exposure to workers in the major quarries and three mines where levels approach or exceed the Australian National Health and Medical Research Council limit of 200 μg alpha quartz per cubic metre of air for an eight hour shift (9). The crystalline alpha quartz concentration range for dusts at each site is also shown.

TABLE 2. RESPIRABLE ALPHA QUARTZ EXPOSURE OF QUARRY WORKERS IN THE NORTHERN TERRITORY

QUARRY \ DUTY	ALPHA QUARTZ ($\mu\text{g m}^{-3}$)						% CRYSTALLINE
	DRILLER	CRUSHER OPERATOR	LOADER DRIVER	TRUCK DRIVER	TUNNEL ATTENDANT	BULLDOZER DRIVER	ALPHA QUARTZ IN DUST
ABM, Darwin	1900	110	80-240	310			10-50
DCM, Darwin		90- 330	90-540	90			10-40
Batchelor		300-1400	310	360			35-45
Mt Bundy	100	70- 280			320		4-10
Emily Gap, Alice Springs	920-4300	85-4900	100-230	2500	2000		20-50
Undoolya, Alice Springs	2800	290-670	40-100	200-530			7-20
Tennant Ck			150-240			320-560	10-20
Katherine	10-160		110-210				4-11

TABLE 3. RESPIRABLE ALPHA QUARTZ EXPOSURE OF SOME MINE WORKERS IN THE NORTHERN TERRITORY

MINE \ DUTY	ALPHA QUARTZ ($\mu\text{g m}^{-3}$)							% CRYSTALLINE
	DRILLER	CRUSHER OPERATOR	LOADER DRIVER	TRUCK DRIVER	MINE WORKERS	MILL OPERATOR	SAMPLE PREPARATION	ALPHA QUARTZ IN DUST
Noble's Nob		20-1600				10- 50		3-8
Plenty River	100-2200	5- 80	70	15-45		80-190	25	9-16
Ranger Uranium	5-70	5- 150		5	10-60	5-15	5-115	3-36

Detailed discussion of these results is beyond the scope of this paper. Some aspects are, however, worthy of brief comment.

Essentially, they have provided the information necessary to enforce the installation of dust suppression equipment to operations of high risk and have supported temporary shutdown of some plant until these measures have been made effective.

The variability of results from day to day for many of the operations shows the necessity for regular sampling at frequent intervals. Spasmodic monitoring programs by government officials are not sufficient. In the Northern Territory, responsibility for routine sampling is being placed on the operating company and the validity of this sampling checked by less frequent government monitoring. The large number of samples generated by these programs can easily be handled by the above X-Ray diffraction technique.

Workers in air-conditioned cabins of earthmoving equipment and haulage trucks often express the opinion that they are not at risk to excessive silica exposure. Personal monitors sometimes contradict this. Levels as high as $500 \mu\text{g m}^{-3}$ alpha quartz have been recorded for drivers of airconditioned trucks.

In interpreting results consideration must be given to the fact that Threshold Limiting Values are set for an 8 hour shift. Mine and quarry workers frequently work 10-12 hours per day.

ASBESTOS

Asbestos-Containing Materials

Although asbestos is seldom used in Australia today, in the past many building and insulation materials contained various asbestos minerals from a few percent in pipes or plasterboard to near 100% in woven lagging. These materials are frequently used where conditions are extreme - eg boiler rooms, engine exhausts, factory roofs and ceilings - and degradation from heat, moisture and vibration rapidly occurs causing fracturing, peeling and flaking and releasing particles and fibres into the workplace atmosphere.

Materials investigated include:

- ceilings and wall flakes;
- dust;
- wall panelling;
- acoustic tiles;
- steam pipe woven lagging;
- steam pipe foam insulation;
- steam pipe fibrous insulation;
- water drum lining;
- diesel exhaust lagging;
- fibrous sheeting;
- ships funnel lagging;
- air conditioner insulation;
- electrical cable insulation; and
- solvent cupboard doorseal.

Seventy percent of samples examined to date have been found to contain asbestos. The most commonly occurring asbestos minerals are chrysotile and anthophyllite. Most woven pipe insulation lagging contains chrysotile, often in very high concentrations. With age and exposure this becomes brittle. This type of material is often used on suspended pipes near heavy machinery or boilers, is subject to vibration and can pose an unacceptable hazard to workers. At least three major installations have been faced with the difficult and expensive task of removing this material. Anthophyllite occurs in building materials usually in association with other components. Contamination occurs when coatings crack and peel, flaking occurs and particles are released into the atmosphere.

Incidence of crocidolite and amosite has been less frequent and generally in lower concentration but at times associated with other asbestiform minerals.

Analysis

For 90% of samples the method is simple. The sample is dried, broken up and an aliquot ground for 3 minutes in a Rocklabs ring grinder. The powder is hand-pressed into a standard specimen holder and scanned from 60° to $5^\circ 2\theta$ at $1^\circ 2\theta$ per minute. A copper anode broad focus X-Ray tube is used at 50 kV 40 mA, curved graphite crystal monochromator, 1° divergence slit, 0.3 mm receiving slit and scintillation counter. All components are identified.

The d-spacings of the reflections of greatest intensity of the four most common asbestos materials are shown in Table 4.

TABLE 4. D-SPACINGS OF THE MORE INTENSE DIFFRACTION LINES OF THE COMMON ASBESTOS MINERALS

Mineral	d Å	Relative Intensity	hkl
Chrysotile	7.3	100	002
	4.56	50	020
	3.66	80	004
	2.50	50	202
	2.45	65	
	1.53	65	060
Crocidolite	8.3	100	110
	4.50	25	040,021
	3.10	55	310
Anthophyllite	9.3	25	200
	8.9	30	020
	8.3	55	210
	3.25	60	421,440
	3.05	100	610,501
Amosite	8.2	100	110
	3.25	20	240
	3.06	65	310
	2.76	20	151

Preferred orientation may distort relative peak intensities.

The presence of other, non asbestos, components can hinder identification by dilution and by line overlap. Gypsum and other calcium sulphates, calcite and other calcium carbonates, magnesium sulphates and carbonate, sodium and calcium silicates, cellulose, fibre glass, rutile (from paint), quartz and clay are among the more frequently encountered materials in various combinations. Magnesium sulphates and other water solubles are readily removed by hot water leach. Cellulose and other carbonaceous matter can be burnt off. Temperatures should be kept below 500°C to avoid alteration of the asbestos minerals. The (020) reflection of gypsum overlaps chrysotile (002) and gypsum (041) may mask anthophyllite (610), (501), amosite (310) and crocidolite (310). Gypsum may be leached from the material with ammonium chloride solution or converted to anhydrite by heating - anhydrite not diffracting with significant intensity near these lines. Calcite (100) may overlap amosite (310), anthophyllite (610), (501) and crocidolite (310). These three asbestos minerals are resistant to acid attack and calcite and other carbonates may be removed with, for example, dilute HCl. Chrysotile may react with the acid. Calcite and gypsum are often present in high concentration in building and insulation materials.

The presence of any amount of asbestos in materials is considered hazardous and quantification is not normally required. Investigations are, however, currently being undertaken to determine the feasibility of a double dilution X-Ray diffraction technique of quantitative analysis (10).

X-Ray diffraction is as yet not used in the Northern Territory for the analysis of samples of airborne asbestos fibres. These are sent to other laboratories for phase contrast microscopy or scanning electron microscopy determination. XRD techniques have, however, been suggested by other workers (11, 12) and interferences reported (13).

OTHER WORKPLACE CONTAMINANTS

The major non-agricultural industries of the Northern Territory are manganese mining, the mining and treatment of bauxite and the mining and extraction of uranium. A smaller lead mine at Plenty River has employed up to 100 people. X-Ray diffraction is a potential analytical method for any crystalline material associated with these industries which may cause health problems to the workforce. Realistically, however, the method must be compared with others available.

Manganese in ore may be in several mineral forms. Total manganese is monitored and atomic absorption is a most suitable method.

Alumina dust is a potential hazard in work areas adjacent to the calciner and post calcine conveyers in the bauxite treatment plant at Gove. Particle size is small and diffraction methods are applicable. However, threshold limiting values are the same as total dust limits and total weight is an adequate monitor.

Dust control is stringent in uranium extraction plants. Radiation monitoring is the accepted measurement method.

Lime is used in association with bauxite and uranium ore treatment. X-Ray diffraction is a useful technique as it distinguishes between Ca(OH)_2 and other calcium compounds.

Plenty River Mining Company have been mining a mixed oxidized and sulphide lead ore. X-Ray diffraction allows distinguishment between the lead minerals. Some peak overlap needs to be overcome for quantitative work.

HOW USEFUL IS X-RAY DIFFRACTION?

X-Ray diffraction is the preferred method for the analysis of free silica in respirable dust. It is a reliable and usually fast method for the qualitative identification of asbestos minerals and has the potential to be at least a semi quantitative technique. There are some attractions in quantitative X-Ray diffractometry for other workplace contaminants but its main usage here under the present Northern Territory industrial structure will be in the qualitative identification of potentially hazardous crystalline materials.

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A TIN-119 N.M.R. STUDY OF A POSSIBLE MECHANISM TO EXPLAIN THE SYNERGISTIC
EFFECTS EXHIBITED BY MIXTURES OF ALKYLtin MERCAPTOESTERS AS P.V.C.
STABILIZERS

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ABSTRACT

Although the phenomenon of synergism observed with mixtures of mono- and dialkyltin stabilizers for P.V.C. has been known and exploited for some time, it remains largely unexplained. Whilst a similar effect in mixed metal (Ba/Cd or Ca/Zn) carboxylate stabilizers has been elucidated, mechanistic studies of the organotin systems have hardly appeared. In this paper, tin-119 n.m.r. spectroscopy has been utilized to study the Cl/mercaptoester exchange equilibria of alkyltin mercaptoester (isooctylthioglycollate)/chlorine compounds which are produced when organotin mercaptoesters act as stabilizers for P.V.C. The exchange process is shown to be facile and based on these observations, a regenerative mechanism is proposed to explain the synergistic effect.

INTRODUCTION

Chlorine-mercaptoester exchange equilibria have long been known to exist in mixtures of dialkyltin dichlorides with dialkyltin bis (mercaptoesters)¹(1).

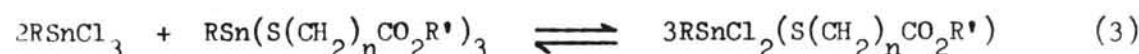
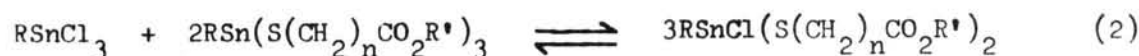


R, R' = alkyl

n = 1, 2

These equilibria have been investigated by means of I.R. spectroscopy and N.M.R. spectroscopy and it has been suggested^{2,3} that such equilibria may play a significant role in the stabilization of P.V.C.

Equilibria similar to (1) which exist in monoalkyltin systems have also been studied,¹ (2), (3).



By analogy, equilibria (2) and (3) should also be involved when monoalkyltin mercaptoesters are utilized as P.V.C. stabilizers. In fact, the addition of monoalkyltin compounds to dialkyltin mercaptides has been claimed to boost the performance of the latter compounds (as P.V.C. stabilizers). Klinsch and Kuhnert⁴ reported that the addition of monobutyltin tris(2-ethylhexylthioglycollate to dibutyltin bis(2-ethylhexylthioglycollate) results in a significant improvement in mill stability.

A full interpretation of these results has not been proposed but Nass⁵ has suggested that the action of the monoalkyltin compounds may be regenerative although no proof was offered. Subsequently, tin-119m Mössbauer spectroscopy⁶ and infrared spectroscopy⁷ have been utilized to study the mode of action of organotin stabilizers in P.V.C. This paper reports a tin-119 N.M.R. study of mixtures containing mono- and dimethyltin mercaptoester chlorides with the objective of obtaining an explanation of the observed synergistic effects.

A Tin-119 n.m.r. Study Of A Possible Mechanism To Explain The Synergistic Effects Exhibited By Mixtures Of Alkyltin Mercaptoesters As P.V.C. Stabilizers

EXPERIMENTAL

Dimethyltin dichloride and methyltin trichloride were obtained from ICN Pharmaceuticals Inc. Dimethyltin bis(isooctylthioglycollate), methyltin tris(isooctylthioglycollate), dimethyltin isooctylthioglycollate chloride, dimethyltin bis(isooctylthioglycollate) chloride and methyltin isooctylthioglycollate dichloride were prepared by previously described methods.^{1, 8-11}

Equimolar mixtures of the mono- and dimethyltin compounds were prepared by stirring the two compounds together at room temperature.

The tin-119 n.m.r. spectra were recorded in the Fourier transform mode with proton decoupling by using a Varian XL-200 n.m.r. spectrophotometer with an operating temperature of 30 °C. Tetramethyltin was the external reference used.

The results are shown in TABLE 1.

RESULTS AND DISCUSSION

The tin-119 n.m.r. spectra of mixtures of mono- and dimethyltin mercaptoester chlorides containing different numbers of isooctylthioglycollate (IOTG) groups shall now be examined.

Mixtures of Mono- and Dimethyltin Mercaptoester Chlorides Containing One IOTG Group

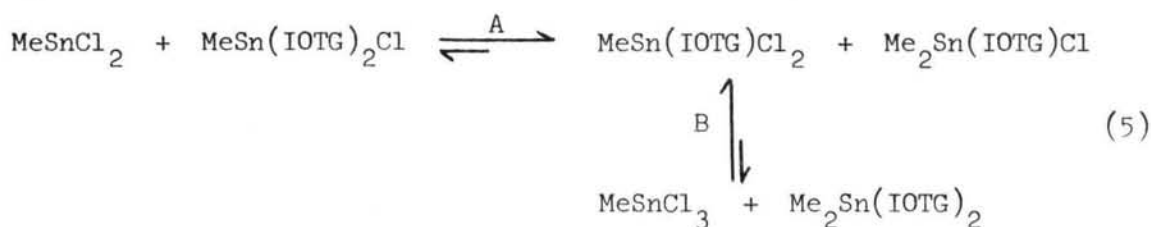
The tin-119 n.m.r. spectrum of a mixture of MeSnCl_3 and $\text{Me}_2\text{Sn}(\text{IOTG})\text{Cl}$ shows absorption peaks at -56.0 and +136.2 p.p.m. indicating the presence of $\text{MeSn}(\text{IOTG})\text{Cl}_2$ and Me_2SnCl_2 respectively. Conversely the spectrum of a mixture of Me_2SnCl_2 with $\text{MeSn}(\text{IOTG})\text{Cl}_2$ indicates the presence of MeSnCl_3 and $\text{Me}_2\text{Sn}(\text{IOTG})\text{Cl}$. These observations suggest that equilibrium (4) is set up via Cl/IOTG exchange. The former reaction proceeds much faster than the latter and the addition of excess Me_2SnCl_2 to either of the above mixtures does not cause any change in their respective n.m.r. spectra. These results suggest that equilibrium (4) lies strongly to the right hand side.



Dilution of the mixtures with hydrocarbon (benzene) and ethereal (DME) solvents had no effect upon their spectra, showing that the spectra of the mixtures are not determined by coordination effects.

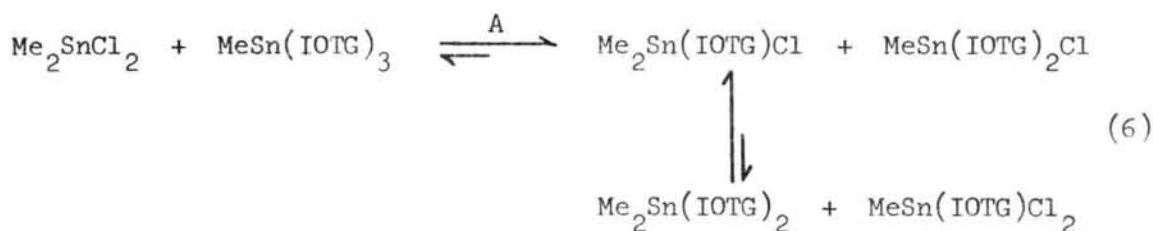
Mixtures of Mono- and Dimethyltin Mercaptoester Chlorides Containing Two IOTG Groups

Increasing the number of IOTG groups present in the mono/dialkyltin mercaptoester chloride leads to a more complicated situation. However, mixtures of Me_2SnCl_2 with $\text{MeSn(IOTG)}_2\text{Cl}$, MeSn(IOTG)Cl_2 with $\text{Me}_2\text{Sn(IOTG)Cl}$ and MeSnCl_3 with $\text{Me}_2\text{Sn(IOTG)}_2$ all yield identical tin-119 n.m.r. spectra indicating that equilibria (5 (A and B)) operate in this case.



Mixtures of Mono- and Dimethyltin Mercaptoester Chlorides Containing Three IOTG Groups

Mixtures of Me_2SnCl_2 with MeSn(IOTG)_3 , MeSn(IOTG)Cl with $\text{MeSn(IOTG)}_2\text{Cl}$ and $\text{Me}_2\text{Sn(IOTG)}_2$ with MeSn(IOTG)Cl_2 all give identical spectra indicating the existence of equilibrium (6 (A and B)).

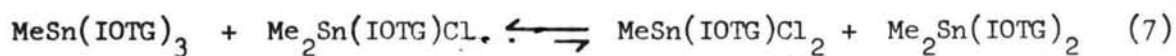


Mixtures of Mono- and Dimethyltin Mercaptoester Chlorides Containing Four IOTG Groups

Mixing MeSn(IOTG)_3 with $\text{Me}_2\text{Sn(IOTG)Cl}$ gives a mixture of $\text{Me}_2\text{Sn(IOTG)}_2$ and $\text{MeSn(IOTG)}_2\text{Cl}$ very slowly. However when the latter two compounds were mixed, reaction occurred very quickly to give MeSn(IOTG)_3 and $\text{Me}_2\text{Sn(IOTG)Cl}$.

These observations suggest that equilibrium (7) lies to the left hand side.

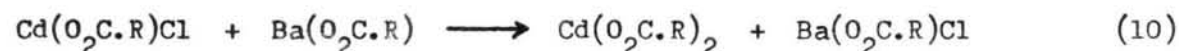
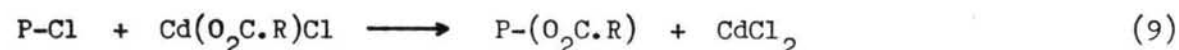
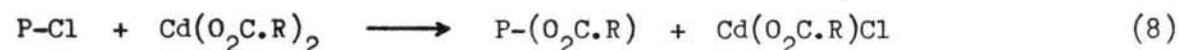
A Tin-119 n.m.r. Study Of A Possible Mechanism To Explain The Synergistic Effects Exhibited By Mixtures Of Alkyltin Mercaptoesters As P.V.C. Stabilizers



P.V.C. Stabilization

The preceding discussion has established the occurrence of facile Cl/IOTG exchange in mixtures of mono- and dimethyltin mercaptoester chlorides. It is interesting therefore to consider the relevance of this phenomenon to the stabilization of P.V.C. There are many claims to synergistic effects obtained with mixtures of mono- and dialkyltin mercapto compounds but explanation for these effects had only begun to appear recently.^{6, 7}

However, the synergism observed with mixtures of barium and cadmium (or calcium with zinc) carboxylates has been explained in terms of Cl/carboxylate exchange reactions.^{12, 13} In the case of the mixed Ba/Cd carboxylates, the role of the cadmium carboxylate is to react with the chlorine atoms (usually allylic in origin) within the P.V.C. while barium carboxylate reacts with CdCl_2 to regenerate the active cadmium carboxylate. These processes, (8) - (11), which are depicted below results in the replacement of CdCl_2 , an active prodegradant for P.V.C., with inert BaCl_2 .



(P = Polymer)

It seems logical to suggest that a similar mechanism would operate in mixtures of mono- and dialkyltin mercaptoester stabilizers whereby the regenerative process involves either the transfer of IOTG groups from a dialkyltin species to a monoalkyltin species or the converse reaction of exchange of IOTG groups from a monoalkyltin species to a dialkyltin species.

In an attempt to differentiate between these two possibilities Burley and Hutton⁷ studied the degradation times of P.V.C. samples stabilized with mixtures of alkyltin mercaptoesters and mercaptoester chlorides. The results of the study indicate that the partial replacement

of either $R_2Sn(IOTG)_2$ or $R_2Sn(IOTG)Cl$ ($R=alkyl$) results in increased stabilization whereas the converse procedure of partially replacing mono- alkyltin stabilizers such as $RSn(IOTG)_3$ and $RSn(IOTG)_2Cl$ with R_2SnCl_2 does not result in increased stabilization. Hence, it seems reasonable to conclude that the regeneration mechanism essentially requires the conversion of a monoalkyltin salt $RSn(IOTG)_xCl_{3-x}$ ($x=0,1,2$) to $RSn(IOTG)_{x+1}Cl_{2-x}$ and the conversion of a dialkyltin salt $R_2Sn(IOTG)_yCl_{2-y}$ ($y=2,1$) to $RSn(IOTG)_yCl_{2-y}$ ($y=2,1$) to $RSn(IOTG)_{y-1}Cl_{3-y}$. Therefore, by analogy with the Ba/Cd carboxylate system, the role of $RSn(IOTG)_3$ would be similar to that of the cadmium carboxylate whilst that of $R_2Sn(IOTG)_2$ would be similar to that of the barium carboxylate. Hence the regeneration process would mainly involve reactions such as (12) and (13) which are analogous to reactions (11) and (10) respectively.



Work carried by Wirth¹⁴ and co-workers (dehydrochlorination of P.V.C.) suggest that neither of the organotin chlorides are prodegradants but that each imparts some degree of stabilization to P.V.C. However, the results of Burley and Hutton¹¹ suggest that while R_2SnCl_2 does not have prodegradant activity in comparison to unstabilized P.V.C., $BuSnCl_3$ has a definite prodegradant character. Nevertheless both sets of results agree that R_2SnCl_2 is a better P.V.C. stabilizer than $RSnCl_3$.

Normally, temperatures between 160 to 200 °C are involved in the fabrication of P.V.C. articles. However, the present work on equilibria (4) - (7) does show that there is a change in the distribution of the IOTG ligands between the mono- and dimethyltin entities as the total number of IOTG ligands present in the mixture changes. When four IOTG ligands are present in the equimolar mixture, the equilibrium (7) favours the location of IOTG ligands on the monomethyltin entity. With only one IOTG ligand in the mixture (4) its location on the monomethyltin entity is also preferred. However, when two or three IOTG groups are present ((5) and (6) respectively) there is a greater tendency for IOTG ligands to be located on the dimethyltin entity. Hence, when a mixture of mono- and dimethyltin iso-octylthioglycollates is employed in the stabilization of P.V.C., there will be a continual change in the distribution of IOTG ligands between the mono- and dimethyltin entities as the stabilizer is consumed (IOTG ligands are replaced by Cl atoms).

TABLE 1 N.M.R. SPECTRA (TIN-119 CHEMICAL SHIFTS) FOR METHYLTIN CHLORIDES, METHYLTIN MERCAPTOESTERS AND MIXTURES OF MONO- AND DIMETHYLTIN MERCAPTOESTERS

Compound or Mixture	δ (^{119}Sn) (p.p.m.)	
Me_2SnCl_2	+ 136.2	
MeSnCl_3	+ 12.7	
$\text{Me}_2\text{Sn}(\text{IOTG})_2$	+ 72.8	
$\text{Me}_2\text{Sn}(\text{IOTG})\text{Cl}$	+ 35.5	
$\text{MeSn}(\text{IOTG})_3$	+ 59.6	
$\text{MeSn}(\text{IOTG})_2\text{Cl}$	- 18.1	
$\text{MeSn}(\text{IOTG})\text{Cl}_2$	- 56.0	
$\text{Me}_2\text{SnCl}_2 + \text{Me}_2\text{Sn}(\text{IOTG})_2$	+ 35.5	
$\text{MeSnCl}_3 + 2\text{MeSn}(\text{IOTG})_3$	- 18.1	
$2\text{MeSnCl}_3 + \text{MeSn}(\text{IOTG})_3$	- 56.0	
$\text{Me}_2\text{SnCl}_2 + \text{MeSn}(\text{IOTG})\text{Cl}_2$	- 12.7	+ 35.5
$\text{MeSnCl}_3 + \text{Me}_2\text{Sn}(\text{IOTG})\text{Cl}$	- 56.0	+ 136.2
$\text{Me}_2\text{SnCl}_2 + \text{MeSn}(\text{IOTG})_2\text{Cl}$	- 56.0	+ 35.5
$\text{MeSnCl}_3 + \text{Me}_2\text{Sn}(\text{IOTG})_2$	- 56.0	+ 35.5
$\text{MeSn}(\text{IOTG})\text{Cl}_2 + \text{Me}_2\text{Sn}(\text{IOTG})\text{Cl}$	- 56.0	+ 35.5
$\text{Me}_2\text{SnCl}_2 + \text{MeSn}(\text{IOTG})_3$	- 18.1	+ 35.5
$\text{Me}_2\text{Sn}(\text{IOTG})\text{Cl} + \text{MeSn}(\text{IOTG})_2\text{Cl}$	- 18.1	+ 35.5
$\text{Me}_2\text{Sn}(\text{IOTG})_2 + \text{MeSn}(\text{IOTG})\text{Cl}_2$	- 18.1	+ 35.5
$\text{Me}(\text{IOTG})_3 + \text{Me}_2\text{Sn}(\text{IOTG})\text{Cl}$	- 18.1	+ 72.8
$\text{MeSn}(\text{IOTG})_2\text{Cl} + \text{Me}_2\text{Sn}(\text{IOTG})_2$	+ 35.5	+ 59.6

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CHEMICALS IN THE ENVIRONMENT - THE NEED FOR INFORMATION

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A B S T R A C T

Although chemicals are beneficial to modern society they are also the chief pollutants of the human environment. A large number and variety of chemicals are in use today; their effects on man and his environment have to be scientifically evaluated. International groups of experts have identified the type of data on chemicals which are essential for such evaluation. National and international organisations have set up data banks to collect, classify, store and disseminate the data; international groups of experts have used these data to evaluate the effects of the chemicals on man and his environment. The International Register of Potentially Toxic Chemicals, the International Programme on Chemical Safety and the International Agency for Research on Cancer play a major role in these tasks.

Not all the data necessary for evaluation are available and experts have therefore often recommended more research to obtain these data.

EXTENT OF THE PROBLEM

Over six million chemicals are known today, an increase of two million during the past six years; 1000 new chemicals are being identified every day. The vast majority of chemicals are isolated from natural products or synthesised for research purposes. About 75% of them have been mentioned only once in the literature and can therefore be considered as laboratory curiosities. The best estimate of the number of chemicals in common use is 60,000 to 70,000, about 1% of all chemicals known to us; of these about 3,000 account for almost 90% of the total chemicals used, by weight⁵.

NEED FOR INTERNATIONAL COOPERATION

The collection and the classification of the essential data on a single chemical and the subsequent evaluation of its effects on man and his environment are time-consuming processes requiring the outlay of vast human and financial resources; where a population is exposed to more than one chemical, the process is more complicated as their antagonistic and synergistic effects have to be assessed; the process is further complicated by climatic, geographical and population differences. All this may be beyond the capacity of even a developed country.

Secondly, it should be emphasized that pollution knows no national boundaries, the atmosphere and seas are common to, and rivers run through several countries. Fluorocarbons, acid rain, the Mediterranean sea and the Rhine river pollution problems are notable examples.

International cooperation in the collection of data on chemicals and evaluation of their effects on man and environment is therefore vital.

INTERNATIONAL REGISTER OF POTENTIALLY TOXIC CHEMICALS (IRPTC)

Recognising the need for a systematic collection of data on chemicals and for international cooperation in this area, the United Nations Conference on the Human Environment held in Stockholm in 1972 recommended that "the Secretary-General drawing on the resources of the entire United Nations system and with the active support of governments and appropriate scientific and other international bodies, develop plans for an International Registry of Data on Chemicals in the Environment, based on a collection of available scientific data on the environmental behaviour of the most important man-made chemicals, and containing production figures for the potentially most harmful chemicals together with their pathways from factory via utilization to ultimate disposal or re-circulation"⁶.

INTRODUCTION

Chemicals are essential to modern life and protect and enhance the quality of life and environment. Though they have made possible many of the benefits modern society enjoys, they also pose many hazards to man and his environment. These hazards have been recognised over the years. Roman slaves working in mercury mines used bladder skin masks in a futile attempt to avoid inhaling the toxic mercury fumes; the first smoke abatement law in England dates back to 1273; sixteenth century grinders suffered from a lung ailment they called "grinders' disease" (now known as silicosis) due to inhalation of silica dust; in 1661 John Evelyn, an Englishman, presented a petition to King Charles II complaining against the pollution of the atmosphere of London by arsenical, sulphurous and other "vapours" and suggesting that the brewers, dyers, lime-burners, soap and salt-boilers who were responsible be removed away from the city. He even attributed the annual decrease of 10,000 in London's population to this pollution². The 4,000 deaths that occurred during the four days (December 5 - 8, 1952) of the fog in London were attributed to the presence of sulphur dioxide probably in conjunction with sulphuric acid and mist³. The phrase, "mad as a hatter" arose as a result of workers being poisoned by the mercury nitrate used in the felt hat industry; the symptoms of the disease include emotional disturbance, anxiety, depression and even personality changes - hence the rather unkind reference to madness.

The harmful nature of some chemical agents were thus known in early times so that they were even used in warfare; in 423 B.C. the Spartans saturated wood with pitch and sulphur, shoved it under Delium's walls and set the wood ablaze. The poisonous fumes prevented the defenders from putting out the fire. In 1456, Belgrade was saved from invaders by a poisonous gas cloud prepared by an alchemist; rags were dipped into his preparation (formula unknown) and burnt when dry.

RECOGNITION OF THE PROBLEM

Although such isolated instances of chemical pollution have been with us for several centuries it was only during the last few decades that the problem has become so acute that people have become concerned about the urgent need to protect man and his environment from the adverse effects of chemicals. To evaluate the effects of these chemicals it is essential to have complete information on their identity, physical and chemical properties, acute and long-term toxicity, persistence, degradation amounts produced, used and entering the environment, pathways into the environment and breakdown products and the population group exposed to them. Part of this information is known but often buried in scientific publications and not readily usable form so that the effects of the chemical can be evaluated and presented to those responsible for the protection of man and his environment. Where information is lacking, research efforts may be directed towards obtaining it⁴.

IRPTC was established in 1976 within the United Nations Environment Programme. With the assistance of international experts IRPTC has identified 17 broad groups of data on chemicals necessary for the evaluation of their effect on man and the environment; these groups are subdivided into several individual parameters which are classified according to organism, country and medium (See Annex I). With the assistance of its national correspondents and others it has selected about 350 chemicals on which it collects data. These data collections are called "Data Profiles" and are published by IRPTC.

The United Nations Environment Programme has directed IRPTC to provide countries with information on legal and administrative limitations, basis and regulations placed on potentially toxic chemicals in the producing countries. Although this information forms an integral part of the IRPTC data profile, it is also published separately as the legal file. Regulatory and other legal information and recommendations on about 450 chemicals are contained in this 2 volume publication.

IRPTC in addition publishes a quarterly bulletin devoted to information on chemicals and related activities in English, French, Russian and Spanish. It provides a query response service on Chemical information which can be contacted through its 106 national correspondents in 97 countries or directly if the national correspondent has not yet been appointed.

INTERNATIONAL PROGRAMME FOR SAFETY

Following the recommendation of the Conference on Human Environment (Stockholm 1972) that the World Health Organisation (WHO) should guide programmes for the assessment of the potential risk to human health of environmental agents and for provision of early warning and prevention of the deleterious effects, the International Programme on Chemical Safety was established in 1980. It is sponsored by the (International Labour Organisation), UNEP and WHO and managed by WHO. 15 member states have so far joined the programme which operates through a network of 19 national institutions which undertake specific tasks and two international institutions: IRPTC and IARC. (International Agency for Research on Cancer). About 100 other institutions assist IPCS. IRPTC is responsible for the collection and dissemination of information and IARC for chemical carcinogenesis.

The principal objectives of the programme are to

- (i) evaluate the effects of chemicals on man and the environment and disseminate the results of these evaluations.
- (ii) encourage the use, improvement and validation of methods for laboratory testing and epidemiological studies for health risk evaluations.
- (iii) promote international co-operation in emergencies and accidents involving chemicals.
- (iv) promote the training of the necessary man-power

The outputs of the programme are

- (i) Environmental health criteria documents which review present knowledge and evaluate the risk to human health and environment of exposure to chemicals selected from internationally agreed priority lists. 20 of these documents have so far been published and 48 are in preparation. Executive summaries of 16 of the 20 documents have also been published; these highlight the essential health issues and are designed for the direct use of the decision-maker.

(ii) Evaluation of Food additives and pesticide residues. Since 1981 the Joint FAO/WHO Expert Committee on Food Additives has evaluated or re-evaluated 119 food additives, 4 good contaminants and 2 growth promoters and established "acceptable daily intakes" (ADIs) for several of them. The joint WHO/FAO meetings on pesticide residues have evaluated 101 pesticides and established "acceptable daily intakes" (ADIs) and "maximum residue levels" (MRLs) for them. The ADIs and MRLs are used by regulatory agencies in the member states of the United Nations and by the Codex Alimentarius Commission to establish safe levels of these substances in food.

(iii) Development of methodology for health risk assessment. The following monographs have been published

- a. Development and possible use of immunological techniques to detect individual exposure to chemicals.
- b. Approaches to classifying chemical carcinogens according to mechanisms of action.
- c. Methods for assessing effects of chemicals on reproductive functions.
- d. Guidelines on studies in environmental epidemiology
- e. Principles for evaluating health risks to progeny associated with exposure to chemicals during pregnancy.

The following monographs are in the press :

- f. Principles and methods for evaluating the toxicity of chemicals.
- g. Methods for estimating risks in humans and chemical damage in non-human biota and ecosystems.

(iv) Manpower development. Ten courses of training courses were conducted; these were in two categories, intensive short-term courses on principles of experimental toxicology and short-term training on chemical safety procedures. In addition, an international workshop on manpower development and training in toxicology and chemical safety was held.

These were all organised by the WHO regional office for Europe which has been given the responsibility on behalf of WHO.

(v) Management of chemical emergencies The WHO Regional Office for Europe has, within the framework of IPCS, prepared draft guidelines on reducing the risk of chemical accidents and the rehabilitation of population, water resources, soil, buildings and facilities following the accidents; these have been reviewed at a workshop and specific technical documents have been initiated.

(vi) Computerised data base. The vast resources, both human and financial, required for the testing of an ever growing number of chemicals make it imperative that (a) these resources are used efficiently and duplication of tests are avoided and (b) information on criteria documents is made available. IPCS & IRPTC are jointly developing a computerised data base for chemicals being tested (other than carcinogenicity and mutagenicity) and for criteria documents.

OTHER U.N. AGENCIES

Apart from IPCS and IRPTC which are specifically concerned with chemicals there are other UN Agencies and Groups which have specific programmes dealing with particular aspects of chemicals. These include Economic Commission for Europe (ECE), Food and Agriculture Organisation (FAO), Joint Group of Experts on Scientific Aspects of Marine Pollution (GESAMP), International Atomic Energy Authority (IAEA), International Labour Office (ILO), Intergovernmental maritime Consultative Organisation (IMCO), World Meteorological Organisation (WMO), UN Expert Committee on Transport of Dangerous Goods and UN Statistical Office.

The need to protect man and his environment from chemical hazards, the need for information, the type of information necessary and the international sources of information have been described above. It should be emphasised that several national sources of information are available. International sources of information are derived basically from the national sources; however they have the advantage of easy availability to all member states of the UN System and particularly of general acceptability because of international consensus.

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ANNEX I

Data necessary for the evaluation of the effects
of chemicals on man and his environment

1. Identifiers Physical and Chemical properties, Hazard classification.
2. Production/Trade (Classified by Country)
3. Production processes
4. Use
5. Pathways into the environment (See. 8)
6. Concentrations (classified by organisms)
 - a. Loss/Persistence
 - b. Concentrations
 - c. Human intake
7. Environmental fate tests
 - a. Biodegradation/Biotransformation
 - b. Photodegradation
 - c. Hydrolysis
 - d. Sorption
 - e. Evaporation
 - f. Oxidation
 - g. Model Ecosystem/Ecosystem studies
8. Environmental fate and pathways into the environment
9. Chemobiokinetics (Classified by Organism)
 - a. Absorption
 - b. Distribution
 - c. Bioconcentration factor
 - d. Metabolism
 - e. Excretion
10. Mammalian toxicity and special toxicity studies (classified by organism)
 - a. Mammalian toxicity parameters
11. Special toxicity studies (classified by organism)
 - a. Biochemical interactions
 - b. Carcinogenicity
 - c. Mutagenicity
 - d. Neurotoxicity
 - e. Behaviour
 - f. Sensitization
 - g. Interacting agents
 - h. Primary irritation
 - i. Immunotoxicity
 - j. Reproduction
 - k. Teratogenicity
12. Effects on organisms in the environment (classified by organism)
 - a. Aquatic toxicity
 - b. Terrestrial toxicity
13. Sampling/Preparation/Analysis (Classified by Medium)
14. Spills
15. Treatment of poisoning
16. Waste management
17. Recommendations/Legal Mechanisms (classified by country)

LEAD IN PETROL

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A B S T R A C T

Lead tetraalkyls had been used as additives in petrol for over fifty years. However, in the past twenty years, there is increasing concern over the possible ill effect of airborne lead on human health and people begin to question the wisdom of using the lead additives in petrol. Literature abounds with research and review papers dealing with this controversial matter. This paper is an attempt to examine and present the scientific evidences in a systematic and critical manner so that a logical and rational decision can be made on this issue.

INTRODUCTION

Lead is added in petrol in the form of tetra-alkyl lead compounds, predominantly tetraethyl (TEL) and tetramethyl lead (TML) to boost the octane number to the required value. Since the seventies, faced with mounting evidences of lead pollution due to increasing number of cars in urban areas and its possible detrimental effect on the health of urban population, the developed countries had taken steps to reduce the amount of lead in petrol progressively. Thus, in West Germany and Sweden, the amount of lead in petrol is 0.15 g/l. In the U.K., maximum amount of lead allowed in petrol stands at 0.40 g/l but there is strong public pressure for the level to be lowered further. Lead-free petrol is mandatory in the U.S. for new cars fitted with catalytic converter to meet the stringent emission standards. In contrast, the amount of lead in petrol marketed in most of the developing countries is alarmingly high. Typically, both premium and regular grade petrol marketed in Malaysia contain 0.84 g lead per litre (1).

GASEOUS LEAD TETRAALKYLS

The major portion of lead emitted from the exhaust is in the form of particulate inorganic compounds. Undissociated lead alkyls in the gaseous phase, too, are emitted in variable quantities with the exhaust. Recently, improved experimental techniques have enabled the gaseous lead tetraalkyls to be measured. Harrison et al. (2) reported a contribution of 0.3 - 2.6% and 4 - 10% of tetraalkyl lead compounds to total lead in London streets and petrol station respectively whilst Rohbock et al. (3) found that the ratio of gaseous to particulate lead varied from 3.5% $\pm$ 1.4% in resort area to 27.9% $\pm$ 9.9% in basement car park. Thus, except in petrol stations and underground car parks, the particulate lead is a greater health risk compared to the gaseous lead compounds at the present level.

AIRBORNE PARTICULATE LEAD IN LEAD SOIL

A lot of work had already been carried out to measure the airborne particulate lead which accounts for the bulk of the emitted lead from car exhausts. In general, in the absence of industrial emissions, the average atmospheric lead level is the highest in urban areas. Suburban and rural areas have comparatively lower lead level. Airborne lead level is also a function of traffic density and distance of locality from traffic. These points are borne out by data in Tables 1, 2, and 3. Tables 1 and 2 compiled by Blokner (4) show the airborne lead levels in the U.S. and Europe respectively in the Fifties and Sixties before the curtailment of the use of lead in petrol. Table 3 compiled in the Lead and Health Report (5) shows the airborne lead levels at urban sites in the U.K. Tables 4 and 5 show the airborne lead levels at sites in Penang (6) and Singapore (7) respectively.

According to the findings of Habibi (8) and Ganley and Springer (9), lead particulates appear to be emitted in two distinct

size ranges, small particles less than $1\ \mu\text{m}$ in diameter and larger particles between 5 and $50\ \mu\text{m}$. The larger particles settle close to the source due to turbulent deposition. Thus, it is not surprising to find lead content of dust next to roads of high traffic density the highest compared to those of other roads of lesser traffic. Day (10) found that lead concentrations of road-side dust in Christchurch, New Zealand were closely related to the average traffic density of the roads in question. The average lead levels for various location were:

A	Heavy-medium traffic roads	3100 ppm
B	Medium-light traffic roads	1400 ppm
C	Light traffic roads	830 ppm
D	Children's playgrounds	700 ppm
E	Rural areas close to city	40 ppm

In a similar study done earlier in Manchester (11), the difference in lead concentrations at localities A to D was found to be statistically not significant but locality E did show a lower lead level comparatively. In an environmental lead survey near motorways in West London, Little and Heard (12) also concluded that traffic density and lead level were correlated. Thus, from the above discussion, it can be concluded that both airborne lead and lead in dust levels are dependent on the traffic density and proximity of locality from the streets. Naturally, a reduction in the lead content of petrol will result in a reduction in ambient lead level and lead in dust. This was substantiated by the findings of Jost and Sartorius (13) and Byrd et al. (14). In their survey of the effect of limiting the maximum lead concentration in petrol from $0.40\ \text{g/l}$ to $0.15\ \text{g/l}$ on the ambient lead level in West Germany, Jost and Sartorius observed a reduction in ambient lead level of about 65% in main roads and city centres. Byrd et al. reported that the mandatory use of unleaded gasoline in the U.S. has decreased the lead concentrations in soils near highways.

BLOOD LEAD AND TOOTH LEAD LEVELS AS INDICATORS OF LEAD EXPOSURE

Lead is undoubtedly a toxic substance which in sufficient quantities can cause permanent brain damage to babies and children. It can enter the body by absorption from the gastrointestinal tract of a proportion of ingested lead and by absorption from the lower respiratory tract of a proportion of inhaled airborne lead. What type of index should be used to indicate the level of absorption of lead by human body has been a subject of much debate for a long time. Many biologic indices such as lead concentrations in blood, urine, faeces and hair had been used. For a long time, lead level in blood has been accepted as the most valid and reliable indicator of the amount of exposure to lead a subject has undergone. Table 6 from Bryce-Smith et al. (15) shows significance of lead contents of human blood. Many papers had been written attempting to associate blood lead level with traffic density and hence airborne lead exposure. Caprio et al. (16) found higher percentage of children who lived at distance less than 100 ft. from roadway with blood lead level exceeded $40\ \mu\text{g}/100\ \text{cm}^3$ compared with those who lived further away from

the traffic. In contrast, Jones et al. (17) found no statistical significant difference between the blood lead levels of fifty night shift and day shift London taxi drivers. And despite the constant exposure to urban air of relatively high lead content, the mean blood lead level of the taxi drivers was $28.7 \mu\text{g}/100 \text{ cm}^3$. Flindt et al. (18) essentially came to the same conclusion after he carried out the survey on forty Manchester taxi drivers but the mean blood lead level was lower, $22.8 \mu\text{g}/100 \text{ cm}^3$. Tsuchiya et al. (19) measured the blood lead levels of Tokyo inhabitants residing in houses facing a main street and a side street and they found no statistical significant difference between the blood lead levels of these two groups of inhabitants.

In the case of lead in dirt and dust as related to the children's lead problem, Ter Haar et al. (20, 21) attempted to show that the elevated blood lead level in children was due solely to dilapidated housing and that the proximity of the children's residence from the road did not have a measurable effect on their blood lead levels. Barltrop et al. (22) suggested that soil lead level of 10,000 ppm might result in increased absorption of lead in urban children but it was unlikely to be of biological significance. On the other hand, Lepow et al. (23) suggested that the ingestion of airborne lead fallout accounted for the elevated blood lead level in urban children.

Criticism on blood lead level measurement is that it only reflects the instantaneous lead level at the time of measurement and does not provide a true description of the cumulative exposure of the subject to lead. As an alternative, lead content in deciduous teeth of children were measured because it was demonstrated that lead in deciduous teeth offers a good indicator of cumulative exposure. Needleman et al. (24) found that both household paint and airborne lead were the operative factors which caused relatively higher concentration of lead in the teeth of urban children as compared to that of their suburban counterparts. Lockeretz (25) and Fosse et al. (26), on the other hand, ruled out airborne lead from car exhaust as an important source of undue lead absorption among children. Admittedly, this kind of measurement could only be carried out on a particular group of the population - children. For the adults, the search is still going on for a more clearcut and reliable index to monitor the body lead level.

HEALTH EFFECTS

With regards to the question of whether lead emitted from motor exhaust poses a health hazard to the public, the debate still goes on. The most comprehensive and authoritative review of this issue to date is the Lead and Health Report (5). In the report, Professor Lawther's Working Party on Lead in the Environment estimated that between 10 to 20% of blood lead for city dwellers is contributed from airborne lead derived from vehicle emissions. They also concluded that there is no firm evidence thus far to show that the contribution made by lead from petrol has caused harm. However, a crucial question which cannot be answered with certainty is whether

there is any chronic effect associated with relatively low levels of exposure to lead which would cause slow but permanent damage especially to the central nervous system of young children and other high-risk groups in the absence of overt clinical signs and symptoms. In this sense, any source of lead, however small the contribution may be, which will cause an increase in the body burden of lead should be considered as undesirable. The Lead and Health Report (5) has recommended among other measures that lead content of petrol be reduced to keep the annual mean concentration of lead in air to less than $2 \mu\text{g m}^{-3}$ in places where people are liable to be continuously exposed for long periods.

VARIOUS ALTERNATIVES TO REDUCE LEAD EMISSIONS AND THEIR IMPLICATIONS

The pertinent question to ask next is how will the reduction of lead content in petrol affect the motor industry, the oil industry and the average motorist. The following cost analysis was based on references and data compiled in the West and may be applicable in the local scene. Assuming that the present 98 RON (Research Octane Number) is to be maintained for premium grade, this would necessitate the blending of more catalytic reformates in petrol. In order to do that, the existing refinery facilities would need to be modified. According to the CONCAWE Report (27), it was estimated that, at 98 RON, a reduction of lead from 0.45 g/l to 0.15 g/l would entail an extra consumption of about 20 tonnes of crude oil by refinery per 1,000 tonnes of petrol produced. The additional amount required for reducing lead from 0.6 to 0.4 g/l would be in the order of a half to a quarter times that when reducing lead from 0.4 to 0.15 g/l . Thus, a reasonable figure for reducing lead from 0.8 to 0.45 g/l should be in the order of 20 tonnes of crude oil per 1,000 tonnes of petrol produced. Based on the premium petrol consumption figure of 987,000 tonnes for West and East Malaysia in 1980 (1), the extra crude oil consumed by the refineries per year would be $987 \times 20 \text{ tonnes} = 19,740 \text{ tonnes}$. This approach which does not affect the motor industry has been adopted by West Germany. Other than the penalty of needing more crude oil and an initial capital cost for modification of refinery plants, this approach also suffers from the following drawbacks:

- i) Increase in the use of catalytic reformates to maintain the RON implies more aromatics being used in low lead petrol. Whether these aromatics pose a health hazard or not remains an open question;
- ii) Restriction on lead whilst maintaining the octane quality removes the flexibility in matching the right RON with different types of crudes currently enjoyed by the oil industry.

An alternative approach is to allow the octane quality of petrol to fall to reflect the reduction of lead in petrol. According to information supplied by Campbell (28), it was estimated that a reduction of lead from 0.8 g/l to 0.45 g/l would entail a loss of RON by about 3 units in premium grade petrol. The corresponding figure is about 8 units if the reduction is from 0.8 g/l to nil lead.

Forrester et al. (29) concluded that increasing compression ratio needed higher octane requirement, in the range 4.3 to 6.3 octane numbers per compression ratio. Thus, a drop of 3 RON would necessitate the compression ratio to be decreased in the range of 0.5-0.7 units. The British Technical Council (30) found that the fuel consumed increased by 7.6% for each unit drop in compression ratio, and the Committee of Common Market Automobile Constructors obtained the figure of 5.6% (31). Based on an average value of 6.6% per unit drop in compression ratio, a loss of 3 RON implies about 3% - 5% more fuel used.

A third option is to install lead traps in the exhaust system of vehicles and maintain the present level of lead in petrol. In addition to reducing the total amount of lead emitted, the lead traps also reduce the level of the small, air - suspendible lead particles emitted to the atmosphere. Cantwell et al. (32) found that with the muffler lead traps installed, the percent reduction in lead particles of size less than 1.0 μm reached 68%; the corresponding figures for particles of size 1 to 9 μm and greater than 9 μm were 82% and 98% respectively. Moreover, it was observed that there was no deterioration in lead trap performance with mileage. The drawback of this option is that the disposal of the concentrated lead in the trap may present a problem. Of course, irrespective of which alternative is adopted, the motorist is the one who ultimately pays. The costing analysis in the ENDS Report (33) considered more options and it contended that the motorist has to pay more in order to have a greater reduction in lead emission. To reduce lead level from 0.40 g/l to zero, the quoted annual cost to a motorist was £17 - £18.

CONCLUSION

Any measures to reduce lead in petrol which involves energy penalty may impose some strain on a nation's economy especially in the case of developing countries. In view of the conceivable crude oil price hike in the long run, any pollution abatement measure which involves energy penalty would be unpopular. In this sense, the installation of lead trap offers a workable measure because it carries no energy penalty and at the same time offers a marked reduction in lead emission. Technically, there is no difficulty in having all the petrol-engined vehicles, irrespective of old or new, installing lead traps. Of course, the public has to bear the economic cost but this cost is lower and predictable. In short, in view of the as-yet unanswered question of possible subclinical effect of low level exposure to lead and lead tetraalkyls on human health, every effort should be made to reduce the lead level in the environment. Measures which do not impose an undue economic burden on the public and at the same time prove effective in reducing the lead level in the environment should be considered and adopted by the concerned authority.

TABLE 1. ATMOSPHERIC LEAD LEVELS IN THE U.S.A.

Area or city	Year	Sampling Site Locations	Average Lead Concentration ($\mu\text{g m}^{-3}$)
Remote mountain	1961-62	Estimation	0.12
California countries			
Composite rural U.S.	1961-62	Estimation	0.5
Composite urban U.S.	1961-62	Estimation	1.4
Cities < 0.1 million	1954-55	Central city	1.2
Cities 0.1-0.5 million	1954-55	Central city	1.3
Cities 0.5-1 million	1954-55	Central city	1.3
Cities 1-2 million	1954-55	Central city	1.6
Cities > 2 million (except Los Angeles)	1954-55	Central city	2.3
Detroit	1960-65	5-150 m from traffic	4.8
New York	1960-65	2-75 m from traffic	4.1
Los Angeles	1960-65	4-20 m from traffic	7.6
Los Angeles	1966	12 m from freeway } ground level	13.2
	1966	1600 m from freeway	4.6
	1966	90 m from freeway 4th floor	6.4
Los Angeles	1954-55	Central city	6.6
	1961-62	Central city	4.3
Los Angeles	1961-62	ca. 2-20 m above ground	2.5
Philadelphia	1961-62		1.6
Cincinnati	1961-62		1.4
30 cities	1957-60	Central city 8-65 m above ground	0.5
Detroit	1958	Central city 27 m above ground	0.4
Los Angeles	1958	Central city 24 m above ground	1.7

Source: Blokner (1972)

TABLE 2. ATMOSPHERIC LEAD LEVELS IN EUROPE

City	Year	Sampling Site Locations	Average Lead Concentrations ($\mu\text{g m}^{-3}$)
Berlin	1966-67	Busy streets	3.8
		Quiet streets	0.4-0.5
Hamburg	1961-62	Quiet streets	2.0
Munheim		Quiet streets	
Dusseldorf	1965	$\frac{1}{2}$ mile from traffic	3.2
Meuss			
Wuppertal			
Duisburg			
Milan	1956	-	2.4-7.4
Paris	1964	Central streets	4.8
Rotterdam	1968	Mostly 10-15 m high in city	0.4
		Main street	3.5
Warwick,	1965-66		
England			
London	1964	Busy street	3.2
Zurich	1963	Near traffic	2.8

Source: Blokner (1972)

TABLE 3. AIRBORNE LEAD LEVELS AT URBAN SITES IN U.K.

Location	Period	Lead Concentrations ($\mu\text{g m}^{-3}$) (24 hour sampling)
Chiswick, W4	Apri 72-Mar 73	1.3
Warwick	Mar 65-Feb 66	0.8
Barnsley, town centre	Apri 76-Mar 78	0.36
Motherwell, town centre	Apri 76-Mar 78	0.46
London, Neasden,	Apri 76-Mar 78	0.64
Close to busy road		
Belfast, edge of housing estate	Apri 76-Mar 78	0.31
Leeds, close to busy road	Apri 76-Mar 78	0.65
Leeds, city centre	Apri 76-Mar 78	0.51
Leeds, park	Apri 76-Mar 78	0.27
Newcastle, old housing area	Apri 76-Mar 78	0.28
Coventry, city centre	Apri 76-Mar 78	0.49
Newport, town centre	Apri 76-Mar 78	0.38
Bristol, city centre	Apri 76-Mar 78	0.35
London, busy road, central area	Apri 76-Mar 78	0.72
Bolton, hospital grounds	Apri 76-Mar 78	0.39
Sheffield, close to busy road	Apri 76-Mar 78	0.53
Cambridge, close to busy road	Apri 76-Mar 78	0.48
Glasgow, close to busy road	Apri 76-Mar 78	0.93
London-Endell St, WC2	Jan-Dec 75	0.9
London-Endell St, WC2	Jan-Dec 76	0.8

Source: Lead and Health (1980)

TABLE 4. AIRBORNE LEAD LEVELS AT SITES IN PENANG ISLAND

Location	Period	Lead Concentrations (g m^{-3}) (24 hour sampling)
Sekolah Menengah St. Xavier (Commercial/residential)	Sept-Dec 1982	0.7
Sekolah Kebangsaan Kampung Java (Industrial/Commercial/ High density residential)	Sept-Dec 1982	0.7
Universiti Sains Malaysia (Institutional)	Aug-Dec 1982	0.3
Island Park (Medium density residential)	Sept 1982-Jan 1983	0.5
Bayan Baru (Medium density residential/Industrial)	Oct 1982-Jan 1983	0.5

Source: Lim et al. (1984)

TABLE 5. AMBIENT AND ROADSIDE LEAD LEVELS IN SINGAPORE

Site	Average Lead Concentration in $\mu\text{g m}^{-3}$	
	1980	1981
Ambient		
1. Princess House, rooftop	0.8	1.5
2. Fullerton Building, rooftop	0.8	0.7
3. Jurong Industrial Water Works	0.5	-
4. Serangoon District Office	0.6	0.8
Roadside		
1. Western Urban District Office Jalan Bukit Merah	1.1	2.2
2. Beach Road Police Station	2.6	1.8
3. PUB Substation Alexander Road	0.8	1.0
4. Faber Walk Communitor, Ayer Rajah Rd.	1.7	1.2

Source: Annual Report 1981, Anti-Pollution Unit, Singapore.

TABLE 6. LEAD CONTENTS OF HUMAN BLOOD AND THEIR SIGNIFICANCE

Lead ($\mu\text{g}/100\text{ ml}$)	Significance
< 1	"Natural" blood lead before man began using lead, and still found in some primitive populations remote from modern technology
10	Lower limit of "normal" blood level in the U.S.
20	Mean blood lead level in Birmingham pre-school children (Lead Pollution in Birmingham, HMSO, London (1978))
25	Mean blood lead level in the U.S.
30	Mean blood lead level for a group of Glasgow children
30	Lowest lead level found in industrially exposed adults having mild symptoms of lead poisoning
40	Upper limit of "normal" blood lead level in U.S.
40	Lowest approximate level found in industrially exposed adults having severe symptoms of lead poisoning
80	US "danger" threshold for occupational poisoning

Source: Fryce-Smith et al. (1978)

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STUDY ON THE DETERMINATION OF THE EXHAUSTED GASES WHICH
EXPELLED FROM 2½T TRUCK, BY THE METHOD OF GC-MASS SPECTROMETRY

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ABSTRACT

For the prevention of the air pollution and the saving energy which would be shortened in future, we analyzed an exhausted gas which was expelled from 2½T truck, by the method of GC-Mass spectrometry.

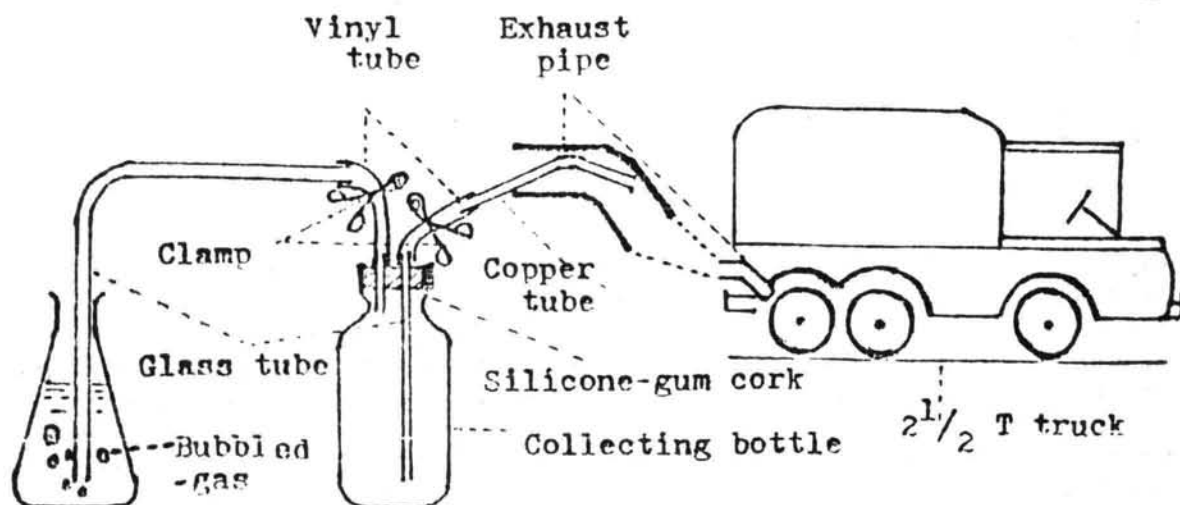
Under the abnormal driving condition, we had identified a small amount or a trace of the hazardous gas on GC and Mass spectrum, by the Molecularsieve-5A connected with Porapak-Q column, for the separation of gases which was produced from incomplete combustion. These were a small amount of carbon monoxide, toluene and low hydrocarbons etc. on the GC spectrum, and a trace of hydrogen sulfide on the Mass spectrum.

From the analytical data shown, the greater the acceleration, the more hazardous gases were produced from the incomplete combustion. Under the abnormal driving conditions which means the combustion assemblies had disassembled, the more assemblies had disassembled off, the more hazardous gases were produced.

EXPERIMENTAL PROCESS AND DETERMINATION

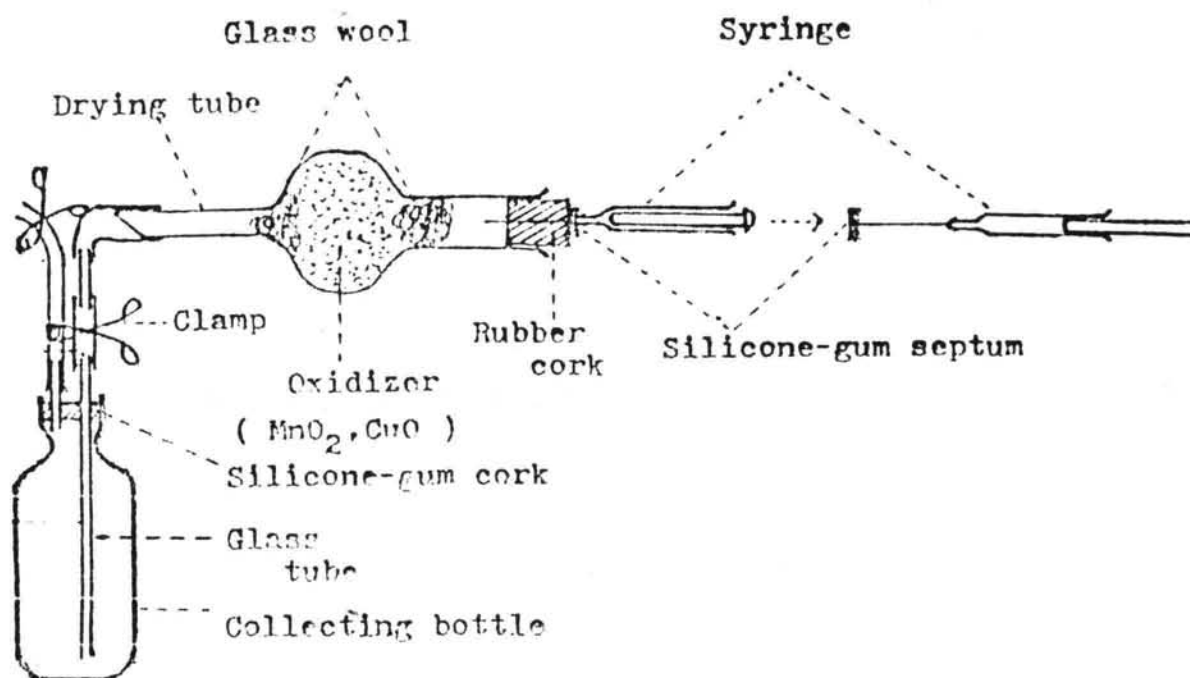
The sample gases for analysis are collected by a method of the air displacement, under an atmospheric state, as shown in the Figure-1.

FIG.-1: APPARATUS FOR THE COLLECTION OF THE GAS SAMPLE.



Some of the collected gas samples are an exhaust gas which collected under a condition of the normal combustion assemblys, one of the disassembled air-cleaner, another one of the dissassembled air-cleaner and turbo-charge. And each conditional gas is reclassified into a state of the idle speed, one of the high speed and another one of the continuous high speed. So that, there are nine gas samples had been determined by us. At first, the exhausted gases which collected in the bottles, were carried out by a syringe with septum of the silicone-gum which was used as a sealling of the needle. After determining the original gas components which contained in the bottle, the bottle was adapted with a drying tube which packed 15 grammes of oxidizer. We had carried out the oxidized gases, through the heat tube of oxidizer, by the syringe. The oxidized gases, such as carbon dioxide, water, sulfur oxides and nitrogen oxides etc., had determined, too. Then, the used oxidizer is a mixture of equal amount of manganese dioxide and cupric oxide. And the apparatus of carrying out sample gas is shown as Figure 2.

FIG.-2: APPARATUS OF THE CARRYING OUT SAMPLE GAS.



The sample gases were determined by RMU-6GC Mass spectrometer, with 2 meters length, 0.3 centimeter I.D. of stainless steel column which packed Molecularsieve-5A connecting with an equal amount of Porapak-Q material.^{(1),(2)} And the carrier gas flowed with 30 milliliters per minute (about 0.6 kilogramme per square centimeter) of a helium gas. The programming temperature increased from 40° to 250°C, with 10°C per minute. The components of sample gas were identified by the Mass spectrometry as above mention. And the data of pattern percentage of abundance about the main components, such as oxygen, nitrogen and carbon dioxide etc., are shown in Table 1.

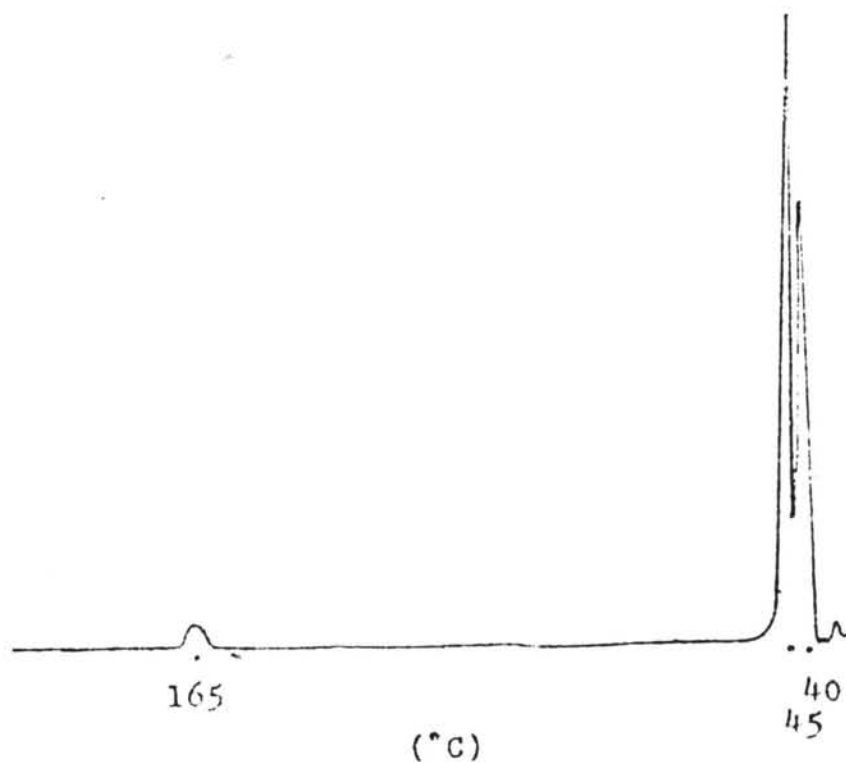
TABLE 1: The Presentational Origin Gas which was Determined by the GC Mass Spectrometry.³

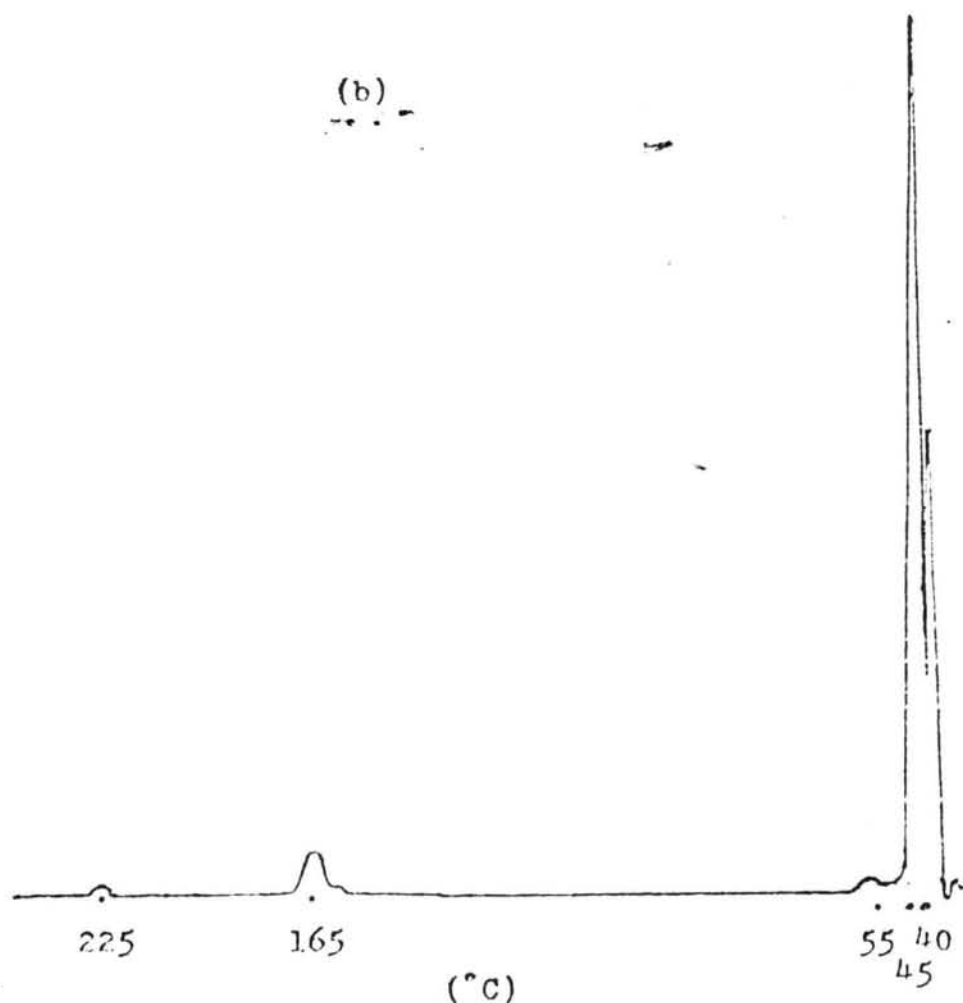
Condition	Speed	Temp. of oven (°C)	Pattern intensity of abundance (div.) of the probable fragment mass-number (M/e)
Normal	High speed	40	4(2.5), 16(19.2), 18(2.7), 20(2.0) He O H ₂ O Ar ²⁺
			28(15.5), 32(64.5--), 40(27.0). CO O ₂ Ar
		45	4(3.5), 14(25.8), 18(2.8), 28(64.5) He N H ₂ O N ₂ ,
			--), 29(3.5), 32(6.6), 33(0.1), C ₂ H ₄ C ₂ H ₅ S HS
			34(0.5), 37(0.2), 39(0.2), 40(6.8) H ₂ S C ₂ H ₃ C ₂ H ₃ C ₂ H ₄
			4(3.0), 12(4.7), 16(1.7), 28(64.5) He C O, CH ₄ CO,
			--), 29(1.2) C ₂ H ₄ C ₂ H ₅
		165	4(4.0), 12(1.7), 16(3.0), 17(4.0). He C O, CH ₄ HO
			18(12.5), 22(1.0), 28(8.5), 41(1.0) H ₂ O CO ₂ ²⁺ CO, C ₂ H ₄ C ₂ H ₅
			44(48.0) CO ₂ , C ₃ H ₈
		225	4(6.0), 14(8.3), 16(4.0), 17(10.0) He CH ₂ CH ₄ , O HO
			, 18(35.2), 28(58.0), 29(3.2), 32 H ₂ O C ₂ H ₄ , CO C ₂ H ₅ O ₂
			(64.5--), 36(4.5), 40(8.6), 44(9.0) C ₃ C ₂ H ₄ C ₂ H ₈ ,
			, 91(26.0), 92(20.5) CO ₂ C ₆ H ₅ ·CH ₂ C ₆ H ₅ ·CH ₃

Though those informations of the Mass spectrum of each kind of the sample gas were much similar each other, but only the GC spectrum of the sample gas which exhausted under the idle speed, were contained less of the incomplete combustion components, such as carbon monoxide and low hydrocarbons, than the other high speed and continuous high speed contained. The above result is shown in Figure-3.

FIG. 3: GC SPECTRUM OF AN IDLE SPEED (a) EXHAUSTED GAS WHICH CONTAINED LESS CO AND HC COMPONENTS, THAN THE OTHER HIGH SPEED OR CONTINUOUS HIGH SPEED DID (b)

(a)





Now, the nine kinds of the exhaust gas collected was identified, and the main components, shown to be oxygen, nitrogen and carbondioxide etc. Its relative pattern intensity of abundance was calculated into the pattern percentage of the abundance against the most abundance of nitrogen component. And the original exhaust gas compared to the oxidized one.

Three kinds of the exhaust gas were collected under a condition of normal driving. Its relative pattern percentage of the abundance are shown as Table 2.

TABLE 2: PATTERN PERCENTAGE OF THE ABUNDANCE OF THE MAIN COMPONENTS WHICH WERE CONTAINED IN AN EXHAUST GAS, AND COLLECTED UNDER A CONDITION OF THE NORMAL DRIVING.

State Speed	Original gas %		Oxidized gas %		Increased CO ₂ %
	O ₂	CO ₂	O ₂	CO ₂	
Idle speed	27.78	2.61	34.31	22.00	19.39
High speed	23.13	4.42	25.05	46.71	42.29
Continuous high speed	25.53	4.57	24.62	29.14	24.57

The other three kinds of the exhaust gas were collected under a condition of the disassembled air-cleanner. Its relative pattern percentage of the abundance are shown as Table 3.

TABLE 3: PATTERN PERCENTAGE OF THE ABUNDANCE OF THE MAIN COMPONENTS WHICH WERE CONTAINED IN AN EXHAUST GAS, AND COLLECTED UNDER A CONDITION OF THE DISASSEMBLED AIR-CLEANNER.

State Speed	Original gas %		Oxidized gas %		Increased CO ₂ %
	O ₂	CO ₂	O ₂	CO ₂	
Idle speed	32.49	4.61	31.5	54.31	49.70
High speed	29.75	1.22	20.84	55.32	54.10
Continuous high speed	17.17	4.92	32.12	15.01	10.09

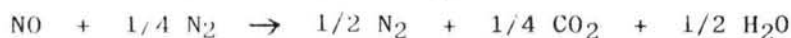
Another three kinds of the exhaust gas were collected under a condition of the disassembled air-cleanner and turbo-charge. Its relative pattern percentage of the abundance are shown as Table 4.

TABLE 4: PATTERN PERCENTAGE OF THE ABUNDANCE OF THE MAIN COMPONENTS WHICH WERE CONTAINED IN AN EXHAUST GAS, AND COLLECTED UNDER A CONDITION OF THE DISASSEMBLED AIR-CLEANNER AND TURBO-CHARGE.

State Speed	Original gas %		Oxidized gas %		Increased CO ₂ %
	O ₂	CO ₂	O ₂	CO ₂	
Idle speed	24.29	1.81	35.30	36.78	34.97
High speed	33.74	2.82	31.32	13.83	11.01
Continuous high speed	34.05	5.08	33.09	130.76	125.68

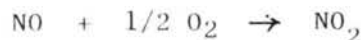
DISCUSSION

From an above showed data of the Table 1 and features of the Figure 3, we can see that exhausted gases which collected under an atmospheric condition, had a small amount of the hazardous carbon monoxide and low hydrocarbons, and had only a trace of hydrogen sulfide on the GC and the Mass spectrum. However, we could not find out other hazardous components, such as nitrogen oxides NO_x and sulfur oxides SO_x , since the atmospheric exhaust gas was too dilute in the bottle, and also the nitrogen monoxide was so unstable below 700°C . Because it is easily absorbed by an active carbon, hydrogen, hydrocarbons and amines, such as carbon monoxide, methane and ammonia gases etc., at that low temperature. And it's also easy to react with catalytic exhaust-pipe wall of the metal oxides, such as Fe_2O_3 , Cu_2O and NiO etc. Those reactions are shown below (4).



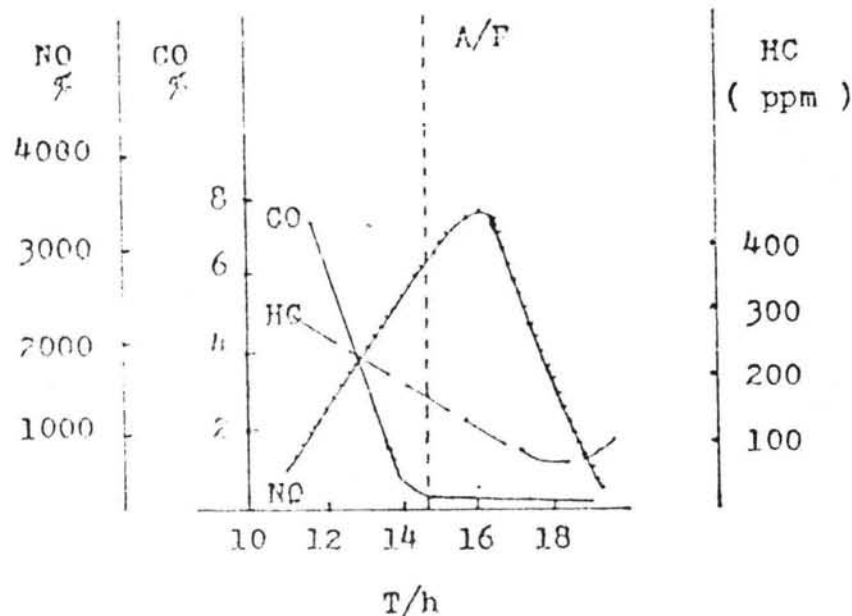
In generally, the 2½T truck exhausted gases always contained only 500 ppm of the nitrogen monoxide within 1% of the contained oxygen (5), since it had assembled the transmission-controlled spark (TCS) and the exhaust-gas recirculation (EGR) etc. devices. (6)

Though the nitrogen monoxide is easy to oxidized to a stable nitrogen dioxide by the oxygen in air, it is only able to occur at 1000°C . The reaction is as below. (1)



On the other hand most of nitrogen monoxide is produced only on a right ratio of the air versus fuel, A/F relation. According to the relation, on the less or excess amount of the air, the nitrogen monoxide may be less produced out. Same as the engine has accelerated its speed or disassembled its combustion devices, the exhaust gas may contain less NO_x gases, as the following Figure 4 showed. (5)

FIG. 4: THE MOST OF NO GAS PRODUCED ON A RIGHT RATIO OF THE AIR VERSUS FUEL



So that, we hadn't determined out the nitrogen dioxide, too. But we could see that why a gas exhausted on the idle speed contained a less amount of carbon monoxide and hydrocarbons. In other words, a gas exhausted on the high speed or on the continuous high speed, had plenty of incomplete combustion components, such as carbon monoxide and hydrocarbons. And we also could find out that oxidized exhaust gas had increased the amount of carbon dioxide, more than the original exhaust gas had, as Table 2, Table 3 and Table 4 showed.

Now, if we postulate these data into an other form of Table 5 and Table 6, as the shown below, then we could see the relation clearly.

TABLE-5: THE PRODUCED CO₂ WHICH CONTAINED IN THE ORIGINAL EXHAUST GAS.

% Condition Speed	Normal	Disassembled air-cleaner	Disassembled air cleaner and turbo-charge	Average
Idle speed	2.61	4.61	1.81	3.01
High speed	4.42	1.22	2.82	2.82
Continuous high speed	4.57	4.92	5.08	4.86
Average	3.87	3.58	3.24	

TABLE-6: THE PRODUCED CO₂ WHICH CONTAINED IN THE OXIDIZED EXHAUST GAS.

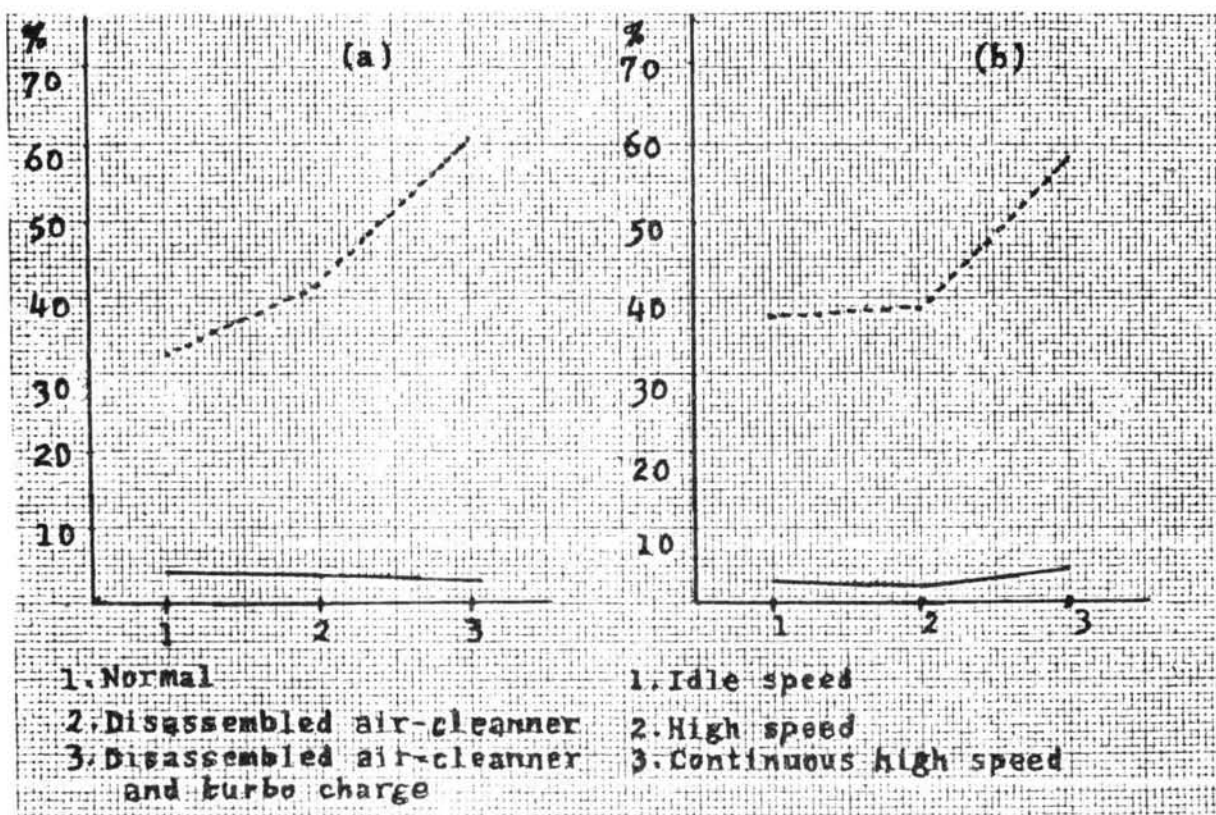
% Condition Speed	Normal	Disassembled air-cleaner	Disassembled air cleaner and turbo-charge	Average
Idle speed	22.00	54.31	36.78	37.70
High speed	46.71	55.32	13.83	38.62
Continuous high speed	29.14	15.01	130.76	58.30
Average	32.62	41.55	60.46	

From an above data of Table 5, we can see that the more combustion assemblys had disassembled, the more carbon dioxide had decreased. In other words, the more combustion devices had disassembled the more incomplete combustion gases was produced such as carbon monoxide and low hydrocarbons etc. So that, the oxidized exhaust gas would produce a carbon dioxide more than the original exhaust gas, as above data showed. By the same reasons, the more speed had accelerated, the more carbon dioxide had decreased. Though the continuous high speed had increased its average carbon dioxide up to 4.86% value disproportionally, but it might be an abnormal operation which occurred on the experimental less correctness. We can refer to the Table 6, for the understanding relation, too. Though these produced carbon dioxide was a product which had oxidized from the original exhaust gas, but the produced carbon dioxide could cause a similar relation, the more combustion assemblys had disassembled, the more carbon dioxide had increased, which was inverted to the Table 5. And also, the more speed had accelerated, the more carbon dioxide had increased.

Now, if we plot the average value of data on the following Figure 5, we could clearly find that relations, between the disassembling devices or not and accelerating speed or not. So that, we can prefer to the best driving conditions and take the appreciated technics.

FIG. 5: THE RELATIONS BETWEEN THE ORIGINAL EXHAUST GAS AND THE OXIDIZED ONE. (a) THE PRODUCED CO_2 AGAINST TO THE DIFFERENT CONDITIONS OF COMBUSTION DEVICES. (b) THE PRODUCED CO_2 AGAINST TO THE DIFFERENT SPEED OF DRIVING.

Solid line ——— denotes the original exhaust gas.
Dash line - - - - - denotes the oxidized exhaust gas.



CONCLUSION

Depend on the result of the above analysis, the exhausted gases which expelled out of the 2½T truck had shown the relations, the more combustion assemblies had disassembled, the more incomplete combustion gases, such as the hazardous carbon monoxide, low hydrocarbons and hydrogen sulfide etc., was produced. And we could be sure, the more speed had accelerated uncorrectly, the more incomplete combustion gases was produced, too. These hazardous gases are not only to make an air pollution, to harm our mankind's health, but also to consume our fuel and money.

So that, we would like to tell all drivers "Do not accelerate your speed or to disassemble your combustion devices unrighteously". And also to advise all vehicle makers that they should develop combustion control devices which could consume oil regularly, even though at greatest acceleration.

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APPLICATION OF ION CHROMATOGRAPHY IN ENVIRONMENTAL CHEMICAL ANALYSIS

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ABSTRACT

Since 1975, ion chromatography (IC) has become a widely accepted method for the determination of ionic species. The basic limitations of conventional IC come from the combined characteristics of the suppressor column and electrical conductivity detector. However with the improvement in new detectors, column technologies, and special eluent systems, working range of IC can be further extended. We have applied new techniques in IC for analyzing ionic species in industrial waste and pollutants. Our results summaries as follows.

1. The analysis of sub-ppm level of cyanide and sulfide by potentiometric method using ion-selective electrode and amperometric method.
2. Determinations of polyvalent anions like polyphosphonate, EDTA, NTA by UV-Vis spectrophotometric method with post-column reacting system (PCR).
3. Using single-column chromatography and PCR system to detect certain ions of inner transition metals and lanthanides.
4. Monitoring ionic surfactant in waste streams with mobile phase ion chromatography.
5. Tracing the hydrolysis degradation products of organophosphorus pesticides by dual detector device.

INTRODUCTION

With the industrialization trend in most of the countries, a world-wide pollution problem becomes more and more serious in the Asian region. To ensure the healthy individuals with a clean environment for the people living in this area, the key chemicals and the toxic/anti-toxic pathways in human being and surrounding environment have to be continuously investigated and monitored.

Many of the pollutants, which severely affect the physiological environment, are anions (cations) or capable be converted to anions (cations). Conventional methods for the analysis of anions (cations) are either complicated or expensive.

H. Small and T. S. Stevens (The Dow Chemical Company) introduced ion chromatography (IC) method in 1975. They tried to develop a simple, reliable method for the analysis of the water soluble polypollutant ions.¹ Since then, the applications of

IC method on analyzing various environmental genotoxics have increased rapidly. But there are basic limitations of conventional IC due to the combined characteristics of the suppressor column and electrical conductivity detector.

In this paper, we intend to apply or develop certain new IC techniques in order to further extend its application range in five particular environmental analyses. The first effort is to determine the sub-ppm level cyanide and sulfide. The second is polyvalent anions, such as polyphosphate, ethylene-diamine tetracetic acid (EDTA) and nitrilotriacetic acid (NTA), detection techniques. The third is inner transition metals and lanthanides determinations. The fourth part includes monitoring the ionic surfactants in waste streams. The fifth part is tracing the hydrolysis degradation products of organophosphorous pesticides.

EXPERIMENTAL

DIONEX Model-10 Ion Chromatograph was used in most of our works. The fabrication of the silver sulfide and silver sulfide-silver iodide working electrodes has been described elsewhere.² For post column reacting (PCR) system, Sage Model 375A tubing pump was used to transfer the secondary electrolyte. A Beckman Model 3500 digital pH meter was used for potentiometric measurements. For amperometric method, the Metrohm Model 656 electrochemical cell and Model 641 VA detector were used. The separator used was a 3x250mm column, slurry packed with 250-325 mesh XAD-1 anion exchange resin prepared by chloromethylation and amination.³ $1 \times 10^{-5} \text{M}$ potassium hydrogen phthalate with pH=6.25 was used as eluent. A DIONEX HPIC-AS4 column was also used. For the latter columns, the solution consisting of 14.7mM 1,2-diamino ethane, 10mM sodium dihydrogen borate and 1.0mM sodium carbonate was used as eluent. For the determination of polyvalent anions, the system consists of Tracor Model 950 HPLC pump, HPIC-AS7 separator, 0.03-0.07N Nitric acid eluent and 0.6 g/l Ferric nitrate with 2% perchloric acid PCR reagent. In the detection of transition metals and lanthanides, gradient elutions were performed with two M6000A Water Associates pumps equipped with a Water M660 gradient programmer. Spectra physics Model 770 UV-VIS spectrophotometer was used as the detector. Vydač 401 TP 4.6 20 μm , Nucleosil SA 10 μm and Partisil SCX 10 μm 4x300mm columns were used as separators. Different types of chelating eluents such as citric acid, tartaric acid, 2-methylsuccinic acid and lactic acid were studied. The pH effect of eluents were also tested. In MPIC, the C₁₈ reverse-phase column was used as the separator. quaternary ammonium hydroxide solution with acetonitrile or methanol as organic modifier were used as eluents for the sepa-

ration of anionic surfactants and metal cyanide complexes.

RESULTS AND DISCUSSION

Determination of Cyanide and Sulfide

The calibration curve of cyanide with the silver sulfide electrode in a XAD-1 separator and 0.01N sodium hydroxide eluent was shown in Fig. 1. Non-Nernstian response was observed for on-column preconcentration sample (fig.2). The interferences from bromide, iodide and thiocyanate were obviously reduced after the separator was employed. Fig.3 showed the separation chromatogram of cyanide, bromide and iodide by both conductivity and potentiometric methods.

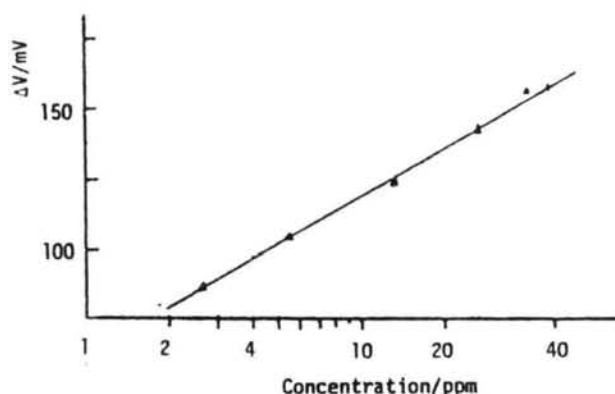


Fig.1: The calibration curve of cyanide

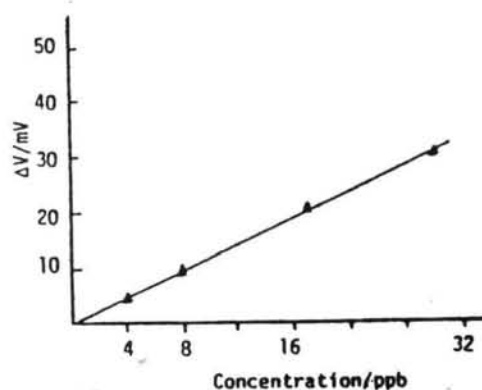


Fig.2. The calibration curve of 1 ml preconcentrated cyanide sample.

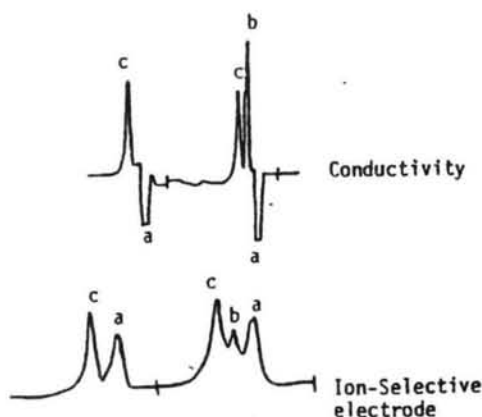


Fig.3. The separation of cyanide from bromide and iodide (a) $H_2O + HCN(CN^- 2.6ppm)$; (b) $Br^- 5ppm$; (c) $I^- 5ppm$.

As the H_2S and HS^- species exist under these eluent conditions, sulfide interference was still present. By using a HPIC-AS4 column, the cyanide and sulfide were well separated and quantitated. The chromatogram with amperometric detection was shown in Fig.4. This method gave a better sensitivity than that of potentiometric method in the determination of both cyanide and sulfide. But oxidizing reagents such as hydrogen peroxide and hypochlorite would seriously interfere the results.

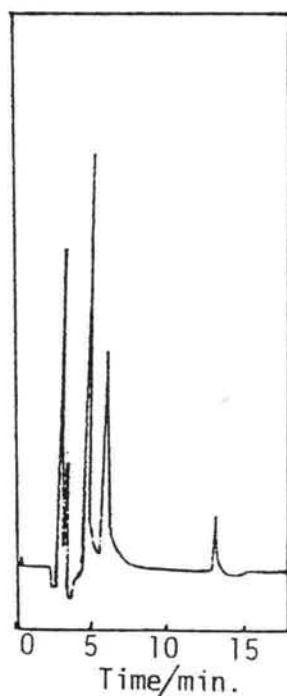


Fig.4. Separation of cyanide, sulfide and bromide.
Column: HPIC-AS4; Sample size: A= HS^- 20ppb, B= CN^- 20ppb, C= Br^- 30ppm; Eluent: 14.7mM diaminoethane + 10mM sodium dihydrogen borate + 1.0mM sodium carbonate.
Flow Rate: 2 ml/min.; Detection: Amperometric, silver electrode, 0.0V.

Determination of Polyvalent Anions

In the normal IC column, the capacity is about 0.03 meq/g. Most polyvalent anions would be retained strongly in the column. In order to achieve reasonable elution time and good separation, a very low capacity anion separator HPIC-AS7 was employed, and nitric acid was used to further reduce the coulombic interaction between stationary phase and analyte. The post column reacting system provided excellent sensitivity for these polyvalent anions. Fig.5 showed a typical chromatogram of certain polyvalent anions which might be practical for detergent plant.

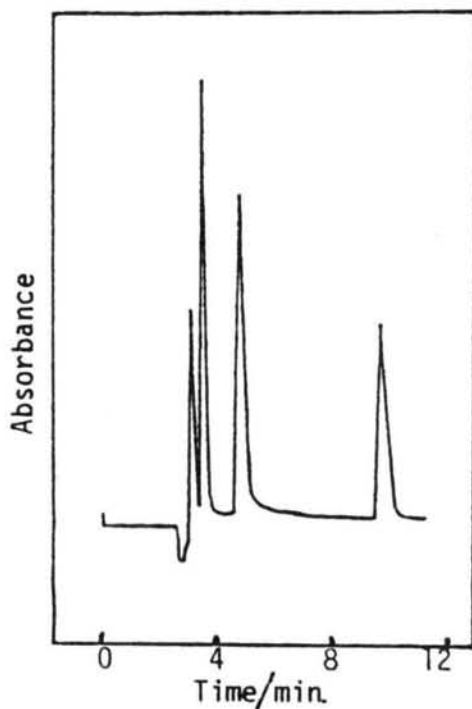


Fig.5. Separation of polyvalent anions. Column: HPIC-AS7; Sample size: A=NTA 25ppm, B=pyrophosphate 40ppm, C=EDTA, D=tripolyphosphate 80ppm; Eluent: 0.07N HNO₃; Flow Rate: 0.5 ml/min.; Secondary Electrolyte: 0.6g/l ferric nitrate + 2% perchloric acid; Detection: spectrophotometric detection, 330nm.

Determination of Transition Metals and Lanthanides

The result shown in Fig.6 was a diagram of the isocratic separation of transition metals by 10µm Nucleosil SA. Lactic acid and 2-methylactic acid have been shown to be the best complexing reagents suitable for the ion-exchange separation of both transition metals and lanthanides.

The effect of pH value on the separations was examined and it was found that at the start of the separation on bonded phases the eluent was susceptible to significant pH changes as a result of protons liberated on complexation with lactic acid.

The isocratic separation of some metals under pH3.5 was shown in Fig.7. A few cases of better separation of transition metals and lanthanides with gradient elution were shown in Fig.8, 9 and 10. Iron(III) and iron(II) could be determined simultaneously. The changes in the elution time of lead(II) were due to its different complex formation constants with tartrate and lactate. Fig.11 showed the application of on-column concentration for sub-ppm metals.

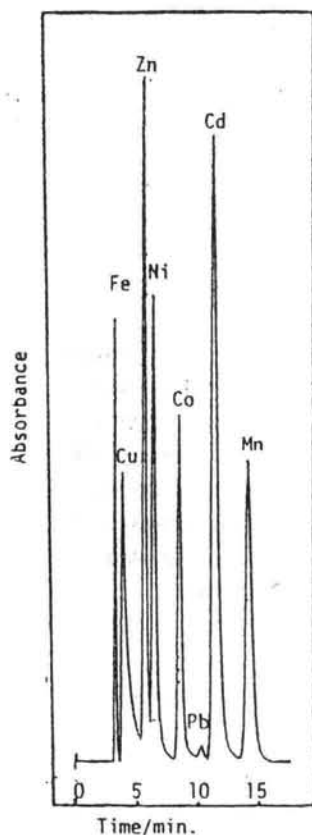


Fig.6

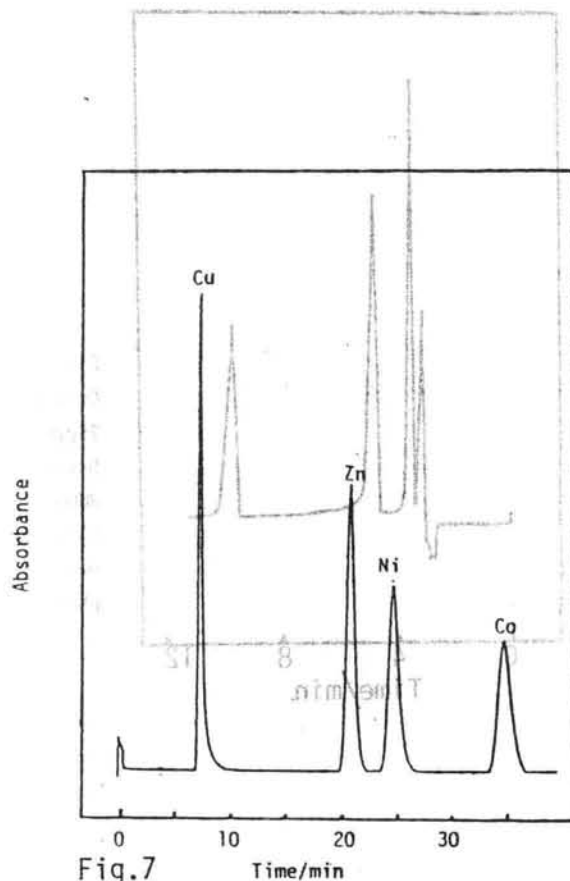


Fig.7

Fig. 6. Separation of the transition metals on 10µm Nucleosil SA.

Sample size: Fe(III) 10 ppm, Cu 10 ppm, Zn 10 ppm, Ni 10 ppm, Co 10 ppm, Pb 0.5 ppm, Cd 50 ppm, and Mn 10 ppm. Experimental conditions: 4mm x 300nm column; 20µl sample loop; 0.1 M sodium lactate and pH 4.5; detection at 498 nm after post-column reaction with PAR-THAM.

Fig.7. Separation of the transition metals on

10 µm Nucleosil SA. Experimental conditions:

Same as Fig. 6 , Except the pH of sodium lactate is 3.5.

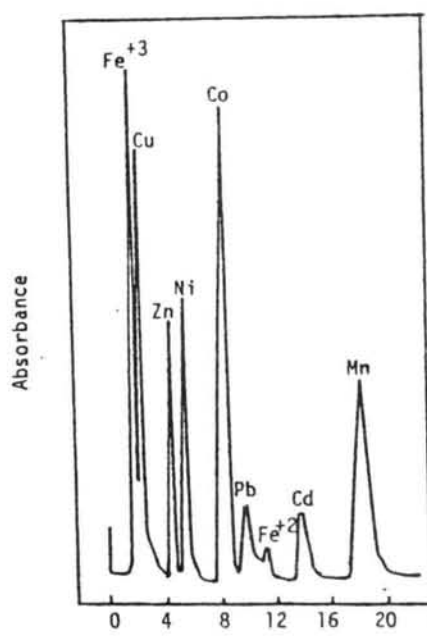


Fig.8 Time/min

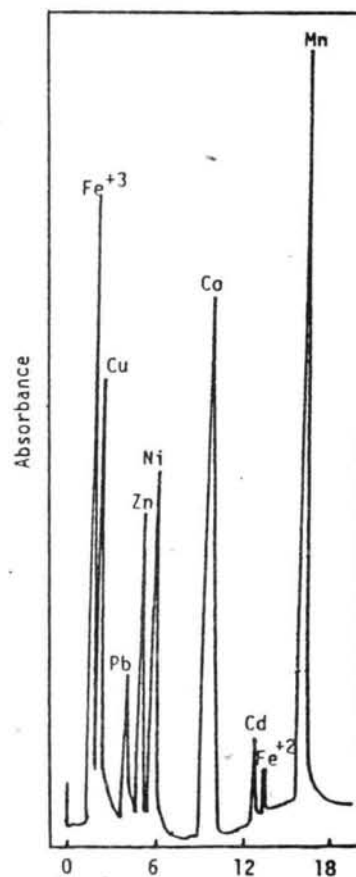


Fig.9 Time/min

Fig. 8.. Separation of the transition metals on 10µm Nucleosil SA. Sample size: Fe(III) 22 ppm, Cu 10 ppm, Zn 10 ppm, Ni 10 ppm, Co 26 ppm, Pb 4.4 ppm, Fe(II) 5 ppm, Cd 10 ppm, and Mn 50 ppm. Experimental conditions: 4mm x 300mm column; 20µl sample loop; linear program from 0.04 mol·l⁻¹ to 0.12 mol·l⁻¹ sodium lactate over a 20-min period at 1 ml/min flow rate and pH 4.5; detection at 510nm after post-column reaction with PAR-ZnEDTA.

Fig. 9. Same as the above, except linear program from 0.04 mol·l⁻¹ to 0.18 mol·l⁻¹ sodium tartrate eluent was used.

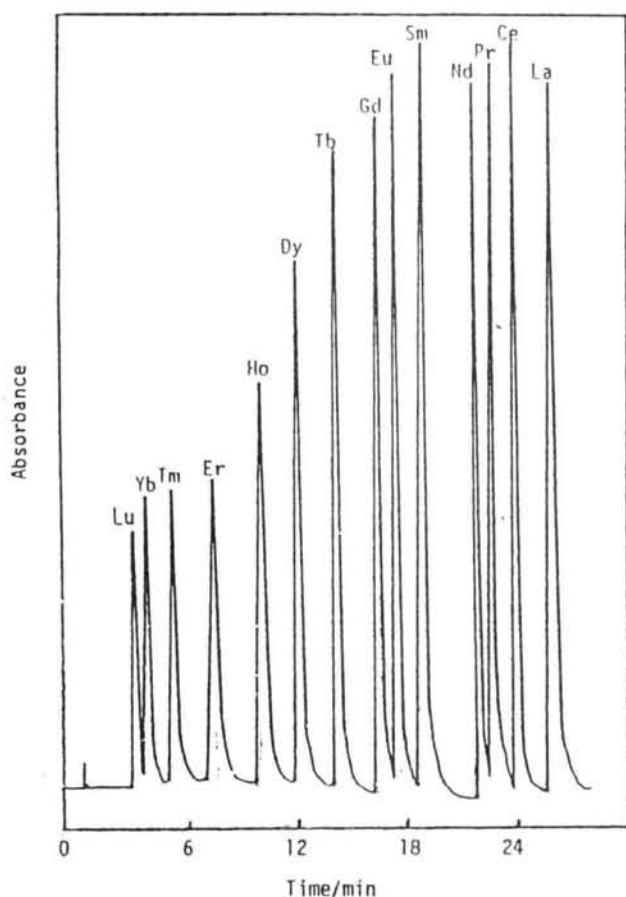


Fig.10. Separation of the lanthanides on 10 μ m Nucleosil SA. Experimental condition: 4mm x 300mm column; 20 μ l of a solution containing $\sim 10\mu\text{g}\cdot\text{ml}^{-1}$ of each lanthanides; linear program from 0.01 mole $\cdot\text{l}^{-1}$ to 0.04 mole $\cdot\text{l}^{-1}$ 2-methyl lactic acid over a 30-min period at 1 ml $\cdot\text{min}^{-1}$ and pH 4.6; detection at 600 nm after post-column reaction with Aresenarzo I.

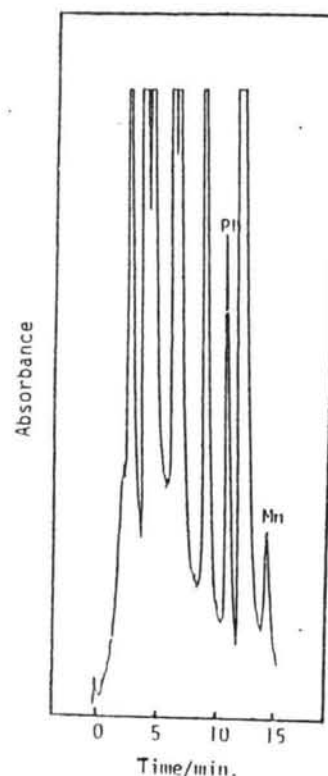


Fig.11. Separation of the transition metals after on-column preconcentration of 5 ppb Pb, 5 ppb Mn, and 0.1 ppm other six metals. Experimental condition as Fig. 6.

Mobile Phase Ion Chromatography (MPIC)

Mobile phase ion chromatography is the optimal separation mode for hydrophobic ions such as alkyl and aryl sulfonates and sulfates, metal cyanide complexes, SCN^- , BF_4^- , ClO_4^- , and quaternary and alkylamines. The mechanism of separation is ion-pairing and adsorption which occurs on a neutral resin. This separation theory has been discussed in detail by Bidlingmeyer⁴ and Iskandarani.⁵ Figures 12 and 13 showed some applications of MPIC to anionic surfactants and iron cyanide complexes. C_{18} was used as the column packing material, but the eluent system with rather higher basicity obviously reduced the life time of column by hydrolyzing the silica gel backbone. Therefore in the future work, a polymer type of reverse phase packing material would be tested and compared.

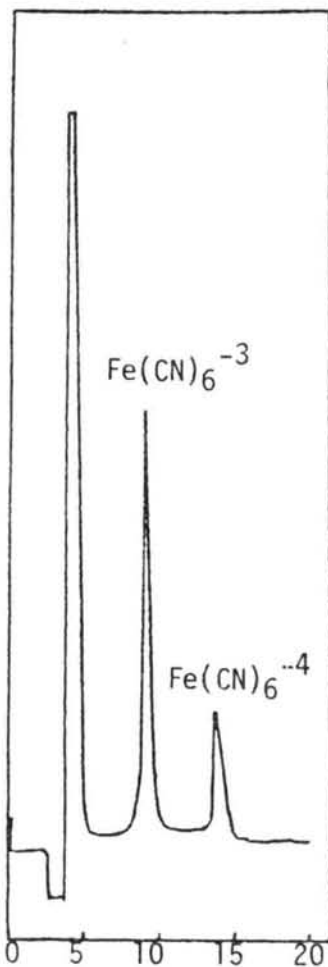


Fig.12 Time/min.

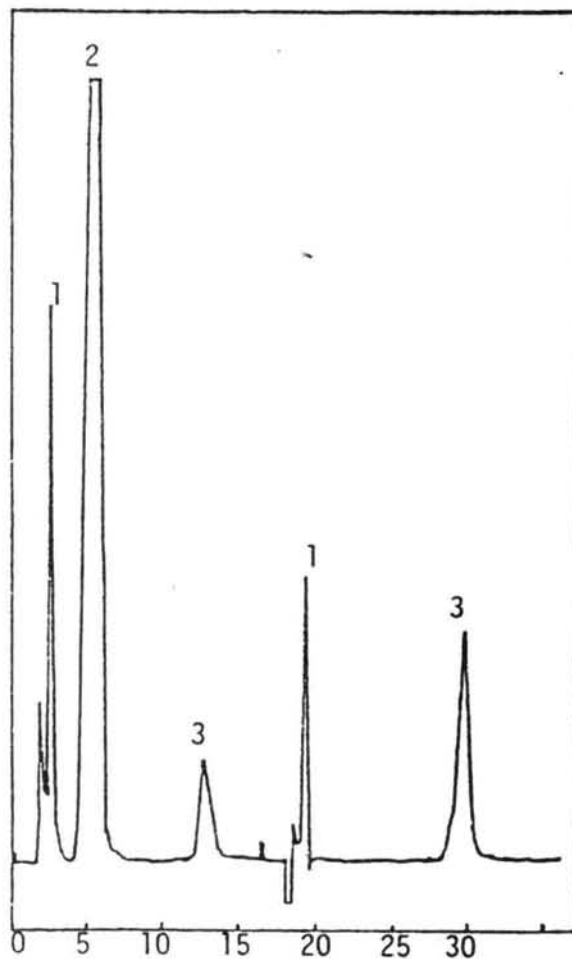


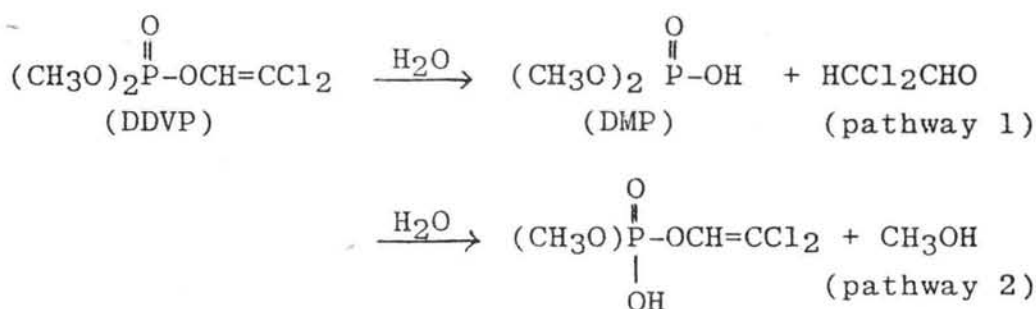
Fig.13 Time/min.

Fig.12. Separation of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. Column: Partisil C18, 10 μm , 3x400mm
Sample size: $\text{Fe}(\text{CN})_6^{3-}$ 23.6ppm, $\text{Fe}(\text{CN})_6^{4-}$ 29.2ppm; Eluent: 40% CH_3CN + TBAH 2mM + Na_2CO_3 0.02mM; Flow Rate: 1ml/min.; Detection: Conductivity.

Fig.13. Separation of anionic surfactants. Column: Partisil C18 10 μm 3x400mm;
Sample size: A: 1=aerosol AY 10ppm, 2=SDS 200ppm, 3=aerosol OT 20ppm,
B: 1=aerosol AY 6ppm, 3=aerosol OT 50ppm; Eluent: 60% CH_3OH + 0.01g/l NH_4OAc ;
Flow Rate: 1ml/min.; Detection: Conductivity.

Dual Detector System

Figures 14, 15 showed the separation and detection of certain anions by conductometric detector coupled with UV-VIS spectrophotometric detector. The obvious advantages of UV detection for nitrite and nitrate over conductivity are better sensitivity and less interference from chloride. Therefore this system offered a better method for the determination of nitrite in preserved foods. In Fig.16, the coupled amperometric and conductometric detectors demonstrated more applications in the study of hydrolysis mechanism of DDVP pesticide. DDVP may hydrolyzed in the following two possible pathways.



With the strong oxidizing potential set on the first amperometric detector, the dimethoxylphosphonic acid (DMP) and dichloroacetaldehyde can both be detected as ionic form in the second conductometric detector. The result showed that pathway 1 is predominant.

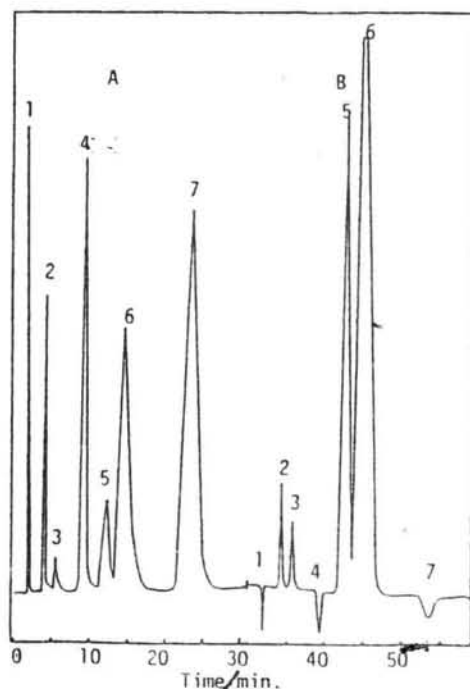


Fig.14. Detection of normal anions by dual detectors. Column: HPIC-ASC-1 +ASC-1; Eluent: 0.003N NaHCO₃ + 0.0024N Na₂CO₃; Sample Size: 1=F⁻ 3ppm, 2=Cl⁻ 4ppm, 3=NO₂⁻ 2ppm, 4=PO₄⁼ 50ppm, 5=Br⁻ 10ppm, 6=NO₃⁻ 30ppm, 7=SO₄⁼ 50ppm; Detection: A: conductivity, B: spectrophotometric 192nm.

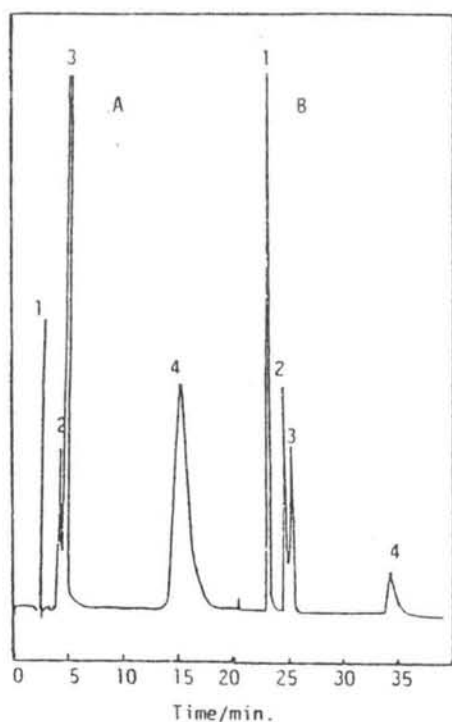


Fig.15. Detection of iodate and bromate by dual detectors. Column: HPIC-AS1 +ASC-1; Eluent: same as Fig.14; Sample Size: 1= IO_3^- 16ppm, 2= BrO_3^- 14ppm, 3= Cl^- 10ppm, 4= ClO_3^- 80ppm; Detection: A: conductivity, B: spectrophotometric 195nm.

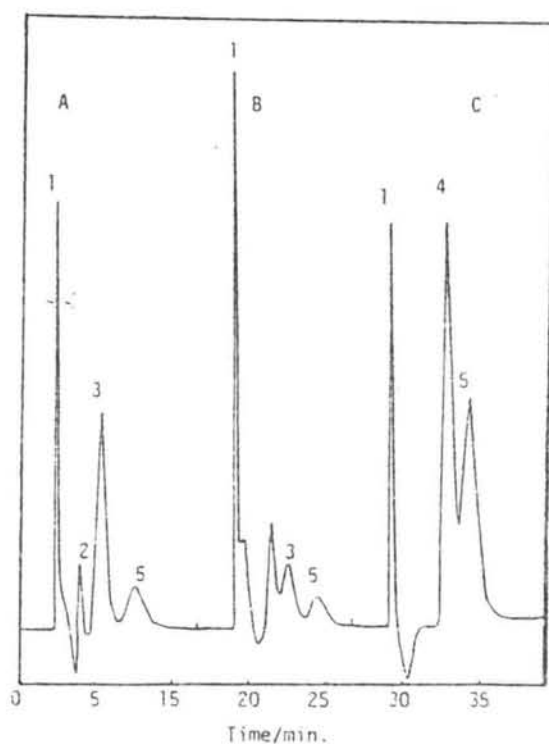


Fig.16. Identification of ionic species from the hydrolysis of DDVP by dual detectors. Column: HPIC-AS + ASC-1; Eluent: 0.0024N Na_2CO_3 + 0.003N NaHCO_3 ; Sample Size: A: standard: 1=DMP 10ppm, 2= Cl^- 1ppm, 3= $\text{CHCl}_2\text{COO}^-$ (DA) 15ppm, 5= PO_4^{3-} 4ppm, B:hydrolysis products of DDVP, 1=DMP, 3=DA, 5= PO_4^{3-} ; C:hydrolysis products of DMP 1=DMP, 4= PO_3^{3-} , 5= PO_4^{3-} .

CONCLUSION

Potentiometric measurement using a silver sulfide based ion selective electrode and amperometric detector using silver working electrode both proved to be a promising method in detecting and quantification of cyanide and sulfide. The UV-VIS spectrophotometric method with suitable postcolumn reacting system provides a new sight for the polyvalent anions, transition metals and lanthanides detections. MPIC offered another means to monitor the ionic surfactants, metal cyanide complexes and many other hydrophobic ionic species. The dual detector system certainly enlightened a new approach to enable us to understand more thoroughly and deeply the influence of toxicants or genotoxicants perhaps still unknown to us. Continuous efforts to develop advanced analytical techniques for the environment assessments would be essential to sustain healthy living surrounding for future.

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SURVEY OF ENVIRONMENTAL WATER IN THE BASIN OF LAKE KASUMIGAURA

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ABSTRACT

A simple and inexpensive method of survey of environmental water was developed and applied to the basin of Lake Kasumigaura by citizens and scientists.

This method is very simple, so anyone can practice easily, who has scientific knowledge and technique about average of a high school student.

It consists of three parts; observation of surroundings, biological survey, chemical analysis.

Results were plotted on maps to show local pollution and classified into histograms.

NATURE OF LAKE KASUMIGAURA

Lake Kasumigaura is located in Ibaraki prefecture, almost center of the Japan islands and near the Pacific Ocean. It is the second largest lake in Japan. The size of the lake and the area of the basin are about 220 Km^2 and 2200 Km^2 respectively, but it is very shallow as 4m in depth on average.

It lies in agricultural zone; rice field in lower alluvial plain and bean and vegetable field on heights.

Since the highly economic growth age (1960S), petro-chemical and steel industrial plants and other industries have been constructed around the lake. Recently this area also becomes residential section of Tokyo.

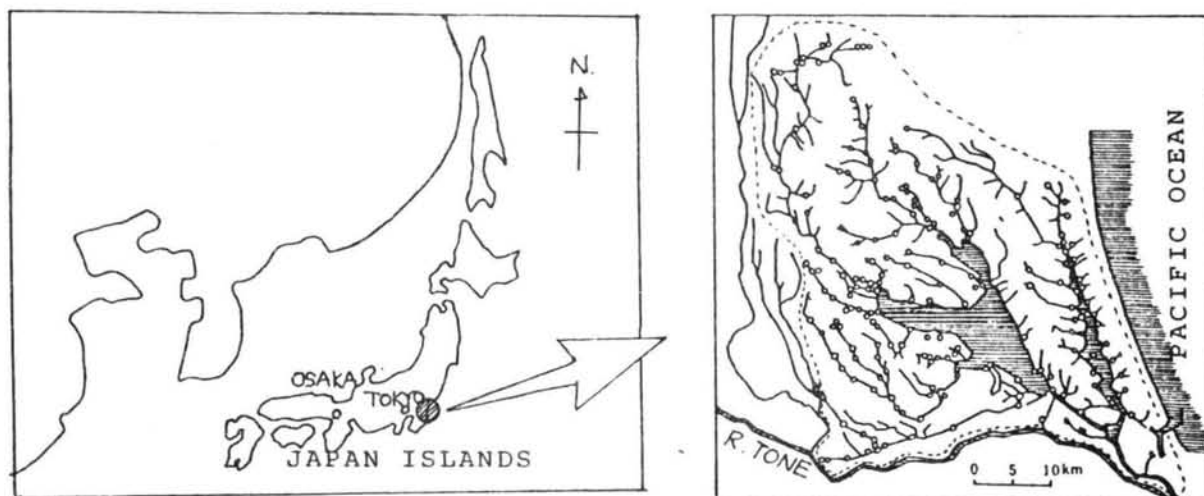


Fig.1 LOCATION OF LAKE KASUMIGAURA

Water quality of Lake Kasumigaura has been getting worse for this 30 years, with development of the basin. Till 1965, levels of COD were kept between 4 to 5 ppm, but afterwards the values were increasing and in the 1980s exceed 10 ppm.

To solve the problem of eutrofication of a lake, we must consider flow of chemicals among living and non-living things, that is ecosystem. Fig.2 shows the relationship between survey items and the ecosystem of a lake.

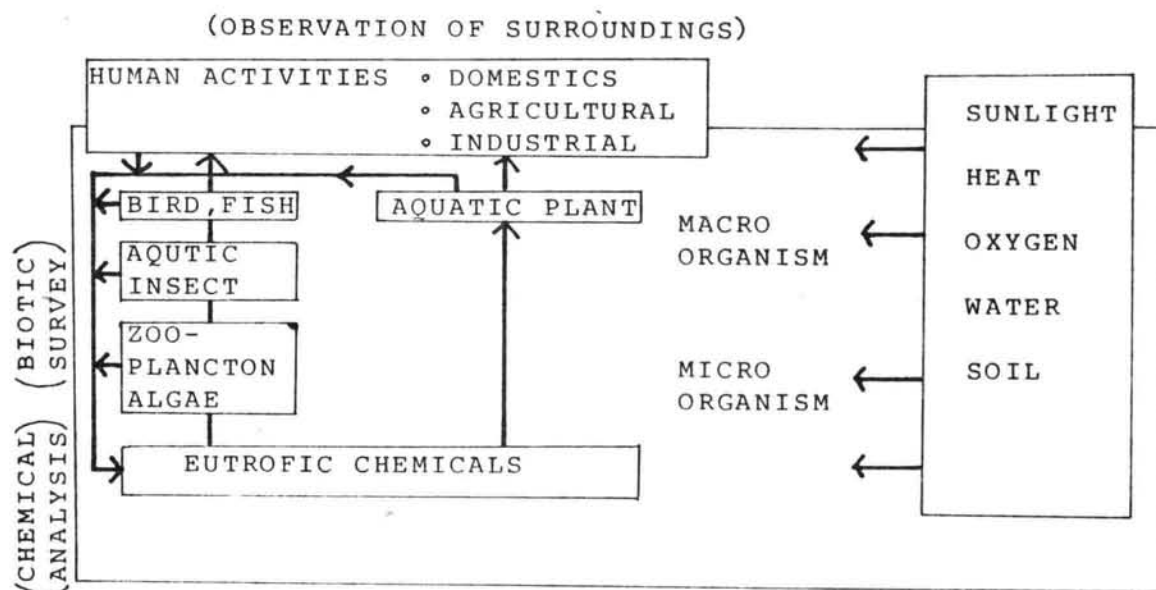


Fig.2 RELATIONSHIP BETWEEN SURVEY ITEMS AND ECOSYSTEM

SURVEY ITEMS

Observation of Surroundings

Contents of observation of surroundings are

- (1) date, name of the river, situation,
- (2) temperature of atmosphere and water, climate,
- (3) depth and width of the river, velocity of the flow,
- (4) sketch of the surroundings,
- (5) state of the inside of banks, water course, muddiness, color, smell of the water, state of the bottom,
- (6) aquatic life (biological survey).

Index of artification (or conservation of nature) is estimated from the results of observation of surroundings. Each item of observation of surroundings has three stages; A (the nature is conserved), B (partially artified), C (the nature is lost).

An index of artification at a surveyed point is formulated as $(3A+B)/(A+B+C)$ for A, B, C; the sum of the number of each stage at this point

Chemical Analysis

Water sample was collected in a well-washed beer bottle with a rubber stopper. Analytical methods are listed Fig.3.

$\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and total-N were measured with a simple colorimeter by Dr. AMAYA. His colorimeter has very simple circuit, but rather sensitive and stable.

Fluorescence of the water sample was observed through the protective glass under a UV lamp in a blackbox.

OBJECT	METHOD
PH	glass electrode PHmeter
COD	pottasium permanganese (100°C) method
$\text{PO}_4\text{-P}$	molybdenum blue simplified method
$\text{NH}_4\text{-N}$	indophenol blue simplified method
$\text{NO}_2\text{-N}$	GR reagent simplified method
total-N	reduced to NH_4 by Devarda's metal
fluorescence	irradiation of UV lamp
CO_3^{2-}	alkalinity by phenolphthaleine
HCO_3^-	alkalinity by methylorange
SO_4^{2-}	liquid chromatography
Cl^-	liquid chromatography
Na^+	emission spectroscopy
K^+	emission spectroscopy
Ca^{2+}	atomic absorption spectroscopy
Mg^{2+}	atomic absorption spectroscopy
Fe	o-phenanthroline spectrophotometry

Fig.3 ANALYTICAL METHODS

RESULT

In the 18-day survey of 1982, more than 170 participants jointed and collected samples at 202 points.

According to the histograms, main streams are more polluted than branches. The former flow through cultivated plain, and the latter do through less developed forest.

From the maps, it is clear that rivers are polluted through crowded city areas.

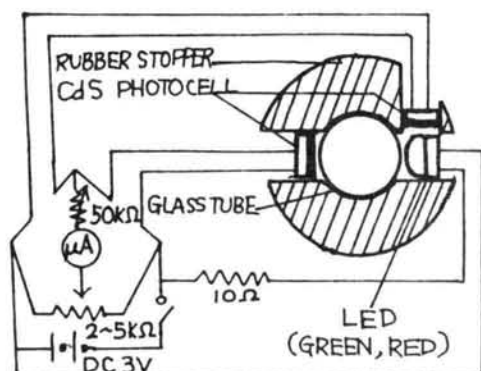


Fig.4 CIRCUIT OF COLORIMETER

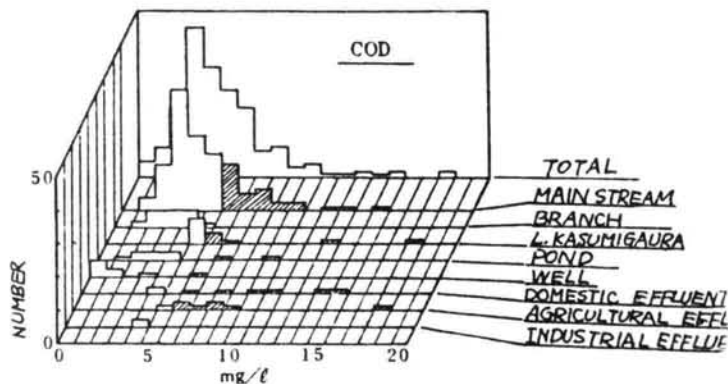


Fig.5 HISTOGRAM OF COD(Mn)

TERNARY COMPLEXES OF COPPER (II) AND THEIR
BIOLOGICAL SIGNIFICANCES

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A B S T R A C T

Much efforts have in recent years been directed towards the study of ternary complexes of copper (II) containing an α , α' -diimine or α , α' , α'' -triimine as the first ligand and an oxygen donor ligand as the second one. This is due to the fact that such complexes display unusual stability and can possibly serve as models for enzyme-metal ion-substrate complexes. In this paper a review will first be made of the recent development in the chemistry of these ternary complexes. Various aspects of the biological significance of these complexes will be examined. Finally results from our laboratory will be presented and discussed.

Introduction

In many biological systems, multiligand-multimetal ion equilibria dominate; that is mixed ligand or higher order complexes are formed. The simplest form of these species namely, a ternary complex², consists of a metal ion and two different ligands (other than the solvent). Such ternary complexes play an important role in metal ion catalyzed reactions³, as is exemplified by the enzyme-metal ion-substrate complex in biological fluids. However the roles assumed by ternary complexes of copper(II) extend beyond this. In the following the recent development in the chemistry of the copper(II) ternary complexes will first be reviewed. The biological significances of some ternary complexes will then be discussed.

Recent Developments In The Chemistry Of The Copper(II) Ternary Complexes

As part of the efforts to understand the roles of metal ions in biological systems, simple ternary metal complexes have been extensively studied in solution. In particular those of copper(II) have aroused considerable interest. This follows from the finding that, in solution, ternary systems in which Cu^{2+} is bound to a bidentate aromatic amine such as 2,2'-bipyridyl and a second bidentate ligand with oxygen atoms as donors, are more stable than the corresponding binary complexes⁴. Such enhanced stability has been attributed to the discriminating behaviour of the $[\text{Cu}(\text{bpy})]^{2+}$ species towards the incoming ligand. Thus when the bidentate oxygen donor ligand is replaced by a bidentate nitrogen donor ligand such as ethylenediamine the stability of the resultant ternary complexes is reduced to that expected statistically while with a 'mixed' ligand such as glycine containing N and O donor atoms, the observed stability is intermediate between the value for the bidentate nitrogen donor ligand and that for the bidentate oxygen donor ligand. The basic conditions for the formation of ternary copper(II) complexes have been reviewed by Sigel et. al.⁵

Following the solution studies, some of the ternary complexes of copper(II) have actually been isolated and characterised⁶⁻⁸ [Table 1]. In our laboratory we reported⁷ the synthesis and characterisation of ternary complexes containing o-phenanthraline (phen) as well as a bidentate oxygen donor ligands shown in Table 1. The electronic spectral absorptions of these complexes suggest D_{2h} symmetry around Cu(II). The mode of bonding of the oxygen donor ligand with the $[\text{Cu}(\text{phen})]^{2+}$ was examined through their electronic as well as infrared absorption spectra. Subsequently another series of ternary complexes was prepared⁸ in which the oxygen donor ligands were replaced by some amino acids [Table 1]. The bonding characteristics of these were studied and compared through infrared spectral, electronic spectral,

polarographic and electron paramagnetic resonance measurements.

Biological Significance Of Copper(II) Ternary Complexes

It has now been recognised that ternary complexes of copper(II) participate in several biological processes of which the roles of these complexes in the following four are comparatively well established : (a) enzyme-metal ion-substrate interaction, (b) transport of copper in blood plasma, (c) action of several antitumor drugs and (d) therapeutic action of pencillamine with respect to Wilson's disease. Selected examples of model ternary systems synthesized for study related to the above will be examined in the following sections.

A common feature of the ternary complexes of copper(II) designed for study of the specific function of cuproproteins is that histidine is often employed to be the first ligand. This arises as histidine has been found to participate in complex formation in many biological systems such as the carboxypeptidase A⁹, carbonic anhydrase B & C¹⁰, plastocyanin¹¹ and superoxide dismutase¹². A significant number of ternary amino acid complexes containing histidine has been prepared for various study. For example, an appreciation of the noncovalent interaction has been said to be one of the keys to understanding the specificity and high efficiency displayed by enzymes. Thus to investigate such interaction, the second amino acid of several ternary complexes was selected¹³ so that significant intramolecular ligand-ligand interaction would likely ensue. Of the different pairs of amino acids experimented, it was found that with each of the three pairs (Table 2) histidine-asparagine, histidine-glutamine and histidine-threonine in the coordination sphere of Cu(II), significant intramolecular hydrogen bonding occurs under favorable conditions. As it has also been shown that histidine in proteins are typically nonchelating, the imidazole moiety¹⁴ has consequently assumed much significance as the binding site of the histidyl residue for Cu(II) in a number of biological systems¹⁴. The latter include human albumin, sperm whole myoglobin, hemocyanin, bovin serum, ceruloplasmin and ribonuclease. The effectiveness of the imidazole group acting as a metal binding site has been attributed to its great flexibility, its availability at physiological pH and its capability to form both σ & π bonds with metal ions. Some examples of its ternary copper(II) complexes are given in Table 2^{15,16}. Those with dipeptides serving as the second ligands were shown to possess enhanced stability¹⁶. It is also interesting to note that the order of the stabilities of these ternary complexes is determined by steric effects imposed on by the side chain substituents in the dipeptides.

That the copper(II)-mixed amino acid complexes may play a part in the transport of copper(II) through the blood and between blood and tissue, was first suggested by the identification of such complexes in normal human serum. It has now been established¹⁷ that a significant proportion of the complexed copper(II) is in the form of a mixed ligand complex containing l-histidine, l-threonine and Cu(II) in the ratio 1:1:1. The molecular structure of this complex has been elucidated by X-ray diffraction method¹⁸. The histidine residue is shown to function as a tridentate chelate bonding through its imidazole N, amino N and carboxyl O, while the threonine residue binds copper through its amino N and carboxyl O.

A third area where the participation of ternary copper(II) complexes is considered likely, deals with the action of antitumor agents. This follows from the recent finding that degradation of DNA can be brought about by a copper(II) complex of phen in the presence of a reducing agent such as the thiol¹⁹. Although the chelating agents phen and bpy are the ones shown to retard the growth of Sarcoma 37 tumor²⁰ and inhibit the cell proliferation

of Ehrlich ascites ²¹, the copper complexes of these ligands are expected to act as the carriers of the antitumor agents. This follows from the fact that the neutral copper complexes are expected to permeate through the cell membranes more readily, thus enhancing the antitumor activity of these agents. In their free uncoordinated forms the hydrophilic groups of the phen and bpy molecule render them less effective in permeating through the cell membrane and consequently reduce their antitumor activities. As the search goes on for more effective antitumor agents, renewed efforts are being made in the study of ternary bpy and phen copper(II) complexes, with the second ligand being one of biological relevance.

Ternary copper(II) complexes have also been found to be useful models in the investigation of the therapeutic action of penicillamine (pen) with respect to Wilson's disease ²². This disease is a genetic defect ensuing in an excessive accumulation of copper in the liver, kidney and brain. Such accumulation, in turn, leads to neurological and other disorders and ultimately death if it is not detected and treated at an early stage. Although penicillamine is used in the treatment, the mechanism by which pen successfully removes copper, i.e. the mode of interaction between pen and copper under biological conditions, is not known. A knowledge of the mechanism is vital in determining the requirements for a more effective therapeutic agent. As it has also been established that even in blood plasma there is negligible amount of free copper, the study of the interaction of pen with chelated copper(II) rather than the free copper(II) is considered to be more appropriate. In this connection, two systems ²² viz., Cu(II)-glycylglycine-pen and Cu(II)-histidine-pen have been investigated by electronic spectral and epr studies. The spectroscopic data were used to relate the formation of the ternary complexes with the mode of mobilisation of the excess copper in Wilson's disease.

In this final section, the catabolism ²³ of histamine is presented to illustrate the potential uses of ternary complexes of copper(II) in many other biological processes. Histamine, the decarboxylation product of histidine, exists mainly in its protonated form in blood plasma. This highly polar form of histamine is not expected to readily cross cell membranes to reach tissue in which it can be catabolised. On the other hand the formation of a metal complex ought to facilitate the diffusion process of histamine. Thus it was not entirely surprising when several metal complexes have actually been found to be effective in reducing histamine toxicity ²⁴. To probe the mode of action of metal ions with respect to histamine catabolism, ternary complexes are considered since there are other low molecular weight amino acids also present in the blood plasma. There has, therefore, been study on possible formation of ternary systems of copper(II) with histamine and some amino acids. Results thus far obtained ²³ indicate that formation of such ternary complexes is somewhat selective, being dependent on the nature of the second ligand.

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TABLE 1

SELECTED EXAMPLES OF TERNARY COMPLEXES ISOLATED FROM SOLUTION

A.	[Cu(phen)(acac)]Cl
	[Cu(phen)(sal)]
	[Cu(phen)(pyr)]H ₂ O
	[Cu(phen)(oxa)]
	[Cu(phen)(mal)]2H ₂ O
	[Cu(phen)(suc)]H ₂ O
	[Cu(phen)(glu)]H ₂ O
	[Cu(phen)(adip)]H ₂ O
B.	[Cu(phen)(gly)](SO ₄) _{1/2} H ₂ O
	[Cu(phen)(ala)](SO ₄) _{1/2} 2H ₂ O
	[Cu(phen)(val)]Cl·2H ₂ O
	[Cu(phen)(tyro)]Cl·H ₂ O
	[Cu(phen)(ser)](SO ₄) _{1/2} H ₂ O
	[Cu(phen)(asp)]
	[Cu(phen)(glut)]2H ₂ O
	[Cu(bpy)(gly)](SO ₄) _{1/2}
	[Cu(bpy)(ala)]Cl·2H ₂ O
	[Cu(bpy)(val)]Cl·H ₂ O
	[Cu(bpy)(tyro)]Cl
	[Cu(bpy)(ser)](SO ₄) _{1/2}
	[Cu(bpy)(asp)]2H ₂ O
	[Cu(bpy)(glu)]

TABLE 2

EXAMPLES OF TERNARY Cu(II) COMPLEXES [CuLL']
DESIGNED FOR STUDY OF SOME BIOLOGICAL PROCESS

<u>L</u>	<u>L'</u>	<u>Ref</u>
A. Histidine	L-,D- asparagine	[13]
	L- glutamine	
	L- serine	
	L-homoserine	
	L-citrulline	
B. Imidazole	DL-2-amino butyric acid	[15]
	DL-3-amino butyric acid	
	DL-4-amino butyric acid	
	DL-4-amino-3-hydroxy butyric acid	
	DL-2,3-diamino propionic acid	
	DL-2,4-diamino butyric acid	
	DL-ornithine	
	<u>dipeptides</u>	
C. Imidazole	glycyl glycine	[16]
	glycyl-L-alanine	
	L-alanylglycine	
	glycyl-L-leucine	
	L-leucylglycine	
	glycinamide	
D. bpy phen	glycylglycine	[19]
	glycyltyrosine	
	glycylphenylalanine	
histamine	cystinate	[23]
	lysinate	

CHEMICAL INDUSTRIES IN DEVELOPMENT OF NEPAL

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A B S T R A C T

A brief introduction to Nepal relating to its topographical and climatological features including Nepals resources, population and labour force, ethnic and linguistic diversity, out-put labour force and productivity is undertaken. A review of industrial situation and industrial growth with special emphasis to chemical and allied industry is discussed. Technical manpower in the field of chemical and allied industry is also shown. In R & D section research and developmental works in different institutions and their status is taken into consideration. In chemical industries relevant to Nepal section the policy and programme underlying the growth of overall industries in Nepal including chemical and allied industries are shown against well established statistical data, figures and surveys. Lack of technology, proper information of R & D and shortage of trained manpower are considered in regional co-operation.

Information on Nepal

Nepal is a landlocked country lying in South East Asia at the longitude between 80°15' to 88°15' East and 26°15' to 30° North. She is surrounded by the Tibetan region of China in the North and India on the other three sides. This country is roughly rectangular in outline. It covers an area of 147,181 sq.km. The population is 15.20 millions. The annual growth rate of population is 2.3 percent. GNP per capita is US\$ 130. The population density is 102 persons per sq.km. Nepal abounds in a diverse set of caste & creed and language which has amalgamated into a homogeneous culture and religion. (1,2).

Topographical features and climate. The geography of the kingdom is such that its character varies from the temperature terai (plain area, altitude of about 100 meters from the sea level) to the peak of Sagarmatha (Mount Everest 8550) meters). Thus the climate and vegetation of Nepal vary according to altitude.(3)

Resources. Nepal has an agrarian economy with 90 percent of the population dependent on agriculture. Forests are only second to agrobased industries and are very important natural resource. It is reported that one third of the country is covered with forests. The third important resources of the country are minerals, though, mineral deposits that are commercially exploitable are very few in numbers. So non-metallic industries have already gained ground. Nepal is very rich in hydro-power potential. This energy is yet to be harnessed to its fullest possible extent. This is one of the main natural resources of the country and, if exploited in diverse fields, this could contribute very strongly to national economy.(4)

Output labour force and productivity. Maximum labour force in the country is involved in agriculture. Only 5 percent of them are in service and only 2 percent of them contribute their labour in industry. The annual growth of labour force is 2.1 percent. According to the World Bank report, productivity per worker of these labour force was lowest in agriculture and highest in industries.(5,6)

Development and Status of Chemical Industries in Nepal

Review of industrial situation (development). Only very recently Nepal has embarked on industrialisation. So the history of industrialisation is not very old. The process of industrialisation took place for the first time in 1938 A.D. with the establishment of a jute mill. This inspired many others to set up new industries due to which many agro-based industries like rice, jute, oilseed extraction, flour mill etc. came into existence. Between 1952 and 1956 not more than 15 public and private limited companies were registered. By 1956, when the first five year plan was launched, out of 68 public companies registered 24 had been dissolved due to the lack of equity capital, 13 were in liquidation, 15 reported operating at a loss and a few were apparently reasonably successful.(7) As a precursor to this step of industrialisation, an organisation by the name of Nepal Industrial Development Corporation (NIDC) was set up in 1959 A.D. which provides financial loans and prerequisites to those people interested in establishing industries. Even before this, the Government did not appear

to have shown any interest to set up industries in the public sector. Any industry that came into being was only in the private sector. The assistance provided by the Nepal Industrial Development Corporation to various industries financially is shown in Appendix-1. It has helped in the opening of 387 big and small industries investing 566.97 million Rupees (shown in Appendix-2). Actually, the industrialisation process started during the First Five Year Plan (1957-1962) as a sequel to planned development in the country.(8)

Industrial growth. Only during the First Five Year Plan (1957-1962) serious attempts were made to encourage and support the industrialisation process. This resulted in a considerable increase in the number of industries in the public sector as well as private sector. This was a very encouraging trend, specially in comparison with the fifth plan. The contribution of the industrial sector in GDP is only 5 percent. From the viewpoint of employment also this sector employs only one percent of the labour force. The contribution of other industries is negligible in comparison to cottage industry. For a big & small scale industries, investment is high and employment is less.(7)

TABLE NO. I: A COMPARATIVE STUDY OF SMALL, MEDIUM AND BIG INDUSTRIES

	TOTAL INDUSTRY	MEDIUM & BIG INDUSTRIES	COTTAGE AND SMALL SCALE INDUSTRIES	% OF COTTAGE INDUS- TRIES	% OF MEDIUM & BIG INDUSTRIES
NUMBER OF INDUSTRIES	7,54,154	3,570	7,50,575	99.5	0.5
NUMBER OF EMPLOYEES	12,71,340	56,340	12,15,000	95.6	4.4
PRODUCTION (MILLION Rs)	32,88.141	2575.140	713.00	21.7	78.3
INVESTMENT (MILLION Rs)	826	485	341	41.3	58.7
VALUE ADDED (MILLION Rs)	698.26	479.5	218.7	31.3	68.7

The cottage industry sector is estimated to contribute more than 6 percent to the GDP. In fact, cottage industries comprise 99.5 percent of all industrial units and employ 95.6 percent of all industrial labour (9) as mention in Table No. 11.

TABLE NO. II: CONTRIBUTION OF COTTAGE INDUSTRIES

YEAR	TOTAL NATIONAL INCOME	CONTRIBUTION OF MANFG. SECTOR	PERCENTAGE	CONTRIBUTION OF COTTAGE INDUSTRIES (Rs. IN 000)	PERCENTAGE
1972/73	9,968	312	3.1	650	6.6
1973/74	12,080	387	3.1	885	6.9
1974/75	14,802	463	3.1	995	6.7
1975/76	17,394	518	3.0	1161	6.7
1976/77	17,344	680	3.9	1081	6.2

According to the industrial statistics carried out during 1977/78, industrial units, either mechanised or having more than 10 employees, shows a remarkable increase in the first interval (1972/73) as shown in Table No. III. But in the second interval (1972/73-1977/78) it was poor. Also the growth rate of industrial output during the period is less than the growth rate of GDP. Whereas, in the developing countries, increase in the industrial output rate was higher than GDP rate during the same period. (7)

TABLE NO. III: INDUSTRIAL GROWTH STATISTICS OF NEPAL

	COTTAGE			BIG OR MECHANISED		
	SMALL SCALE OR NON	MECHANISED		1965/66	72/73	77/78
	1965/66	72/73	77/78	1965/66	72/73	77/78
NO. OF INDUSTRIES	-	376632	750575	1260	2434	3574
NO. OF EMPLOYEES	-	1040000	1215000	18176	41367	56340
PRODUCTION						
(MILLION RS.)	-	303.8	713.0	507	1798	2575
INVESTMENT						
(MILLION RS.)	-	143.1	341.1	-	257	485
VALUE ADDED						
(MILLION RS.)	-	122.5	218.8	89.6	322.0	474.5

In short, the contribution of cottage industries is still very important in comparison to other industries. The non-sectoral and cottage industries are taken up in the home circumstances and are unorganized and practised during the leisure hours. So their products are of low quality and they are produced for internal domestic and private use only. These products do not reach the market. This shows that industrial development in Nepal is still in the stage of infancy. To shift the dependency of the national economy from agriculture to industry, emphasis has been given in the second plan by allocation of 20 percent of the financial disbursement, as compared to 8 percent in the First Plan, for the development of the industries.

Chemical and allied industry. There is no chemical & allied industry at all in the country in a flourishing condition and, even if there are any, they are quite negligible in number. For example, according to Nepal Foreign Trade figures (1980/1981), we have imported miscellaneous materials worth Nepali Rupees 4802 millions and exported materials worth only Nepali Rupees 1423 millions. This amounts to a trade deficit of Rupees 3379 mill millions. From amongst the imported goods worth of Nepali Rupees 4802 millions, we have imported a total Nepali Rupees 1380 millions worth of chemicals and allied products alone as shown in table IV.

TABLE NO. IV: IMPORT OF CHEMICAL & ALLIED PRCDUCTS (IN Rs. 1,000000)

NAME	IMPORT (IN MILLION Rs.)	NAME	IMPORT (IN MILLION Rs.)
1. PETROLEUM FUELS	510	13. STEALITE AND TALC	9
2. FERTILISERS	203	14. ORGANIC DYESTUFFS	8
3. CEMENT	150	15. GLUCOSE	6
4. MEDICINE	149	16. LIME	6
5. PAPER & PAPER PRODUCT	96	17. SHAVING SOAPS	5
6. SUGAR	72	18. COSMETIC AND PERFUMES	7
7. PETROLEUM LUBRICATING OIL	39	19. VEGETABLE COLOURING	4
8. LAUNDRY SOAPS	27	MATTER	
9. SURFACE ACTIVE AGENTS	15	20. INCENSE STICKS	5
10. TOILET SOAPS	11	21. INSECTICIDES	22
11. PAINTS AND ENAMELS	10	22. OTHERS (SO ₂ , MnO ₂ ,	15
12. WRITING INKS	10	Cu-ore, NaNO ₃ etc.	
		TOTAL	1380

SOURCE: Food of Thought, Nepal Chemical Society.
(1 US\$ = Nepali Rupees 14.40)

The figure is 28% of the total imported goods. These do not include other goods such as textiles, polythene materials, vegetable oils, fats, powder milk, tyres, mineral binding substances, glass, etc. This shows that plight of chemical and allied industries - they are still in a very primary stage.(10)

STATUS

Research and development. In the modern world, technological changes are so swift that it is imperative for us to, at least, keep abreast of the new development if we are not to be left far behind. It is even for this reason that some local capacity in science and technology is needed, and this is not likely to be achieved unless some investment is made on research and development at even minimum levels. However, what we generally find here is that research and development is not only absent but there is also a lack of appreciation for its need. As an indicative of this general situation, it is better to mention some of the results of a survey (which is not yet published) carried out by NCST (National Council for Science and Technology) a few year ago. This survey was mainly intended to find out the kind of R & D our industries and manufacturing concerns carry out in their operations. That survey was mainly interested in finding out whether our industrial establishments have in their operations such activities as quality control and testing, standardization of product and process improvement, raw material substitution, by-product utilization, new product development etc. Among the 96 industries and manufacturing concerns surveyed, only 27 responded. Among those responded, only 9 industries appeared to have some activities in the above mentioned areas. But most of them were limited to quality control and product standardization. Very few of them had R & D components, if any, in area such as process improvement, raw materials substitution and new product development. Even recognizing the limitations of this survey, it may be said that our industries do not quite recognize the need for R & D as this component does not quite effect their profitability. The result of this survey shows that our industrialists take very short time measures in

their calculation of return on their investments. They do not feel the competitive urge of the market place to back up the profitability of their operations with R & D efforts. Hence, what is needed first, it to drive home the fact that R & D efforts pay off, and can be made to pay off handsomely in their operations, and to create a congenial environment for the same. (11) When we talk of R & D in other countries, institution that meet production levels spend 2-10% of their income in R & D. Even in India there are certain institution which help to promote and encourage R & D, like, for instance, CSIR (Council of Scientific and Industrial Research). In Nepal, this task will be undertaken by the newly founded Royal Nepal Academy of Science and Technology (RONAST). For R & D we have developed a very narrow infrastructure in our country. As I have mentioned above, our organizations and institutions has involved a very few people in the field of R & D. For instance the Department of Medicinal Plants, Royal Drugs Research Laboratory is presently engaged in carrying out phytochemical, pharmacognostical, formulation of pharmaceutical and allied products and biological investigation in plants. Technological methods have been developed for the extraction of Vasaca, Xyntho xylum, Gaittheria, Belladonna, Pyrethrum, Dioscorea and Finerosin. The Department of Mines and Geology works for the development of different minerals based industries including oil & gas; similarly, exploration & evaluation of the mineral deposits are also being carried out. The Food Research Laboratory has developed suitable techniques for the preservation of fruits and produces preserved fruits & fruit products besides carrying out the standardization of vegetable oil, ghee, milk & milk products. Some basic research has been carried out by Tribhuvan University. Similarly RECAS (Research of Applied Science and Technology) is engaged in R & D in the field of industrial waste products and towards the utilization of natural products. (12,13,14,15)

Technical manpower (chemists). The step of imparting chemical education in Nepal started only some 60 years back. According to our available manpower, we have 300-350 Chemists in the country. About 60% of them are engaged in teaching institutions while the remaining 40% of them are engaged in different institutions of His Majesty's Government. They are active in carrying out the routine analysis on the departmental works. A few of them are involved in R & D activities. According to the Science and Technology Directory published by the National Council of Science & Technology (NCST) in 1977, the total number of Scientists and Technologists in the country is 2377 among which 450 are Natural Scientists, 108 of them are Chemists and 64 of them are technologists. But according to the present report, "chemical" manpower is 320. Among them 64 are technologists. However, after the implementation of the First Five Year Plan, as it was felt that more and more of the Chemists should be involved in chemical research and, as they began to get absorbed in different institutions, chemistry emerged as a prospective subject. So the teaching and training of Chemistry so as to produce adequate technical personnel for different chemical and allied industries was undertaken by Tribhuvan University and its affiliated institutions. In the Sixth Five Year Plan, the number of varicus technical manpower to be produced, their supply and their shortage etc. is defined and in the same period about 70 Chemists, and about 45 Technologists that are to be produced as per target have been kept in view which is as shown in Appendix 3. (16,17)

Chemical industries relevant to Nepal

Data from Appendix 4 shows that although there is slight increase in the percent share of chemical industries during the period 1965/66 to 1977/78, its share compared to other industries is the least. The highest share in the list is of the agro-based industries. The chemical and plastic industries according to the Department of Industries includes oxygen, pesticides, pharmaceuticals, fertilizer (bone mill), soap, solvent, oil and katha (Catechu). Moreover, some more chemical and allied industries involving chemical or chemical process like match, soft drinks, sugar, alcohol, beverage, animal feed, cement, agriculture lime etc. have been included in this report. Even on including these industries, the subsector share is not much compared with the other industries. The major contribution is seen to be that of nonmetallic products, drinks and metallic products whose complete shares are itself not big. A study has been carried out by industrial service centre which is shown in appendix 5. As per these finding, it can be seen that the total number of chemical & allied units in operation at present are 78 in number. Appendix 5 also presents the volume of production and the manpower employed in these units. The chemical and allied product industries are not operating at full capacity. This is because of unavailability of raw materials and inadequate market for the products. (7,18,19)

Policy and programme (1980/81-1985/86). The achievements of the Fifth five year plan, although substantial, was inadequate in the sense that industrialization of the economy as desired could not be achieved. In the sixth five year plan policy measures with the goal, enabling people to participate in industrial development, were laid down. Along with this, in the sixth five year plan, foreigners have also been invited to open big industries in the country. Priority is given to the development of the agricultural sector because of the availability of raw materials for this sector in the country. Emphasis has been given to cottage & small scale industries. Stress has been laid to promote export trade, utilization of the infrastructure that has been developed so far in the country and to make the economy effective with regard to more utilization of natural resources. Appendix 6 is a compact list of the total industrial development programmes for the sixth five year plan. This appendix gives the probable investments in the different sectors, the number of projects likely to be implemented, the additional man power required, energy consumption and the out put along with the value added. Appendix 7 shows the sixth five year plan programme for the small, medium and large chemical and allied industries. This appendix gives, under the different categories of the chemical and allied industries, details regarding the number of units likely to come up, e.g. manpower required, electricity consumption and the gross output. Similarly, appendix 8 gives informations regarding cottage scale chemical and allied industries. From appendix 7 and 8 it can be seen that the gross out put from the chemical and allied industries during the sixth five year plan will be of the order of 2461 million Nepali rupees which, on an average, works out to an annual output of 492 million Nepali rupees. From table IV we know that the present annual consumption of chemical and allied products in Nepal is about 1380 million Nepali rupees. Thus it can be seen that a very large annual gap of the order of 888 million Nepali rupees exists between production and consumption of chemical and allied products. Thus it can be seen that a tremendous scope exists for setting up of new units in the chemical and allied industries both in

the small, medium and large scale sector as well as in the cottage scale sector. As a result, during the current sixth plan period, foreign companies have been invited to set up mineral based industries viz. magnesite, lead and zinc. Also forest based industries viz. rosin and terpentine are being set up. (4).

Regional co-operation in the development of chemical industries co-operation in the field of R & D. R & D is an expensive and time consuming process. Therefore it would be advantageous and economical if the finding of R & D is easily available from different countries. This will help spreading out the cost involved in R & D. This is advantageous for the country having low R & D activities.

Training of manpower. We can fulfill the shortage of skilled and trained manpower by giving higher education and training in the different institutions of this region. This will fulfill our demand for manpower which is needed for chemical and allied industries.

Collection of funds. Being in the process of development, we have shortage of funds due to which big industries cannot come up. This gap can be eliminated by foreign companies who are interested in opening the industries in Nepal.

Exchange of technology. In the field of technology we are still in an infant stage. So exchange of technology is possible on the basis of regional co-operation.

Exchange of raw material. The raw materials that we cannot utilize properly will be exported and in exchange of that, we may get machinery or products whichever is necessary for our chemical industries.

Exposure to new industries. Inexperienced industrialists and entrepreneurs could visit different countries developed in the respective fields, and gain fruitful experience useful in the context of Nepal.

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APPENDIX-1 NEPAL INDUSTRIAL DEVELOPMENT CORPORATION SECTORWISE DISBURSEMENT OF FINANCIAL ASSISTANCE
(F.Y. 1977/78 - 1982/83)

INDUSTRIAL SECTOR	(Rs. in million)					
	1977/78	1978/79	1979/80	1980/81	1981/82	1982/83 (NINE MONTH)
1. AGRO-BASED	32.56 (48.7%)	16.29 (35.7%)	9.25 (35.6%)	11.63 (25.0%)	28.52 (53.2%)	26.94 (72.6%)
2. FOREST BASED	2.09 (3.1%)	0.25 (0.5%)	0.26 (1.0%)	0.48 (1.0%)	0.06 (0.1%)	0.07 (0.2%)
3. MINING AND MINERAL BASED	0.20 (0.3%)	3.54 (7.7%)	1.27 (4.9%)	1.26 (2.7%)	0.67 (1.2%)	0.63 (1.7%)
4. TOURISM	27.93 (41.7%)	22.77 (49.8%)	14.35 (55.3%)	30.33 (65.2%)	21.59 (40.3%)	6.96 (18.7%)
5. MISCELLANEOUS	4.12 (6.2%)	2.83 (6.3%)	0.82 (3.2%)	2.20 (4.1%)	2.77 (5.2%)	2.53 (6.8%)
6. TOTAL	66.90 (100%)	45.68 (100%)	25.95 (100%)	46.50 (100%)	53.61 (100%)	37.13 (100%)

Source : Nepal Industrial Digest - Silver Jubilee Issue vol 10, 1983.

**APPENDIX-2 NEPAL INDUSTRIAL DEVELOPMENT CORPORATION DISTRIBUTION OF TOTAL FINANCIAL ASSISTANCE BY
INDUSTRIAL SECTOR AS AT MID APRIL 1983.**

INDUSTRIAL SECTOR	UNIT	AMOUNT (Rs. IN MILLION)	PERCENTAGE
1. HOTEL & TOURISM	75	224.79	39.7
2. RICE, OIL, FLOUR & SUGAR	59	63.09	11.1
3. CEMENT & OTHER CONSTRUCTION/MATERIALS	18	42.05	7.4
4. BISKERY & SOFT DRINK	3	39.52	7.0
5. TEXTILE & JUTE	16	20.08	3.6
6. BISCUITS & CONFECTIONERIES	3	17.78	3.1
7. TRANSPORT SERVICES	93	13.55	2.4
8. SHOES & LEATHER GOODS	3	14.97	2.6
9. LIGHT ENGINEERING	22	10.33	1.8
10. ELECTRIC POWER	4	8.11	1.4
11. STRAW BOARD, SAW MILL & WOOD WORKS	17	7.48	1.3
12. OTHERS	74	105.22	18.6
TOTAL	387	566.97	100.0

Source : Nepal Industrial Digest - Silver Jubilee Issue vol 10, 1983.

APPENDIX-3 MANPOWER REQUIREMENT FOR SIXTH FIVE YEAR PLAN (1980/81-1985/86)

MANPOWER CLASSIFICATION	UP TO 1979/80	ESTIMATED EXCESS MANPOWER REQUIREMENT	FULL- FILL	SHORTAGE
1. HIGH LEVEL	2,608	3,381	2,072	-1,309
(a) SCIENTISTS & TECHNICAL LOGISTES		217	225	+ 8
(b) CIVIL ENGINEERS		751	431	- 320
(c) OTHER ENGINEERS		372	206	- 166
(d) AGRICULTURIST		1,456	737	- 719
(e) FORESTERS		191	150	- 41
(f) MEDICAL MAN		394	323	- 71
2. MEDIUM LEVEL	7,784	7,134	7,807	+ 673
(a) ASSISTANT SCIENTISTS & TECHNOLOGISTS		454	408	- 46
(b) CIVIL OVERSEERS		1,355	1,398	+ 43
(c) OTHER OVERSEERS		1,083	760	- 323
(d) J.T.A's		3,011	2,062	- 949
(e) FORESTERS (JUNIOR)		247	755	+ 508
(f) HEALTH ASSISTANT & C.M.A.		984	2,364	+1,380
3. BASIC LEVEL	7,268	8,972	6,304	-2,668
TOTAL		19,487	16,183	-3,304

SOURCE : Development of Science in Nepal, Royal Nepal Academy-Silver Jubilee Issue Vol-7, pp. 159.

SOURCE : Proceedings of the first Annual Function, Nepal Chemical Society Vol-1, 1981.

APPENDIX-4 STRUCTURE OF INDUSTRY, SUB-SECTOR SHARES

SL. NO.	SUB-SECTOR	1965-1966			1972-1973			1977-1978		
		EMPLOY- MENT	VALUE ADDED	%	EMPLOY- MENT	VALUE ADDED	%	EMPLOY- MENT	VALUE ADDED	%
1.	Food & Allied	51.0	11.2	61.0	16.7	76.7	51.4	35.8	73.5	57.5
2.	Textiles & Allied	25.2	7.2	7.8	14.65	4.36	2.87	16.7	8.3	12.26
3.	Chemicals, Pharmaceuticals, Plastics, Rubber	0.24	0.34	0	0.25	0.17	0.08	1.35	0.87	2.07
4.	Non Metallic Mineral Products	8.07	1.5	3.38	10.8	2.63	11.05	14.34	3.61	6.95
5.	Metals, Fabrication	2.32	1.74	-	2.12	1.25	2.3	3.04	2.02	3.42
6.	Jewellery, Curio	1.06	0.12	0.44	0.42	0.15	0.5	0.33	0.03	0.03
7.	Miscellaneous	17.8	0.8	16.37	5.25	6.86	14.16	0.14	0.11	0.13
		18176	507	89.6	49048	1798	322.4	56341	2575	479.5
		(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)

NOTE : that for 1965-66 the miscellaneous category has only been broken down for gross output. Therefore the three estimates-employment, gross output and value added do not correspond in some cases. However, individual industries included in miscellaneous are usually quantitatively small. Of the sectoral shares, rice and oil milling alone accounts for the following shares in total employment and output.

RICE, OIL MILLS & SHARS 25.6 78.9 61.7 38.6 73.3 47.8 24.2 65.0 44.3

SOURCE : Industrial Sectoral Plan study (1980/81 - 1990/91) Volume 1, Industrial Services Centre, 1979.

APPENDIX-5 PERFORMANCE OF SOME OF THE CHEMICAL & ALLIED INDUSTRIES IN NEPAL

ITEM	NO. OF OPERATING UNITS	LEGAL STATUS	PRODUCTION (MILLING)		MARKET		TOTAL EMP- LOYMENT
			CAPACITY PER ANNUM	VOLUME	DOMESTIC	EXPORT	
1. SUGAR	3	3 PVT. LTD.	24100 TONS	14219 TONS	100	-	3102
2. KHANDSARI (BROWN SUGAR) #	4	4 PVT. LTD. 4 PARTNERSHIP.	2000 TONS	533 TONS	100	-	975
3. LIQUOR*1	6	6 PVT. LTD. 2 PARTNERSHIP.	17.25 LAKH LITRES	8.5 LAKH LITRES	100	-	302
4. BEER	2		LAKH LITRES		100	-	
5. SOFT DRINKS* 2	3		24.5 LAKH LITRES	14.4 LAKH LITRES	100	-	107 One
6. ANIMAL FEED*3	5	5 PVT. LTD.	20487 TONS	11165 TONS	100	-	263
7. PROCESSED LEATHER*4	7	7 PVT. LTD.	29.9 LAKH PCS.	19.8 LAKH PCS.	14	86	286
8. MATCHES	6	2 LTD. CO. 4 PVT. LTD.	2376 LAKH BOXES	1022 LAKH BOXES	100	-	1104
9. SOAP*5	5	3 PVT. LTD. 2 PRIVATE.	4010 TONS	1712 TONS	100	-	170
10. SOLVENT EXTRACTION	3	3 PVT. LTD.	2688 TONS	2057 TONS	12	88	382
11. KATTHA & KHAIR	3	3 PVT. LTD.	510 TONS KATTHA	369 TONS KATTHA	6	94	768
12. PHARMACEUTICALS	3	1 LTD. CO. 2 PVT.	1020 TONS KHAIR	626 TONS KHAIR			
13. PESTICIDES	1	1 PVT. LTD.	2400 TONS	412 TONS	100	-	20
14. BONE MILL (FERTILISER)	1	1 PVT. LTD.	10000 TONS	268 TONS	100	-	41
15. CEMENT	1	1 PVT. LTD.	48000 TONS	29200 TONS	100	-	500
16. AGRICULTURE LIME	1	1 PVT. LTD.	13000 TONS	5590 TONS	100	-	70
17. CIGARETTES	3	1 LTD. CO. 2 PVT. LTD.	406 CIGARETTE STICK	181 CIGARETTE STICK	100	-	1823
18. POLYTHENE PIPE	3	1 PVT. LTD. 2 PARTNERSHIP	660 TONS	356 TONS	100	-	154
19. PLASTIC FILM # 1	7	4 PVT. LTD. 1 PARTNERSHIP 1 PRIVATE.	290 TONS	139 TONS	100	-	72
20. SEASONED WOOD* 2	2	2 PVT. LTD.	25000 cu.ft.	5000 cu.ft.	100	-	
21. OXYGEN	1	1 PVT. LTD.	168000 M	52080 M	100	-	20
22. VEGETABLE GHEE	1	-	-	-	-	-	-

*1 Review relates to 7 units only.

*2 " " 2 " "

*3 " " 4 " "

*4 " " 6 " "

*5 " " 5 " "

#1 Review relates to 6 units only.

#2 " " " "

NOTE 1 - One Lakh = 100000

One Crore = 1000000

SOURCE:- A country paper by - ...Pradhan 1983.

**APPENDIX-6 THE COMPACT LIST OF INDUSTRIAL DEVELOPMENT PROGRAMMES FOR THE SIXTH PLAN
(1980/81 - 1985/86)**

SL. NO.	SUB-SECTOR	TOTAL PROJECTS NOS	INVESTMENT Rs. (MILLIONS)	MAN POWER NOS	ENERGY POWER KW	OUT PUT Rs. (MILLIONS)	VALUE-ADDED Rs. (MILLIONS)
1.	FOOD & ALLIED	68	282.97	2202	1845	210.87	57.51
2.	DRINK & TOBACCO	8	27.93	219	211	27.30	9.03
3.	TEXTILE, WEAVING APPAREL & FIBRES	1384	481.09	13927	5928	346.70	105.78
4.	WOOD PAPER PAINTING	329	696.9	6157	9479	604.2	193.0
5.	RUBBER & PLASTICS	43	35.75	501	703	107.24	18.66
6.	CHEMICAL & PHARMACEUTICAL	85	192.10	1652	1795	276.28	67.03
7.	NON METALLIC MINERAL	36	2123.80	5976	27010	847.07	688.56
8.	METAL PROCESSING PRODUCTS	9	96.82	311	3741	69.02	43.82
9.	MACHINERY EQUIPMENT AND COMPONENTS	12	30.49	218	720	46.66	18.34
	TOTAL	1874	4027.25	31663	51432	2557.34	1201.93
	(a) Small to Large Scale	187	3902.12	18125	48602	2212.34	1101.16
	(b) Cottage Scale	1737	125.13	13538	2830	345.00	100.77

SOURCE : - Industrial Sectoral Plan Study 1980/81 - 1990/91, Volume*1, Industrial Services Centre-1979.

APPENDIX-7 SUMMARY OF CHEMICAL & ALLIED INDUSTRIAL PROJECTS IN THE SIXTH YEAR PLAN
(1980/81 - 1985/86)

SCALE : - SMALL, MEDIUM & LARGE.

Sl. No.	INDUSTRY	CAPACITY	SCALE	TOTAL UNIT	TOTAL MAN POWER NO.	ELECTRICITY REQUIRED KW	TOTAL GROSS OUTPUT IN (MILL)
1.	SUGAR	1125 TCD	LARGE	2	1395	450 KW	127.73
2.	STARCH & GLUCOSA	20 TON OF STARCH/DAY	LARGE	1	113	700 KW	17.09
3.	ANIMAL FEED	3600 MT / YR	SMALL	2	42	80 KW	13.45
4.	GINGER PROCESSING (OIL EXTRACTION)	180 MT OF DRY GINGER/ YR	SMALL	1	56	60 KW	3.40
5.	SOLVENT EXTRACTION	15 MT OF RICE BARK/DAY	MEDIUM	1	52	60 KW	6.27
6.	SUGAR CANE JAX	100 TON OF JAX/HR	SMALL	1	34	30 KW	-
7.	ACTIVIFIED SPIRIT	75000 LITERS/YR	SMALL	1	22	25 KW	8.00
8.	GENUINE	10000 HL/HR	LARGE	1	73	100 KW	13.98
9.	LEATHER TANNING	72000 SQ FT/YR	LARGE	1	39	200 KW	23.52
10.	WOOD SEASONING	10000 CU. FT	SMALL	4	40	140 KW	14.90
11.	WRITING & PRINTING PAPER	40 TPD(AVERAGE)	LARGE	4	1627	7900 KW	399.00
12.	PENCIL	200 HR/DAY	SMALL	1	35	25 KW	4.30
13a)	RUBBER						
b)	CAMEL BACK	150 MT	SMALL	2	28	150 KW	6.37
c)	MICRO CELLULAR SHEET	150 MT	SMALL	1	21	60 KW	1.53
14	PLASTICS						
a)	ELECTRIC CABLES	6 MM MT	SMALL	4	64	72 KW	38.40
b)	HOUSEHOLD GOODS	60 MT	SMALL	2	16	14 KW	5.28
c)	RDF. PIPE	80 MT	SMALL	4	48	100 KW	14.97
15.	PESTICIDE FORMULATION	200 MT	MEDIUM	3	166	210 KW	18.18
16.	LIME (INDUSTRIAL)	6000 MT	MEDIUM	3	81	165	41.25
17.	SYNTHETIC DETERGENT	300 MT	SMALL	2	80	140	9.24
18.	PAINT & VARNISH	300 MT	SMALL	2	80	140	13.51
19.	CALCIUM SILICATE	120 MT	SMALL	3	51	90 KW	3.24
20.	ROSIN & TURPENTINE	2900 MT & 737 KL	LARGE	2	224	160 KW	24.00
21.	FERTILIZER BLENDING	9000 MT 1 ST PHASE 18000 MT 2 ND PHASE	MEDIUM	1	48	30 KW	26.3
22.	DRUGS & MEDICINES	-	LARGE	1	343	N/A	9.68
23.	OIL REFINERY	5000 BARRELS/DAY	LARGE	1	98	320 KW	618.24
24.	CEMENT	1800 MT (AVERAGE)	LARGE	2	2706	22 950 KW	629.46
25.	MAGNESITE						
(a)	DEAD BURNT	50000 MT	-	-	-	-	-
(b)	BRICKS	20000 MT	LARGE	1	840	4500 KW	169.53
(c)	TALC	10000 MT	-	-	-	-	-
26.	LEAD & ZINC	27000 MT	LARGE	1	500	2800 KW	32.40
27.	DRY CELL BATTERY	12 MILLI PCS	LARGE	1	51	120 KW	22.4

SOURCES : Industrial sectoral plan study (1980/81-1990/91) Volume 1, Industrial Service Centre 1979.

APPENDIX-8 SUMMARY OF CHEMICAL & ALLIED INDUSTRIES PROJECTS IN THE SIXTH YEAR PLAN (1960/61-1965/66)

SCALE - COTTAGE

Sl. No.	INDUSTRY	CAPACITY	SCALE	UNITS	TOTAL MAN POWER REQUIRED (BY NO.)	ELECTRICITY REQUIRED KW	TOTAL GROSS OUTPUT IN RS. MILLIONS
1.	ANIMAL FEED	2500 MT/YR	COTTAGE	1	18	30	4.67
2.	CHIURI GHEE	45 MT/YR	COTTAGE	2	14	-	0.90
3.	CHIURI GHEE	69 MT/YR	"	1	10	-	0.60
4.	FRUIT PRESERVATION	200 MT/YR	"	2	10	4	0.48
5.	RECTIFIED SPIRIT	100000 L. PLIN/YR	"	1	14	-	2.8
6.	HAND MADE PAPER	15 MT	"	6	120	67	1.8
7.	CHALK	172800 PKTS	"	3	54	-	1.3
8.	SAND PAPER	14000 DOL	"	6	6	5	0.1
9.	PLASTICS						
	(a) ELECTRIC ACCK	30 MT	"	1	29	20	2.40
	(b) COMBS	25 MT	"	1	15	20	1.80
	(c) POLYESTER SHEET	10 MT	"	3	15	30	2.29
	(d) TOOTH BRUSH	10 MT	"	2	14	16	2.00
	(e) PLASTIC BANGLES	5 MT	"	4	24	20	2.16
	(f) FOUNTAIN PEN & BALL PEN	1,00,000 PCS	"	5	80	50	9.24
10.	ANIMAL GLUE	40 MT/YR	"	1	16	5	0.39
11.	SODIUM SILICATE	900 MT/YR	"	2	16	20	3.99
12.	COSMETICS	15 MT/YR	"	3	33	75	3.1
13.	POLISHES	7 MT/YR	"	2	14	20	0.81
14.	BONE MEAL	100 MT/YR	"	10	40	100	1.33
15.	RESIN ADHESIVE RUBBER LATEX	100 MT/YR	"	2	22	80	1.80
16.	PRINTING INKS	40 MT/YR	COTTAGE	1	12	50	1.17
17.	WAXED JUNK	200 MT/YR	"	18	126	-	24.48
18.	FOILST JUNK	100 MT/YR	"	14	112	280	23.68
19.	WAXED JUNK	50 MT/YR	"	1	11	25	1.76
20.	WAXED JUNK	12 MT/YR	"	1	7	20	1.17
21.	HYDROLYTIC PRODUCTS	CHANGOL 40 MT/YR JIL 512 MT/YR	"	4	38	5	2.88
22.	WAXED SANDS	36	"	1	61	5	1.29
23.	WAXED SANDS	300 MT	"	2	30	25	1.25
24.	WAXED SANDS	30 MT	"	6	90	150	7.12
25.	PVC BATH CUB	100 MT	"	1	16	6	1.51
26.	WAXED FILM	10 MT	"	1	1	1	1.44
27.	PVC BANGLES	100 MT	"	1	1	25	1.45

Source :- Industrial Sectoral Plan Study 1960/61-1965/66 Volume-1, Industrial Services Centre-1979.

AN ALTERNATE DISINFESTATION TECHNOLOGY FOR
ETHYLENE DIBROMIDE PHASEOUT¹

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A B S T R A C T

Ethylene dibromide has been found to be carcinogenic and its use as fumigant for insect disinfestation is being banned in the very near future. This probable cancellation of ethylene dibromide as fumigant and the recommended clearance in the wholesomeness of irradiated foods up to an irradiation dose of 10 kgy pave the way for utilization of irradiation and hot water dip treatment as an alternative process.

Synergistic effects of the combined process of hot water dip treatment at 55°C for 5 minutes and low dose irradiation at 0.50 - 0.70 kgy have proved effective in the disinfestation of oriental fruit flies and seed weevil.

Added benefits caused by the treatment are the 4 - 6 day shelf life extension of the mango fruits due to delayed ripening and reduced microbial decay which allow for longer travel time of the fruits being exported.

No significant adverse effects were obtained on the acidity, pectin, carotene, ascorbic acid, and reducing sugar contents of the treated mangoes.

No significant differences were also observed between the treated mangoes and the controls by the taste panelists on the sensory attributes of the fruits.

¹ Research funded under IAEA Contract on Integrated Studies on Irradiated Mangoes.

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INTRODUCTION

Philippine mangoes exported to Japan and Australia require disinfestation to rid the fruits of eggs and larvae of the Oriental fruit fly. The United States requires an additional disinfestation for the seed weevil. The present method employed is fumigation by ethylene dibromide. Ethylene dibromide however, causes residual toxicity and is thus considered a health hazard. Its use was scheduled to be banned in 1983, but for lack of substitute has been rescheduled for 1984.

The United States was very active in food irradiation research in the 50's and early 60's but stagnated during the 70's and suddenly revived their interests in the 80's due to the scheduled ban on the use of ethylene dibromide.

The US Food and Drug Administration initiated a new policy for irradiated food in March, 1981 which states that food irradiated at doses of 1 kgy or less is considered wholesome and safe for human consumption. At present, some 45 irradiated food items or groups of related food have already been approved in 24 countries either on an unconditional or restricted basis.

The Codex Alimentarius Commission has also recommended clearance on foods subjected up to an irradiation dose of 10 kgy. This wholesomeness clearance on irradiated food and the cancellation of ethylene dibromide as fumigant for quarantine treatment greatly favor utilization of irradiation or the combined process as replacement for fumigation.

Ionizing radiation has been found to be a practical means of treating fresh fruits and vegetables for disinfestation and shelf life extension. Earlier studies have also shown that heat greatly improves the effectiveness of radiation. Combining ionizing radiation with heat treatment takes advantage of the synergistic effects between the two processes.

Studies were conducted to determine the efficacy of 0.65 kgy dose of irradiation as a disinfestation treatment for mangoes and of irradiation alone and in combination with hot water dip treatment, as a method for extending post harvest marketable life of fresh mangoes intended for the export market.

METHODOLOGY:

Carabao mangoes packed in dried banana leaves in bamboo crates obtained from various provinces depending upon the season were used for the tests. These were actually fruits harvested two or three days before, depending upon distance from Manila.

Disinfestation studies were conducted with mangoes by exposing them to 20,000 adult fruit flies for oviposition and then withdrawn periodically at three 24 hour interval for exposure to 0.20, 0.40, 0.60, and 0.80 kgy. Results showed that infested fruits when irradiated at 0.60 kgy after 24 hours did not develop any larvae thus proving that 0.65 kgy was sufficient to disinfest the fruits against the oriental fruitfly, Dacus dorsalis Hendl.

Fruits were divided according to maturity and according to the treatment methods to be applied, packed in carbon boxes, and transported to the Philippine Atomic Energy Commission in Diliman, Quezon City for irradiation. They were returned to PWU, Manila for storage at the prescribed temperature immediately afterwards.

Mangoes were irradiated at 0.65 kgy and those subjected to the combined treatment were hot water dipped at 55°C for five minutes prior to exposure to an irradiation dose of 0.65 kgy.

During storage at the prescribed temperature, they were observed for ripening changes and percentage decay. Stages of maturity were measured using a modified maturity scale. Periodically, samples were withdrawn for chemical and sensory evaluation to determine any adverse effects of the treatment on the fruit.

For the chemical tests, fruit pulp was homogenized and analyzed for reducing sugars, ascorbic acid, carotene, pectin, and total acidity using standard analytical methods. For sensory evaluation, paired comparison and preferred tests with the nine point Hedonic scale was used by a trained panel in evaluating the aroma, flavor, color, and acceptability of the samples.

Fruits were halved to detect presence of any seed weevil.

RESULTS:

Results show that green mangoes stored at ambient temperature subjected to combined treatment extended shelf life to 5-6 days, irradiation to four days as compared to no treatment at all. For yellow-green mangoes, preservation treatments extended the shelf life of 50% of samples to 4 days. Fruits stored at 15°C extended shelf life for even longer periods regardless of maturity.

This shelf life extension to 4 days makes these fruits exportable to many foreign markets which require a shorter travel time.

For green mangoes, the longer shelf life extension of 5-6 days for those exposed to combined treatment means extended marketability to farther foreign markets.

No significant differences on acidity, pectin, carotene, ascorbic acid and reducing sugar contents were found between the green controls and the treated samples kept at the two storage temperatures. Lower values of components observed in samples subjected to combined treatment were attributed to the physiological changes brought about by the normal ripening process other than the preservation treatment.

Except for color and odor attributes of green mangoes stored at 15°C, no significant differences were observed by the taste panelists on the sensory attributes of mangoes regardless of the maturity, preservation treatment, length and temperature of storage.

Sections of fruits did not reveal presence of any seed weevil.

CONCLUSION:

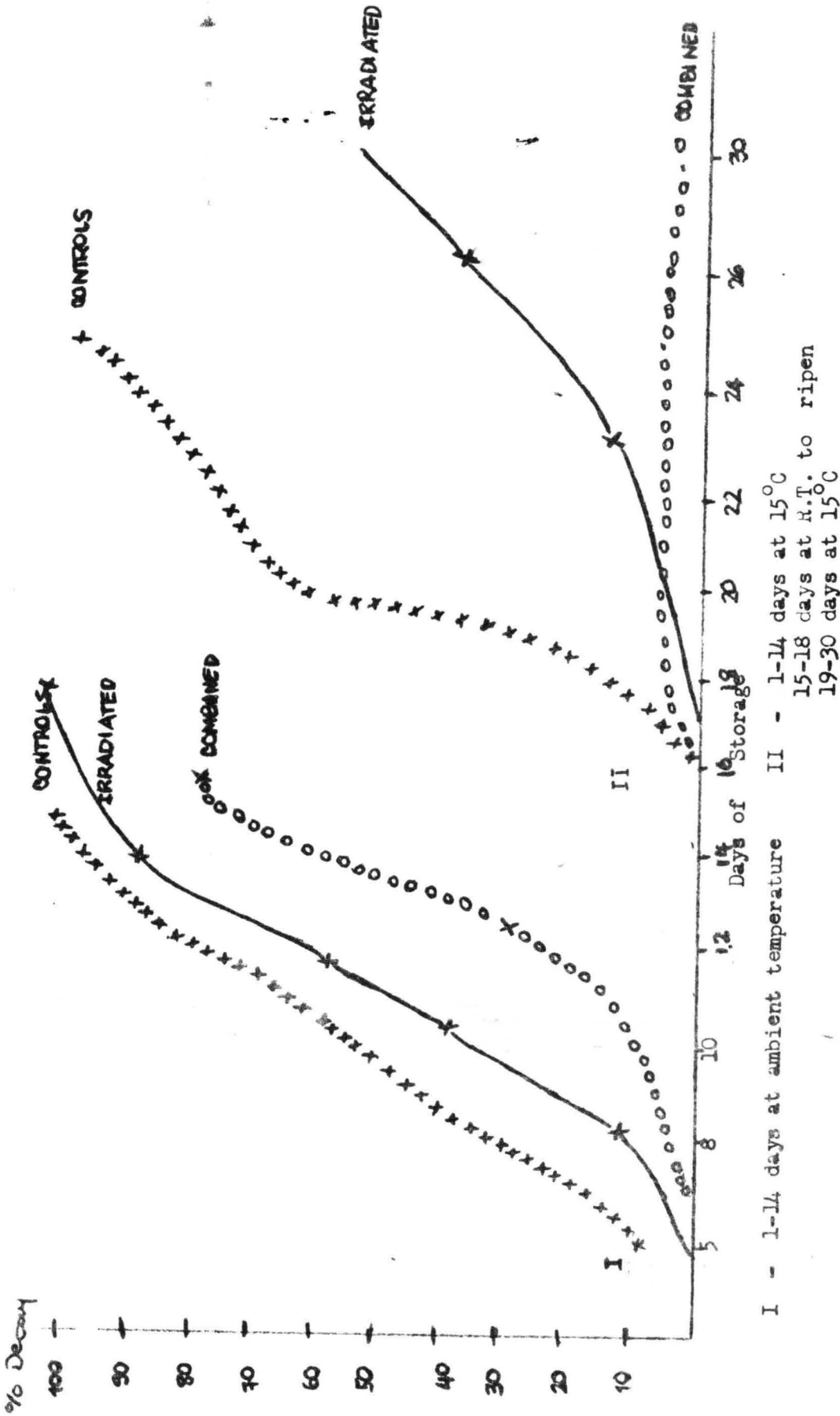
Experiments show that irradiation at 0.65 kgy combined with heat treatment offers the following benefits towards improving the export market for Philippine mangoes:

1. It is an adequate disinfestation treatment against the Oriental fruit fly Dacus dorsalis, Handl and seed weevil. It can thus be used to replace ethylene dibromide as a fumigant.
2. It increases the post harvest marketable life of green mangoes and yellow green mangoes to four days.
3. When combined with hot water dip at 55°C, marketable life is extended to six days.

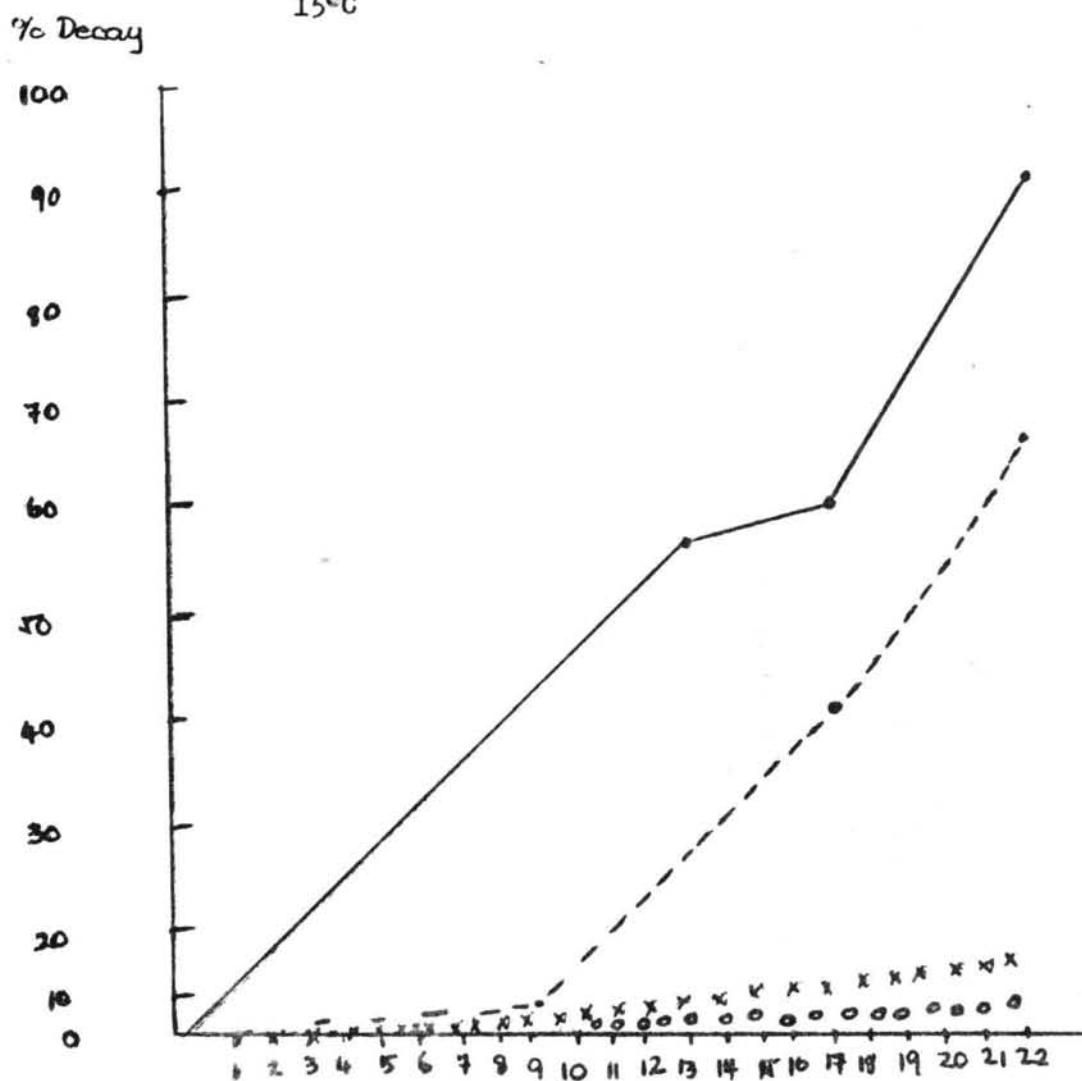
These extension may mean probable expansion of export to farther foreign markets by air or improved marketability at the sales area through improved quality of the fruits.

4. No significant adverse effects on the acidity, pectin, carotene, ascorbic acid and reducing sugar content were observed.
5. No significant differences were observed by the taste panelists on the sensory attributes between the treated mangoes and the controls.

Graph showing % decay of green mangoes subjected to preservation treatments and stored at two temperatures (1,II)



Graph showing effects of Preservation Treatments on
% Decay of Two Maturities of Mangoes stored at
15°C



————— Green Controls (GC)
 - - - - - Yellow Green Controls (YGC)
 xxxxxxxxxxxx Green Irradiated (GI)
 ooooooooooooo Yellow Green (YGI)
 00000000000 Green Combined (GC)
 Yellow Green Combined (YGC)

Graph showing effects of preservation treatments on total ascorbic acid content of green mangoes stored at two temperatures.

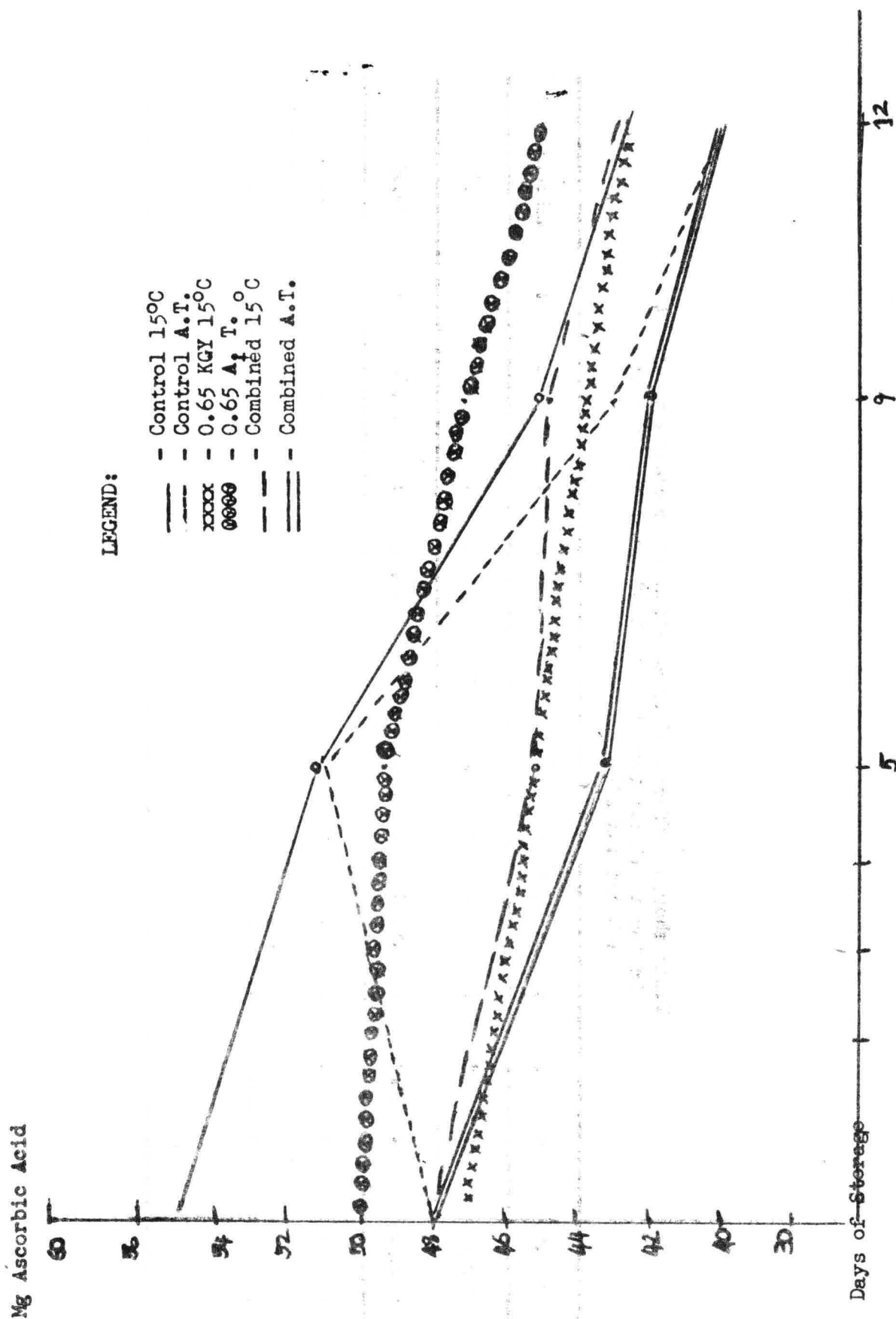


Table showing effects of irradiation and combined treatment
in the total carotenoid content of mangoes stored at
ambient and 150C.

Days of Storage :	150C :	Ambient :	150C :	Ambient :	150C :	Ambient :
0 day	8.85	9.60	7.80	9.50	2.05	2.17
5 days	25.32	36.00	20.80	22.40	12.80	19.20
9 days	36.00	28.37	26.00	29.27	15.95	21.40
12 days	40.90	41.70	35.70	41.20	22.95	35.20
Expressed in mg %						

Figure showing total acidity of green mangoes stored at 15°C.

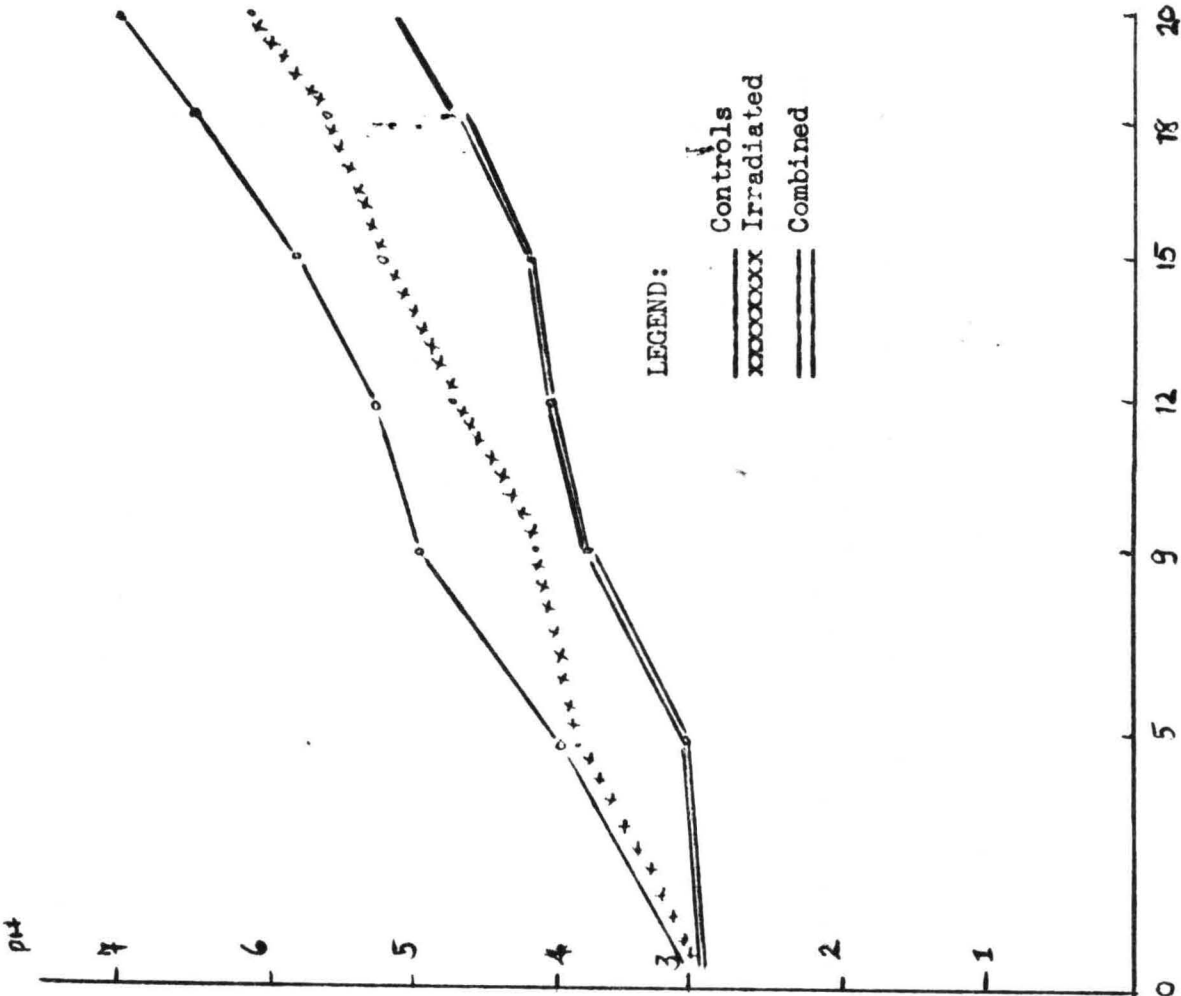


Figure showing reduced sugar content of green mangoes stored at 15°C

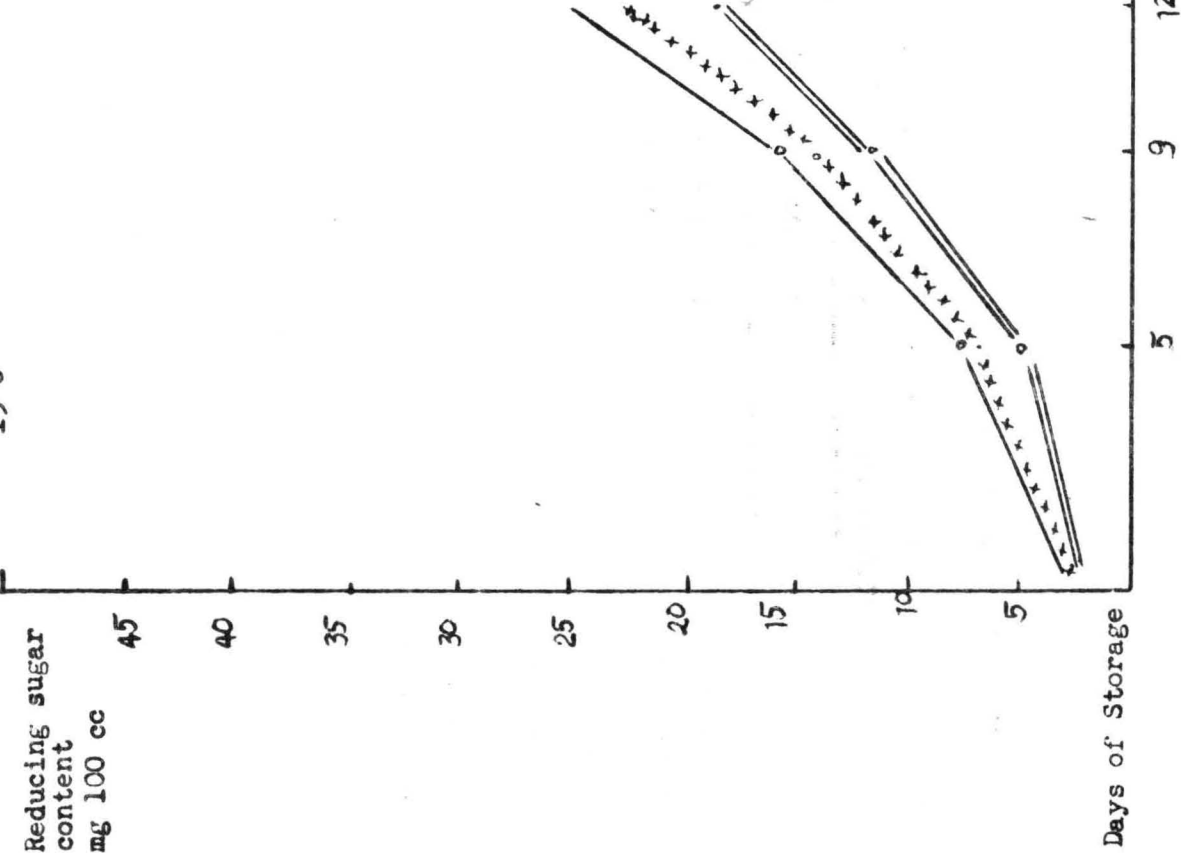


Table showing sensory evaluation results on Green Mangoes stored at 15°C and ambient temperature

ATTRIBUTES	15°C			A M B I E N T		
	:	:	:	:	:	:
: Controls: 0.65 KG: Combined Treatment: Controls: 0.65 KG: Combined Treatment						
Color	:	6.5 :	6.4 :	6.5 :	6.8 :	6.8 :
Odor	:	6.7 :	6.5 :	6.7 :	6.8 :	6.7 :
Flavor	:	6.8 :	6.5 :	6.8 :	7.0 :	6.9 :
Texture	:	6.4 :	6.3 :	6.3 :	:	:
General Acceptability	:	6.7 :	6.6 :	6.8 :	7.0 :	7.0 :
						6.8

Table showing evaluation results on Yellow Green Mangoes subjected to preservation treatments and stored at 15°C.

SENSORY ATTRIBUTES	:	CONTROLS	:	0.65 KGY.	:	COMBINED TREATMENTS
Color	:	6.6	:	6.4	:	6.6
Odor	:	6.5	:	6.3	:	6.5
Flavor	:	6.3	:	6.4	:	6.4
Texture	:	6.6	:	6.4	:	6.5
General Acceptability	:	6.7	:	6.6	:	6.6

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PRIORITIES IN THE DEVELOPMENT OF CHEMICAL ENGINEERING IN KOREA

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Development of chemical industries in Korea since 1950 is described, and the size and growth of key chemical industries are shown. The development of Korean chemical industries in the future will be towards the improvement in the productivity and the manufacture of high value-added products such as fine chemicals.

1. Chemical Industries in Korea

Chemical industry in Korea has developed in 4 stages since 1950 as shown in Table 1.

Virtually all of industries in Korea were destructed during the Korean War between 1950 to 1953. After the war, major concern of Korean industry was to produce necessities of life. Chemical industry in 1950s was developed mainly on such consumer products as sugar, paper and textiles.

Industrialization plan was announced by the Government in 1962 with the start of the first 5 year economic development plan. The objective of Korean industry was shifted to the production of raw materials. The development of chemical industry during this period was centered on the manufacture of fertilizer, cement, synthetic fibre, and petroleum refining.

In 1970s, the main objective of the industrialization plan was to lay a foundation for Heavy and Chemical industries in Korea. Petrochemicals industry was developed in this period. From 1980 to the present is called the period of the adjustment of the industrialization plan. New plan for the development of Korean industry is fomulated by the Government and industry.

The total amount of production of the chemical industry in Korea in 1980 was about 13 billion U.S. dollars which is about 28% of the total production amount of the manufacturing industries in Korea.

Petroleum Refining

First refinery was constructed in 1964 with a capacity of 35,000 barrels per day (BPSD). In 1981, the capacity increased to 790,000 BPSD, which is a 22-times increase within 20 years.

Petrochemicals

First petrochemical complex was constructed at Ulsan in 1972 and the second complex in 1979. Total naptha cracking capacity on ethylene base is 505,000 MT per year. There are 45 plants producing petrochemicals in Korea.

Synthetic fibre

The development of fibre industry in Korea has been very rapid since 1967. The production in 1981 was 646,000 MT and Korea is now the 6th largest producer of synthetic fibre in the world. Including natural fibre, the total production is 965,000 MT.

Plastics

PVC was produced first in 1967, and other general purpose resins were produced with the development of the petrochemical industry. In 1981, the total demand was 774,000 MT. The consumption of resin per capita was 3.77 kg in 1971 and 16.5 kg in 1981, about 4 times increase in 10 years.

Rubber

Demand of rubber in 1961 was 12,000 MT and this is 270,000 MT in 1981, 22 times increase in 20 years. Consumption of rubber in Korea is the 8th largest in the world and the export is about 1.5 billion U.S. dollars.

Caustic Soda

Production of caustic soda was 45,000 MT in 1974 and 190,000 MT in 1981, 4 times increase in 7 years.

Sulfuric Acid

Production of sulfuric acid in 1974 was 474,000 MT, and in 1981 it was 1,760,000 MT, 4 times increase in 7 years.

Hydrochloric Acid

There are 14 acid plants and the total production capacity is 284,000 tons (35% HCl) per year in 1982.

Fertilizer

There are 10 large fertilizer plants in Korea. The largest fertilizer plant in the world is in Korea. The total production capacity is about 3 million tons per year.

Cement

Production in 1958 was 248,000 MT and in 1981 it was 15 millions tons, indicating 58 times increase in 23 years. The total production capacity in 1981 is 23 million tons per year.

2. Priorities in the Development of Chemical Industries

In the last 20 years, Korean chemical industry played a major role in the development of Korean industry. It helped other industries such as machinery, electric and electronic industries to develop by supplying necessary materials. The chemical industry provided much needed jobs to help increase the employment. The operation of modern chemical plants also gave to Korean engineers and technicians the opportunity to learn and experience the modern technologies.

However, entering 1980s, the increase in the price of raw materials and energy following the oil shock, and the wide spread market protectionism of many countries appeared as obstacles for further development of Korean chemical industry. Korean Chemical industry has become less competitive, and we have to find out a solution to overcome these difficulties. Such difficulties are, in fact, those encountered by almost all industries in Korea.

Plans suggested for a new turn of the Korean industry are:

- (a) Rapid completion of the Heavy-and Chemical industries such as steel, machinery and petrochemicals industries in order to lay a firm foundation for the development of industry.
- (b) Productivity increase of the existing industries. Quality of the products should be improved and new multi-functional products should be developed.

- (c) Development of Technology-intensive industries. Energy and material saving new technology should be adopted and high-added value products should be produced.

In next 20 years from 1980 to 2000 priorities in the development of the chemical industry in Korea will be:

(1) Basic Chemicals

As a backbone of Korean chemical industry which supplies basic raw materials to other industries, this industry will continue to develop.

Priorities will be placed on

- o Process improvement
- o Quality improvement
- o New product development

At this stage, this industry produces mostly general purpose chemicals and supplies about 50% of the demand. Until the year of 2000, chemicals for special use will be developed. This industry will supply most of basic chemicals demanded in Korea.

(2) Petrochemicals

Priorities will be placed on the increase in productivity and diversification of products and raw materials.

By-products such as C₄-fraction will be vigorously utilized to make intermediate chemicals for fine chemicals 80% of the demand of petrochemicals will be met in 2000.

(3) Polymers

Korea produces general purpose resins such as polypropylene, polyethylene, PVC and polystyrene, synthetic fibres such as acryl, polyester and Nylon, and synthetic rubber such as SBR and BR in large scale. However, inspite of the rising demand of engineering plastics from machineries and electric and electronic industries, only small quantity of composite materials from general purpose resins are made.

Polymer industry in Korea will be developed in the following direction:

- o The grade of the general purpose resins will be diversified and high value-added products will be developed based on the general purpose resins.
- o High value-added and technology-intensive materials such as engineering plastics and functional polymers are developed.

(4) Fine Chemicals

Special emphasis is placed upon the development of fine chemicals industry in Korea. Characteristics of fine chemicals industry are shown in Table 7. It is seriously considered that the fine chemicals industry with such characteristics is best suited to Korea.

World wide production of fine chemicals amounts to about 230 billion U.S. dollars in 1981. Comparing 160 billion dollars in 1974, this shows an increase of 40% in 7 years. It is anticipated that the amount will be 300 billion dollars in 1986. In 1977, production of fine chemicals in U.S.A amounted to 31 billion dollars, and those of Western Europe and Japan in 1974, were 52 and 16 billion dollars, respectively. The proportion of the fine chemicals industry relative to the whole chemical industry in industrial countries is well above 50%.

In Korea, the amount of production of fine chemicals in 1980 was 2.5 billion dollars and import was 800 million dollars. Thus the total demand was about 3.3 billion dollars worth. Export amount was 150 billion dollars. The size of the fine chemical industry relative to the whole chemical industry in Korea is around 15-20% which is far below the figure of 50% in other industrial countries. In 1986 this figure will be 35% when the demand will be 4.8 billion dollars.

The demand of fine chemicals in Korea increases rapidly. Especially the rate of increase in agricultural chemicals and pharmaceuticals were remarkable, being 66% and 57%, respectively, during 1977 to 1980.

At present, Korea produces some fine chemicals as agricultural chemicals, pharmaceuticals, dyestuff, paint and food additives, of which demand is big in Korea, but does not produce such chemicals as high grade dyestuff, special pharmaceuticals, photographic and electronic chemicals which require very sophisticated technologies.

The development of the fine chemicals technology in Korea was:

- o In 1960s most of the raw materials and active ingredients were imported and these were diluted, formulated and packaged. Only very simple chemicals were synthesized.
- o In 1970s, some raw materials and active ingredients were synthesized.
- o About 50% of agricultural chemicals demand was produced and some pharmaceuticals were exported.

Within next 10 years, a great emphasis will be placed on the development of technology of making intermediates and active ingredients for fine chemicals.

Priorities in the development of fine chemicals industry in Korea in the next 20 years will be on the following area,

- o Agricultural Chemicals
- o Pharmaceuticals
- o Intermediates
- o Inorganic Materials for electronics
- o Photographic Chemicals
- o Dyestuff
- o Catalysts
- o Textile Additives

3. Conclusion

Last 20 years, chemical industries in Korea have been developed by producing mostly commodity chemicals employing the turn-key plants. The production of commodity chemicals consumes large quantities of raw materials and everygy.

In an age of high prices of raw materials and everygy, in order to remain competitive, Korean chemical industries will seek new technologies to improve productivity and quality and to diversify the products. In Korea whose natural resources are scarce, priorities in the chemical industries in the future will be the production of technology-intensive and high value-added products such as fine chemicals and specialty polymers.

TABLE 1. DEVELOPMENT OF CHEMICAL INDUSTRY IN KOREA

Stages	year	Emphasis	Type of Industry
Stage 1	1950's	Consumer goods	Sugar Paper, Textile
Stage 2	1960's	Raw Materials	Fertilizer, Cement, Synthetic Fibre, Refining
Stage 3	1970's	Heavy & Chemical Industry	Petrochemicals
Stage 4	1980 (present)	Adjustment of Heavy & Chemical Industry	Fine Chemicals

TABLE 2. CHARACTERISTICS OF FINE CHEMICALS INDUSTRY

1. Technology-Intensive
2. Energy and material saving
3. High added value products
4. High profit
5. Noncapital Intensive
6. Small quantity

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THE DEVELOPMENT OF FINE CHEMICAL INDUSTRY

- KOREAN EXPERIENCE -

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THE DEVELOPMENT OF FINE CHEMICAL INDUSTRY

- KOREAN EXPERIENCE -

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ABSTRACT

The fine chemical industry in Korea is at the stage of improving and modifying foreign technology. The ultimate goal is directed toward the development of our own technology and the products by early nineties. Currently, however, this industry is confronted with the shortage of the basic raw chemicals and the intermediates. The solution to the problem is sought in the supply and the demand theory. If the fine chemical industry flourishes, the sufficient demands for the basic chemicals and the intermediates will be created. The government is now promoting the development of the fine chemical industry. The industry and the research institutes are actively engaged in the research and development activities. Hopefully, by early nineties, the imbalanced structure of our chemical industry will be corrected. Some of the research areas in the fine chemical industry are listed.

1. THE HISTORY AND THE TECHNICAL LEVEL OF THE INDUSTRY.

The chemical industry in Korea started with the fertilizer plants in the late fifties. Korea, being an agricultural country, and in order to feed the nation, sufficient production of the crops has been the utmost priority. From 1960's to 1970's, oil refineries were built and petrochemical complexes were formed under the government plans. Our initial petrochemical industry was based on "turn-key" base foreign technology. They have expanded their capacities continuously and presently the petrochemicals are almost at the self-sufficient level.

Then how was the fine chemical industry and what has been the technical level of the industry ?

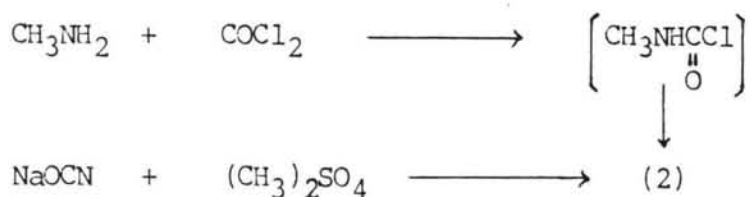
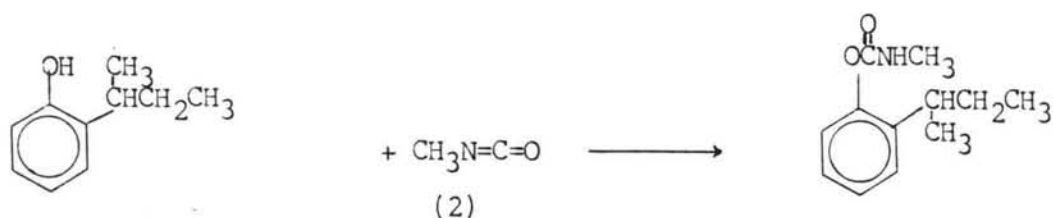
In the sixties, we imported the finished products or active ingredients for the pesticides and pharmaceuticals. We just diluted these biologically active ingredients and tabulated. In the seventies, imitation synthesis began for the pesticides and pharmaceuticals. Main effort was for the domestic production of the imported fine chemicals.

In the early eighties, I mean at present, we have digested the foreign technology and are at the stage of modifying or improving the foreign processes for our own pruposes.

From the middle and late eighties, the researches will be directrd toward the development of the new technology or new products which will be sold in the world market with our own trade marks.

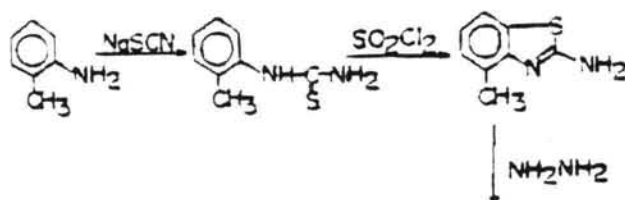
One of the improvements we have made is the synthesis of methylisocyanate. This compound is the indespensable chemical to make the carbamate insecticides.

SHORT CUT ROUTE TO METHYLISOCYANATE

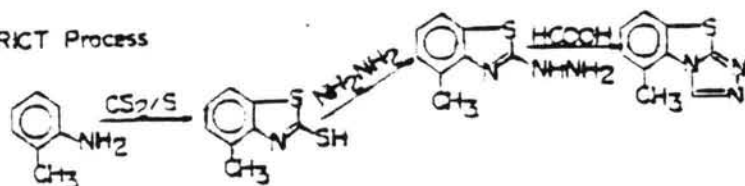


Instead of using methylamine and phosgene to go through three step reaction, we synthesized the product from sodium cyanate and dimethylsulfate. Handling of the toxic and corrosive phosgene was avoided. Another innovation we have made is the process of making a pesticide Beam^R for the rice blast. As you have noticed, we have improved the process to make methylbenzothiazole and made the product cheaper.

Ell Lilly Process



KRICT Process



Synthesis of 5-methyl-1,2,4-triazolo[3,4-b]benzotriazole

with the low labor cost of scientists and engineers, we can bring down the expenses of products development. If the developed country spend \$50 million for a new product, we are of the opinion that we can make similar compound with one hundredth of that expenses.

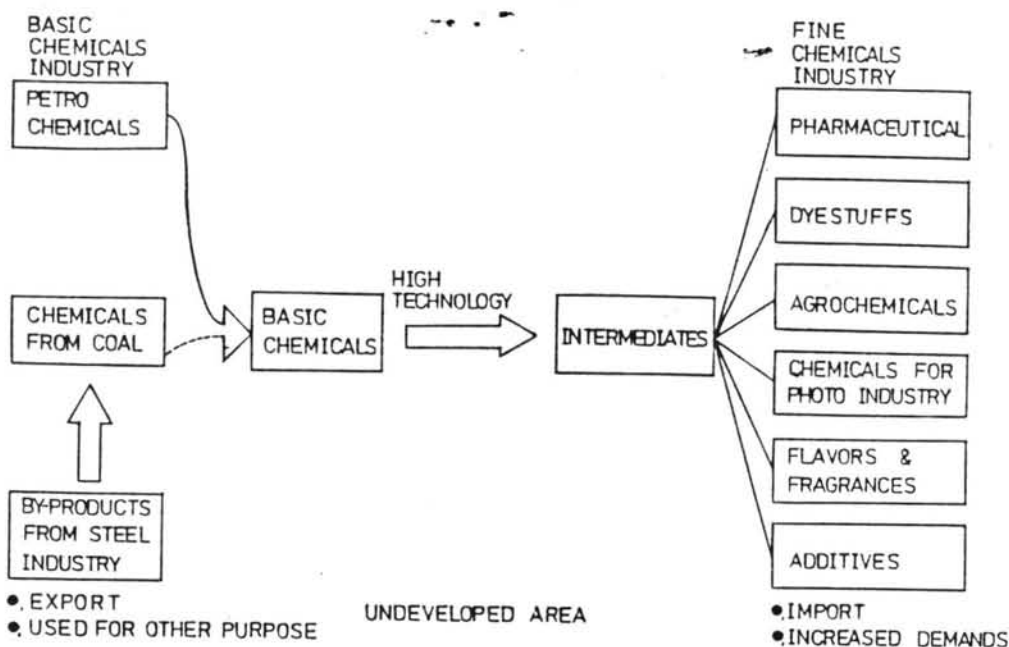
The advantage of technical improvements are two fold. It not only brings the accumulation of technology but also brings down the prices of the imported fine chemicals. I presume we all share the same experiences that once the imported products are manufactured domestically, the products are offered lower price by the developed countries. We have numerous cases in which import prices of fine chemical have been slashed down this way.

2. THE DIFFICULTIES IN THE DEVELOPMENT OF THE FINE CHEMICAL INDUSTRY

The fundamental problems the fine chemical industry in Korea faced are the imbalanced structures of our chemical industry. The present status is that the products from the oil refineries are not adequately utilized. The portions of the refinery products intensively used are only for the plastics and the synthetic fibre industry. The production of the fundamental chemicals which are essential for the specialty chemical industry are at an infantile stage. Accordingly, the intermediate chemicals are also in a great shortage.

The paradoxical phenomenon is that once processed refinery products are exported in cheap prices and are imported back as high priced refined products. The good example is the case of cresols. The crude mixed cresols in the crude tar acid are exported and they are imported back as ortho-, meta- and para-cresols.

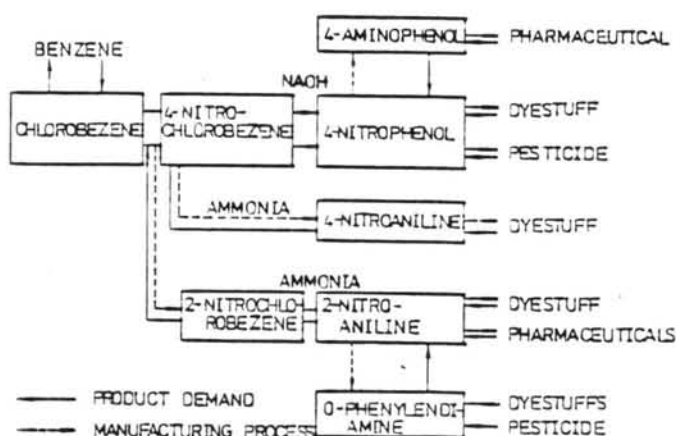
CURRENT STRUCTURES OF KOREAN CHEMICAL INDUSTRY



3. THE POSSIBLE SOLUTIONS FOR THE PROBLEM

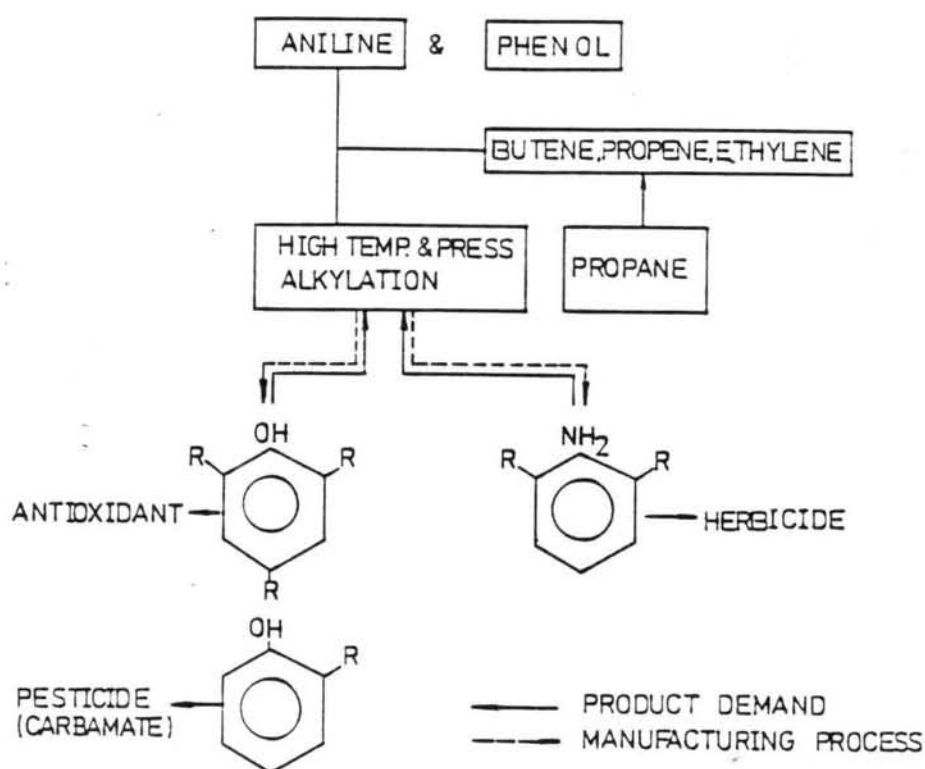
The situation of our chemical industry, as you have noticed, needs remedies. The only solution we consider is that if there are sufficient demands for the raw chemicals and intermediates, these industry will grow by itself accordingly. In order to create the demands, our fine chemical industry has to grow in the first place. For example, to create the demands for chlorobenzene and its derivatives, like nitro-anillines nitrophenols, there should be big market for the fine chemicals using them.

INTER-RELATIONSHIP OF PRODUCT



Likewise, we can exhaust the C_4 fractions more effectively instead of using them as fuel if the related fine chemical products are in demands.

C₄ FRACTION



Recognizing the needs and the importance of the specialty chemicals for the balanced development of the chemical industry, as a whole, our government included the development of the fine chemical industry as one of the projects to be supported in our fifth five year economical development plan.

The way the government assist the fine chemical industry is by way of subsidizing R & D expenses for the industries. The companies which are capable of carrying out researches and developments by themselves, do their own works. The small & medium sized enterprises ask the research institutes to do the researches for them on contract bases. The financial subsidies are in the form of interest-free loans. If their R & D works succeed and the products are sold in the open markets, they are supposed to pay back the loans to the government.

Some of the researches in our fine chemical industries and research institutes are currently engaged in include the following

Organic Chemicals ;

Synthesis and test of new biologically active compounds.
Resolution techniques of optical isomers.
Energy saving reactive dyes.
Synthetic sugar substitutes.
Other known specialty chemicals.

Inorganic Chemicals ;

The materials for electronic industries, i.e., synthetic quartz single crystals, silicone single crystals and pure gases.
Researches on zeolites.
New homogenous catalysts for chemical reactions.
Utilization of the waste gypsum.

Polymer Areas ;

Specialty polymers - conductive polymer, photo sensitive polymers.
New composites - Electromagnetic interference shielding materials, carbon fibres.
Chlorinated polyethylene.
Co-polymers for reaction injection molding.

Photographic Areas ;

Color film and the paper.
Photographic chemicals.
The photographic film for aerial image.

4. THE PROSPECTS OF THE FINE CHEMICAL INDUSTRY IN KOREA

Currently, production of the fine chemical industry occupies only 22 % of the total chemical industry.

ANTICIPATED GROWTH RATE OF KOREAN CHEMICAL INDUSTRY
(ON THE FIXED VALUE OF 1980)

	1980	1986	1991
Average annual growth rate (%)	20.5*	8.03	4.16
Production (\$ Million)	6,355	10,104	12,390

* Average growth rate during 1972 - 1980.

PROJECTED GROWTH OF FINE CHEMICAL INDUSTRY
(ON THE FIXED VALUE OF 1980)

	1980	1985	1991
Average annual growth rate (%)	25.5	17.5	10.3
Production (\$ Million)	1,373	3,622	5,908
Ratio to total Chemical industry (%)	21.6	35.8	47.7

Our projection is that this ratio will become around 50 % in 1990's. This assumption is based on the previous growth rate of the fine chemical industry.

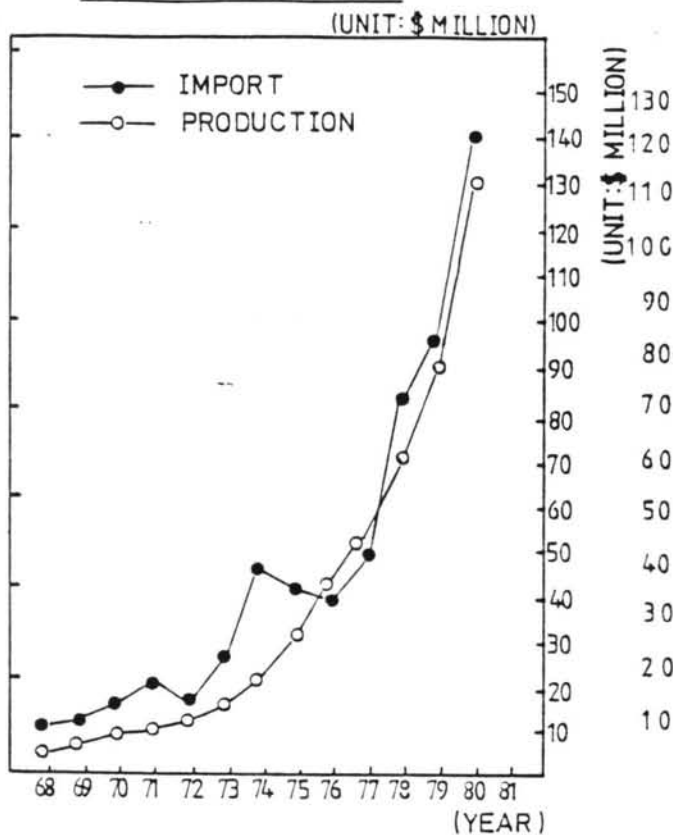
THE FINE CHEMICAL MARKET

(unit ; \$Million)

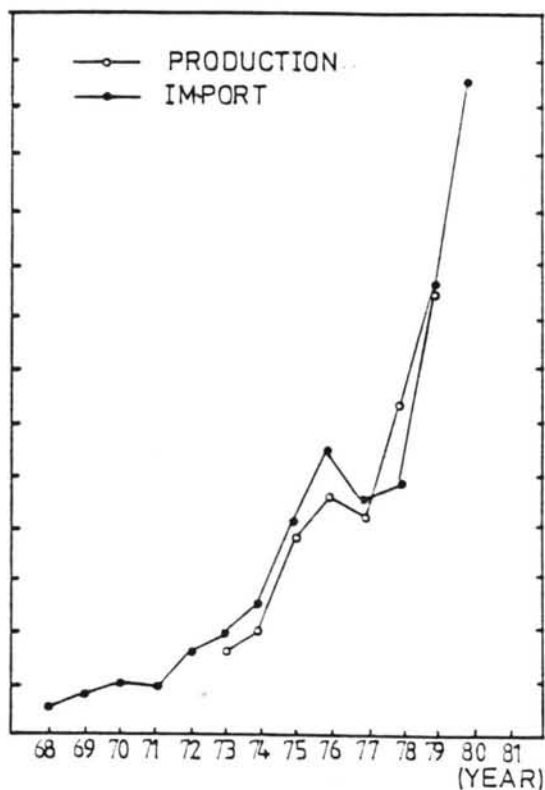
		1976	1980
Pharmaceuticals	Production	415	902
	Import	43	107
	Export	23	43
Agrochemicals	Production	104	240
	Import	53	110
	Export	0.6	5
Dyue Stuffs	Production	24	45
	Import	52	79
	Export	4	14
Pigments	Production	13	34
	Import	11	28
	Export	0.4	5
Surfactants	Production	23	44
	Import	14	26
	Export	2	9
Paints & Printing Ink	Production	110	108
	Import	12	32
	Export	1	3
Other	Production	16	20
	Import	11	425
	Export	4	70
Total	Production	705	1,373
	Import	200	827
	Export	40	149

The production of fine chemical industry almost doubled in 1976 - 1980 period. Especially in the pharmaceutical and the agricultural industry, the market size increased 3 - 4 times during these periods.

IMPORT & PRODUCTION TRENDS OF PHARMACEUTICALS



IMPORTS & PRODUCTIONS OF AGROCHEMICALS



In conclusion, by early 1990's, if our present projection is right, the fine chemical industry will be large enough to create the demands for basic chemicals and the intermediates. In other words, the structures of our chemical industry will be the sound and balanced one.

UNIVERSITY-INDUSTRY INTERACTION: THAI EXPERIENCE

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A B S T R A C T

Most of the chemists involved in industry in Thailand are chemical technologists and analytical chemists, who act as consultants to solve problems in factories and plants. Some technologists are invited to teach industrial courses. University students including chemistry students receive on-the-site training for about two months in the summer vacation. Thus, certain university-industry interactions do exist, but the university has not yet earnestly worked for industry since funds for research projects are not provided by the latter.

The Thai Government is at present paying more attention to research and development in science and technology; it encourages both industry to provide funds for research, and the researcher to aid industry in the investigations provided with such funds. The Ministry of Industry supports the establishment of liaison offices in universities for a closer tie between these two sectors.

Thai universities are empowered to conduct research projects, analysis, surveying, among others, for industry, and to receive fees as their income, which may be allotted to the researchers concerned. The university has its own rights in cooperating with industry; it is able to patent inventions and processes useful to industry.

INTRODUCTION

It is generally accepted that a developing country needs industrial advances in its path towards becoming a developed country. Such advances are hard to come by, since scientists and technologists quite often do not work on matters which will solve problems of their country; cooperation is lacking and there are too few qualified personnel to achieve progress in these two allied fields. Moreover, scientists are so much occupied with their routine work that they hardly have time for industry, which mostly involves a rapidly growing in number of purchased technology.

However, a sizable number of chemists with knowledge in industry also act as part-time consultants for 1 - 2 factories or plants. They do not have many opportunities to use their knowledge and experience since industrial processes including production systems are more or less fixed. These chemist consultants are university teachers. Their colleagues in other disciplines also give consultation in business administration, engineering, quality control and pharmacy.

For the large industry employing the production system and machinery as parts of the package of purchased technology from abroad, only little consultation is needed since most information comes from its parent foreign company. True benefits usually develop between the university and the small industry, in which purchased technology is not employed extensively, and experience and error are still valuable in the operation. In most industries, scientists are employed for quality control and pollution control, such work is routine and does not call for consultation from university teachers. Even state-owned enterprises employ scientists and do not need university teachers, since production processes have not changed from the start.

Although university-industry interactions are not extensive they do not exist at the degree which varies from university to university. The basic interactions, which may be considered to be indirect rather than direct, are education, personnel, training, etc.

1. Education

The teaching of chemistry is included in secondary education, with the emphasis on its usefulness in many chemical industries, eg. caustic soda industry, soap industry, paper industry, etc. It arouses more interest in science among students. Knowledge on production processes, however, are given together with other details at the university level. Students usually receive training, with cooperation of the industry, in the vacation before ~~their~~ final year. Such

training is directed at acquainting the students with working practice and products, rather than the reactions taking place in each step of production.

Every university has agreed to participate in the revision of science curricula. For this purpose, committees whose members consist of the heads of science departments or their representatives have been appointed, by the Ministry of University Affairs, to standardize science curricula for universities. They have prepared textbooks in basic sciences with adequate contents for science students. Certain details, however, may be left out in classes for students specializing in other fields, eg. engineering. These science curricula have been designed with industry in mind from the first year of university education.

In later years, eg. in the year before the final for chemistry students, industry-oriented courses are offered, with special lectures from industry, as electives in every university. In the vacation that year, chemistry students will have their first-hand experience, from training in factories and plants, to work in industry and the private sector.

Under this heading should be mentioned the in-service training courses organized by the Chemical Society of Thailand and the Chemistry Section of the Science Society of Thailand, with the objective of providing technologists with recent advances in chemistry and industry so that they can use them to improve their work. The topics of these courses included treatment of waste water, etc. In addition to technologists university teachers and government officials have also participated in these training courses, thus making it possible for exchange of views, discussions and scientific cooperation.

2. Personnel

University teachers, students and technologists are all involved in university-industry interactions.

The university teachers who are most active in these interactions are not members of chemistry departments, since they are mostly involved in teaching and research in pure chemistry. The departments involving in applied chemistry, and hence industry, are those of chemical technology, chemical engineering, and industrial chemistry, which exist only in a few universities. Lecturers with industrial education and back ground are often invited to act as consultants in factories and plants. They usually give advice on problems involving raw materials, production processes, and products. Some of them are so involved in their extra work that their main responsibility is jeopardized.

Most chemistry students in Thailand have an opportunity to take a certain number of industry-oriented courses, which are taught by lecturers with industrial background, and special lecturers from industry. These courses only introduce students to become acquainted with industry, since it is not possible to go into detail of all the chemical industries operating in the country. These students usually receive training in a factory or plant for about two months in their vacation. It is rather haphazard for the students to work in what type of factories; it all depends on the types and number of cooperating factories, and also the number of students for each year.

Technologists usually do not have much time available for teaching. For this reason and for the reason of specialization, a number of them are required for each course.

3. Research

In departments which involve chemical technology or industrial chemistry, research projects on the development of new products for general use are common, but none has produced the end-use. For this reason, most of the research funds, which amount to not much, come from the government budget.

4. Other Cooperations

The government has established the National Standards Office to set up and control, for the benefit of the consumer, the standard of goods produced in the country. Some tests for quality control are carried out in a number of university chemistry departments.

Mechanism for University-Industry Interaction

At present the Ministry of Industry is collecting data on the Industrial Consultancy Units (abbreviated at ICUs) operated by various offices, since it has realized that the use of expertise in science technology and management that exists in universities is vital to industrial development in developing countries. The link between the university and industry, therefore, should be strengthened. One way of achieving this goal is to set up ICUs in universities in order to increase cooperations between the university and industry. It can be seen that in addition to the university-industry interactions through personnel as already described, the government is going to strengthen such interactions through the operation of ICUs.

Commercialisation of Research Findings

Universities are entitled to market their research products, to keep the income therefrom and to distribute it to the researchers concerned. University teachers who provide private consultation to industry, of course, earn for themselves. At present there are hardly any research contracts from industry since most technologies in the country have been purchased from abroad, with processes supplied by parent companies. Research in universities to discover new processes or to improve products, therefore, does not exist since there is no need for the industry concerned. At present the government, acting through the Ministry of Science, Technology and Power, and the Ministry of University Affairs are planning for industry to make more use of the expertise in science and technology that exists in universities.

Industry's Contributions to Universities

From this move made with good intention and spirit of the government, university personnel of different professions will be able to give better services to industry in the future. One foreseeable impact is that there will be more applicants for science and technology professions. The government's idea to promote industry through assistance of the academic necessitates the promotion of research conducted by qualified personnel, not necessarily university teachers. A scheme is under way to persuade the industry to donate money, which is exempt from tax, for research.

Thailand now has the Copyright Act, and inventions can be patented. Inventions and research products in high technology are in the electronics field, and none, as far as I know, in chemistry. From what is described above it can be seen that Thailand is aiming at more university-industry interactions and Thai scientists are making it possible. This is for the benefit of industry, which paves the way for the country to achieve development and, of course, progress.

A COLLABORATIVE RESEARCH PROJECT BETWEEN
UNIVERSITY OF PERADENIYA AND CEMENT CORPORATION

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A B S T R A C T

This paper describes an 8-year collaborative research program, of which I was Director, between the Chemistry Department of the University of Peradeniya and the Ceylon Cement Corporation. Four graduate chemists from the Cement Corporation participated in this project which involved studies on: the raw materials of importance to the cement industry; the properties of various types of latex-cement mixes; the manufacture of masonry and pozzolanic cements; and operational research studies. The project was successful in many ways; it led, for example, to the industrial manufacture of masonry cement and also established the feasibility of manufacturing good quality pozzolanic cements using industrial waste.

INTRODUCTION

A collaborative research program, entirely financed by a generous grant from the Ceylon Cement Corporation, was initiated in 1968 between the Cement Corporation and the chemistry department of the University of Peradeniya. I was appointed Director of this project in which four Chemistry Special graduate employees of the cement corporation were released, during different periods, to carry out full-time research work. Part of the research was done at the cement corporation laboratories, and part at the University. Many aspects of importance to the cement industry were investigated and the results have been published in many papers. The studies included investigation of raw materials of importance to the cement industry, properties of various types of latex-cement mixes, pozzolanic cements, masonry cements, red cement and operational research studies.

In this paper some of the work done under this program, the results obtained and the significance of the work will be outlined. The success and limitations of the program will also be evaluated.

PROPERTIES OF RUBBER LATEX-CEMENT MIXES

This work was done by Mr. A. Thevarasah who did two years full-time research. The objective was to study the effect of various types of rubber latices on the physical properties of 'Kankesan' cement. Four types of rubber latices were studied: field latex, centrifuged latex, prevulcanized latex and grafted latex. Physical properties measured were compressive strength, tensile strength, modulus of elasticity and setting times.

A detailed report of the work, complete with literature references, is available (1). The first technical problem that had to be solved was to control the time of coagulation of latex when it is added to cement. The relationship between the time of coagulation of latex and the cement-setting time is important since it determines the structure and properties of the product obtained. If the latex remains stable during the setting of cement, rubber globules tend to become surrounded by the cement hydration products and thus do not form a continuous phase. In contrast if latex coagulates before the cement sets, the cement particles get coated with rubber which will inhibit further hydration and setting. It is therefore necessary to select conditions under which latex coagulates simultaneously with the setting of the cement. Since latex coagulates almost immediately when added to cement, it is necessary to add stabilizers. The effect of various stabilizers was studied. The actual stabilizers used and their concentrations are indicated, along with the tensile strength and compressive strength results, in Tables 1 and 2.

The most significant point to note from the results in Tables 1 and 2 is that the compressive strength of concrete was not changed significantly by the addition of even 8% field latex when 1.3% Vulcastab + 4% KOH was used as stabilizer. At the same time the modulus of elasticity was halved (i.e. elasticity is doubled) and the tensile strength is increased. These results are in agreement with those obtained by earlier workers, and suggests that properly stabilized rubber-latex mixes will be less likely, than normal concrete, to crack due to expansion and contraction brought about by thermal changes and moisture movements.

Some practical trials were carried out, jointly with the Rubber Research Institute of Sri Lanka, using the vulcastab stabilized field latex-cement mixes (as damp-proof flooring material, for cricket pitches). The trials were successful.

Another useful observation was that methylmethacrylate grafted latex-cement mixes gave a smooth marble like surface on setting. This could have useful applications.

OPERATIONAL RESEARCH STUDIES

Operational research studies were also carried out. The most important technical limiting factors that affect the production and also the efficiency at the various factories in Sri Lanka were identified.

A method was developed (2) for the 'kinetic' analysis of the operation of a factory: for identifying the slow steps in production, for revealing 'mis-matches' in the utilization of the various operations, and for providing a basis for the deduction of possible methods for increasing production. By making use of actual production data, the known rated capacities of the various machines used and the stoichiometric

TABLE 1: TENSILE STRENGTH /lb per sq. inch

Tensile strengths were measured using the standard procedure. Details are given in reference (1).

cm ³ of latex per 100 g cement	Field latex (2% KOH + 2% Na ₂ CO ₃ as stabilizer)	Centrifuged latex (3% Na ₂ CO ₃ + 3% KOH as stabilizer)	Pre-vulcanized latex (2% KOH as stabilizer)	15% grafted field latex (20% KOH as accelerator)	30% grafted field latex (20% KOH as accelerator)
0	575	575	575	575	575
3	540	440			
7	480	430	450	450	450
10		300			
14				385	325
16	400		400		
20				335	310
25			250	315	300

TABLE 2: COMPRESSIVE STRENGTHS /lb per sq. inch

cm ³ of latex per 100g cement	Field latex (3.3% vulcastab + 4% KOH as stabilizers)	Pre-vulcanized latex (3% KOH as stabilizer)	15% grafted field latex (20% KOH as accelerator for setting)	30% grafted field latex (20% KOH as accelerator for setting)	Centrifuged latex (20% Na ₂ CO ₃ + 20% KOH as stabilizer)
0	3000	3600	3600	3600	3600
0.8					2300
1	3410	3000	3100	2980	
1.2					1970
1.6					1860
2	2000	1860	1860	1970	

Note 1. The results given are the average values of several sets of readings

2. By varying the amounts of KOH and vulcastab LW it was observed that about 3.3% vulcastab and 4% KOH with respect to latex gave the maximum tensile strength; this percentage was used for compressive strength measurements.

relationships between the various steps in the manufacturing process, the percentage utilization (% Ut.) of each of the operations at a factory, which is defined by the equation

$$\% \text{ Ut.} = \frac{\text{actual output}}{\text{maximum possible output}} \times 100$$

can be calculated. The percentage utilization data gives useful quantitative insight into the operation of a factory.

The percentage utilizations of the important operations at the three cement factories in Sri Lanka are given in Table 3. It can be deduced from the data that the burning of the raw meal in the kilns is the slowest step. To increase production, attention has to be focused on this step. Many suggestions have been made for improving this step and hence for increasing the rate of production in a detailed report sent to the Ministry of Industries and to the Cement Corporation. The significant parts of this report have also been published in an Industrial journal (3).

The data given in Table 3 indicates at a glance the overall operation of the factory: it indicates for example the 'mismatch' in some of the operations and the low percentage utilization of most of the operations.

MANUFACTURE OF POZZOLANIC CEMENT

Pozzolanic cement is a special type of cement that is obtained when pozzolans are finely ground with portland cement. By pozzolans is meant siliceous and aluminous substances which, though having no cementitious qualities themselves, react with lime in the presence of water to form compounds having cementitious properties. The pozzolans available in Sri Lanka include bricks, roof tiles and clays.

The feasibility of the manufacture of pozzolanic cement in Sri Lanka was studied by Mr. Thevarasah at the cement corporation laboratories. The results of this work have been published elsewhere (4) and so will not be given here. What we did was to first find out by experimental studies (reactivity with lime and with alkali) the conditions (pre-treatment required etc.) under which broken tiles (and also some other pozzolans) exhibit maximum pozzolanic activity. The pozzolan was then ground with cement and the relevant properties (e.g. tensile strength, compressive strength, sulphate resistivity, initial and final setting times, workability) of the pozzolanic cements so obtained were studied so as to evaluate their quality. The effects of the ratio of pozzolan to portland cement, grinding procedure, and also particle size (this depends on grinding time) on the quality of the portland cement were studied to optimize the quality of the product.

TABLE 3

Actual Production (in tons) and Percentage Utilization of the Various Operations

	<u>Limestone Crusher</u>	<u>Clay Dryer</u>	<u>Raw Mills</u>	<u>Kilns</u>	<u>Cement Mills</u>	<u>Packing Plants</u>
<u>Kankesanthurai:</u>						
Production 1974	3.14x10 ⁵	4.33x10 ⁴	3.53x10 ⁵	2.02x10 ⁵	1.86x10 ⁵	1.81x10 ⁵
Production 1973	3.86x10 ⁵	7.06x10 ⁴	3.58x10 ⁵	2.20x10 ⁵	1.82x10 ⁵	1.85x10 ⁵
Production 1972	3.53x10 ⁵	5.64x10 ⁴	3.77x10 ⁵	2.08x10 ⁵	1.77x10 ⁵	1.76x10 ⁵
%Ut 1974	12	41	58	62	40	13
%Ut 1973	14	46	62	68	38	13
%Ut 1972	14	37	60	64	36	13
<u>Puttalam:</u>						
Production 1974	4.88x10 ⁵	1.08x10 ⁴	4.36x10 ⁵	2.67x10 ⁵	2.30x10 ⁵	2.23x10 ⁵
Production 1973	3.20x10 ⁵	0.70x10 ⁴	3.90x10 ⁵	1.80x10 ⁵	1.50x10 ⁵	1.50x10 ⁵
%Ut 1974	14	3	40	58	31	13
%Ut 1973	10	2	27	38	21	9
<u>Galle:</u>						
Production 1974	-	-	-	-	5.50x10 ⁴	5.50x10 ⁴
Production 1973	-	-	-	-	5.00x10 ⁴	5.00x10 ⁴
%Ut 1974	-	-	-	-	26	13
%Ut 1973	-	-	-	-	24	12

Our work showed that good quality pozzolanic cements conforming to ASTM specifications could be manufactured in Sri Lanka by grinding Portland cement with powdered roof tiles (40 to 50% by weight of tile powder). Pozzolanic cements are better than Portland cement for certain applications, and they are also cheaper. An approximate cost analysis showed that pozzolanic cement will be about 75% cheaper than portland cement. The pozzolans required (broken roof tiles) are easily available in Sri Lanka, being a waste material. No new machinery would also be required for its manufacture.

Plans for the manufacture of pozzolanic cement in Sri Lanka were drawn up some years ago (and even announced over the radio). For some reason nothing more was heard about these plans. The Industrial Development Board is now pressing the case for the manufacture of pozzolanic cement in Sri Lanka.

MANUFACTURE OF MASONRY CEMENT

Masonry cement is obtained by intergrinding a mixture of portland cement clinker, crushed limestone (about 50%), gypsum and a small amount of an air entraining agent. Masonry cement is not only cheaper but superior to portland cement for use in masonry work, i.e. for use as a mortar, because the plasticity, workability, water retention and adhesion of this type of cement is better. These are the properties that are important in a mortar (not so much its strength).

The feasibility and necessity for manufacturing masonry cement in Sri Lanka was first studied under this program in 1973 by Mr. T.G.A. Premadasa. Mr. Premadasa estimated that 60% of the cement used then was for masonry work and that considerable savings would be effected if masonry cement was manufactured and used for masonry work. Experimental work was subsequently done by Mr. Navaratnam. The experimental studies were very similar to those described under pozzolanic cement. The percentage of limestone, the amount of air-entraining agent, the grinding procedure and the particle size of the cement (this depends on grinding time) were varied so as to find optimum conditions for the manufacture of masonry cement. It was shown both by laboratory and pilot plant studies that good quality masonry cements could be manufactured. These results were made use of for starting the manufacture of masonry cement in Sri Lanka.

OTHER STUDIES

Many other studies have also been carried out under this program. For example Mr. Mikadawa made a study, for two years, under the supervision of Prof. H.W. Dias, of the composition and quality of limestone and dolomite deposits in the Central Province. Mr. Herat Banda studied, under the supervision of Prof. S.G. Canagaratna, the grafting of acrylonitrile to natural rubber latex, and the properties of cement-acrylonitrile grafted rubber latex mixes. Studies were also carried out and suggestions were made in the Report

sent to the cement corporation and the Ministry of Industries on various other topics such as the transport and drying of clay, prevention of pollution, necessity for diversification of products, etc.

A GENERAL REVIEW

There is a strong emphasis nowadays, in many parts of the world, for the initiation and promotion of University-Industry interaction. An important form of this interaction is collaborative research between industry and University. Some comments on our program, and the factors that may determine the success of such collaborative research programs will be made now.

Our program can be considered to be successful for the following reasons. It trained four Honour graduate chemists of the corporation in research methods and cultivated research awareness in them. It led to the manufacture of masonry cement and established the feasibility of manufacturing pozzolanic cement. Many limiting technical factors in the operation of the factories were also identified and simple suggestions were made for overcoming these limiting factors.

The success of our program in due, in my view, primarily to the fact that the then Chairman of the Cement Corporation (Dr. V. Perampalam) was actively involved in the project. In fact he is coauthor of one of our research papers (4). He strongly encouraged and provided facilities that would lead to the implementation of the research findings. Another reason for the success of our research collaboration is the fact that the Corporation's chemists themselves were actively involved in the work. This is absolutely essential if implementation of any research findings is to be expected. It is not sufficient for an industry to identify a research problem of importance to them and hand it over to the University scientists for a solution (as is sometimes done). It is essential, I believe, for the Industrial chemists themselves to be directly involved in the research work; otherwise implementation of any research findings is unlikely.

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UNIVERSITY - INDUSTRY INTERACTION: THE PHILIPPINE EXPERIENCE

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ABSTRACT

The more than 7,000 islands that comprise the Philippines is more oriented to agro-business concerns rather than chemical industries which had its beginnings during the Spanish regime when the missionaries taught the people the manufacture of simple medicines from native plants and the cultivation of sugar.

The distribution of industries throughout the islands follows a similar pattern as the distribution of universities and colleges (a total of 42) offering B.S. Chemistry and B.S. Chemical engineering.

Among the university-industry interactions practiced in the Philippines today are: campus recruitment program, extra-curricular industrial experience, part-time study, continuing education, scholarship grants, professorial chairs, contracted research and development work. The Philippine Institute of Pure and Applied Chemistry (PIPAC) is mentioned as a model of University-Industry Collaboration.

However, constraints in the practice of the professions are encountered when violations of the laws governing chemistry, chemical engineering and pharmacy occur due to unavoidable overlapping of their respective functions.

INTRODUCTION

The Philippines, with its more than 7,000 islands, is more oriented to agro-business concerns rather than chemical industries.

The historical background of chemical industries has shown that as early as the 16th century, when the Philippines was then a Spanish colony (1521-1898), the missionaries taught the people

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the manufacture of simple medicines from many native plants as well as the cultivation of sugar cane which later became a chief export product of the Philippines.

At present, the chemical and chemical products industries, although considered as one of the large scale industries, is not a major industry of the country. The reasons for this are twofold: one, the inadequate supply of locally produced raw materials for use in the manufacture of the chemicals and related products and two, the difficulty of transferring the required technology.

In presenting the problems arising from university-industry interaction, the consequences of government regulation of the professions must be taken into consideration. Another factor is the proliferation of both private (30) and chartered (12) universities and colleges scattered over the islands with varied curricular offerings.

CHEMICAL INDUSTRY

The chemical industry is one of the fast expanding areas of investments in the country today. Its growth is due to the increasing demands of the country's rapidly growing manufacturing sector. In view of this, it has been included in the country's First Investment Priorities Plan for manufacturing. This is to assure the industry of low-cost domestic raw materials, cheap hydro-electric resources and relatively low labor cost.

Figure I shows the provincial and regional map of the Philippines, and the geographical distribution of companies dealing with industrial and other chemicals. Region I (Ilocos) - 14 companies, Region II (Cagayan) - 0, Region III (Central Luzon) - 13, Region IV (Southern Tagalog) - 12, Region V (Bicol) - 5, Region VI (Western Visayas) - 14, Region VII (Central Visayas) - 29, Region VIII (Eastern Visayas) - 3, Region IX (Western Mindanao) - 7, Region X (Northern Mindanao) - 7, Region XI (Southern Mindanao) - 4, Region XII - 4.

The chemical industries accounted for less than one percent of the total non-profit private expenditures gross capital formation and in net industry change.

UNIVERSITIES AND THE CURRICULUM

There are 30 private industries and 12 chartered colleges and universities offering B.S. Chemistry and B.S. Chemical Engineering degrees (not necessarily both). Table I presents the distribution of these schools by regions throughout the country.

Most universities within the period 1960 to 1970, offered Industrial Organic and Inorganic Chemistry in the curriculum for

FIG.1 REGIONAL DISTRIBUTION OF COMPANIES DEALING IN INDUSTRIAL AND OTHER CHEMICALS

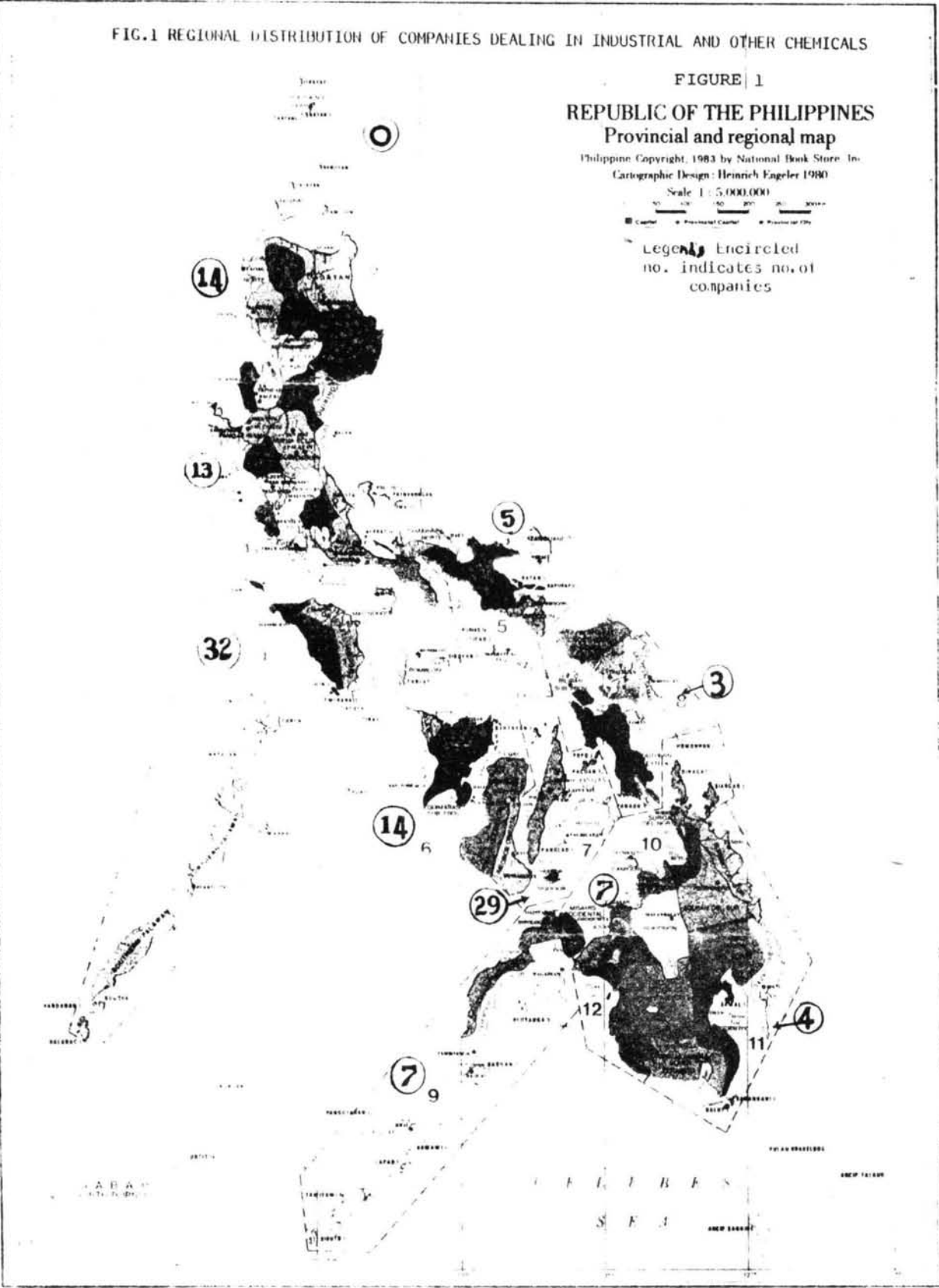


TABLE I. UNIVERSITIES/COLLEGES OFFERING B.S.CHEMISTRY
AND CHEMICAL ENGINEERING COURSES

S.CHEM.	B.S.CH.E.	UNIVERSITY/COLLEGE	SECTOR	LOCATION
		: Region I		
x	x	: Saint Louis University	: Private	: Baguio City
	x	: University of Baguio	: "	: Baguio City
x		: Mariano Marcos State University	: Chartered	: Batac, Ilocos North
x		: University of Northern Philippines	: "	: Vigan, Ilocos Sur
x		: Luzon Colleges	: Private	: Dagupan City
		: Region II		
x		: St. Mary's College	: "	: Nueva Viscaya
		: Region III		
x		: Centro Escolar University	: "	: Malolos, Bulacan
		: Region IV		
	x	: Golden Gate College	: "	: Batangas City
x		: U.P. at Los Banos	: Chartered	: Los Banos, Laguna
		: Region V		
	x	: Aquinas University	: Private	: Legaspi City
x		: University of Northeastern Philippines	: "	: Iriga City
	x	: University of Nueva Caceres	: "	: Naga City
		: Region VI		
	x	: Aklan College	: "	: Kalibo, Aklan
x	x	: University of San Agustin	: "	: Iloilo City
x	x	: Central University of the Philippines	: "	: Iloilo City
x		: University of Iloilo	: "	: Iloilo City
x	x	: Western Institute of Technology	: "	: Iloilo City
	x	: University of Negros Occidental Recoletos	: "	: Bacolod City
x	x	: Colegio de San Agustin	: "	: Bacolod City
x	x	: West Negros College	: "	: Bacolod City
		: Region VII		
	x	: University of Bohol	: "	: Tagbilaran City
x	x	: University of San Carlos	: "	: Cebu City
x	x	: Southwestern University	: "	: Cebu City
	x	: Cebu Institute of Technology	: "	: Cebu City
x		: Silliman University	: "	: Dumaguete City
		: Region VIII		
	x	: Divine Word University	: "	: Tacloban City
	x	: Leyte Institute of Technology	: Chartered	: Tacloban City
x		: University of Eastern Philippines	: "	: Northern Samar

TABLE I, cont.

B.S.CHEM.	B.S.CH.E.	UNIVERSITY/COLLEGE	SECTOR	LOCATION
		: Region IX		
x		: Western Mindanao State University	: Chartered	: Zamboanga City
		: Region X		
x	x	: Xavier University	: Private	: Cagayan de Oro City
		: Region XI		
x		: Notre Dame of Marble College	: "	: South Cotabato
x	x	: Ateneo de Davao University	: "	: Davao City
	x	: University of Mindanao	: "	: Davao City
x		: Immaculate Conception College	: "	: Davao City
	x	: Rizal Memorial College	: "	: Davao City
		: Region XII		
x		: University of Southern Mindanao	: Chartered	: North Cotabato
x	x	: Mindanao State University	: "	: Marawi City
x	x	: Iligan Institute of Technology	: "	: Iligan City
	x	: St. Michael's College	: Private	: "
		: National Capital Region - Metro Manila (Chartered University/College		
	x	: Pamantasan ng Lungsod ng Maynila	: Chartered	: Intramuros Manila
	x	: Eulogio "Amang" Rodriguez Institute of Science & Technology (EARIST)	: "	: Sampaloc Manila
x		: Philippine Normal College	: "	: Taft Avenue Manila
x	x	: University of the Philippines, Diliman	: "	: Diliman, Quezon City

B.S. Chemistry degree. This is to prepare students for a job in industry if they can find such an employment opportunity after graduation. Industrial Chemistry subsequently was made as one of the major board exam subjects given by the Board of Examiners of the Professional Regulation Commission, a government licensing organization. In the Philippines, a graduate must have to pass the corresponding government board examination before he could practice his profession. But later, the academe and the Board of Examinees realized that the industrial chemistry subject taught in the universities were either obsolete or did not keep pace with the more modern processes employed so that by the 1970's the subject was distributed among the basic branches of chemistry, organic and inorganic chemistry, while physical chemistry replaced it as a major subject in the Board exam. This was effected after a consultation among the Board of Chemistry, composed of three examiners, and the heads of chemistry departments of various schools.

UNIVERSITY-INDUSTRY INTERACTIONS

Some of the university-industry interactions practiced in the Philippines are as follows:

1. Campus Recruitment Program - This is a deliberate effort of some industries to bring academic and business worlds closer to one another by promoting a better understanding between corporate management and the student community. The mechanics of the program consists of the following steps:

- Step 1 - Identification of priority degrees/preferred schools by taking into consideration division/plant requirements through the personnel officers.
- Step 2 - Designing of training programs suitable for the trainees and presentation of training programs to the Deans of preferred degrees and schools.
- Step 3 - Submission of list of the names of the top 10 percent of college juniors, as per requirements of the Company division.
- Step 4 - Processing of qualified college juniors for placements and pool and for possible employment of those who passed company tests and interviews.
- Step 5 - Conduct of performance evaluation of each student trainee by the immediate Supervisor.
- Step 6 - Appraisal of the effectiveness of the training program.
- Step 7 - Classification of trained college juniors according to functional areas for pooling.
- Step 8 - Renewal of contacts with company trained students for possible placements on or before graduation.

2. Extra-curricular Industrial Experience - Students enrolled in industrial chemistry subjects are required to make visits to selected industries. The faculty teaching the subject requests selected factories for permission for a plant visit. The industry usually conducts a two to three hours plant visit.

3. Part-time Study - Some government and private industries encourage deserving employees to pursue studies in the universities by allowing them time off to attend classes, on a full-time salary. The work schedule of the employee is arranged to fit his schedule of classes at the university. This is however feasible, if the industry operates on a two-shift or three-shift timetable.

4. Continuing Education - This is offered to industries by some universities and professional organizations for continual assessment of all technology relevant to the country's present and future needs. Studies are made of the possibility of adopting a particular program or extending it to suit particular needs of the country. The needs must be analyzed to distinguish between those that are specialized and non-specialized. A quantitative assessment is required as well as a qualitative determination. It is, in effect, a market survey to determine the magnitude of the response to programmes which maybe offered.

5. Scholarships - Some industries support deserving students through college scholarships. Examinations are administered to qualified students. Usually the scholarship includes free tuition fee, a living allowance and book allowance.

6. Professorial Chair - is awarded as an appropriate rewards system by some industries for outstanding achievements. A fixed sum per month is given to the faculty member awardee. In exchange, the awardee is required to give a seminar on a topic within his line of expertise within the year.

7. Research and Development Schemes - Small industrial concerns which may find it expensive to maintain a laboratory to solve some of their industrial problems, seek out university laboratories for joint project ventures, or they may simply enter into a research contract with the university.

THE PIPAC - A MODEL OF UNIVERSITY-INDUSTRY COLLABORATION

The Chemistry Department of the Ateneo University in view of its better facilities, involved itself not only in academic research and teaching, but also in industrial concerns. Initially, the problem of training in the use of modern chemical instrumentation was met by offering special training seminars on the various current chemical instrumentation techniques.

The second phase of involvement with industry dealt with analytical problems and occasionally involved a major piece

of development work.

By the end of 1969, serious consideration was made to establish a separate organization closely linked but then separate from the University to service industries. An in-depth interview with the management and technical personnel of some thirty six companies showed that some 75% of these will need analytical services, 75% -R & D; general consultation-70%, personnel training-46%, and quality control-25%.

Eventually, the Philippine Institute of Pure and Applied Chemistry, or PIPAC was organized in 1972. The Board of Trustees consists of three members from the university, one from the government on a technical basis, and five from various industrial sectors.

The activities in which PIPAC was envisioned to be engaged are:

1. Analytical Services
2. Chemical Research
3. Training Program and Workshops
4. Standards Testing Laboratory
5. Environmental Pollution Monitoring
6. In-plant Analytical Procedure
7. General Chemical Consultation

Table II below shows the increase in the number of chemists serviced by PIPAC, as well as the increase in the income, and operating expenses indicating the extent and growth in the operations of PIPAC:

TABLE II. SUMMARY OF THE EXTENT AND GROWTH OF PIPAC ACTIVITIES FROM 1975-1979

Growth Indicator	1975	1976	1977	1978	1979*
No. of Chemists served	15	40	70	66	80
Gross Income	₱11,600	₱105,500	₱328,000	₱379,000	₱450,000
Operating expenses	₱ 6,800	₱ 68,000	₱157,000	₱243,000	₱350,000

* From January to August 1979 only.

SOME LIMITATIONS IN THE PRACTICE OF THE RELATED PROFESSIONS

The legal definition of the practice of chemistry, pharmacy, and chemical engineering contained in the laws controlling the practice of these three professions clearly shows the unavoidable overlapping of their functions. Chemistry, in its various facets,

along with cognate principles of physical and biological sciences, is essential in the practice of pharmacy. The different methods used to determine whether a certain pharmaceutical preparation is efficacious, of a standard and consistent potency and purity, and acceptable as to color, flavor, and physical appearance are definitely chemical in nature and these analytical procedures are within the sphere of operation of a chemist. The same can be said of chemical engineering. It is a branch of engineering concerned primarily with the application of chemistry, physics, and mathematics in the manufacturing processes of modern industry. Chemical engineers are now employed in quality control laboratories of industrial firms, and as such they perform the work of a chemist.

It is indeed not an easy task to delineate the sphere of these three professions as it is not easy to determine with precision and certainty the sphere of the three departments of the government. In the words of Justice Holmes of the United States Supreme Court in the case of *Government vs. Springer*, 27 U.S 189:

"The great ordinances of the Constitution do not establish and divide fields of black and white. Even the more specific of them are found to terminate in a penumbra shading gradually from one extreme to the other. When we come to the fundamental distinctions, it is still more obvious that they must be received with a certain latitude or our government could not go on."

"It does not seem to need argument to show that however we may disguise it by veiling words, we can not carry out the distinction between legislative and executive action with mathematical precision and divide the branches into water-tight compartments, were it ever desirable to do so, which I am far from believing that it is, or the constitution requires".

The principle of separation of powers and delienations of functions and responsibilities envisioned by the law cannot be enforced with pedantic rigor. It is only a relative theory. The more practical way of looking at it is to consider the professions as circles which partly overlap. There must be some ground which each of the three professions may occupy. However, there should be no absorption of legitimate functions of each group and short of that, the merging or blending of functions is allowable. These professions while separate and coordinate, should not be antagonistic to each other. One should not frustrate the other. They should work hand in hand to attain their objectives.

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ASIAN CHEMICAL CONFERENCE ON PRIORITIES IN CHEMISTRY IN
DEVELOPMENT OF ASIA

UNIVERSITY-INDUSTRY INTERACTION:

THE SINGAPORE EXPERIENCE IN AN INDUSTRIAL ORIENTATION
PROGRAMME FOR SCIENCE STUDENTS

Much has been and will continue to be written on this all important area of university-industry interaction¹⁻³. Like many other areas of common concerns, concepts alone, though intellectually stimulating and appealing, may be in danger of remaining permanent precepts. On the other hand, a precept that can be translated into practice would be welcomed by both academics and industrialists alike and especially the latter. We believe such an idealised situation may be seen in the Industrial Orientation Programme for science students in Singapore^{4,5}.

This very conference with its apt theme on "Priorities in Chemistry in Development of Asia" is a timely reminder and challenge to all of us especially those concerned with Chemical Education and Industries. The author is grateful for the opportunity of sharing the experiences embodied in this paper and welcomes the comments and suggestions that a gathering of this nature may be able to make to the enrichment of all concerned.

Tertiary Chemical Education in Singapore dates back to the days of Raffles College, more than half a century ago⁶⁻¹⁰. Since then, many chemistry graduates have been produced, whose contributions on both sides of the causeway have been considerable. Conferees here will undoubtedly concur that the challenge of Chemical Education is indeed fascinating. The teaching and learning of this practically all-embracing science call for all the resources at our command. The extent and range of chemistry is indeed expanding rapidly with ever-widening frontiers and demands the very best from us.

These thoughts, together with the take off in the Industrial Programme of Singapore in the early sixties, focussed on the need that the academic training in the University could be beneficially matched with some form of work experience in an industrial environment. Such an experience will go a long way to help students plan their careers and be of better service to the community.

Although tertiary education in chemistry in Singapore has not included a formal programme of industrial training, yet the Science Faculty was open to several possibilities whereby students could obtain this type of experience. One such possibility was to make use of the long vacation for students to be exposed to the working situation outside the University, especially in industry and commerce. This move

was indeed welcome by all quarters as it has been generally recognised that diplomas and degrees are not an end in themselves and that students must also be exposed to the work-a-day world in both government, quasi-government and private sectors.

While it was possible for the Science Faculty and/or the Chemistry Department to make use of their own contacts with various bodies outside the University, especially through its own graduates, to seek places for its students for such training, yet it was thought best that the activities should be carried out through a centralised body. This would help facilitate cooperation with other institutions having similar aspirations. This need was taken up by the Science Council of Singapore, a statutory body established primarily to advise the government on scientific policies and matters and related issues. In turn, the Science Council appointed a body known as the Central Agency, a sub-committee of the Council and comprising representatives from the Council, government ministries and various commercial and educational bodies.

One crucial front-line contribution of the Central Agency is making known this programme to outside bodies. It makes public announcements and invitations to various establishments in the private and public sectors for this programme. Invitation circulars and response forms are sent

out many months before the onset of the student vacation.
On receiving positive replies from these establishments as to the facilities they can offer, the Agency proceeds to place students in appropriate establishments through the University Liaison Officers.

To help launch the programme as well as in its early year Chinese Chamber of Singapore gave financial as well as strong moral support. This has now been followed up by the Singapore Manufacturers' Association, the International Chamber of Commerce and the Singapore Employers' Federation. Recognition of this programme is also afforded by the Ministry of Defence through the granting of deferment to National Service men from any training that coincides with the orientation period. Likewise, these establishments need not apply for work permits for our foreign students engaged in this programme. Other encouraging exemptions are in the areas of the skills development fund levy and the payment of payroll tax in conjunction with the "employment" of these students. Media coverage including those over national television and radio have been supportive and encouraging.

As anticipated, the response on the part of both establishments and students has been warm and appreciative. Table 1 presents an overview of the response by the establishments. The total number of such establishments and the total number of training placements they offered are

listed for the period 1971 to 1983.

Except for a few irregularities the figures show a steady growth. Table 2 elaborates on these establishments and training placements by classifying them into the "public" and "private" sectors. While the private sector comprises a multitude of companies over a wide spectrum, ranging from small family enterprises to the giant multi-nationals, the public sector comprises relatively large government or semi-government bodies with the capacity to offer larger numbers of training placements.

Table 3 provides some indication of the number of years the different establishments have been offering places. There is the constant need to ensure that not only are more and more establishments involved but participating ones encouraged to keep on offering places. This exercise itself is an important aspect of university-industry interaction. Yet another, is the need to ensure that the placements are meaningful to the students who volunteer for this programme. Whenever possible the training and experiences gained should be relevant and/or complementary to the courses they are reading at the University. Wherever possible, students should be given assignments which commensurate with their academic background, training or interest.

Table 4 furnishes the number of places offered in relation

Table 4 furnishes the number of places offered in relation to courses of study. The patterns here is a possible reflection of the employment and career situations prevailing at that time. The high figures for chemistry placements and the fast-growing ones for computer science (listed under mathematics) are certainly good indicators of career opportunities.

Table 5 shows the period of attachment for our students participating in Industrial Orientation. The six week period dominates simply because this is the official length of attachment indicated in all our official correspondence, releases etc. Where the establishment is able to offer good placements even though they may not be able to offer the suggested six week period, we, nevertheless, gratefully accept such placements. It is encouraging to note that in a large number of cases where the training exceeds six weeks it has been due to the establishments' initiative to extend the programme on the basis of the students' keenness, performance, usefulness etc.

It may also be of interest to note the way chemistry students have been placed in the various establishments, classified by their industrial character. These details are given in Table 6. The students' response has been positive. This has been all the more encouraging noting the voluntary/optional nature of the programme and the many competing and attractive alternatives open to our students

in their long vacation. Students who take part in this programme are usually paid a nominal allowance, the current rate being \$7 per day. Where the establishment is able to pay more, it would of course be an added area of satisfaction and/or even motivation for the students. Where the establishment is not able to pay the minimum rate of \$7 to the student per day, the University will make up the difference. Students who have completed their second year are given priority over first and third year students.

Another useful area of interaction is the assessment of our students by the establishment. Attitude towards work, performance, adaptability, reliability, interest/initiative are reported by the establishment (Table 7) and monitored by us in the University. The figures in the table and our own impressions suggest that students do show a sense of responsibility and keenness. These could also be due to the increasing realisation on their part of the intrinsic value of such a programme.

Playing important roles and thereby also benefitting from the same in this university-industry interaction are the academic staff (Table 8). They are appointed Liaison Officers by the University on a voluntary basis. These officers would keep in close contact with the establishment, before, during and after the Orientation Programme. The duties of the Liaison Officers include getting in touch with

the establishment so that the appropriate programme can be drawn up having regard to the facilities that have been made available by the establishments. They keep in touch with both students and the supervisors at establishment throughout the period of training. While no honoraria or allowances are given to the staff, the University however, reimburses them for expenditure incurred in transport. The Liaison Officers are key personnel in this programme in this programme in that they are link between the University on the one hand, and the establishments on the other. At the end of the training programme, reports by the establishments, Liaison Officers and the students are studied with a view to improving future programmes. Table 9 shows the involvement over the years by staff members. A few of these Liaison Officers also serve as faculty co-ordinators to give oversight generally as well as to represent the faculty on the Central Agency.

The voluntary nature of this programme and their role makes understandable the turn-over of staff involvement. Long term commitments are ideal especially in building up relationships, confidence etc with the establishments. Their inputs would help optimise the benefits gained by the students (Table 10). The table also shows that not only have we fulfilled our immediate objectives (example, application of theory, technical knowledge gained) been attained but also seen benefits accrue in other vital areas

like work experience and human relations. The feedback given by Liaison Officers are also valuable (Table 11).

A very important development in this university-industry interaction is the transference of responsibility by the Ministry of Trade and Industry of the work of the Central Agency from the Science Council to the National University of Singapore in 1982. The Dean of Science now heads the programme which oversees the work involving thousand of students in our tertiary institutions.

Through this programme, the University becomes more aware of the problems of the industrial and commercial sectors and will thus be in a better position to advise on the placement and training of graduates more suited to the changing requirements of employers and national economy and development. On the other hand, industries through contact with these Liaison Officers may also become aware of some of the facilities and expertise available in the tertiary institutions.

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UNIVERSITY-INDUSTRY INTERACTION: THE SRI LANKAN EXPERIENCE
(COUNTRY PAPER)

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A B S T R A C T

The growth of University institutions and development of the Chemical industry in Sri Lanka is reviewed. The current state of University-Industry interaction details relevant programmes of research and training.

A mechanism to relate University programmes to local industry and enlist the cooperation of industry has resulted in the formation of the National Committee for University-Industry Interactions in Chemistry (NCUIIC). The scope of NCUIIC and strategies evolved to promote interface activity is discussed. Research, Training and Service are the keynotes of this interaction. A strategy for its promotion is presented.

The Country Paper outlines the roles of Universities, Industries, National professional societies and International organisations for use of this interaction in Chemistry for development. This paper would also illustrate some recent activities and experiences in promotion of University-Industry interaction in Sri Lanka.

INTRODUCTION

A Country Paper should necessarily reflect the theme of this workshop which discusses mechanisms and experiences. The need for University chemistry to orient its priorities for development is increasingly recognised. The concept of a University in a developing country solely as a centre for higher learning needs rethinking. University-Industry relationships recognise the growing perception that industrial products and services are increasing dependent on fundamental scientific understanding. Basic ideas and approaches are used in both Universities and Industry. The distinction between basic and applied work often disappears. This interaction is necessary to resolve problems of national economic importance. Experiences and factors inhibiting such interaction need to be examined.

UNIVERSITY CHEMISTRY IN SRI LANKA

Since 1920s to the early 1940s, University Chemistry in Sri Lanka was a model of the curricula of the University of London, since it was a University College reading for the examinations of that University. Although the University structure in Sri Lanka saw several changes with the establishment of the University of Ceylon in 1942, programmes in Chemistry have only first begun to show some awareness to local needs. There now exist 6 independent Universities and 2 University Colleges coordinated by a University Grants Commission. The Chemistry curricular in the Universities vary somewhat in structure. However, a 3-year general science degree in Chemistry as one of three subjects and a 4-year Special degree in Chemistry reflect the general pattern.

University of Colombo provides for a 2-year basic course in three subjects. In Chemistry, this includes emphasis on such basic concepts as structure, bonding, reactions, quantum mechanics, thermodynamics, kinetics, mechanisms, electrochemistry as well as introductory analytical and industrial chemistry. The laboratory course is intended to teach skill and methodology rather than an ability to solve defried chemical problems - this is so planned as effective laboratory instruction at pre-University classes leaves much to be desired.

A 1-year 'build' on this basic course, provides for optional oriented Course units in Chemistry for a General Degree in Science, requiring 9 Courses among the subjects. This orientation bear some relevance to industry, as well as to basic academic needs. These by design lack rigid entrenchment in the traditional areas and so reflect the integration that is so essential in the practice of Chemistry -

Topics in Natural Products Chemistry	
" "	Polymer Chemistry
" "	Analytical Chemistry . . .
" "	Solid and Surface State Chemistry
" "	Biochemistry

This coverage provides a base and emphasises fundamental aspects. The laboratory course attempts to teach skill and methods related to the lecture courses.

The 2 year build on the basic course which includes both scheduled and optional courses in special topics, provides for the Special degree in Chemistry. These graduates are primarily intended to fit into research and development positions in academic, agriculture and industrial sectors. The course is largely with an academic orientation and does provide the base for graduate study and research. Special features include: research project, seminar industrial work experience, and industrial visits. The evaluation, tests understanding and application. In addition, exercises in literature survey, planning for research projects and basic knowledge in Chemistry are built into the examination scheme. At present, universities in Sri Lanka are regionally positioned in the North, South, East and West to promote liaison between University and Industry.

CHEMICAL INDUSTRY IN SRI LANKA

Prior to independence in 1948, Sri Lanka exported raw materials from the main plantation sector - tea, rubber and coconut to import finished goods. A programme of industrialisation was begun after World War II, with a view to diversifying the economy to meet reduced imports of consumer goods. A department of Industries was set up in the early 1940s, to meet some of the immediate needs. Production of acetic acid for use as a coagulant in the rubber industry; a Shark liver oil industry as a substitute for Cod liver oil; glass factory; tyre retreading; leather products etc.

With independence in 1948, several industries have been set up, largely based on local natural resources - tyre, ceramics, mineral sands, oils and fats, sugar, paper, salt and salt based industries, as well as production units, on imported raw materials such as for steel and petroleum.

Small scale industries as Paints, soap, food, cosmetics etc and some cottage industries are largely private owned.

Innovation and development of natural resources to advantage, have largely been the private sector initiative. Illustrations include: manufacture of alkyd resins from rubber seed oil - the seed once an agricultural waste posing problems of disposal. There is an estimated availability of 4000 million tons per annum. Most of the oil finds a ready export market while some is converted to epoxidized rubber seed oil for a variety of purposes. There are yet other uses for its fatty acids in manufacture of factice. Castor oil - a dry zone crop, is used in the manufacture of Turkey red oil for use in the textile industry as well as for motor oils, medicines and paints industry. This oil awaits further exploitation.

Kaolin and China clay for ceramics and paints; activated carbon from coconut shells; perfumery from essential oils are other areas of activity. The mineral resources of Sri Lanka include - limestone, dolomite, mica, apatite, mineral and glass sands, gems and peat. Their location and those of the University institutions bear special significance.

MECHANISMS

National Committee for University Industry Interactions in Chemistry was formed in March 1982 by the Ministry of Higher Education - a 5-member committee representative of the University, State industry, private industry and UNESCO, with the Chairman, U.G.C. as its Chairman. A small but workable group with firm commitments to promote this interaction. The inauguration of this national committee was followed by a regional workshop on 'Chemistry, Industry and the Citizen' organised by the Institute of Chemistry, Ceylon and a UNESCO meeting of the national representatives of UIIC, both held in June 1982. The guidelines for action formulated at these meetings could be set out as follows:

Preparation of the National Chemical Directory on Chemical Industries.

University facilities for Industry - services, consultancy and training.

University-Research Institute-Industry interaction.

Resources development.

Interaction of National Committees in the region for promotion and exchange of know-how and transfer of technology.

Incentives and academic recognition to university staff contribution to industry.

Creation and strengthening of centres of excellence on the primary resources of the country.

University-industry interaction is a "two-way" process; just as much as the university is not always aware of the nature and needs of industry, the industry itself is unaware of the curricula and programmes of the University Chemistry. The National Committee has brought out its first issue of a biannual Newsletter. This is intended to be informative, as well as provide the incentive for interaction. The second issue includes research results of universities of relevance to industry. They have long remained accomplishments on the laboratory bench and require exploitation and commercialisation. The problems of chemical industry, trouble shooting

and studies on potential of natural resources will no doubt highlight the needs of industry. This is one way of bridging a gap of awareness between these two groups.

There is little research and development activity in the industrial sector in Sri Lanka. Multinational organisations continue to be served by the research and development centres in developed countries. There is little research and development centres in developed countries.

There is still much dependence on expertise from industrialised countries to develop natural resources to advantage. It is essential that local activity should have control over its resources, if they are to get the best economic benefit. Skills in Chemistry for research and development, production and quality control need therefore to be acquired. 'Fertilizers provide a case in point. About four fifths of all phosphate raw material comes from the third world. Yet the third world makes only 8 per cent of all fertilizer and consumes about 15 per cent'. A find in early 1970s in Sri Lanka, is a vast deposit of Apatite. The economic potential of this phosphate bearing rocks is yet to be realised. Mining of Graphite is one of the oldest industries of the country. Development of this rich resource to give value added products as collodial graphite, graphite crucibles and electrodes has still to receive attention.

Much of the chemical knowledge, expertise and resources needed to solve problems already exist. Problem perhaps, is mobilisation of this expertise and to adapt knowledge to local conditions, constraints and opportunities. A mechanism to promote this interaction for development could include the following components:

Orientation of university programs for industry.

Problem solving in chemical industry.

Utilisation of local raw materials in industry, adding value to our resources.

Dissemination of information between universities and industry.

EXPERIENCES

Orientation of University programmes should provide for research, training and services as the keynotes of this interaction. These should necessarily be built on a solid core of fundamental or basic chemistry and include ingredients for awareness and relevance. Special degree students at the University of Colombo, who form about 10% of the annual admissions for Chemistry, take an 8-week WORK EXPERIENCE programme in industry at the end of their examinations. This required careful planning and monitoring. It has enabled industry,

both from the private and the State sector to identify problems for study. Illustrations of these projects are:

Preparation of a fat liquor oil from castor oil for use in the leather industry - the product was tested in a local leather tannery.

Study of the components of smoke of fuel sources deposited on rubber smoked sheets.

Study of corrosion problems in heat exchanger tubes in Ammonia/Urea plants in fertilizer manufacturing industry.

Polar lipid degradation during manufacture of black tea.

Removal of clay and stain from the feed to a rutile/zircon processing plant.

Phenol absorption capacity of activated coconut shell-charcoal.

These are but a few, representative of exposures to problem solving activity. This program was intended to provide opportunities to put theory into practice in real life situations. It has had the added advantage of work with local resources as ilmenite, tea, rubber, coconut, castor oil etc.

The next phase of this programme was centred around the larger number (90%) that read Chemistry for a General degree. University of Colombo had the advantage of streaming students into a Special degree and a General degree at the end of a 2-year grounding in the three science subjects. A proposal for a cooperative programme with industry was formulated to provide a third stream for a selected group. It sought to provide for a one-year employment placement in a local chemical industry. These students on completion of this industrial exposure would return to the university to complete the final third year of the General degree. In essence, a "SANDWICH" one-year to allow the students to increase their awareness of the needs of local industry. An orientation programme which is intended to achieve a number of objectives:

Opportunity to observe professionals at work.

Lessons in human relations through association with people in an adult environment.

Period of growth as students put learning into practice in real life situations.

Acquire attitudes, working discipline and maturity.

Enhance employment potential in industry.

This programme will provide the necessary feed-back from industry to the university to orient the teaching programmes. Career counselling, ease of transition from university to the work world, partnership between student, employer and the university, constructive work experience to relate to academic study are additional credits of this programme.

There are of course other advantages that accrue from this programme to the employer, industry and the student. The employer of such a student is taking on an individual who has completed two years of a degree course and who, having two-thirds of the way to graduation, is capable of making a useful contribution, while using the opportunity to acquire further skills and techniques from seasoned practitioners. For many employers, who cooperate with the university in finding places for students in their 'industrial' year, it is no doubt a chance to assess talent for themselves. Student could return to their employers on graduation. Industry may as well support youngsters through their academic years. In either way, the fact of actively working with the university to train recruits for a real role in local industry should produce considerable benefits to the student, the university and the industry.

An interim programme has been put into effect with the general degree graduates as INDUSTRIAL TRAINEE placements. 6 such graduates commenced this programme last year, in private and state sector industry. Teaching staff assist in monitoring this programme and report on quality of placement, working conditions, students' progress, as well as other factors affecting future placement. The success of this effort would largely depend on the selection of trainees, interest of employers and enthusiasm of academic staff. It is hoped that the experience gained would identify additional inputs as in management, process technology etc. so as to institute a formal postgraduate certificate programme for Chemistry and industry.

COOPERATIVE PROGRAMMES such as these serve the orientation of chemical sciences in development. President Gerald Ford in an address to the Ohio State University calls for this emphasis, "... For you, the time has come to test the theories of the academic world in the laboratories of life. As President, I invite students, graduates and faculties to contribute their energies and their genius in the solution of massive problems facing America Show us how Universities can work with industries and labour unions, to devise a whole new community of learning across this great land. Show us how work study programmes can become a part of the ongoing educational process". How much more would all this mean to the developing nations?

UNIVERSITY RESEARCH has long remained accomplishments on the laboratory bench. Its relevance to industry, value addition processes of our natural resources and control of industrial products have received little attention. Some of the projects carried out by university institutions in Sri Lanka are listed:

Studies on the use of dolomite as a substitute for coral limestone as finishing coats in masonry - a pilot scale application of dolomitic quicklime under recommended conditions have shown promising results.

Electrochemical reduction of the product of hydrolysis of rubber seed oil to form crystalline stearic acid - an 83.5% yield has been recorded, the method has received local patent.

Use of local oils in preparation of analytical reagents for hydrometallurgy.

Reduction of chlorate contaminant in caustic soda from the chemicals corporation.

Isolation of solid pectins from lime and passion fruit peel.

Manufacture of Cassava starch for textile finishing.

Pozzolan cement manufacture from local pozzolans.

Research projects such as these are of direct local relevance. Collation of such information as well as others, re-extraction procedures for essential oils, perfumery materials, alkaloids etc. is being carried out. Its usefulness to industrialists in product development and value addition processes of local natural resources will be disseminated through the Newsletter of the National Committee. Given the right contacts between the two groups, a strong university research effort should contribute greatly to a strong industrial effort in chemistry. The role of individual contacts and initiative are important in the development of such relationships. Yet another recommendation of the National Committee, is the need to provide advisory, analytical and consultative SERVICES to industry. It has recommended the set up of a 'Chemical Services and Consultancy Fund' in all the universities. This needs to be self-financing, provide incentives to staff involved and would maximise utilisation of resources as equipment, expertise and technical library facilities.

There are two aspects of service to industry which provide experiences of university chemistry: University of Colombo, besides providing instrumental facilities has set up facilities for such areas as standardisation of analytical techniques, corrosion service and consultancy, water quality and analysis of pollutants.

University of Peradeniya has accomplished operational research study of industries, for analysis of rate of factory production, revealing mismatches in the utilisation of various operations and to provide the basis for increasing efficiency.

Another area of activity concerns chemical analysis in LOCAL SMALL SCALE INDUSTRY. A national chemical directory is being prepared to provide information on the needs of small scale industry for chemical

analysis of their products. The project is now at its initial stages. The directory is intended as background material for a field oriented analytical chemistry course, of service to small-scale industry. The objectives are to assist industry in making available advice and preparation of a source book of methods for associated chemical analysis. It should also provide the incentives for industry to set up simple analytical procedures at minimal cost. In this effort, the collaboration of the C.I.S.I.R. and the Industrial Development Board has been sought - this is a UNESCO sponsored project of the IOCD.

STRATEGIES

Resources development would necessarily include components of resources monitoring, development and conservation. There are a number of minerals hitherto discovered, like iron ore, apatite, dolomite, magnetite, serpentinite, silica sands (to mention a few) which have yet to be processed. It is here, that chemistry and chemists can play a decisive role to develop and build mineral based industry in Sri Lanka into a major programme and stable one for the future. Resources monitoring is an essential prerequisite to resources development. The need for an integrated expertise of biology, chemistry and geology is important to establish chemical relationships.

Our universities are gold mines of human resources, creativity, know-how and expertise. The combination of knowledge with the enthusiasm of the students constitute an outstanding potential. Curricula should reflect to the students about the world in which they will have to work tomorrow. Multidisciplinary programmes, new work schemes and the recognition of service teaching are important.

The greatest resource is people, who need an informed awareness and learning to solve problems rather than merely discuss them. Any country that wants to develop its industrial and agricultural production and the services it provides to its people, must develop its science and technology for self sustaining development.

Research institutes in Sri Lanka include the C.I.S.I.R. and those of T.R.I., R.R.I. and C.R.I. which cater to the major plantation sector of tea, rubber and coconut. These and such others could be effective catalysts in promoting interaction between the University and Industry. Efforts are being made in this direction by encouraging joint research programmes to enable these research institutes to bridge the communication gap.

Incentives and academic recognition - one of the important aspects of this interaction is the mechanism to provide incentives and academic recognition for university staff to enable contribution to industry. This has proved difficult in Sri Lanka. The reasons are many. There is still the 'hangover' of the postgraduate programmes of study the young recruits are exposed to in developed countries.

A Ph.D. on return to his home country is unable to work with the resources available. He has often been a 'pair of hands' in a research programme of academic merit. This situation needs study and recognition. Cooperation of academics of developed countries is essential in this effort.

One approach could be a collaboration between the academic staff member of the developing country and his counterpart in the developed country where the young student is reading for his post-graduate degree. Project formulation, scope for continued research on return to his home country, relevance of research etc. are basic aspects that need be looked into. A 'split' Ph.D. programme would cater to some extent the constraints and attitudes to research and study on problems of relevance to the developing country.

In Service Programmes in universities of one or two weeks duration could be used to widen the horizons or deepen the knowledge in a particular area of an industrial or university scientist. These could be of the 'recent advances' or 'special technique' type where chemists from the industry and university cooperated in the teaching. Industry and university chemists with mutual interests and enthusiasm would forge a healthy interaction. The role of INSTITUTE OF CHEMISTRY in promoting interaction is effective particularly in areas where opportunities or upgrading technical expertise is provided. The Institute mobilised its membership from activity to interact with national development programmes in industry, agriculture, mineral and natural resources, environmental studies, etc. It has been involved since 1981 in the TRAINING of analytical chemists in the varied sectors of employment. RESEARCH programmes are being actively pursued and its orientation to meet the needs of industry has been important. Analytical SERVICE to industry is being provided. The centre is aimed at interacting with other universities, research institutes and government departments. An international conference on 'Analytical Chemistry in Development', August 1984 marks the fulfillment of the objectives of this project.

Of the practising graduate chemists with professional expertise in Sri Lanka, university academics account for 25%, the research institute, 25%, the government scientific departments, 20% and industry 20% and about another 10% distributed in the private commercial sector, the number of chemists presently serving industry is grossly inadequate. Many industrial corporations employ chemists, but several are without laboratories for study of product quality, analytical controls and for research and development. This number needs to be increased at least five times over. Employment sector in industry for chemists is widespread:

Cement	Paper
Fertilizer	Leather
Oils and Fat	Mineral Sands
Steel	Glass
Ceramics	Distilleries
Sugar	Pharmaceutics
Textiles	Graphite, etc

Over 90% of such chemists are involved in quality control and chemical analysis. It is here, that the scope of the centre at University of Colombo assumes such significance.

INTERNATIONAL ORGANISATIONS

Several international organisations are development oriented. A recent significant feature is the formation of the International Organisation for Chemical sciences in Development, IOCD by UNESCO in 1981. There have been several programmes pursued through specialist panels:

The chemical synthesis programme launched in March 1982 aims to develop new drugs to parasitic diseases. Several laboratories in 8 countries are carrying out the first stage, synthesising new compounds for tests. These diseases account for large proportion of the fatal diseases in African and other developing countries. A concerted research effort becomes an urgent priority.

IOCD has linked into the UNESCO regional networks in chemical sciences such as SCAMAP. Training programmes, exchange visits, workshops, research collaboration etc. in study of medicinal and economically useful plants are some of its activities.

The third programme initiated in 1982 is specifically designed to create links between universities and industries in the third world. Mobilisation of university chemists to help create and set up small scale industries in the developing nations.

These programmes should receive the highest priority among the activities of National and Regional associations of chemists. FACS should become the focal point of action in Asia and use IOCD programmes to "redress the imbalance between countries by directing much effort and expertise in the chemical sciences toward the solution of problems of developing nations".

UNIVERSITY - INDUSTRY INTERACTION

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ABSTRACT

The Department of Chemistry at Osmania University has launched University-Industry collaborative teaching and research programmes to make Chemistry teaching and research meaningful and relevant to the industrial growth in the region. At the post-graduate level the Chemistry courses which have relevance to industries, situated closer to University have been tailored and introduced as elective courses for teaching. We in Hyderabad have a number of industries and research laboratories around the campus of the Osmania University.

For giving instructions for these elective courses the Department has teaching collaboration from the scientists of the industries in the city. All the elective courses are not offered every year. Those of the industries in which more of the Chemistry students are needed for manning the industry are offered as elective subjects to the students to suit the needs and demands of the industry. A constant assessment is made of the utility of the courses offered from the industry and university point of view. A particular elective will be offered for 2 to 3 years then some other electives will be offered depending on the demand and man-power requirements of the chemical industry to make university-industry collaborative teaching programmes more effective and meaningful. Expertise is drawn from the industries to the academic bodies for maintaining and ensuring proper linkage and co-ordination in research and teaching activity. Research which is relevant and useful for the industry is also carried out, maintaining continuous link in teaching and research activities between the Industry and the University. From experience, it has been found that such University-Industry collaboration has been very useful.

A continuous and systematic evaluation of the syllabi in various science subjects including Chemistry enabled the educationists in India to suitably revise the course contents in order to meet the demands of the society. Today chemistry is recognised as a highly organised and systematic science subject. This is in contrast to the past, say till forties and fifties, which students shunned this subject because of the erroneous impression that it is made up of numerous unrelated factors worthy of mere remembrance. But, the present day graduate student of Chemistry not only learns the fundamentals of the subject but also the application of the basic ideas in various fields like industry, medicine, biochemistry, etc.

It is often observed in a developing country like India that an average student of Chemistry gets confused in understanding the relevance to practical life of the knowledge he has acquired in the lecture hall, library and laboratory. He is also at loss to visualise the role he can play for the betterment of the society which not only supports his education but also enables him to acquire several academic honours. It must be accepted that his educational training in Chemistry is not suitably oriented to provide him clear under-

standing of its applications to industries mainly chemical industries related to drugs, dyes, polymers, food additives etc. As the student fails to visualise the transformation of theoretical knowledge to practical purposes, an element of frustration may creep into his young mind. Eventhough a Chemistry teacher takes pleasure in talking to his students about the various benefits that man has been drawing from chemistry-knowledge, he does not play sufficient role in impressing the students about the mechanics of industrial production responsible for such benefits. Also, the course contents in the graduate study do not give sufficient scope in this regard.

Keeping these points in view and taking into consideration the increasing number of talented graduate students in Chemistry, we at the Department of Chemistry, Osmania University, Hyderabad, India, have introduced University-Industry collaboration in teaching and research programmes. In the teaching programme we have introduced elective subjects in the final year of graduate study. It may not be out of context to mention here briefly about the course contents and scheme of evaluation during the four semesters of study, leading to Master's degree in Chemistry.

All the students admitted to the post-graduate courses (M.Sc.) in Chemistry undergo common training during the first two semesters (one year). The candidates take up examination in both theory and practical courses in various brances of Chemistry like inorganic, organic and physical chemistry. These examinations are in addition to continuous evaluation through internal assessment. After the completion of the second semester, the students are admitted into different specialised courses like inorganic chemistry, organic chemistry, physical-organic chemistry and physical chemistry on merit-cum-preference basis in the third semester. The student thus undergoes intensive training in one of the specialised fields in the third and fourth semesters (i.e. second year of M.Sc. degree). Grades are awarded on the basis of over-all performance in the four semesters.

The elective topic mentioned above constitutes one of the theory courses of the fourth semester and has approximate 50-60 contact hours. The different electives offered have relevance to the industries and research laboratories in and around Hyderabad city. They are:

1. Dyes, drugs and intermediates
2. Explosives
3. Medicinal Chemistry
4. Natural Products
5. Polymers
6. Agrochemicals & Fertilisers
7. Nuclear fuels
8. Catalysis
9. Electrochemistry
10. Phtochemistry.

The course contents of these elective have been framed in consultation with the research development personnel of the corresponding industries and research laboratories. This would enable the student to gain a first-hand knowledge of the application of

chemical principles to different industrial uses. This type of collaboration also helps the student to serve effectively in the respective institutions if he gets a chance. Some of the research chemists of these institutions have also been associated with the University academic bodies such as Board of Studies in Chemistry and Academic Council so as to have an effective industry-university interaction. Not all electives are offered at one time. Depending on the demand courses are chosen and offered from time to time keeping in view to avoid unemployment in a particular specialisation.

Both the faculty members of the Chemistry Department and the Research & Development personnel of the industry concerned are involved in training the students in these elective courses. Quite often the training is right in the premises of the industry and the students are taken round the different plants to obtain a close view of the different stages of industrial technology. The Indian Drugs & Pharmaceuticals Limited, The Nuclear Fuel Complex, The Indian Detonators Limited and the Regional Research Laboratories, all situated in the around Hyderabad are some of the institutions that are closely associated with this collaborative venture.

We also have collaborative research programmes with some of these industries. Extraction of natural products from the local plants and forests, removal of the toxic materials from the effluents of the industrial units, to avoid pollution and search for better and effective catalysts are some of the areas of mutual collaborative research programmes. The research scholars and scientist make use of the facilities available at these institutions to the maximum possible extent.

We are glad to note that this experiment of teaching-research collaboration between University and Industry has proved quite successful and well received by both students and industrial personnel. It is also heartening to note that a good number of such students, after successful completion of the training, have been absorbed by the industries and since doing well. It is our earnest hope to enlarge the scope of such co-operation and collaboration with industries which would enable the graduate students in chemistry to serve the society better.

UNIVERSITY AND RURAL INDUSTRIES

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ABSTRACT

Among many facets of "Industry", rural Industries has emerged as one of the major development strategies to pursue during the Sixth Thai National Development Plan period (1987 - 1991). It has been identified that rural industrialisation, if properly promoted, can increase employment and income among the population outside the major cities. A team of scientist engineers and economists from Chulalongkorn University has been commissioned to carry out a study on some aspects of rural industrialisation and employment generation. They will undertake an investigation of specific problems of local entrepreneurs in rural industries in selected provinces. Results of the investigation will be analysed and appropriate policies and programme for action will later be formulated.

HISTORICAL DEVELOPMENT

From the inception of the Fifth National Economic and Social Development Plan in 1981, Chulalongkorn University has set up a number of Task Forces such as the Task Force for Energy Research, the Task Force for Drug Research, the Task Force for the Promotion of Industrial Research and Development etc. within the Office of the Vice Rector for Research. Each Task Force is charged with the responsibility to define topics of interest, create research teams of critical mass and obtain appropriate and worthwhile results. It is obvious that the research topics must be problem oriented multidisciplinary nature which Chulalongkorn University is in a unique position to undertake a research endeavour of that kind since she has 14 Faculties with a full spectrum of Sciences, Technology, Social Sciences and Humanities and over two thousand Faculty members.

During the first two years, the Task Force for the Promotion of Industrial Research and Development has placed the main emphasis on pooling the expertise within the campus to form research teams on few areas of industrial research and development, each team comprises of scientist and/or engineer and economist. Feasibility studies were also included in each project. Researchers were informed prior to their commitment to the projects that the expected results of their work are as much to fulfil their own interests as to stimulate the interest of industries. In the first year, Chulalongkorn University has spent over one million bahts on these industrial research projects in the areas of agro and some basic industries. Few projects were dropped out after the evaluation at the end of the first year while some were received continued support and found to have industrial applications. By the end of the second year, a new aspect of industrialisation emerged, the "rural industry". In order to probe into the interest of our Faculty members and to stimulate the interest of policy makers at the national level, the Task Force for the Promotion of Industrial Research and Development organised a one day seminar last August, entitled "Industry and Employment Generation Outside the Metropolitan Area". The Seminar was successful and was supported rather eagerly by the Office of the National Economic and Social Development Board (NESDB) who was planning to include rural

industrialisation as one of the major development strategies to increase employment and income among the population outside the Bangkok Metropolitan area in the next development plan. However, a preliminary study must be carried out covering several types of problems faced and assistance needed by the existing rural manufacturers before policies and plan of action can be formulated. The Task Force for the Promotion of Industrial Research and Development at Chulalongkorn University as well as other institutes and government departments were invited to join in the study group to be set up by NESDB around last October.

DEFINITION OF RURAL INDUSTRIES

It is deemed appropriate to define rural industries as all types of manufacturing whether it be large or small, modern or traditional which owned by Thais and situated outside the Bangkok Metropolitan.

Scope of the Work

Rural industries are known to have problems relating to technology, finance, management and labour. It was decided at the National Seminar on Employment Generation at Pattaya early November last year that how their problems can be solved must be worked out together by the government departments which are directly responsible to that sort of the problems, in consultation with the entrepreneurs and other specialists on the subject. Successful implementation of the promotional measures and assistance must have institutional base which is local and fairly full autonomy on its own. It was also agreed that in 1984 only eight out of sixty eight towns outside Metropolitan area will be covered by this project. These towns will be uniformly distributed in four provinces. Pitsanulog was selected anonymously as the first town that the study group will conduct the investigation. The main industries of this town are agricultural machinery, processed food, rice mill. The organised group of entrepreneurs has already been formed and may serve as the institution arrangements for dissemination of the government's assistance.

The first workshop was held at Pitsanulog on 10th January 1984. About sixty participants from local industries and various governmental departments involving in the industrial promotion, a team of experts comprising the representatives of IFCT, SIFO, NESDB, Industrial Service Division, Centre for the Industrial Promotion in Northern Region, Chulalongkorn University were present. The main objective of the workshop was to introduce the project to the local entrepreneurs and to get a general first hand informations relating to their problems in the area of Finance, Management, Technology and Labour. The workshop has achieved that goal of objective reasonably well and the follow up workshop was scheduled to take place in mid February among entrepreneurs and officers in charge of the industrial promotion in Pitsanulog when more specific problems would be listed and compiled in group. The entrepreneurs and the specialists in the four areas of problems mentioned above will meet again in March and the major problems will be discussed and technical solutions to the problems will be dealt with by the experts who have seen and studied those problems before hand from the compiled list obtained from the second workshop. As far as the technological problems are concerned, the problems will first be screened by the Centre for Industrial Promotion in Northern Area. Only those lie beyond the capability and responsibility of the Centre will be sent to the Universities/Institutes for further investigation. Other form of

co-operation is also formed i.e., the universities/institutions will, on request, make available a team of experts to serve as lecturers or trainers in the training courses or workshop organised by Industrial Service Division or Centre for Industrial Promotion in Northern Area.

CONCLUSION

It may be too early to report the results of the activities of this study group. It is however, believed that such a kind of assistance should alleviate the problems of the rural industries to such an extent that it will increase local employment in a long run as well as to induce a more stable economy in the region. For the universities, it is about time to start "marketing" their capabilities and research facilities to the industrial public and it is up to the universities to make the first step forward.

UNIVERSITY-INDUSTRY INTERACTIONS:
INDIAN EXPERIENCE (COUNTRY PAPER)

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ABSTRACT

India is considered to be a developing country. However, there has been a phenomenal growth of chemical industry in India during the past three decades after Independence. The contributions of the chemical industry to the total gross output has been of the order of 15.5% and ranks second only to food products which account for about 15.6%. In the early stages of development the chemical industry depended heavily on foreign collaboration. Hardly any attempt was made to establish in-house R and D capability.

There has been an equally phenomenal rapid growth in the development of Scientific ManPower during the same period. Over 120 Universities and Institutes of Technology turn out a large number of graduates, post-graduates and doctorates in Science and Engineering every year. Several of them have active research centers on their Campus specially in the field of Chemical Sciences. R and D programmes, leading to the development of technology, are in progress in several National Laboratories and other Government establishments. Thus India has already invested significant amounts in setting up R and D facilities and building a vast industrial infra-structure.

Technology Policy Statement adumbrated by the Government of India (1983) is aimed towards the attainment of technological self reliance making use of indigenous resources available both in industry and academic sections. Appropriate financial incentives and tax benefits are given for setting up R and D units in industry and collaborative programmes with academic institutions. With such support and encouragement as well as interaction between academics and industry, it has been possible to develop indigenous technology and build commercially viable chemical industries in India in the recent past. This will be illustrated with a few successful case studies.

INTRODUCTION

India is considered to be one of the developing countries in the modern world. However, in the earlier period India was one of the leading workshops of the world like China. India was known for its manufacture of speciality chemicals like indigo and steel. Indian steel was the best steel until the BESSEMER PROCESS became popular in the WEST during the latter half of the nineteenth century. The local technology and industry suffered practically a total destruction during the colonial rule of eighteenth and nineteenth centuries.

A century of industrial development based on modern technology during the colonial rule pales into insignificance when compared with the industrial stride made during the past three decades of planned development after independence. The rate of growth of the Chemical Industry

has been faster than the average of all manufacturing industries. The contributions of the chemical industry to the total gross output has been of the order of 15.5% and ranks second only to food products which account for about 15.6%. The products of Chemical Industry are used extensively in widely dispersed sectors of the economy producing vital materials such as drugs, textiles, fertilisers, other agricultural products, and so on. The Chemical Industry is dependent on inputs from a variety of other sectors like power and transport. The developments of Chemical Industry are closely linked with the rest of the economy.

It is well known that Chemistry is the only branch of Science devoted to transforming matter into useful products. Chemistry is the obvious means of bringing intellectual power to bear on satisfying the needs of the society. The nature of chemical industry is different from much of the rest of the industrial sector. Its basic strategy is to start from naturally occurring ores, or man made chemicals or agricultural products as raw materials and finish up with consumer products through a series of physico-chemical changes. In this it differs from manufacturing industries which are assembly oriented and not creative in the sense as are the chemical and allied industries. Chemical Industry plays a prominent role in the development of Indian economy.

CURRENT STATUS OF INDIAN CHEMICAL INDUSTRY

The basis of economic development of India is Government Planning through a series of 5 year plans. The first plan was implemented in 1951 by the Planning Commission of the Government of India. While we are running currently through the Sixth Plan, the seventh plan is under preparation. Rapid industrialisation has been the continued aim of planning through public and private enterprise. A comparative set of statistics is given for a few important chemical and allied industries in Tables I to V. The data have been classified under five broad headings: (I) INORGANIC CHEMICALS, (II) CHEMICALS BASED ON NATURAL AND AGRICULTURAL PRODUCTS, (III) SYNTHETIC ORGANIC CHEMICALS, (IV) METALLURGICAL AND MINERAL PRODUCTS AND (V) TEXTILE PRODUCTS.

RAW MATERIALS PICTURE

A brief account about the RAW MATERIALS PICTURE for these Chemical Industries in India may be appropriate at this stage. India is well endowed with a large varieties of minerals. Iron and coal reserves are in abundance, 20 and 40 billion tons respectively. Current annual output is of the order of 40 million tons of iron ore and 120 million tons of coal. India ranks third in the world deposits of manganese (116 MTS). India is the major producer (80%) in the world supply of MICA. India is rich in BAUXITE and mine over 5 million tons every year. Substantial amounts of other ores and minerals are scattered over the country and these include: BERYL, BARYTES, CLAYS of different kind and quality, CHROMITE (111.2 MTS), CHALCO PYRITES (455 MTS), CALCITE, DOLOMITE, LIMESTONE, DIAMOND (5.5 lakh carats), GYPSUM (1205 MTS), ILMENITE (540 MTS), LEAD and ZINC (160 MTS), NICKEL ORE (160 MTS). India is also rich in atomic minerals in the form of beach sand of KERALA containing monozite, zircon, silliminite and others. Kolar Gold Mines are the deepest in the world and continue to supply gold bearing rocks (0.8 MTS) for the extraction of the precious metal (65 tons). Raw materials for organic, pharmaceutical and textile industries are also

in adequate supply. India produces over 7 million tons of sugar and about 700 million liters of industrial alcohol. While the oil reserves are estimated to be over 350 million tons, 15 million tons of petroleum crude is produced in the country. Oil refineries supply feed stock for petrochemicals and other industries.

FOREIGN COLLABORATION

It is important to point out that most of the chemical plants thus far established have been supplied by foreign collaboration in the push to meet the growth demand. Out of 7,000 collaborative industries, over 2,000 come under chemical and allied industries. A DIRECTORY OF FOREIGN COLLABORATION IN INDIA (1974) provides some details of the capital, source of the foreign technology production capacity, etc., for all these industries. Hardly any attempt was made to establish any in-house Research and Development capability in the early stages. Even now R and D activity in Indian chemical industry is not adequate enough to generate technology which will enable the industry to design, engineer and commission new plants or even to expand existing plants. Very few opportunities exist for Indian chemists and chemical engineers in these industries for innovation and creative approach through R and D programmes. The center of gravity of R and D programmes of these collaborative industries lies in their home organisations. There is no need to belabour the point that Chemical Industry must invest in Science to secure its future and at the same time seek opportunity in a country where the vast majority has been denied the fruits of modern industry. There is vast scope for future improvements and innovation. Such developments could come out of collaborative efforts of both industry and R and D laboratories in the country. Now let us have a look at these Research and Development Centers in India.

DEVELOPMENT OF SCIENTIFIC MAN POWER AND R & D CENTRES

It is of interest to observe that an equally phenomenal growth is witnessed in India on the development of Scientific Man Power and R and D Centers after independence. Today there are over 120 Universities and 11 Institutions deemed to be Universities. 9 other Institutions including Indian Institutes of Technology (IITs) which have been declared by Parliament to be Institutions of National Importance. Hundreds and thousands of graduates, postgraduates and doctorates come out of these academic institutions every year. Quite a good number of these well-trained Scientists and Engineers take up overseas assignments while others fill the national needs. Several of these academic institutions have flourishing centers of research specially in Chemical Science and Technology. There are many R and D programmes leading to the development of indigenous technology in several of the Laboratories established by the Central and State Governments and these include: Laboratories of Council of Scientific and Industrial Research (CSIR), Defence Science, Department of Atomic Energy and Space, Indian Council for Agricultural Research (ICAR), Indian Council for Medical Research (ICMR), Railways, Post and Telegraphs, etc. Thus India has already made substantial investments in setting up R and D facilities and in building a vast industrial infrastructure. The technological potential inherent in this system of interlinking capabilities must be fully utilised for further development from within the system. In-house R and D units in industry and sponsored or collaborative projects between industry and

university and National Laboratories provide a desirable and essential interface for both the sectors.

The Technology Policy Statement enuciated by the Government of India is aimed towards the attainment of Technological self-reliance and to reduce vulnerability, particularly in strategic and critical areas making the use of indigenous resources. Appropriate financial and other incentives and tax concessions are provided to induce the Industry for setting up in-house R and D units on their camps. About 1,000 industries have so far registered with the Department of Science and Technology and are making substantial investment.

FROM LABORATORY TO INDUSTRY

It has been well recognised that the problem of technology transfer from laboratory to industry is much more complicated than horizontal transfer of technology from one industry to another in which case technologies are already proved on an industrial scale. There is no doubt about the success of production and the buyer can confidently take up the venture. On the other hand, technologies in a Laboratory (industrial or academic) will only be on a bench scale and the problem of scaling up will always be there before the establishment of a commercial unit. Invariably work on a pilot plant becomes necessary. Even with successful pilot plant work, it is difficult to prove the success of the technology on a commercial scale. It is needless to emphasise the limitations on the resources and infrastructure needed for carrying out the task on a large scale in an academic laboratory.

The inputs required for transferring technology from laboratory to industry are of various kinds. First of all it may become obligatory to prove the success of a laboratory process on a pilot plant scale before an entrepreneur takes up the technology for scaling up further. Setting up of commercially viable Chemical Plants will be a cooperative effort among many disciplines. A chemist will have to learn to work with engineers (Chemical, Electrical, Instrumental and Mechanical) which he is not obliged to do while he is working in his laboratory.

It is therefore, necessary that when the process is being considered for ultimate commercial uses, the engineers are brought into the scheme at the early stages of the innovative chain. Such cooperative efforts will give the R and D project an orientation which would make the whole scheme go in such a way that when ultimately the results are to be used in industry, there would be as little trouble as possible. It is also desirable that a competent consulting engineering firm be associated closely with the development phase of the project. They can be involved in the design of the pilot plant and carrying out economic analysis of the various processes steps so that an optimum technology can be evolved. There are a number of Indian Consultancy firms which are ready to offer their services for such projects. The industrial infrastructure available in the country could be gainfully employed for this purpose provided there is a complete understanding and agreement between the academics and industrial experts in working out a cooperative and collaborative project. There is always a considerable amount of time lag in technology transfer from laboratory to industry, invariably of the order of 8-10 years before a process developed on bench scale becomes a successful and well established industry run on a commercial scale as

it has to go through several stages of assessment including pilot plant, market development, etc.

In India one often observes that there is a great amount of resistance and reluctance in buying indigenous technology from R and D laboratories. There is always a loud cry and demand that the indigenous technology should be proved on a commercial scale before the entrepreneur can accept to purchase it. Entrepreneurs in India are invariably not prepared and willing to take the kind of risks which entrepreneurs in other countries have taken before such technologies have been established and hence the rush for import of foreign technology. Indian chemists and chemical engineers have to win over the confidence of industry and build up credibility to attract venture capital.

The National Research Development Corporation of India (NRDC), New Delhi, a public sector undertaking of the Central Government set up in 1953 acts as a link between research and industry. It is also entrusted with the task of promoting inventive talents in the country. The NRDC will also provide RISK CAPITAL to induce industries to become partners in the development of technology. Many processes developed at the National Laboratories and other R and D institutions in the country are now in actual production. NRDC helps to streamline these operations. Among the more prominent chemical industries for which the technology has been developed in these laboratories are (1) Infant food, (2) Pine oil, (3) Mica insulating bricks, (4) PENTAERYTHRITOL, (5) BENZYL Chemicals, (6) Plasticsizers, (7) Insecticides, (8) Ferro alloys and several others. For purposes of illustration, a few case studies of successful technologies are presented briefly.

CASE STUDIES (1 TO 8) (Attached)

CONCLUSIONS

We observe that chemicals and chemical products rank first (with 12.2%) among the industries according to their contribution to the net value added to the raw materials followed by basic metals and alloys (11%). Thus the chemical industry is today in the forefront of economic activity in India, with over dependence on purchases of technology from foreign countries. It has become imperative to the chemical industry to seriously consider the establishment of a meaningful R and D base without which the pace and cost of growth are likely to become increasingly costlier and progressively uneconomical. Such efforts will also make the country self-reliant and free from vagaries and vicissitudes of the commercial policies of industrially advanced countries. This is possible only with the joint efforts of both industry and academics. The potential role of the chemical community is tremendous.

Chemists should get involved in solving the fundamental problems of economic production and productivity in a developing country like India. Innovative R and D programmes should not remain merely as laboratory curiosities but should contribute with co-operation and collaboration with industry to the commercial realisation of the fruits of the experimental results which in its turn will improve the quality of life of our people by aiding to provide clean air, drinking water, nutritious food, adequate housing and clothing,

improved health, effective population control and for satisfying the aesthetic and intellectual needs.

ACKNOWLEDGEMENTS

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CASE STUDIES

1. MANUFACTURE OF SILICON BASED MATERIALS

R and D programmes on silicon based materials have been in progress at the Indian Institute of Science for over two decades. The technical knowhow generated in the laboratories have been transferred to industry for commercial exploitation. In collaboration with the Institute, M/S METTUR CHEMICAL AND INDUSTRIAL CORPORATION LTD., METTUR DAM, have set up manufacturing units for the production of silicon tetrachloride of about 1,000 tons per annum. Ethyl silicate-40 is also manufactured on a similar scale. Silicon tetrachloride has become an important industrial chemical for the manufacture of a variety of silicon based materials. Ethyl silicate finds extensive uses in foundry industry, refractories, paint and varnishing industry and for silicone processing and in electrical industry. Commercial reactors have been designed, fabricated and commissioned, totally based on the indigenous technology. These chemicals conform to the international specifications and are competitive in the world market and exported to industrially advanced countries such as U.S.A., U.K. and other countries in Europe and Australia. A plant is under commission to manufacture semi conductor grade silicon to meet the demands of electronic industry and photovoltaic solar cells for harnessing solar energy.

2. INFANT FOOD

A good deal of work has been done in developed countries on standardisation of conditions for production of infant food from cow's milk. In India, while cow's milk is in short supply, buffalo milk is available in abundance. Scientists at the Central Food Technological Research Institute (CFTRI) at MYSORE have been successful in developing a process for production of infant food from buffalo milk, with a digestibility comparable to that of infant food based on cow's milk. The indigenous process involves pasturization of fresh buffalo milk, its standardisation to optimal fat content (2.5%) and addition of buffer salts, sugar solution and vitamin premix. The infant food base thus obtained is homogenized, concentrated and roller or spray dried. The process is found to be economical and commercially viable.

The work was carried out on 50-100 liters/batch pilot plant scale. Two plants based on the above technology having a total capacity of about 4,000 tons per annum are in production in the country.

3. BENZYL GROUP OF CHEMICALS

(i) BENZYL CHLORIDE, (ii) PHENYL ACETIC ACID, (iii) BENZYL ALCOHOL, BENZYL ACETATE and BENZYL BENZOATE.

Benzyl chloride is an important intermediate for a variety of chemicals like phenylacetic acid, phenyl acetamide, pheno-barbital benzyl cyanide, pathadine, AMPHETAMINE, benzyl alcohol, benzyl acetate and benzoate. These chemicals find extensive application in pharmaceuticals, perfumery, textile chemicals, dyes and intermediates. All the raw materials (BENZENE, TOLUENE, CHLORINE, ETHYL ALCOHOL, HYDROCHLORIC ACID, SODIUM CYANIDE) are available in India.

The processes have been developed at the REGIONAL RESEARCH LABORATORY (R.R.L.), Hyderabad on a pilot plant scale of 200-300 kg/day. Based on these processes, commercial plants are in operation with the following capacities.

(1) BENZYL CHLORIDE	(Two plants)	15 metric tons/ year
(2) BENZYL ACETATE	(One plant)	20 MT/year
(3) BENZYL BENZOATE	(One plant)	40 MT/year
(4) PHENYL ACETIC ACID	(Two plants)	160 MT/year

4. METHYL CHLOROSILANE

Chlorosilanes are the basic raw materials required for the manufacture of SILICONES which have number of industrial applications in the form of soils, emulsions, resins, greases. The National Chemical Laboratory (Poona) has successfully developed a technology for the manufacture of methyl chlorosilanes. Silicon metal is treated with methyl chloride in the presence of catalysts and promoters in a mechanically agitated fluidized bed reactor and the crude methyl chlorosilanes are fractionated into individual components in continuous distillation columns.

The laboratory had developed the technology on a 3.5 kg/hour scale. A pilot plant with a capacity of 100 tons/annum was designed, built and commissioned in collaboration with industry (HICO). The process is now being commercially exploited by the firm with a capacity of 1,000/1,200 tons per annum. has been just commissioned to meet the entire national demand and there is a possibility for export market also.

5. TITANIUM SUBSTRATE INSOLUBLE ANODES

Till recently chlor-alkali industry was completely dependent on graphite anodes in India in spite of their inherent limited life and other drawbacks. Titanium Substrate Insoluble Anodes (TSIA) have been found to be quite stable anodes not only for the manufacture of caustic soda but also in the production of chlorates and perchlorates. The process involves the preparation of insoluble anodes by depositing platinum or a combination of platinum group of metals (Rhodium, Indium, Ruthenium and palladium) or their oxide on a sheet of titanium or titanium tantalum alloy. The technology was developed by Central Electrochemical Research Institute in collaboration with a chloroalkali industry.

The technology has been licenced to two firms one of which went into production 5 years ago and has been able to convert 30% of the total installed capacity of the caustic soda in the country from graphite anodes to TISA. Anodes manufactured by this firm have been installed in more than 16 chlor-alkali plants and this has resulted in substantial savings of power.

6. CINEMA ARC CARBONS

India is one of the world's largest producer of motion pictures. Normally two pairs of carbon electrodes are consumed in

show of three hours. The National Physical Laboratory (New Delhi) has developed a technology for the manufacture of carbon electrodes making use of raw materials available in the country which include petroleum coke, carbon black, coal-tar pitch, rare earth salts and graphite. Cinema arc carbons based on this technology are at present produced by three firms.

7. BETA-NAPHTHOL

The beta-naphthol industry is directly linked with the dye-stuff industry which not only meets the demand of home needs but also is exporting to the industrially advanced countries. The Central Fuel Research Institute (Jealgora) has successfully developed a process for the manufacture of Beta naphthol using indigenously available raw materials, viz., naphthalene and sulphuric acid. The process involves sulphonation of naphthalene and separation of α -naphthalene sulphuric acid by steaming. Beta naphthalene sulphonic acid neutralised with caustic soda at 300 - 380°C, quenched with water and acidified to liberate Beta naphthol and purified by solving extraction and vacuum distillation.

A Beta-naphthol plant of 1,000 tons per annum capacity based on the above technology is in operation and a 5,000 tons per annum capacity is under construction.

8. ENDOSULFAN

Endosulfan also known as THIODAN is a broad-spectrum of synthetic organic contact pesticide useful to control of pests and mites which infest fruits, vegetables and also useful for crop protection. In spite of its high effectiveness against pests, it has a very low toxicity towards mammals and therefore is a highly valued pesticides in great demand.

The process developed at National Chemical Laboratory (Poona) involves two steps: (1) DIELS-Alder reaction in which hexachlorocyclopentadiene (HCCP) is reacted with cis-2 butene-1,4-diol to obtain endosulfan alcohol and (2) condensation reaction in which the endosulfan alcohol is reacted with thioryl chloride ENDOSULFAN. The first step was standardised on 25 kg/batch scale and the second on 35 kg/batch scale.

The process has been taken up by a reputed firm manufacturing organic chemical will go into production soon. Another public sector industry has already commissioned the plant on a commercial scale.

9. MAGNESIUM DRY BATTERY

The development of the magnesium-manganese dioxide dry cell is relatively a recent one, having mainly evolved in U.S.A. The Indian Institute of Science took up a project for the development of the magnesium dry battery in close collaboration with the BHARAT ELECTRONICS LTD., BANGALORE in 1973.

The magnesium dry battery stands out from the conventional dry cell in such respects as energy input, cell voltage and the range of operating temperature. It also has a longer shelf life than the conventional dry cells.

During this development project, several scientific and engineering problems were encountered and solved. Some of these problems were to do with compatibility for scale up, process control measures, acceptance tests and indigenisation of raw materials. With the completion of the project, magnesium dry cells of acceptable quality are now being produced on a pilot plant scale at the B.E.L., BANGALORE. A large scale manufacture unit is also coming up and will be commissioned soon.

TABLE I: COMPARATIVE STATISTICS OF SOME CHEMICAL AND ALLIED INDUSTRIES

Industry of products	Production metric tons x 10 ³				
	1950 - 51	1960 - 61	1970 - 71	1978 - 79	1980 - 81
I. Inorganic Chemicals					
1. Sulphuric acid	101	368	1050	2500	
2. Soda ash	45	152	331	541	568.8
3. Caustic soda	12	101	371	562	571.3
4. Cement	2700	7970	14400	19300	187000
5. Fertilizers					
(a) Nitrogenous (N-basis)	9	98	830	2264	2164
(b) Phosphatic (P ₂ O ₅ basis)	9	52	229	749	842
6. Marine chemicals					
(a) Common salt	2.9		5588.2		(Imported earlier 0.5MT)
(b) Bromine			0.3		
(c) Sodium alginate			0.1		
7. Barium chemicals			93		
8. Hydrogen peroxide			5		
9. Lime			25000		
10. (a) Graphite			85		
(b) Activated carbon			15		
(c) Cinema arc carbons			18 million pairs		
11. Calcium carbide			8		
12. Silicon carbide			8		
13. Phosphorus					

TABLE II: COMPARATIVE STATISTICS OF SOME CHEMICAL AND ALLIED INDUSTRIES

Industry of products	Production metric tons x 10 ³				
	1950 - 51	1960 - 61	1970 - 71	1978 - 79	1980 - 81
II. Chemicals based on natural products and agricultural products					
1. Paper and paper board	116	350	755	1008	1148.8
2. Petroleum refining	0	5800	17100	24100	24000
3. Petro chemicals					
(a) Ethylene)				210	
(b) Propylene)				123.3	
(c) Butadiene)				54.4	
(d) Benzene				139	
(e) O-xylene)				21	
(f) p-xylene)				17	
(g) Formaldehyde				155.8	
(h) Methanol				99	
(i) Phenol				209	
(j) Phthalic anhydride				273	
(k) Ethylene oxide				28	
(l) Ethylene glycol				30	
(m) Caprolactum				20	
(n) DMT				24	
4. Sugar	1130	3030	3740	5867	51.99
(a) Alcohol (in liters)				700000	
(b) Acetic acid				23	
(c) Acetic anhydride				6.3	
(d) Acetone				15.6	
(e) Ethyl acetate				6	
5. Rubber (natural)				150	132
6. Tea	27.7	32.2	42.1	53.7	56.7
7. Coffee	21	54.1	72.7	110	139.5
8. Cashew nut				150	
9. Arecanut					
10. Spices					
11. Tobacco					
12. Vanaspathi	170	340	558	678	742

TABLE III: COMPARATIVE STATISTICS OF SOME CHEMICAL AND ALLIED INDUSTRIES

Industry of product	Production metric tons x 10 ³				
	1950 - 51	1960 - 61	1970 - 71	1978 - 79	1980 - 81
III. Organic (synthetic) chemicals					
1. Drugs					
2. Plastics		0.9	2	10	
(a) L.D.P.E.				110	
(b) H.D.P.E.				30	
(c) P.V.C.				85.8	
(d) Polypropylene				30	
(e) Polystyrene				23.5	
(f) P.F. Moulding powder				3.3	
(g) M.F.				0.24	
(h) U.F.				2.4	
3. Synthetic rubber					
(a) S.E.R.				30	
(b) P.B.R.				20	
4. Insecticides					
(a) D.D.T.				4.5	
(b) B.H.C.				2	

TABLE IV: COMPARATIVE STATISTICS OF SOME CHEMICAL AND ALLIED INDUSTRIES

Industry of product	Production metric tons x 10 ³				
	1950 - 51	1960 - 61	1970 - 71	1978 - 79	1980 - 81
IV. Metallurgical and mining					
1. Pig iron	16.90	43.10	69.90	94.90	85.8
2. Steel	1470	3420	6140	8160	73.5
3. Steel (salable)	1040	2390	4480	6590	62.9
4. Steel (castings)		34	62	75.4	71.3
5. Aluminium (metal)	4	183	166.8	213.7	200.4
6. Copper (metal)					25.4
7. Zinc (metal)	7.1	8.5	9.3	21.9	44.54
8. Lead					11.37
9. Coal	32800	55700	74300	1054000	1188000
10. Iron ore	3000	11000	22500	38200	40700
11. Bauxite					

TABLE V: COMPARATIVE STATISTICS OF SOME CHEMICAL AND ALLIED INDUSTRIES

Industry of product	Production metric tons x 10 ³					
	1950 - 51	1960 - 61	1970 - 71	1978 - 79	1980 - 81	
V. Textile						
1. Jute	837	1097	958	1046	1387	
2. Cotton						
(a) Yarn	53.4	80.1	92.9	127.3	(Crore kg)	
(b) Cloth	421.5	637.8	759.6	864.0	(Crore meters)	
3. Woollen						
(a) Worsted yarn						
(b) Fabrics						
4. Silk						
5. Man made fibers						
(a) Viscose filament yarn						
(b) Rayon tyre yarn						
(c) Viscose staple yarn						
(d) Acetate filament yarn						
(e) Nylon filament yarn						
(f) Nylon tyre yarn						
(g) Polyester staple yarn						
(h) Polyester staple fiber						
(i) Acrylic staple fiber						
(j) Caprolactum						
(k) D.M.T.						

STUDENT SEMINARS AND PROJECTS IN CHEMISTRY
IN DEVELOPMENT OF ASIA

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Abstract

The introduction of programmes like seminars and projects would not only enrich the curriculum in chemistry but would also enhance the quality and standard of chemical education imparted in schools and colleges in Asian countries to a considerable extent. Years of experience in conducting these innovative programmes have revealed the marked influence on students in developing their self confidence and skills and the impact on society.

The success of implementing these stimulating programmes depends mostly on teachers and guides who plan, organise, supervise and evaluate seminar presentation and project work activity. The motivation, commitment and the helpful attitudes of teachers and guides towards their students along with their deep knowledge and wide background in the field of study, would influence and inspire students to participate enthusiastically in seminars and projects.

Problem of the local community and industries could be identified and tackled through project work activity. Relevant project work programmes if organised effectively could serve as a bridge between the educational institutions and local industries and act as a potential instrument for industrial development and social progress in Asia.

In this presentation the author shares his experience in conducting seminars and project work in chemistry and discusses the useful roles that Community, Industry and State could play in supporting relevant project work programmes for the welfare and progress of societies in Asian countries.

SEMINAR PRESENTATION

Innovative Programmes

Training students of Chemistry through seminar presentation and project work activity¹ enhance the quality and standard of chemical education imparted. Inclusion of such innovative programmes in teaching chemistry at all levels of education (in schools, colleges and universities) in Asian countries would not only enrich the curricula but would also develop sound teaching and training methods with far reaching impacts on students in particular and on society in general.

The stimulating courses like seminars and projects have received enthusiastic response from majority of students as these programmes are forward looking and challenging to their abilities and imagination. Through active participation in seminar and project work programmes students develop the sense of self confidence and variety of skills, in logical preparation of materials for writing a concise report and in precise oral presentation of matter during seminar, employing visual aids and charts. Further students develop their skills in communication and in carrying out systematic experimental work. Thus the versatile programmes of seminar and project occupy unique positions in educational methods of training and would help student effectively to aim at excellence in their field of work and study.

Role of Teachers and guides

The success of implementing seminar presentation and project work, programme effectively depends entirely on the teachers and guides who plan, organise, supervise and evaluate these programmes. The motivation commitment and the helpful attitudes of teachers and guides towards their students, along with their deep knowledge and wide background in the field of study would influence and inspire students to participate actively in seminars and projects.

Teachers and guides have a special responsibility in identifying local problems of chemical interest from the community and nearby industries that could be tackled through carefully planned and well organised project work in consultation with officials of industry and leaders of community. Results of such investigations would help to solve some problems of the industry and the community. Thus project work would serve as a bridge between the educational institution and local community and industry². It is indeed a potential instrument for social progress.

Purpose and plan of presenting seminars

The main purpose of training students to participate in the seminar programme is to provide a convenient forum, to present and

discuss their chosen problems of scientific interest freely and frankly in presence of their fellow students and staff advisers. Such presentations would help them to overcome stage-fear and develop in them a sense of self confidence. In addition seminar presentation develops and strengthens skills in communication, in collecting and reviewing materials for report and in preparation of slides charts and transparencies for projection.

The moment a student decides to present a seminar he has to choose a topic that has excited his curiosity and interest and start collecting materials from several books, journals and magazines. The collected material has to be rearranged and organised for presentation with details of introduction, earlier work, recent work and present state of knowledge on the chosen topic with references. For exhibiting tables, graphs and figures he has to prepare slides and charts and transparencies well in advance. He must study the materials prepared thoroughly, consult his staff advisers and fellow students and give a rehearsal seminar before final presentation.

Pre-requisites of a good seminar³

For making seminar presentation quite interesting, informative and stimulating the student must take care to choose a good subject matter of current interest, arrange the matter collected, in logical order with facts and figures and present the materials in loud and clear voice taking care of the language and style of presentation. He must employ visual aids to make his presentation quite impressive informative and enlightening to the audience. If necessary he may have to use the black board, writing neatly and clearly to explain his points. He must stop his presentation few minutes earlier before the allotted time and must be ready to answer questions from the audience with confidence. He must be prepared to acknowledge when good suggestions are made or when useful additional informations are given. These are some of the essential ingredients of a good seminar presentation.

Conduct of seminars at Loyola College

The Department of Chemistry of Loyola College has provided staff advisers, to help the participating students in choosing suitable topics, in preparing seminar reports with references and in presenting the matter with the aid of the blackboard, projectors and charts. Twenty five minutes were set apart for seminar presentation. The last five minutes were set apart for answering questions from the audience. Two such seminars were conducted during the seminar hour every week to keep the attention and interest of the students active and alive. It was found quite useful enlightening and enjoyable.

Encouraged by the favourable response from the students and the influence of the seminar programme on undergraduate students in training them to face the audience confidently, present the matter precisely and participate in the discussion effectively, the department has introduced with the approval of College Academic Council, one credit seminar course for the final year B.Sc. Chemistry major students. This weekly seminar has become a regular feature in the Chemistry Department.

Seminar programme for the semester is worked out well in advance, fixing the date, time, speaker, topic and staff advisers for each seminar. The list is exhibited in the notice board indicating the programme. Students have been advised to attend the seminar regularly, participate in the discussion and note down the salient features in a separate note book. To earn the credit for this course, students must attend the seminar regularly, present a seminar for 30 minutes submit a well-written or neatly typed seminar report with references and face an oral examination on the topic of his choice and some general questions from the other seminars he has attended.

Evaluation of the seminar

At Loyola, the seminar is evaluated by half a dozen staff advisers. Standard of the subject matter and mode of presentation are taken into consideration for evaluation. Critical evaluation is attempted by the staff who follow the seminar closely looking into the various points stated in the evaluation slip provided for grading. The format of the evaluation slip employed at Loyola College is reproduced below for information.

LOYOLA CHEMISTRY SEMINAR

Topic	:	
Speaker	:	
Class	:	D. No.: Date:
<u>SUBJECT MATTER</u>		
1) Standard of subject & plan		10
2) Preparation & mastery		10
3) Originality & logical development		10
4) Answers to questions		10
5) Summary & references		10
		<u>50</u>
<u>MODE OF PRESENTATION</u>		
1) Economy of time		10
2) Voice as a tool of communication		10
3) Blackboard use & teaching aids		10
4) Language & diction		10
5) Relating to the audience		10
		<u>50</u>
Evaluator :		Total mark%
Name :		
Signature :		

Marks are awarded by staff advisers in the evaluation slips, for each seminar and the average mark is taken for seminar presentation. Students are further encouraged by the award of prizes and certificates of merit for their participation and for their outstanding performance in the seminar course.

PROJECT WORK PROGRAMME

Aim and impact of Project Work

Project work aims at thorough investigation of a specific problem within a limited period under the supervision of a competent staff adviser or guide. It offers an opportunity to concentrate and work on a small area and make an indepth study of the specific problem chosen. Participation in project work programme provides interesting and exciting experience in the pursuit of truth employing scientific method.

The programme of project work develops a spirit of adventure, and a sense of discovery. It is found to enhance the skill in devising an appropriate scheme for studying a problem and in handling, classifying, interpreting and presenting information through tables, graphs and charts. Project work develops courage and self confidence and helps students to apply previously by acquired knowledge to the new situations. Thus training in project work induces originality and independent outlook to face challenging problems effectively.

Project work has made deeper impact on students in schools and colleges than the routine laboratory exercises some of which are dull and sterile. Project work excite the interest and curiosity of students as it is forward-looking and challenging. Even students of ordinary calibre and average ability were found to take deep interest in project activity, concentrating on their programmes outside the class hours and on holidays. It is evident that carefully planned and well organised project of relevance is bound to have marked influence in training students and in solving the local problems of society and industry.

Search of problem for Project Work

Ideas for selecting suitable problems for tackling, through project work, may be obtained from science books, journals, magazines and research reports and also from attending of seminars and symposia. Discussion with competent persons in the field of study and careful observation of life situations in and around the community and local industries would provide fresh ideas for identifying relevant projects of interest.

Once the problem is identified extensive search for materials should be undertaken by referring the relevant literature. In the process of reviewing the collected materials, new and fresh ideas and suggestions will emerge for identifying problems for project work.

Project work experience of Loyola College, Madras

In the light of experience gained for over ten years in conducting project work for M.Sc. students in the department of chemistry of Loyola College, Madras, an effective programme of training has been developed.. The author wishes to share his experience in organising and conducting project work programme which received good response from students and teachers.

M.Sc. chemistry programme is a two year post-graduate course at Loyola College, Madras. The course is conducted in four semesters. Students are initiated into project work, during the third and fourth semesters in the second year of M.Sc. course. Project work is conducted in two phases in the third and fourth semesters.

In third semester only three hours per week are allotted for project work. During this period student is permitted to discuss freely with members of the faculty and read in the library to identify his problem and choose a guide for his work. Later he starts collection of materials from recent books, journals and research reports on his chosen problem. From the collected material a concise report is prepared, reviewing earlier work and indicating his aims, objectives and programmes of his proposed project work. The report is evaluated and graded by the staff adviser at the end of the third semester after oral examination.

Further the student is directed to present a seminar on his proposed project work from the materials he has already collected. The seminar is critically evaluated by staff, offering suggestions and guidance for his future project work. In addition the student is advised to plan and secure the necessary chemicals and equipments for his experimental work to be conducted in the fourth semester. Thus, by the end of the third semester the student is fully equipped with sufficient knowledge, and definite programmes and plan to carry out his experimental investigations with confidence and courage.

During the fourth semester the student is free to concentrate on his experimental work althrough the week. He carries on steadily his laboratory and library work according to definite

plan and programme, approved by his guide. He notes down carefully all his experimental results in his record. The progress of his work is reviewed every week and discussed through short seminars. During this period he works systematically and seriously almost like a research scholar creating an atmosphere of a research institute in the college laboratory.

After completion of his experimental work of his project, student starts writing his final project report following the standard pattern and procedure. In the introductory chapter, the earlier work is briefly reviewed followed by the aim, programme and scope of the proposed project work undertaken. It is followed by chapters on Materials and Methods, Experimental Results (with tables, graph, figures and charts), Discussion and Summary and ends with bibliography. The manuscript of the report is critically reviewed by the guide and the neatly typed and attractively binded project report is submitted for evaluation by experts appointed as examiners. The project is evaluated and graded after oral examination.

After completing the course in project work, the student is encouraged to present his results in the Annual Inter-collegiate symposium regularly organised by The Indian Institute of Technology, Madras with transparencies and slides. Later he is advised to write a paper under the guidance of his staff adviser, on the results of his project work and present it for publication in a reputed journal, thus providing him all the opportunities to develop his talents, personality and professional competence. In the years to come the staff of Loyola College would strive their utmost to improve Project Work Programme further to serve the students effectively.

At Loyola College several project work programmes of relevance have been undertaken to stimulate teaching and research in chemical education. Projects on analysis and preservation of milk and milk proteins, analysis of local ores and minerals and nearby canal water involving pollution and soil and coal ash analysis have been attempted. In addition projects like construction of models as teaching aids and development of question bank are being perused with great interest.

The impact of project work in training students effectively for a scientific career and its influence on industrial development and social progress have been well recognised. For strengthening and developing such innovative programmes in educational institutions, the local community, industries and State should take active interest and participate in planning and organisation of project work in schools and colleges, offering all assistance and help, for the welfare of the society.

Teachers in consultation with local community and industries can identify relevant problem for project work and plan and prepare the programme of work. Industries must share freely their problems and encourage visits of students to the factories and workshops and provide them short training programmes to develop skills and appreciation for industrial work.

The community and State should help in organising workshops for teachers on project guidance to enhance their competence in the field. Summer camps for project work, may be organised for talented high school boys and girls to develop their curiosity and interest and exciting a sense of discovery. These workshops and summer camps would certainly provide opportunities to create future scientists to serve teaching, research and industry for the welfare of the nation.

While concluding this presentation the author wishes to recall the statement of D. McCormick⁵ of Manchester and Region Centre for Education in Science, United Kingdom on the role of science teacher in revolutionising chemical education through project work. "If every science teacher were to examine critically the relationship between the teaching of his subject and its potential scope in rapidly changing world and in the light of this had to justify to himself every topic taught, not only with regard to the logical framework of the subject, but also with regard to its far wider implications - then we might have a revolution in science education. If one occurs, I hope, project work will be recognised as an essential aspect of chemical education".

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UNIVERSITY - INDUSTRY INTERACTION: THE MALAYSIAN EXPERIENCE
(COUNTRY PAPER)

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Abstract

This country paper outlines University-Industry Interaction in Malaysia. Although a relatively new endeavour in this country, it is officially encouraged and is gaining momentum. A case study, using Universiti Sains Malaysia is documented.

I am presenting a country paper from Malaysia. For the benefit of participants from overseas, Malaysia is divided into Peninsular Malaysia and East Malaysia. The latter consists of the States of Sabah and Sarawak while in Peninsular Malaysia there are eleven states. There are five universities in the country namely:

Universiti ~~Sains~~ Malaya - University of Malaya
Universiti Sains Malaysia - University of Science, Malaysia
Universiti Kebangsaan Malaysia - National University of
Malaysia
Universiti Pertanian Malaysia - University of Agriculture,
Malaysia
Universiti Teknologi - University of Technology, Malaysia.

Other than Universiti Sains Malaysia which is situated in Penang, 400 kilometers north of Kuala Lumpur, the other four Universities are situated within a few miles of Kuala Lumpur.

A sixth University situated near the Thai border in the State of Kedah will begin its first session in June 1984. It is tentatively to be called the Universiti Utara Malaysia (The University of

Northern Malaysia). In addition there is an international university known as the Islamic University.

Industry University interaction or Industrial Liaison is a relatively new concept in Malaysia. In March 1980 a Malaysian National Workshop on Cooperation among Industries, Research Institutions and Universities was held in Kuala Lumpur under the auspices of the United Nations Development Programme. At this workshop there was consensus regarding the need for cooperation between the three sectors. One of the main recommendations which arose was the establishment of Industrial Liaison Units in order to promote active collaboration between the Universities, Research Institutes and Industry.

On his return from the workshop, the Vice-Chancellor, Universiti Sains Malaysia instructed the Deputy Vice-Chancellor (Research and Development) to carry out a feasibility study on the possibility of setting up such a Unit at Universiti Sains Malaysia. It was found that staff were already providing services to industry but on an ad hoc basis. A report was prepared and accepted by Senate in November 1980. A month later, Council agreed in principle that an Industrial Liaison Unit could operate without any commitments or funds as a service. In April 1982, the Deputy Vice-Chancellor visited a number of industrial liaison units in Australia and he returned favourably impressed with what these units had achieved in that country. In May 1981, the Industrial Research and Consultancy Service (IRCS) was started at Universiti Sains Malaysia. The IRCS deals in all matters related to the science based Schools (departments). In addition the University has another body called The Centre for Policy Research (CPR) which deals with matters related to socio-economic problems. It was founded in 1974 to enable the University to undertake research (including commissioned research, mainly for government and other public bodies) on a scale and over a range of problems that would not have been possible within the existing academic structure. The aims of the centre could be summarised as follows:

"In very broad terms, it was hoped that through its projects the Centre could collect, analyse and store data on crucial subjects on a continuing and systematic basis so that it would be easier at any time to monitor the nature of change, assess trends in development, measure the impact of existing policies and evaluate the need for new orientations in public policy. It was also hoped that the Centre would, through its own as well as through commissioned studies, generate information that could assist in the solution of specific problems. The data collected through these studies could, in addition to being used in policy formulation and review, also enhance the relevance and quality of teaching and research in areas where knowledge was lacking or was deficient."

Thus at Universiti Sains Malaysia we have two separate bodies interacting with the public.

As I had mentioned, earlier, Industrial Liaison is relatively new in Malaysia. There is encouragement from the Government to start Industrial Liaison Units at all the Universities. Presently, each University is carrying out studies on how best to carry out these aims. Universiti Kebangsaan Malaysia has a Bureau of Research and

Consultancy similar to that of the Centre of Policy Research at the Universiti Sains Malaysia. They are working on how to incorporate the Science-based Departments into the Bureau to do consultancy work. The Engineering Faculty at the University of Malaya have been providing consultancy services on an ad hoc basis for a long time. Staff members at the Faculty are very keen to formalise their present arrangements. I gather that they are working out a scheme for the whole University to get involved in liaison activities. Work at the University of Agriculture is related to food and agricultural problems while that at the University of Technology is related to architecture, building and engineering problems.

I shall now elaborate on the Industrial Research and Consultancy Service (IRCS) at Universiti Sains Malaysia. The principal function of IRCS is to develop contacts and contracts with industry, government agencies and the community at large in areas of mutual interest. All contracts leading to fee for service are undertaken on a strictly commercial and confidential basis in accordance with established professional conduct and practice. The IRCS acts as the interface and coordinating centre for such contacts and contracts. The resources of the University can be marshalled to advise, assess, service and solve problems using the expertise and facilities available in the Science based Schools. The public can contact individual staff members themselves if they know the staff members personally or they could ring the Coordinator with their enquiries who will then arrange to contact the necessary expertise who are interested in the problems presented. Fees are charged by the Service for the professional services of academic staff and for access to scientific equipment and other facilities. The Service has a responsibility to conduct its affairs in a businesslike manner and to provide services of a high professional standard. A breakdown of the type of services provided can be divided into the following categories:

- (a) Research and Development
- (b) Consultancies
- (c) Use of facilities and equipment
- (d) Routine tests and services
- (e) Courses.

Since this is a chemical conference, it was suggested that we should give as many examples from chemistry as possible. In the areas of (a) Research and Development and (b) Consultancies, it has to be stated with much regret that it is very difficult to arrange such work at the present state of our industrial development. The main reason is that the chemical industry is a capital intensive industry and the large plants that are operating in this country are mainly run by multi-national corporations. Smaller plants are tied by technical agreements and do not do any development work locally. The main area where we do extensive work for industry is in routine testing. Here we have a policy of not competing with commercial testing laboratories and to do this we price ourselves above that of commercial laboratories. With this limitation, industry still comes to the University for two main reasons (a) they need verification from an independent source and (b) the University has equipment to carry out tests which are not obtainable at commercial

laboratories.

Before concluding, I shall briefly outline with figures the amount of work that we have carried out in the two years that we have operated. The work was carried out in the Science based Schools and include the following:

School of Applied Sciences
 School of Biological Sciences
 School of Chemical Sciences
 School of Mathematical Sciences
 School of Medical Sciences
 School of Housing, Building and Planning
 School of Pharmaceutical Sciences
 School of Physics.

The total value and volume of work for 1983 are as follows:

(1982 figures are in brackets)

ROUTINE TESTING	\$53,254.00 (\$15,451)	175 (57)
HIRE OF FACILITIES	2,402.50 (\$14,032)	20 (25)
CONSULTANCIES	91,075.60 (\$21,913)	13 (6)
COURSES	16,693.00 (\$10,530)	4 (3)
	\$163,425.10 (\$61,926)	212 (91)
	=====	

It can be seen that there is an increase in the amount of work done in 1983.

In addition we have major research contracts where staff accept to do work usually during the vacations. Such contracts can be divided into three categories:

- (a) Staff undertake to do such work for the experience gained. They receive no payment but all their expenses in the project are paid for e.g. pollution studies on behalf of the State Government.
- (b) Staff are paid an honorarium and have all expenses of the project paid for.
- (c) Staff receive a consultancy fee according to commercial rates.

In conclusion it can be stated that the establishment of an Industrial Research and Consultancy Service at Universiti Sains Malaysia has marked a formal commitment by the University to interact with industry. The overall objective is to contribute to Malaysia's industrialisation by establishing strong links between

Universiti Sains Malaysia and industry. Experience gained in two years of operation indicates that there is ample scope and need for such a service that will prove beneficial to both the University and industry.

UNIVERSITY - INDUSTRY INTERACTION:
THE BANGLADESH EXPERIENCE

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ABSTRACT

The reasons for the ill-defined process of University-Industry interaction in most developing countries as in Bangladesh have been summarised on the basis of purely commercial and solely profit-oriented motivation of industries both in private and public sectors ignoring the vital need of development of endogenous scientific and technological infrastructures. Industries mainly established on turn-key basis depend on imported technology, foreign expertise and advisory services for production rather than having rapport with the universities and research organisations for innovation, modification, expansion and invention of techniques and materials. Some examples of the efforts extended toward university-industry interaction in Bangladesh have been cited to show how much benefit have been derived by developing the collaborative programmes. In order to achieve this objective collaboration between university administration, industrial management and modification of the course contents research and training programmes have been suggested. The methodology of establishing the university-industry interaction and the fields of collaboration have been identified.

WHY UNIVERSITY-INDUSTRY INTERACTION IS NECESSARY ?

The modern concept of development is based on the generation of skill and increase in endogenous industrial infrastructure and production. In Bangladesh there is the crying need to develop skills through education, training and research so that the production rates in the fields and factories can be expeditiously increased. It has been universally recognized that the industrial progress, creation of technological infrastructure and the programmes of education, research and training are mutually beneficial and interdependent. The pressing need in all development sector is the improvement of skill in management and technical know-how aimed at achieving the goal of continually increased production. The national development therefore emphasizes the urgency of university-industry interaction for the purpose of raising the standard and quality of products and advancement of normal academic programmes. The university has to be involved with the industries for the generation of new ideas, innovation of processes, development of the quality of goods. The strengthening of national technological capabilities of developing countries in line with the philosophy of self-reliance in a wide range of

activities demands the collaboration between the educational systems and the industrial enterprises. Naturally, the goal can only be reached with the help of a strong foundation for academic plans in science and technology education directed to develop the endogenous industrial, agricultural, medical and technological capabilities so as to create the local expertise for absorption, adaptation, innovation and expansion of the practice of science and technology in terms of experience in enquiry and the realization of the practical values and applications of knowledge for socio-economic benefit of man in the region.

What is to be Done at the University Level ?

We may summarise the basic needs of a university for collaboration with industries particularly concerning those of a developing country like Bangladesh:

1. Planning of academic training and research activities of the university based on relevance to the need of the industrial development of the country.
2. The production of skilled manpower resources for the management and progress of industries.
3. The generation of facilities for changing the requirements of teaching and research according to the changing needs of the industry from time to time.
4. A strong research and training programme of the university contribute greatly to develop a strong industrial base in the long run.
5. Looking to the developed world we know that the research and training programmes of the universities have contributed to the modern technological superiority in fields such as petrochemicals, agrochemicals, plastics, paper, pharmaceuticals, housing, building, heavy structural industries, metals, alloys, glass, ceramics, oils, fats, health, family planning textile, fibres, pollution control, transport, communication, electronics, instrumentation, new sources of energy, space exploration etc etc.
6. The training and research programme of the university have also been conducive toward development of the production of consumer goods of daily use.

BANGLADESH EXPERIENCE OF UNIVERSITY-INDUSTRY INTERACTION

The practical courses in chemistry and applied chemistry particularly of Dhaka University have been designed from the very inception of the University in 1921 so as to serve the commercial, technical and industrial needs of the then Indian sub-continent. But in view of the rapid pace of industrialization and enhanced activities in the fields of manufacture, imports and exports etc. in the area now known as Bangladesh, the existing facilities appear to be extremely

limited. The interaction between industries and the universities in Bangladesh is lacking because of many reasons such as:

1. The attitude and the motivation of the large industrial sectors mainly established on turn-key basis, both in public and private, sectors, which thrive only on imported technology and depend entirely on foreign expertise and technical know-how.
2. Lack of interest in research and development by the industries considered as economically nonproductive.
3. Policy of suspicion and industrial secrecy by the industrial sectors.
4. Communication gap between the university and industry on account of isolation of both from the common socio-economic structures.
5. University faculties are too busy in course work and fundamental research to give attention to industrial problems.
6. Degree and diploma-oriented education system mainly for the purpose of acquisition and distribution of the stamps of the university as the end product of learning process without training in skills and having no relevance to the need of the country.
7. Lack of properly trained staff for the purpose of establishing liaison between the university and the industry at both ends.
8. Lack of industrial funds to support research and academic programmes of universities for healthy rapport between the university and industry.

Nevertheless, of late, we have developed some meaningful interactions between the universities and industry based on programmes involving the institutions and mostly the individuals:

1. Arrangements have been made for a four week in-course training of our post-graduate students in different industries. The students receive a nominal per diem from the industries and in return they perform duties dealing with processing and production.
2. Every year batches of general students visit industries for a period of two weeks to have on-the-spot experience of production under the guidance of teachers.
3. Occasionally university staff are involved in training of industrial staff particularly in courses of analytical chemistry and use of laboratory equipments. We have also developed courses for industrial workers in relevant fields.
4. Consultancy service on individual contact basis to assist the industries exist but at present there is no institutional arrangements to offer such services and the industries mainly depend on foreign imported expertise.

5. In general, the communication between university teachers, research workers and industrial staff takes place during seminars, symposia and national conferences. These are of transitory nature and has not been much significant for a meaningful rapport.
6. Private industrial enterprizes which are mostly of small scale or moderate capacity sizes approach university faculty on personal contacts for solutions of problems and analysis. I recount some of my personel experience, both good and bad, in this direction.
 - a. Food and Allied Industries Corporation enquired about the cause of frequent fire in the ware house of oil seeds. The problem was solved by proper arrangements of stacking of the sackings containing oil seeds (rape seeds) and humidity control.
 - b. The starch produced from 'Sati' became brownish in colour. The cause of this was found and steps were taken to get a white product.
 - c. Analysis of raw materials and finished products are normally done in our laboratories frequently.
 - d. A glycerine recovery plant from soap lye set up on consultation and technical know-how of a local research organisation.
 - e. The proposal for setting up a nicotinamide production plant from cigarette factory wastes was submitted.
 - f. A private firm set up a plant to produce the alkaloid, scopolamine hydrochloride, on the basis of work in a local research organisation. The firm, although set up the plant but never went into production.
 - g. We have recently set up a paper and building board plant based on water hyacinth fibres. A private firm came forward to set up the industry on the basis of the research and feasibility report. At one point during discussions I mentioned that research results are not always positive and that the firm should not be disheartened by the negative results at the initial stages. The propriter and the manager fled away from the scene never to be seen again.
 - h. Proposal of utilization of waste iron obtained as a by-product in the Steel Mill industry in Bangladesh has not been successful so far.
 - i. Industries in Bangladesh generally use the services of the Standard and Testing Laboratory which is a Government organisation or utilize better facilities at the Atomic Energy Centre particularly for analytical problems.

How to Establish Better Collaboration between the Universities and Industries ?

The main line of action is to find ways and means to bridge the communication gap in order to increase the universities awareness of the industrial needs and the industries eagerness to make use of the training and research facilities of the university. It may be argued that the industry may have a full-fledged research and development programme of its own without caring to involve the universities for collaboration. But the fact remains that generation of new ideas and innovation of processes and products can best originate through the medium of appropriate and sound educational and training programmes infused into the young mind. The ways and means of establishing the link between the university and industry may be adopted as follows:

1. Incorporation of industrial advisory services in the curricula.
2. Nomination of industrialists representative in appropriate bodies of the university.
3. Financing research programmes at the university on the problem of the industry.
4. Sandwich and In-Service courses for industrial workers at the university.
5. Secondment of industrial staff at the university and vice-versa both on short term and long term basis.
6. Nomination of academic staff on the boards of industries.
7. Arrangements for refresher courses, workshops, seminars on topics of mutual interest and importance to industries at the two premises.
8. Involvement of industry in the supervision work of the research degree at the university.
9. Sharing of capital equipments and instruments.
10. Exchange of information through liaison Centres.
11. Coordinated research programmes between industry and university on topics of current interest having future industrial prospects.
12. Financial assistance to the university by industry as loans, gifts, grants, endowments, scholarships, fellowships, equipments, specialized laboratories in order to effect the general upliftment of the standard of teaching, training and research in the universities.

Unfortunately none of the points of proposal have ever been given any considerations by the industries in Bangladesh for reasons mentioned before.

What are the Areas of Interaction ?

The cooperation and collaboration for research and development between the university and industry in a developing country naturally suffers due to the absence of a policy as regards the areas for interaction. For this purpose the industry has no clear concept of a scientific, social and precisely humanistic approach to industrial production and are involved mainly in profit-oriented goal on commercial lines. The areas of cooperation which can benefit the industries in the long run may be cited as:

1. Improvement of products.
2. Process development.
3. Development of analytical technique.
4. Standardization of existing products.
5. Technical and commercial evaluation of products.
6. Industrial utilization of natural products for economic benefit.
7. Solving problems faced by industries in existing production lines.
8. Research on alternative sources of raw materials.
9. General and technical services to the users of industrial products.

I may mention here that very recently a 12-man Committee of the National Training Council, headed by the Minister of Industries and Commerce has been formed in Bangladesh for the purpose of generating better skills and training in different fields. The ideals working behind the constitution of this Council is to help in implementing properly the programmes related to training of industrial personnels.

We are aware of the historical background which has brought about the scientific and technological advancement of the developed countries in modern times possibly through a lot of trials and tribulations. We in the developing countries have the opportunity to profit from their experience and make rapid strides through the cooperation and collaboration between the universities and industries. But if we continue to depend entirely on turn-key basis for industrial progress our fate as LDC will be sealed for all time to come.

Of course, the international cooperation and assistance as well as the regional links are essential factors for the development of an LDC but the success of all international and regional scientific cooperation will be judged by the extent to which the indigenous scientific and technological capabilities of a developing country have been enhanced and expanded. This should be the goal and mission of all international programme of cooperation and can play a catalytic role in bringing about university-industry interaction.

THE CHEMICAL INDUSTRY IN SINGAPORE

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Economic statistics are presented to illustrate the growth and importance of the manufacturing industries over the last two decades with special reference to the chemical industries and the role of the chemist in industry. The key importance of the multinationals in the export-oriented industries is discussed. The profile of a pharmaceutical multinational is given. The role played by some government institutions in providing technical support to smaller industries is also described. The article ends with a brief account of the emphasis placed on high technology industries and Singapore's attempt to promote R & D activities to support such industries.

INTRODUCTION

When Raffles established Singapore as a British colony in 1819, it was only a small fishing village with about 150 inhabitants. The colony rapidly grew in importance as a trading centre and by the turn of the 19th century, it had developed into a major emporium of the East. However, even before the attainment of self-government in 1959, it had become clear after the 2nd World War that Singapore could no longer depend so heavily on its traditional entrepot trade for its prosperity. The population had swollen greatly over the years (at an annual rate of 42 per thousand). Housing was sadly lacking. All the social facilities - health, education, social welfare and even public utilities - were bursting at the seams. These problems, together with rising unemployment, made it imperative that alternative sources of foreign exchange earnings be found. The advice of experts was that Singapore, which has no natural resources of its own, should add an industrial base to its existing trading economy to create employment and new sources of income. It seemed essential at that time that she should adopt a policy of industrialization basically similar to that of Malaya in order to be an integral part of the proposed Malayan common market and in anticipation of forming a closer political union. This was a policy which emphasized labour-intensive import-substitution type industries, designed primarily to strengthen the Malayan economy. The political union leading to the formation of Malaysia took place in 1963, but it was short-lived. In 1965, owing to irreconcilable political differences, Singapore withdrew from this union. With the loss of the potential Malaysian market, she now had no choice but to shift emphasis to the promotion of more capital-intensive, high technology, sophisticated and export-orientated enterprises with the world as her market.

This change in Singapore's industrialization policy is reflected in the increase in the number and functions of government

industrialization-promotion agencies after 1965 and the Economic Expansion Incentives Act enacted in 1967, as shown in Table 1.

The rest of this article will focus on the growth of the manufacturing industries in Singapore over the last 15 years or so with special reference to the "chemical industries" including the chemist's role in industry. Because of their importance in the industrialization effort, the role of multinational corporations will be discussed. Some prominence will be given to the petroleum industry which, after all, contributed more than one third to total output of manufacturing for many years. Since chemicals and pharmaceuticals constituted one of the four industries which contributed most to the growth of the manufacturing sector in recent years, a brief sketch of the British multinational Beecham Pharmaceuticals in Singapore will be given. The functions of government institutions such as the Singapore Institute of Standards and Industrial Research which provide technical support especially for smaller industries will also be described. However, to avoid unnecessary ambiguity, it would be useful first to explain briefly what we mean by the term "chemical industry" before proceeding further.

CHEMISTRY'S PLACE IN INDUSTRY

The term "chemical industry" is used in this article both in a narrow sense to mean the manufacture of simple chemicals such as sulphuric acid, ammonia, ethylene glycol and similar inorganic and organic chemicals; and in a broader sense to include complex products that are usually thought of as having other primary functions such as plastics and resins, synthetic rubber and fibers, drugs, soaps and detergents, cosmetics and toiletries, paints and varnishes, and fertilizers and pesticides. Since chemistry by definition deals with the molecular transformation that matter undergoes, we should broaden our perspective further to include industries which depend on chemistry in some way or other: those dealing with ferrous and nonferrous metals; petroleum, food; coal and coke; pulp and paper stone, clay and glass; and even electronic equipment.

GROWTH OF MANUFACTURING INDUSTRIES

The growth of the chemical industry in Singapore has been paralleled by the growth of the manufacturing industries as a whole. The position of the manufacturing sector in the national economy over the years is summarized in Table 2. From about 13 per cent in 1960, it grew to account for about 21 per cent of the Gross Domestic Product in 1982. Manufacturing production continued to be increasingly oriented towards exports. In 1982, direct exports of manufactured goods accounted for 60 per cent of total manufacturing output. The general growth of the manufacturing industries can be seen in Table 3 which gives details about number of establishments, number of workers, output, value added, sales, employee's remuneration, and capital expenditure. Materials used cover raw or basic materials, chemicals and packing materials. The gross

output of industries refers to the total value of all commodities produced (including by-products) and services rendered during the year. The valuation of commodities produced is at ex-factory price, excluding outward transport charges and excise duties if any. Value added is derived as the differences between the value of gross output and that of total input and work given out. Total input covers cost of materials, electricity, fuel, water and inward transportation. Work given out refers to payments to other firms or persons for work performed on raw or basic materials supplied by the establishments. Capital expenditure covers the total expenditure on capital assets incurred by the establishment during the year.

The principal statistics for output by industry are given in Table 4 for 1982. In the tables, all values are expressed in Singapore dollars. Examination of these tables shows that chemicals and chemical products including products of petroleum and coal experienced accelerated growth (more than 50 per cent growth rate) between 1969 - 1973 and continue to contribute substantially to the growth of the manufacturing sector.

THE CHEMIST'S ROLE IN INDUSTRY

The chemical industry in Singapore is very young. With the exception of the petroleum refineries and a few other multinationals, "chemical" firms are small in size. The Directory of the Singapore Manufacturers Association shows that the basic chemical industry consists of a few companies making sulphuric acid, alums, hydrochloric acid, chlorine, caustic soda, sodium hypochlorite, industrial gases (oxygen, nitrogen, argon, carbon dioxide, acetylene, hydrogen, nitrous oxide, cyclopropane, helium, neon, ammonia and butane) and formaldehyde and PVC resins. In addition, there are companies which produce a variety of chemical products such as soap, detergents, perfumes, essences, flavours, textile chemicals and dyes, pharmaceuticals, adhesives plastic and rubber goods. Most of the raw materials used are imported. The chemist's role in industry is primarily in quality control. His responsibilities usually consist of various testing and evaluation duties to ensure that the raw materials used are correct and the quality of finished products is maintained at the desired level. Any research or development activity is usually confined to increasing the efficiency of the production process and in possible material substitution using locally available raw materials.

One-third of chemists in Singapore are employed in teaching institutions. Another third work in manufacturing industries. The biggest number of working chemists are to be found in teaching and lecturing, general administration and quality control/teaching/product evaluation. It is probably true to say that most of the chemists working in these two latter areas are in industry.

MULTINATIONAL CORPORATIONS

The unprecedented growth in export sales of manufactured goods since 1969 has been made possible mainly because of the influx of multinational corporations although the American involvement in Vietnam has helped to boost sales until 1974. Most multinational firms in Singapore are either joint ventures with local capital participation or wholly owned subsidiaries of foreign firms. From Singapore's point of view, such foreign investment is particularly welcome because these multinational enterprises bring with them established international markets, thus overcoming the problems of a limited domestic market and the difficulties of domestic manufacturers in penetrating export markets. Singapore has also become attractive to export-oriented foreign investment as a manufacturing and distribution centre for international operations. The comparative advantages for such operations have been stated by the Economic Development Board in their 1970 report.

"In particular, industrialists have found that the quality of Singapore's workers, their productivity, their ability to learn quickly and their high basic educational level have all proved valuable in strengthening their competitive position in their home markets and in international markets. Thus, in increasing numbers and diversity, they come to Singapore with the following objectives - to manufacture high quality parts and components at competitive cost for supplying parent companies in home countries and subsidiaries in various parts of the world; produce finished products in large volume at low cost for international markets; manufacture capital equipment, intermediate products and chemicals with cost advantage for Southeast Asia, Middle East and East African Markets, especially for the offshore oil exploration, mineral resources, agricultural and forestry development and construction projects in these areas; use Singapore as the 'investment base' or 'launching site' for branching out manufacturing operations in surrounding countries."

Other factors which have helped to attract foreign investment include liberal fiscal and financial incentives offered by the government, the entrepreneurship of the business community in diversifying their markets and product range, a well coordinated industrial skill training program, and a highly disciplined work force.

THE PETROLEUM INDUSTRY

Ever since Singapore embarked on its industrialization program, the petroleum industry has dominated manufacturing operations both in terms of capital investment and in domestic exports of petroleum products. The search for oil in Southeast Asia took the region by storm and Singapore found herself in the centre of the black gold rush.

There are at present 5 major refineries in the Republic with a total capacity of more than 1 million barrels per day, representing an investment of about \$2 billion.

The Chemical Industry In Singapore

The big 5 are Esso, Mobil, British Petroleum, Royal Dutch/Shell, and the Singapore Petroleum Company. The SPC is a joint venture between the Singapore Government and two American Companies-Amoco (Standard Oil of Indiana) and Oceanic Petroleum (subsidiary of the U.S. Summit Corporation). In addition, there are two lubricant blending plants owned by Caltex and Castrol.

Petroleum Refining

1982 saw the refineries operating at near full capacity but falling prices and slower growth in demand resulted in a marginal decrease in output and value added.

A number of secondary processing projects were completed in 1983 - Singapore Refinery Company's catalytic reformer and visbreaker and Shell's hydrocracker. Future developments are expected to be in process control systems, energy conservation, and increased storage capacity reflecting the overall effort by oil refiners to increase operating efficiency and flexibility.

With the imminent overcapacity in refining in the region and competition from export refineries in oil producing countries, the industry is expected to face a severe challenge. However, because of its unique geographical location, Singapore will remain an important balancing centre for petroleum products in the Far East supplying the shortfalls and distributing the excess supplies to other markets.

Petrochemicals

The basic infrastructure and utility facilities of the S\$2 billion petrochemical complex have been completely installed. The Petrochemical Corporation of Singapore, the Polyolefin Company (Singapore) and Denka Singapore are ready for start up while Phillips Petroleum Singapore Chemical is close to mechanical completion. Ethylene Glycols (Singapore) the fourth downstream company in the complex will manufacture ethylene glycol and ethylene oxide as well as nitrogen gas for the whole complex.

BEECHAM PHARMACEUTICALS (SINGAPORE)

Beecham's pharmaceutical factory is the result of a two phase development. The first phase, built for the acylation stage of penicillin manufacture and subsequent pharmaceutical processing started production in December 1972. Constructed at a cost of S\$32 million it was in production only 26 months after the decision to proceed with the project was taken.

The second phase of development completed in August 1976, comprised a plant for the production of the penicillin nucleus 6-amiopenicillanic-acid (6-APA), so enabling the factory to begin

operations one stage earlier in the production of semi-synthetic penicillins. This plant together with supporting facilities was built by a local company at a cost of S\$15 million. The plant now produces all the factory's requirement of the previously imported 6-APA. This is made by splitting the Penicillin G molecule using the enzyme amidase immobilised on an inert carrier resin. Beecham Pharmaceuticals is now producing six major antibiotics and will produce more advanced products resulting from the S\$65 million annual expenditure on Research and Development undertaken by Beecham Group. Beecham Pharmaceuticals (Singapore) now has more than 500 employees, of whom about 10 per cent are graduates with degrees in chemistry, pharmacy, microbiology, chemical, electrical and mechanical engineering and accountancy. The remaining staff comprise a group of highly skilled engineers, technicians and production operators, many of whom received their initial training in factories in the United Kingdom.

An encouraging feature is that R and D is being undertaken locally in the development of enzymation process for semi-synthetic penicillins.

SOME RECENT DEVELOPMENTS IN THE CHEMICALS SECTOR

Because of its diversified nature, the chemical industry was one of the growth sectors in 1982 which saw 4.6 per cent increase in output. While products such as household chemicals served a stable domestic market, other more specialised products were in demand from the growing offshore oil exploration and production industry.

Some projects started include

Exxon chemical Singapore-additives (paramins) for lubricating oil. The S\$80 million plant is the first of its kind in Southeast Asia and will supply the Asia Pacific region

Sun Ace Kokoh - PVC stabilisers

Stahl Chemical Asia/Beatrice Chemical - leather finishing chemicals

Major projects under construction include

Lubrizol - a S\$19 million plant to blend additives for lubricating oil which at a later stage will be integrated with the manufacture of chemical components for the additives

National Oxygen/National Iron & Steel Mills Nippon Sanso - a S\$ 20 million air separation plant to produce also high purity gases for the electronics industry

Pharmaceuticals

The three major companies in this section continued their expansion.

The Chemical Industry In Singapore

Beecham is expected to begin commercial production in 1985, Augmentin, a new synergistic formulation effective against a wide range of bacteria.

Gloxchem will increase its production of ranitidine hydrochloride.

Kaneka is widening its range to include valine and phenylglycine, an intermediate material for the production of antibiotics while expanding the capacity for hydroxyphenylglycine.

Food and Beverages

Product development and process improvement are the two new dimensions in the food section. The R & D project by Nestle/Eastreco is based on the concept of using regionally available raw materials to produce Asian food products and subsequently developing the manufacturing process. Other food processing companies have also begun development in their respective product lines. Cerebos for instance, is combining East and West through the introduction of instant Chinese porridge, bottled bird's nest and other oriental specialities.

SCIENTIFIC INSTITUTIONS IN THE SERVICES SECTOR

There are 3 major scientific institutions in the services sector which provide supportive chemical expertise in Singapore. They are (i) the Department of Scientific Services, (ii) Singapore Institute of Standards and Industrial Research and (iii) the Port of Singapore Authority Chemistry Department. These institutions have been set up to meet the demands for scientific services from government departments, statutory boards, commerce and industry.

DEPARTMENT OF SCIENTIFIC SERVICES (DSS)

This department has widened its scope from its traditional role of offering services only to the Government to include the commercial and industrial sectors as well. It assists other Government Departments by providing the Scientific back-up service necessary for the administration of the various Acts. In the commercial and industrial sectors, similar services are offered to enable commercial firms to upgrade the quality of their goods and to develop new ones. In the field of export promotion the Departments quality certification service has been invaluable in enabling exporters to compete in international markets.

The Department comprises six sections:

Forensic Science, Environmental Science, Toxicology, Food Science, Pharmaceutical Science, and Radiation Science.

THE SINGAPORE INSTITUTE OF STANDARDS AND INDUSTRIAL RESEARCH (SISIR)

This Institute was established to help industrialists, especially local ones, meet international standards of quality in their manufactures and overcome technical problems. It also undertakes a certain amount of industrial research. The SISIR quality certificate is now well-accepted as a guarantee of quality of Singapore made products in the international market. The Institute's programs are organised along multidisciplinary lines.

Chemistry enters the program mainly in the Materials Technology and Application Centre which has identified the following areas for development: plastics, metals and chemistry. It may be noted that one of the successes of SISIR's development program has been the production of attractive RISIS gold-plated orchids on a commercial scale, now proving to be quite popular with tourists looking for souvenirs.

PORT OF SINGAPORE AUTHORITY CHEMISTRY DEPARTMENT

The Chemistry Department of the Port of Singapore Authority was set up in 1974 to provide rapid scientific and technical services to all the departments of the port and the shipping community. This was made necessary because of the tremendous increase in the volume of activities in the port in recent years. The PSA Chemistry Department consists of an Inspectorate of Dangerous Goods and an Analytical Services Section. The Inspectorate looks after the safety and health of the port workers by carrying out

- (a) inspection of petroleum carrying vessels to ensure that they are gas-free before they are allowed to enter the port and shipyards for repair.
- (b) inspection of dangerous and toxic cargoes to be discharged from vessels. On-the-spot advice is given to workers on safety precautions in handling poorly packed or broken containers.
- (c) inspection for toxic fumes from vessels arising from leakage or accidental spillage.
- (d) inspection for carbon dioxide and oxygen on board vessels.

The main Analytical Services consist of palm oil analysis, examination of drinking water, analysis of slop oil from petroleum tankers, flash point testing of petroleum and monitoring of sea-water for pollutants. Other services performed include the analysis of marine clay, oil-spilled dispersants, transformer oil, lubricating oil, rice, soya bean meal, cooling water in air-conditioning plants, boiler water and unclaimed dangerous chemicals. The Department fumigated about 3,500 containers and 650,000 tonnes of grains during the year.

CONCLUSION

In conclusion, it can be said that if the will to upgrade skills, processes and the industrial base itself remains strong, there is no reason why given its central location and its record of success, industrial development cannot continue to bring economic gains to the people of Singapore well into the 21st century.

TABLE 2 GROSS DOMESTIC PRODUCT BY INDUSTRY 1960, 1970, 1977-1982
(AT 1968 FACTOR COST)

(S\$ MILLION)

	1960	1970	1977	1978	1979	1980	1981	1982 ^P
Agricultural & Fishing	87.7	128.5	152.3	151.1	156.1	159.1	155.5	145.6
Quarrying	7.5	19.2	41.1	35.6	40.7	43.7	56.7	71.7
Manufacturing	279.7	1,007.0	2,032.7	2,262.9	2,603.0	2,909.6	3,192.3	3,013.5
Utilities	53.4	144.9	265.7	303.0	331.4	357.0	383.0	401.5
Construction	79.3	343.0	557.8	514.9	551.0	611.1	718.1	978.4
Trade	713.4	1,538.1	2,558.8	2,734.4	2,928.6	3,139.3	3,318.7	3,474.8
Transport & Communication	297.6	593.1	1,533.3	1,772.9	2,049.0	2,334.8	2,656.5	2,942.4
Financial & Business Services	247.5	716.4	1,387.0	1,525.4	1,766.8	2,162.7	2,581.3	2,952.6
Other Services	391.9	723.6	1,110.7	1,197.7	1,265.2	1,336.8	1,417.5	1,547.3
Less: Imputed Bank Service Charge	35.7	106.8	349.1	409.3	660.9	893.6	1,110.3	1,309.9
Total	2,122.3	5,107.0	9,290.3	10,088.6	11,030.9	12,160.5	13,369.3	14,217.9

TABLE 3 PRINCIPAL STATISTICS OF INDUSTRIAL PRODUCTION

Year	Establi- shments	Workers	Input	Output	Value Added	Employees' Remuneration	Capital Expenditure	Direct Exports
	Million Dollars							
1972	1,971	175,241	4,230.0	6,126.7	1,820.5	666.2	652.0	2,911.2
1973	2,117	202,713	5,967.3	8,705.6	2,606.2	881.3	791.7	4,778.8
1974	2,219	210,002	10,453.2	14,237.0	3,596.8	1,096.2	626.3	8,520.1
1975	2,424	195,001	9,479.2	13,197.4	3,463.8	1,200.9	629.9	7,609.9
1976	2,545	210,822	11,815.9	16,175.0	4,041.1	1,332.6	631.1	10,160.5
1977	2,674	222,342	13,430.9	18,293.5	4,539.6	1,494.6	756.3	11,411.5
1978	2,979	246,467	14,871.9	20,492.3	5,220.0	1,743.9	824.3	13,087.0
1979	3,156	271,917	19,314.2	26,331.0	6,523.9	2,108.0	1,429.8	16,904.0
1980	3,391	288,165	23,433.7	32,805.8	8,652.8	2,556.2	1,878.4	19,874.9
1981	3,471	284,509	26,836.0	37,694.0	9,866.9	2,971.7	2,012.7	22,893.6
1982*	3,581	274,106	25,914.2	36,266.6	9,391.6	3,163.6	..	21,876.7

Note: Establishments employing 10 or more workers.
Data include rubber processing and granite quarrying.

YEAR BOOK OF STATISTICS S'PORE 1982/83

TABLE 4 INDUSTRIAL OUTPUT BY INDUSTRY

Million Dollars

Industry	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982*
Food	552.0	714.9	930.2	813.5	938.0	1,219.0	1,229.8	1,452.7	1,661.5	1,692.5	1,661.4
Beverage	73.3	80.5	97.8	130.5	150.7	168.3	205.5	219.7	249.1	327.2	323.0
Tobacco Products	102.7	129.8	142.7	144.5	153.6	166.4	171.1	166.0	171.3	193.6	198.9
Textiles & Textile Manufactures	192.9	313.8	292.4	259.7	359.9	346.6	352.6	425.8	488.8	422.1	335.5
Wearing Apparel except Footwear	206.7	289.3	269.1	286.1	406.1	479.5	633.1	737.0	848.4	924.7	937.9
Leather & Leather Products	16.7	27.9	25.6	22.0	31.1	44.2	50.4	51.4	47.0	49.6	38.6
Footwear	25.9	23.7	27.2	30.3	33.9	30.8	34.7	51.5	53.6	54.9	42.0
Sawntimber & Other Wood Products except Furniture	261.0	466.7	358.1	311.5	422.0	437.4	550.2	796.1	749.8	641.0	530.0
Furniture & Fixtures except primarily of Metal, Stone & Plastics	29.0	37.9	44.3	48.7	61.3	79.1	116.9	160.9	227.5	277.1	270.4
Paper & Paper Products	60.6	84.9	103.6	96.8	114.8	127.3	158.7	209.2	272.7	302.2	273.2
Printing & Publishing	143.2	168.3	221.2	225.2	290.2	335.6	375.5	431.2	550.4	674.3	666.1
Industrial Chemicals & Gases	72.9	108.8	172.1	154.5	210.1	227.0	183.3	255.2	346.1	363.7	389.3
Paints, Pharmaceuticals & Other Chemical Products	100.4	184.3	236.7	274.8	311.9	344.9	411.1	429.9	583.3	663.4	685.3
Petroleum Refineries & Petroleum Products	1,680.2	1,967.9	5,705.5	4,753.3	6,118.8	7,022.4	7,498.3	9,308.1	11,520.5	14,453.8	14,370.2
Processing of Jelutong & Gum Damar	13.1	17.6	22.6	20.2	16.4	21.0	19.3	22.8	25.9	28.2	43.6
Rubber Products except Footwear & Toys	43.2	48.0	54.6	54.3	57.8	62.0	66.8	89.9	89.7	76.3	72.1
Plastic Products	60.5	108.2	130.0	120.7	160.7	204.2	277.8	380.7	498.1	519.0	503.1
Pottery, China, Earthenware & Glass Products	15.9	22.6	30.0	28.3	37.0	41.0	49.7	60.9	68.0	90.3	97.7
Structural Clay Products	13.2	17.2	21.8	16.2	20.2	20.4	14.2	21.3	30.7	34.9	35.5
Cement	58.1	74.9	127.2	157.1	161.5	165.9	179.9	225.2	277.1	347.2	426.0
Structural Cement & Concrete Products	14.4	22.1	32.7	58.2	64.4	65.3	71.2	95.5	156.5	263.9	292.5
Non-metallic Mineral Products	30.9	58.0	79.0	88.4	85.0	96.9	89.4	102.8	115.4	138.2	107.4
Iron & Steel	73.3	105.3	176.7	148.3	152.4	145.0	192.9	272.1	338.1	343.1	393.2
Non-ferrous Metals	21.1	33.4	49.4	41.3	33.8	53.7	56.1	135.4	190.4	130.5	127.9
Fabricated Metal Products except Machinery & Equipment	246.4	340.9	454.0	506.9	507.1	597.9	743.8	965.5	1,234.9	1,492.7	1,527.4
Machinery except Electrical & Electronic	223.4	338.5	573.0	754.7	676.9	701.0	844.4	1,183.5	1,662.7	2,484.2	2,545.0
Electrical Machinery, Apparatus, Appliances & Supplies	206.4	332.9	444.0	414.5	531.8	541.1	727.4	758.4	974.4	1,050.3	958.3
Electronic Products and Components	529.3	905.5	1,333.4	1,229.3	1,722.6	2,137.2	2,548.4	3,963.0	5,344.0	5,728.5	4,980.4
Transport Equipment	463.1	636.2	918.2	1,056.8	1,117.6	1,251.3	1,342.8	1,548.0	2,043.5	2,223.8	2,059.2
Instrumentation Equipment, Photographic & Optical Goods	69.2	128.3	115.9	182.3	193.2	184.1	237.6	276.6	382.8	290.6	296.3
Other Manufacturing Industries	123.3	149.9	157.5	151.3	176.4	201.8	228.9	337.5	455.6	505.2	462.4
TOTAL MANUFACTURING EXCLUDING RUBBER PROCESSING	5,722.2	7,938.1	13,346.9	12,610.1	15,317.4	17,518.2	19,666.7	25,133.7	31,657.9	36,787.1	35,650.9
Rubber Processing	385.9	748.6	867.9	555.2	814.0	744.1	801.3	1,170.2	1,052.5	772.6	437.0
TOTAL MANUFACTURING INCLUDING RUBBER PROCESSING	6,108.1	8,686.7	14,214.8	13,165.3	16,131.4	18,262.4	20,468.0	26,303.9	32,710.4	37,559.7	36,087.9
Granite Quarrying	18.6	18.9	22.2	32.1	43.6	31.1	24.3	27.1	95.3	134.3	178.7
TOTAL	6,126.7	8,705.6	14,237.0	13,197.4	16,175.0	18,293.5	20,492.3	26,331.0	32,805.8	37,694.0	36,266.6

THE CHEMICAL INDUSTRY'S CONTRIBUTION TO AGRICULTURAL PRODUCTIVITY WITH PARTICULAR REFERENCE TO DEVELOPING COUNTRIES

J D Rushton

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ABSTRACT

The developing countries have a high proportion of the world's population and it is beneficial for them to improve agricultural productivity in order to increase output of foodstuffs and of plantation crops. The application of agricultural chemicals and fertilisers, together with good husbandry and the use of higher yielding varieties with increased resistance to disease and pests, can substantially improve crop yields and prevent losses from harvested crops. The chemical industry can contribute towards bringing about these increases in yield by developing and supplying agricultural chemicals and by co-operating with national governments in education and training programmes. In this paper examples are cited of the kind of yield improvement which can be possible from effective use of the major groups of agricultural chemicals by which is meant insecticides, fungicides, herbicides, growth regulators and rodenticides. The favourable cost/benefit ratios quoted demonstrate that use of such products leads to substantial yield improvement at low cost both to farmers and to national governments.

INTRODUCTION

Today, the world's population is 4.5 billion of which two-thirds live in the "developing countries" as defined by the United Nations (UN). By the year 2000 the world population is projected to reach 6.2 billion; at that time almost 80% of the population is expected to be resident in the developing countries. Compared with this high proportion of world population, the developing nations at present only produce approximately 40% of the world's total agricultural production.

Large increases in food production are, therefore, necessary if developing countries are to maintain current nutritional standards. To improve on these standards, and to cope with population increases, a growth rate in agricultural productivity above the 2.8% per annum achieved over the last 20 years will be required and the Food & Agricultural Organisation (FAO) has suggested a target growth rate of 3.7%. Improvement in output is also of immense value in plantation crops where these are important to a country's economy.

Let us look at how improvements in output can be achieved. FAO has estimated that only 10% of the growth in South East Asia can be obtained from increases in the available arable land; a further 14% may come from increases in cropping intensity; the majority of the desired growth - 76% in all - will have to be obtained by improvement in crop yields. In Asia as a whole, there is only 0.21 ha of cultivatable land per head and there is emphasis in almost every country on enhanced yields and better cropping patterns. Table I displays the projected contributions to Agricultural Production growth.

TABLE I

Projected Contribution of Area Expansion and Crop Intensification to Agricultural Production Growth in Developing Countries - 1975-2000

(% contribution to output growth)

REGION	ARABLE LAND GROWTH	CROPPING INTENSITY	YIELD	YIELD & INTENSITY
Averages for 90 developing countries	26	14	60	74
Africa	27	22	51	73
South East Asia	10	14	76	90
Latin America	55	14	31	45
West Asia	6	25	69	94

Source : FAO

The farmer or planter and the agriculturalist are able to exert a degree of control over many factors affecting yield such as soil fertility, crop varieties, pests, diseases and weeds. There is a lot to aim for, because it has been estimated that losses due to pests and diseases amount on average to 30-40% of potential production and in some circumstances losses can be total. A further 10% of yield on average is lost in storage. The chemical industry has the capability to help reduce these losses considerably and, allied with the development of higher yielding varieties with increased resistance to disease and pests, to participate in the global drive for improved yields. It is my hope that industry and Governments will together work out how best to harness this capability for the good of people everywhere: yield improvements are not a luxury, they are vital.

AGRICULTURAL CHEMICALS - WHAT ARE THEY ?

My paper considers the role of agricultural chemicals, most of which are the discoveries of some of the large integrated chemical companies, with a huge investment in research and development.

My own company, ICI, is typical of many of these integrated organisations which have large pharmaceutical and agricultural chemical divisions with associated animal health and public health interests. There is indeed a grey area between the pharmaceuticals and agricultural chemical businesses; for example, some insecticides which have been developed for agriculture have been very successful in veterinary science and in improving the health of rural populations, for example in malaria control with DDT. Pharmaceutical and agricultural chemical products are sometimes similar chemically and each group of products can benefit from research work in the other.

For the purposes of this paper I will define agricultural chemicals as products used for the protection of crops against the ravages of pests, diseases and weeds. They include insecticides, fungicides, herbicides, plant growth regulators, rodenticides and other public health chemicals. In this context fertilisers are not included. I shall consider each of these product groups in turn, beginning with insecticides.

Insecticides

Crops are affected by insects whilst growing and during storage. Insects also have an impact on animal health and public health.

I made reference earlier to losses in storage, averaging some 10% of the total crop. For example, in India elimination of storage losses would result in so much more food being available that under-nourishment would be eliminated. The country's foreign exchange position would also be improved. In Nigeria, it has been estimated that half of stored cowpeas are attacked by bruchid beetle and 25% of the harvested crop is lost. Furthermore, damaged seed is not attractive and is less saleable and palatable. Typically, avoidance of losses in store through use of insecticides results in a cost/benefit ratio of 1 : 45; hence the low cost of protecting the harvested crop is a small price to pay for insurance. Losses in store are particularly unfortunate as the means already exist to protect stored crops in most cases against pests. Furthermore, as the harvested crop has already cost the farmer a high price in terms of seed, labour, fertiliser etc, losses in store are especially damaging from a financial point of view.

There are also many examples of favourable cost/benefit ratios in using insecticides to protect growing crops from insects. Taking rice as an example, the International Rice Research Institute (IRRI) has reported, from a survey of over 130 trials on Philippine farms, that yield increases averaging 25% (equivalent to the production of an extra tonne of rice per hectare) are attributable to the use of insecticides. In the Philippines, the total production of rice is 8m tonnes per annum, so that a 25% yield loss is equivalent to 2m tonnes, worth about US\$750m. Expenditure on rice insecticides is of the order of US\$10m, so the cost/benefit ratio to the Philippines is highly favourable and there is the added advantage of maintaining self-sufficiency in rice production.

It is not only food crops which need protection from the ravages of insects. Plantation crops are also liable to attack, often with serious results for both the grower and for the national economy. Cotton, for example, is a crop which frequently cannot be grown at all without thorough protection by insecticides.

Insect attacks often occur sporadically, sometimes locally and sometimes regionally over wide areas, and it can be difficult to anticipate when and where problems may arise. In combating such attacks Governments and large agricultural enterprises often hold strategic supplies of insecticide so that they may act quickly and over a broad area. It is, of course, possible on occasions to kill some insect pests manually, although usually it is a laborious and unrewarding task incapable of controlling effectively even a modest infestation.

The next group of products I shall cover is fungicides and there is no manual procedure which is really effective with these products.

Fungicides

Strictly speaking, fungicides are chemicals to control fungi, but often the term is used incorrectly to embrace bacteriacides and viricides. Some of the world's worst famines have been due to plant diseases; the Irish potato famine was caused by *Phytophthora* blight and the Bengal famine of 1943-44 was the result of an attack on rice by *Helminthosporium oryzae*. As with insect attack, plant diseases are often the result of weather conditions favourable to the development of the disease. When a particular crop suffers repeatedly from disease, the farmer will often have to resort to changing the crop or asking the plant breeder to try to breed varieties with increased resistance to disease.

In South East Asia, fungicides are not widely used in rice but in Japan US\$180m worth of fungicides are used on blast and sheath blight. Fungicides are extensively used in the production of vegetables and fruit, not only for domestic consumption, but also for export and where quality control is critical. Indeed, it is doubtful if there could be any organised horticulture without fungicides.

Whenever there is specialisation in monoculture as, for example, in plantations, the right conditions are created for epidemics to arise. The rubber industry has to be vigilant against the introduction of South American leaf blight whilst the tea industry regularly contends with blister blight. Fungicides play a vital role in the protection of banana plantations from Sigatoka and cocoa plantations from black pod disease. Sometimes, of course, good husbandry alone can go some way to control fungal diseases but often chemical methods are necessary if the farmer or planter is to avoid the serious financial consequences that can arise from taking inadequate precautions.

Fungicides and insecticides may also be applied to the seed before sowing thereby providing a coating to protect the young seedling from soil borne pests and diseases and this is a particularly cheap method of treatment.

Herbicides

The next group of products I shall consider is herbicides which are described as chemicals which destroy unwanted plant tissue totally or selectively either by contact or systemic action.

Compared with insecticides and fungicides, this is a much less understood - and dare I say much more maligned - range of products. People often think of a herbicide as merely a chemical way of killing weeds that could otherwise be controlled using hand labour. There is, of course, some truth in that, and where labour is cheap and plentiful, it may be correct to use manual labour or mechanical methods. Those of you, however, who are familiar with the plantations of Malaysia, will know that labour is no longer cheap and may not be easy to obtain. I do not think, that from my limited experience, I can name any estate in Malaysia which still relies entirely on hand labour.

Experience has shown that over the long-term a four or five fold reduction in weeding costs has been achieved by most plantations using herbicides. In any event, some weeds cannot be controlled/other than by chemical means. Here I will refer to the well-known South East Asian weed Imperata cylindrica (Cogon in the Philippines, alang-alang in Indonesia, lallang in Malaysia) for which the introduction of compounds such as dalapon and glyphosate have been a boon to plantation owners and smallholders alike. /efficiently

Herbicides can be used either to kill weeds outright or to keep them under control in a form of weed management. By leaving the weeds in situ, a mulch of dead weeds and their roots is allowed to build up, thereby binding the soil and preventing erosion. In this way the soil is not disturbed and weeds are destroyed before the seed heads form, thereby avoiding the development of a seed bed of weeds; as a result there are fewer weed seeds and progressively fewer weeds germinate each year. Under a crop such as tea this has led to better soil fertility, less root and crop damage, better humus build up, less erosion, and better fertiliser uptake - these factors taken together give rise to enhanced yields which are obtained at a fraction of the alternative cost of hand weeding.

The advent of herbicides such as paraquat and glyphosate, which are inactivated on contact with the soil, has opened up exciting new horizons through the ability to establish crops with minimal or zero cultivation. Zero tillage is achieved where pasture or cereal stubbles are sprayed with a herbicide and the crop is drilled through the treated weeds, the dying weeds and stubble remaining undisturbed. Quick turn-round from one crop to the next, late grazing for stock, rapid crop establishment, less wind and rain erosion, and lower energy cost are some of the benefits of this technique. In the less extreme intermediary form of minimal tillage, herbicides are used to reduce the number of cultivations that are made to prepare the seed bed. This technique is widely practised in Japan and South East Asia to prepare seed beds for vegetables and rice, and also to allow short maturing rice to be multi-cropped. More efficient use of fertiliser and irrigation water ensues.

In parts of Brazil, double-cropping of soya bean and wheat in rotation calls for two cultivations per annum, thus laying the soil open to the elements and to serious erosion. Zero tillage has reduced erosion by up to 95% and this has brought major economic benefit both to the farmer and to the Brazilian economy. Improved moisture conservation, reduction in terracing costs, improved planting rate, timeliness and savings in fuel have led to increases in wheat yields, and lower production costs. Table 2 shows the effects of different tillage systems on run-off and soil loss. In the USA the growth of minimal tillage and zero tillage has been rapid, with the advent of suitable herbicides and the stimulus of successive oil crises. In 1963, only an estimated 5m acres were planted in any form of minimal tillage regime, yet it is forecast that out of a possible 370m acres of crop land in the USA by the year 2010, 90% may be minimally tilled and as much as 50% of all crops will be grown with zero tillage. These predictions were made in 1975 and may now seem somewhat over-optimistic, but they do illustrate the high potential of the techniques.

TABLE 2

Effect of Tillage Systems on Run-Off and Soil Erosion Under Maize for a
Rainfall of 44.2mm

TILLAGE SYSTEM	SLOPE %	RUN-OFF %	SOIL LOSS t/ha
No Tillage	15	2.2	0.0015
Ploughed	15	13.3	3.92
Bare Fallow	15	21.5	16.0

Source : Rockwood and Lal (13)

It has been estimated that in the tropics 60 - 70% of a farmer's time is taken up with controlling weeds. This is well justified for researchers have reported that in upland rice, for example, early weed competition can reduce yields by at least 50%. In rice crops the use of cheap selective herbicides, supplemented with manual weeding, is now giving way to better and more cost effective broad spectrum chemicals. With direct seeded rice, which is an increasingly popular technique in South East Asia, manual weeding is almost impossible and herbicides have become almost essential. Over and above the significant yield improvements, it should not be forgotten that the use of herbicides also helps to smooth out the peaks in labour requirements that occur seasonally.

One other important aspect of the use of herbicides that I would like to draw to your attention is that of selective activity. I have mentioned the selective activity of herbicides in rice. An even greater challenge to the chemical industry is posed by the idea of an agricultural chemical which can select one species of grass out of an annual grass crop, the effect of which is comparable to the control of wild oats in a crop of cereals. Recently, after many years of research, chemists have begun to invent compounds which will selectively kill grasses in a broad leaf crop such as soya bean, potatoes or tea.

Plant Growth Regulators (PGR)

Let me turn now to Plant Growth Regulators (PGR) which may be defined as compounds which influence plant growth and fruiting habits. Plant Growth Regulators are a diverse group of compounds used to stunt crops, prevent lodging, prune growth, stimulate flowering and hasten or delay ripening. For example, the plantation industry in South East Asia makes use of ethylene generating compounds to stimulate latex in the production of natural rubber. The PGR sector is one which I believe holds much promise for the future and this will be realised most successfully through collaboration of the geneticist, the plant breeder and the chemist.

Rodenticides

The last group of products I want to mention is rodenticides. Rodents are both an agricultural and a public health problem. Diseases are also spread by other organisms such as molluscs.

Rats have been one of mankind's oldest enemies, not only because of the food that they spoil and eat, but the damage that they do to the fabric of buildings and the disease they are capable of transmitting. They attack grain crops as well as stored and harvested produce. A few examples will perhaps serve to illustrate the problems and the considerable benefits, both social and financial, of keeping rats under control.

China - Stored Grain. Losses of as much as 20-25% of foodstuffs in store due to rodents are not uncommon. In China, approximately 4% of the country's grain production is imported, equivalent to 13 million tonnes costing US\$2,400m in a year. Use of rodenticides could prevent destruction of this amount of rice in storage at a cost of only US\$24m, thereby eliminating the import bill and showing a 1 : 100 cost/benefit ratio. Perhaps most importantly, China would be self-sufficient in grain.

Thailand - Rice. Damage of only 1% of rice tillers before harvest by rats is equivalent to a 6-7% loss in yield. In Thailand, with average rice yields of 3 tonnes per hectare (at a value of US\$150 per tonne) a 5% loss of tillers, which is by no means exceptional, results in a financial loss to the farmer of US\$135-160 per hectare. Set against this, protection can be achieved at a cost of rodenticide, including application, which is seldom more than US\$10 per hectare - a cost/benefit ratio of 1:16.

Malaysia - Oil Palm. In a series of trials in Malaysia it was reported that rats consumed on average 479 kg of oil palm mesocarp (the oil bearing tissue) per hectare per annum. This is the equivalent of 240 kg of processed oil (approximately 5% of yield) and at, say, US\$500 per tonne, losses amount to US\$120 per hectare per annum. The cost of rat bait per hectare per annum is US\$4.70 (excluding labour costs) - and this cost is only 4% of the potential saving. It is no wonder most estates attempt to control rodents.

The challenge to industry and governments is to achieve an understanding, among all growers of food and industrial crops which suffer heavily from rodent damage, of how a modest investment in rodent control can lead to such large financial rewards. In order to control rodents effectively, there is a need for co-ordination from the authorities, as an individual farmer or planter cannot adequately control them unless there is control in all farms and estates over very large areas. In this connection I should say that industry has considerable experience in handling the logistics of large rodent control campaigns in agriculture and public health.

The problems which rats cause, because they are carriers of disease, are well appreciated and need not be elaborated here except to mention the increase in labour productivity which can result from an improvement in health in a rural or urban population from which rats have been eliminated. This ultimately is reflected not only in crop productivity but in industrial output.

Application Technology

Following this survey of the various groups of products it is appropriate to mention developments in application technology. Chemists, assisted by formulation experts, have over the years synthesized compounds which are more and more active, to the point where we now talk of application rates of only a few grammes of active material per hectare.

However, until recently, all chemicals were applied through the same spray machinery which had remained virtually unchanged since the development of the hydraulic sprayer. The importance of controlled application is now being recognised and the agricultural chemical industry is playing an active part in working with application specialists to produce new machines and formulations. High volume sprays delivering 200-2,000 litres per hectare are beginning to be replaced by low volume sprays and even ultra low volume sprays capable of spraying as little as $\frac{1}{2}$ litre per hectare. The principles of physics, for example, centrifugal force and electrostatics, are being applied in order to select and achieve the correct droplet size for efficient but safe application.

In my own company a range of formulations is being developed in sealed containers specifically for use with ICI's new invention, the 'ElectroDyn' Sprayer. Droplets of the correct particle size are produced electrically and a charge is imparted to the droplet to ensure its speedy passage from spray nozzle to plant giving even distribution and wrap-around on the crop. A high percentage of the emitted spray hits the target and contamination of the operator and the environment is minimised.

The amount of chemical applied to the crop is also controlled in this technique. The end result is an effective, fast and highly convenient application method which is financially and technically within the reach of most farmers. The development of the 'ElectroDye' project requires a multi-disciplined team effort using the skills of chemists, physicists and application experts as well as the normal biological and commercial skills.

HOW SHOULD INDUSTRY PLAY ITS PART ?

I hope I have indicated that industry has already developed a wide range of cost effective compounds which is capable of greatly increasing agricultural productivity. Research and Development is on-going and, hopefully, will produce more potent and more selective compounds which will also meet the requirements of the registration authorities around the world. Industry should, therefore, work closely and co-operate with national authorities in the evaluation of products. Companies involved in developing agricultural chemicals also need to have a good understanding of the farmers' and planters' requirements and of national aspirations, which means that products must be tested and developed under local conditions before any attempt is made to sell them. Indeed, some chemical companies like mine have their own chemical screening stations based in ASEAN territories.

The final decision as to whether a product is offered for sale and in what form, in any particular country, rests with the national registration authority, which has to be satisfied as to the efficacy of the product as well as its safety, before sales commence. In addition to research aimed at finding new products, it is the responsibility of the agricultural chemical industry to carry out development and prepare submissions to registration authorities, including toxicological, environmental and biological data. The cost of this to the industry is between US\$10-20m for every new product and it may take up to eight years before the first sales are made. In connection with development costs, industry very much welcomes the attempts being made by ASEAN Governments to harmonise registration requirements. Moves of this nature are of benefit to all because through them the highest standards of efficacy and safety can be established on a regional basis whilst at the same time, through harmonisation of standards, unnecessary escalation of costs is avoided.

The commitment to research and development in leading companies is very large indeed and many thousands of products are screened every year for biological activity - in ICI's case the number screened is about 10,000 every year and none of these may turn out to be a worthwhile product. If one major new product could be introduced every year onto our sales range we would consider ourselves fortunate - but successes do not usually come that frequently. The high cost of the sophisticated Research & Development necessary for the invention and registration of new products can only be sustained provided new and effective products are found which can be sold profitably. Without profits there cannot be Research & Development.

Once a product has been approved by national registration authorities, there is still much to be done to ensure that it is used correctly. In many countries in the region national governments have the main responsibility for education and training of many agricultural workers; they also are responsible for extension work. But industry also has a responsibility to ensure that its products are used correctly and safely. Hence, it is of paramount importance for industry to work closely with the relevant government departments in each country. This calls for much free and frank discussions between industry and government so that products can be evaluated objectively and thoroughly and appropriate application procedures developed. Industry must get its evaluations right for the repercussions of being wrong are not acceptable. I, therefore, welcome developments such as the Integrated Pest Management Scheme here in Malaysia which aim to secure the benefits which can be achieved from the use of approved agricultural chemicals but at the same time ensure that they are used in ways which do not give rise to potential hazards. Initiatives of this nature must be given industry's full support. It is in the industry's own interests to do so, for a healthy, thriving agricultural sector is the life-blood of the agricultural chemical industry.

There is one other aspect of introducing effective agricultural chemicals which I want to mention. The agricultural economies of developing countries are a mix between the most sophisticated vegetable, plantation and export enterprises and the fairly basic small scale agriculture which is still sometimes at subsistence level. It is perhaps fairly self-evident that the first sector needs a continuing flow of innovative products, but so, too, do those working on a small scale. For once they have seen evidence of products which under their small-scale basic conditions are capable of transforming yields, then provided they can afford the product which usually means providing some form of credit arrangements, they will be as interested to participate as any farmer or planter anywhere. How else can you explain the improvements in rice production in this part of the world?

The challenge to industry and to our national governments is for both parties to work together to demonstrate the benefits that agricultural chemicals can bring and for the authorities to continue where necessary to improve rural credit facilities so that the small scale farmer, if convinced, can afford to apply products which will give him higher yields and improved productivity.

That eminent agricultural scientist and Nobel prize winner, Norman Borlaug has said that a total ban on the use of agricultural chemicals would not only result in production losses of 50% but could also cause price rises of four or five fold. Let us put that another way; if we want to maintain and improve crop yields - whether food or plantation - within the region, we must improve productivity. With agricultural chemicals today, we already have the proven tools with which to do so. The challenge is for industry and government to pull together to enable that transformation in our agriculture to take place.

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SULPHUR COMPLEXES OF THE TRANSITION METALS WITH SPECIAL REFERENCE TO CHROMIUM

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ABSTRACT

The preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ (1) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5(\text{S}_2)$ (2) from the facile reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ with elemental sulphur, together with their structural features, will be discussed, against a brief background review of available synthetic methods and known structural types of transition metal sulphur complexes. The significance and implications of this area of sulphur research will be noted.

INTRODUCTION

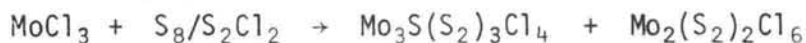
Complexation of diatomic molecules eg. O_2 , N_2 , CO , NO , CN^- , is a subject of continuing research interest, because of its biological and catalytic implications. In the last decade, this area has been extended to cover the S_2 ligand, which shows a remarkable versatility in bonding modes and thus demonstrates a great potential in the synthesis of new metal cluster complexes.¹ So far most of the work has been focussed on Fe, Mo and Mn, for obvious biochemical reasons. Thus the interest in Fe-S clusters lies in their potential applications as models for the active site in non-heme iron proteins such as the ferredoxins. In fact the Fe_4S_4 -cubane geometry of $[(\text{C}_5\text{H}_5)\text{FeS}]_4$ and $[(\text{RS})\text{FeS}]_4^{2-}$ are found in the $[(\text{RS})\text{FeS}]_4$ units in the ferredoxin from *peptococcus aerogenes*.² Likewise a lot of Fe-S and Mo-S chemistry is aimed at unravelling the nature of the enzyme nitrogenase which converts N_2 to NH_3 under normal conditions and is now known to contain 2 proteins, one of which is an Fe protein (the electron carrier) containing subunits of 4Fe-4S clusters and the other a MoFe protein (the reaction carrier) with 2 Mo, about 32-33 Fe and 27-32 "labile" S atoms.³

Sulphur complexes of the rest of the transition elements, other than Fe and Mo, are only occasionally reported.¹ Here in our laboratories, I have chosen to investigate the reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ with elemental S_8 for two main reasons. First, despite much work on Mo-S₂ systems (for reasons mentioned above) sulphur complexes of Cr and W, the lighter congeners of Mo in Group VIA are unknown.* Secondly, by virtue of its very long Cr-Cr bond as shown by Cotton's X-ray structural analysis,⁶ $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ is much more reactive than $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$, as demonstrated by its reaction with $\text{P}(\text{OMe})_3$.⁷ The reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with S_8 in refluxing C_6H_6 for 16h., has been reported to give only an unidentified insoluble polymeric material.⁸ It would be interesting therefore to study the reactivity of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ towards S_8 .

SYNTHESES OF SULPHUR COMPLEXES

Disulphur complexes can be prepared by various methods, which can be grouped together under five main classes of reactions,¹ namely, via.

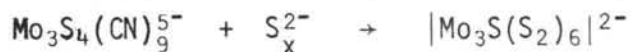
- a) a positive S_2 group (agent: $\text{S}_2^{+\delta}\text{Cl}_2$ or $\text{S}_8/\text{S}_2\text{Cl}_2$), e.g.



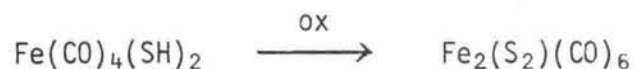
- b) a neutral S_2 group (agent: S_8), e.g.



- c) a negative S_2^{2-} group (agent: S_2^{2-} in polysulphide) e.g.



- d) oxidation of S-containing ligands, e.g.



* During the course of this work the W analogues of some Mo-S₂ complexes⁴ and the first Cr-S₂ complex⁵ were reported.

e) other S-containing reagents e.g.

H_2S , P_4S_{10} , COS , Na_2S_4 or Na_2S , R_2S_x and Na_2SO_3 .

In recent years, method (b) has been found to lead to many new S_2 complexes.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr(CO)}_3]_2$ with S_8

Unlike most reactions of cyclooctasulphur with transition metal complexes, which require either thermal or photochemical activation for prolonged periods,^{4,9} it is found that $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3]_2$ reacts instantaneously with S_8 at ambient temperature. A deep green solution of $[\eta^5\text{-C}_5\text{H}_5\text{Cr(CO)}_3]_2$ in THF or toluene under nitrogen with 1/8 equivalent of S_8 turned immediately to a greenish brown solution from which was isolated $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ (1), as air-stable dark green needle-shaped crystals (m.p. $111\text{--}112^\circ$) in 100% of isolated yield. With 2/8 equivalent or more of S_8 , a deep reddish brown solution resulted, from which was isolated $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5(\text{S}_2)$ (2), as fine dark brown air-stable crystals in 90% yield. The product crystallised as dark-brown rectangular prisms with curved faces from THF/pentane after ca. 20 days at -78° . Both complexes have been characterised by total elemental, complete spectral and X-ray diffraction analyses.¹⁰

STRUCTURES OF S_2 COMPLEXES

Structural Variety

The remarkable versatility of S as a ligand has resulted in a variety of bonding modes and hence a variety of structures, conventionally classified by Muller¹ as types Ia, IIa and IIb, III and IV, illustrated in Table I below. Modifications of these structures arise from the ability of the remaining one pair of electrons on S to coordinate to additional metal atoms.

TABLE I: STRUCTURAL TYPES OF S_2 COMPLEXES¹

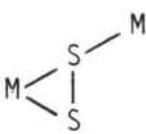
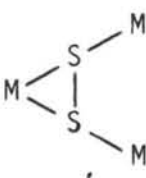
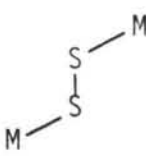
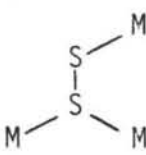
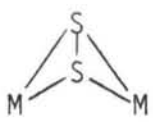
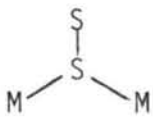
Type	Structure	Example
Ia		$[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$
Ib		$[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$ $\text{Cp}_2\text{Fe}_2(\text{S}_2)_2(\text{CO})$
Ic		$\text{Mn}_4(\text{S}_2)_2(\text{CO})_{16}$
Id		$\text{Mn}_4(\text{S}_2)_2(\text{CO})_{16}$
IIa		$[(\text{NH}_3)_5\text{Ru}(\text{S}_2)\text{Ru}(\text{NH}_3)_5]^{+}$
IIb		$\text{Cp}_2\text{Fe}_2(\text{S}_2)(\text{SEt})$
IIc		$\text{Cp}_4\text{Co}_4(\text{S}_2)_4\text{S}_2$

TABLE 1 (continued)

Type	Structure	Example
IId		$\{\text{SCo}_3(\text{CO})_7\}_2(\text{S}_2)$
III		$[\text{Mo}_2(\text{S}_2)_6]^{2-}$, $\text{Fe}_2(\text{CO})_6(\text{S}_2)$
IV		$\text{Cp}_2\text{Cr}_2(\text{S}_2)_2\text{S}$

Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$ (2)

The complex (2) with a structure as shown in Fig. 1, is the first example of a Cr-S complex based on the Cr_2S_2 unit. The most outstanding feature is the simultaneous end-on and side-on bonding of the S_2 ligand, i.e. S_2 functions as an unsymmetrical bridge between the two Cr atoms, S1 being bound to both Cr1 and Cr2 [$\text{Cr-S} = 2.348(2)$ and $2.466(2)\text{\AA}$ respectively] while S2 is bound only to Cr1 [$\text{Cr-S} = 2.399(2)\text{\AA}$]. This bonding feature, of type Ib in Müller's classification is the first of its kind for a Cr complex and the third of its kind among the transition metals. The two previous examples were $[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$ which possesses four such (S_2) groups. [$\text{S-S} = 2.048(7)\text{\AA}$ av., $\text{Mo-S} = 2.465(5)-2.492(5)\text{\AA}$]¹¹ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{S}_2)_2(\text{CO})$ [$\text{S-S} = 1.993(8)\text{\AA}$ av., $\text{Fe-S} = 2.230(6)-2.293(6)\text{\AA}$]⁹. The S-S distance in (2) [$2.009\text{\AA}$] is close to the above values and to that in octasulphur S_8 [$2.060\text{\AA}$]¹². The coordination geometry around Cr2 is of the 4-legged piano stool type with the metal atom having an $18e^-$ configuration completed via one 6- and four 2-electron donor ligands. In contrast, Cr1 is electron deficient ($16e^-$) and is best envisaged as having a 3-legged piano-stool coordination geometry as found in $(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$ ¹³ with a single $\pi(\text{L})-\text{d}(\text{M})$ σ -bond to the η^2 -bonded S_2 group.

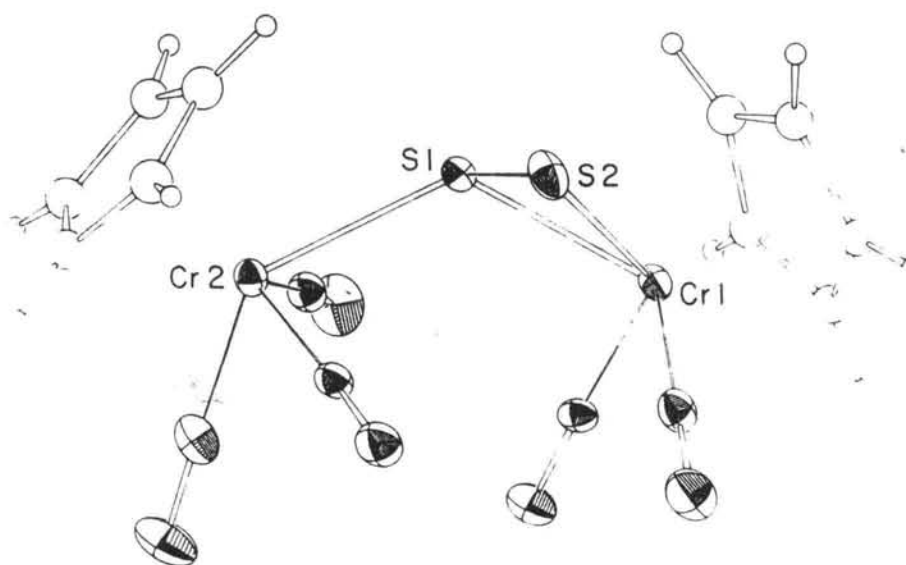


FIG. 1: Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$, (2). Bond angles at sulphur are: $\text{Cr1-S1-Cr2} = 125.8(1)$, $\text{Cr1-S1-S2} = 66.3(1)$, $\text{Cr1-S2-S1} = 63.7(1)$, $\text{S1-S2-Cr1} = 50.1(1)$, $\text{Cr2-S1-S2} = 115.5(1)^\circ$.

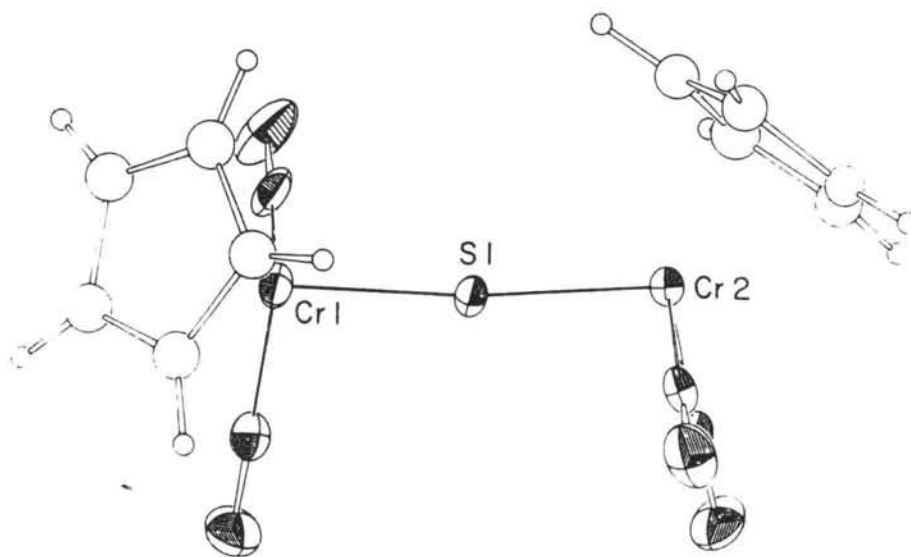


FIG. 2: Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$, (1). Bond angle at sulphur: $\text{Cr1-S1-Cr2} = 174.4(1)^\circ$.

Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ (1)

In (1), as shown in Fig. 2, the two Cr atoms are linked by a single $\mu\text{-S}$ bridge, the ligand arrangement about each metal atom being of the 3-legged piano-stool type.¹³ This is the first example of a binuclear Cr complex based on the Cr_2S unit, i.e. a *single* bridging S. The Cr- μS distances [2.067-2.076Å] are noticeably shorter than those in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$ [av. 2.238Å]⁵. Indeed, the Cr_2S unit [Cr-S = 2.072Å av., Cr-S-Cr = 174.4° av.] is structurally very similar to the Mo_2S unit in $[(\text{CN})_6\text{MoSMo}(\text{CN})_6]^{6-}$ ¹⁴ [Mo-S = 2.173Å & Mo-S-Mo = 169.5°], and as in the Mo complex, the unusually short Cr-S bonds are probably due to the presence of S $\rightarrow$ M π -bonding interactions.¹⁵ The parallel-antiparallel dispositions of the carbonyl groups are also consistent with the presence of Cr-S double-bonding. The observation of a single ^{13}C (CO) resonance in both the 25° and 183°K NMR suggests that the barrier to rotation about the Cr-S-Cr axis is small.

It is of interest to compare the metal-sulphur bonding features of these Cr-S complexes with those of other S complexes of Group VIA elements (Fig. 3). It will be noted that the bonding mode of S in (2) is not observed at all in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$, the only other reported S complex of Cr,⁵ nor in any of the other Mo or W complexes in Fig. 3. Instead, there is a strong structural resemblance between $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2\text{S}_4$.⁴ Both molecules contain a planar arrangement of S atoms perpendicular to the metal-metal bond and parallel to the two $(\eta^5\text{-C}_5\text{Me}_5)$ planes, and both contain S in similar bonding modes, namely, a $\mu\text{-}\eta^2\text{-S}_2$ bonding mode (side-on bonded disulphur bridging two metal atoms) and a $\mu\text{-S}$ bonding mode (bridging two metal atoms). The Cr complex, however, has an additional novel $\eta^1(\mu\text{-S},\text{S})$ ligand with one uncoordinated S atom. The other two complexes in Fig. 3, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}_2\text{S}_3$ ⁴ and $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{MoS}_2]_2$,¹ which possess very similar structures, again show very little resemblance to (1), other than the presence of $\mu\text{-S}$ bridging ligands and the anti-parallel disposition of the M-CO and/or M-S groupings in all of them.

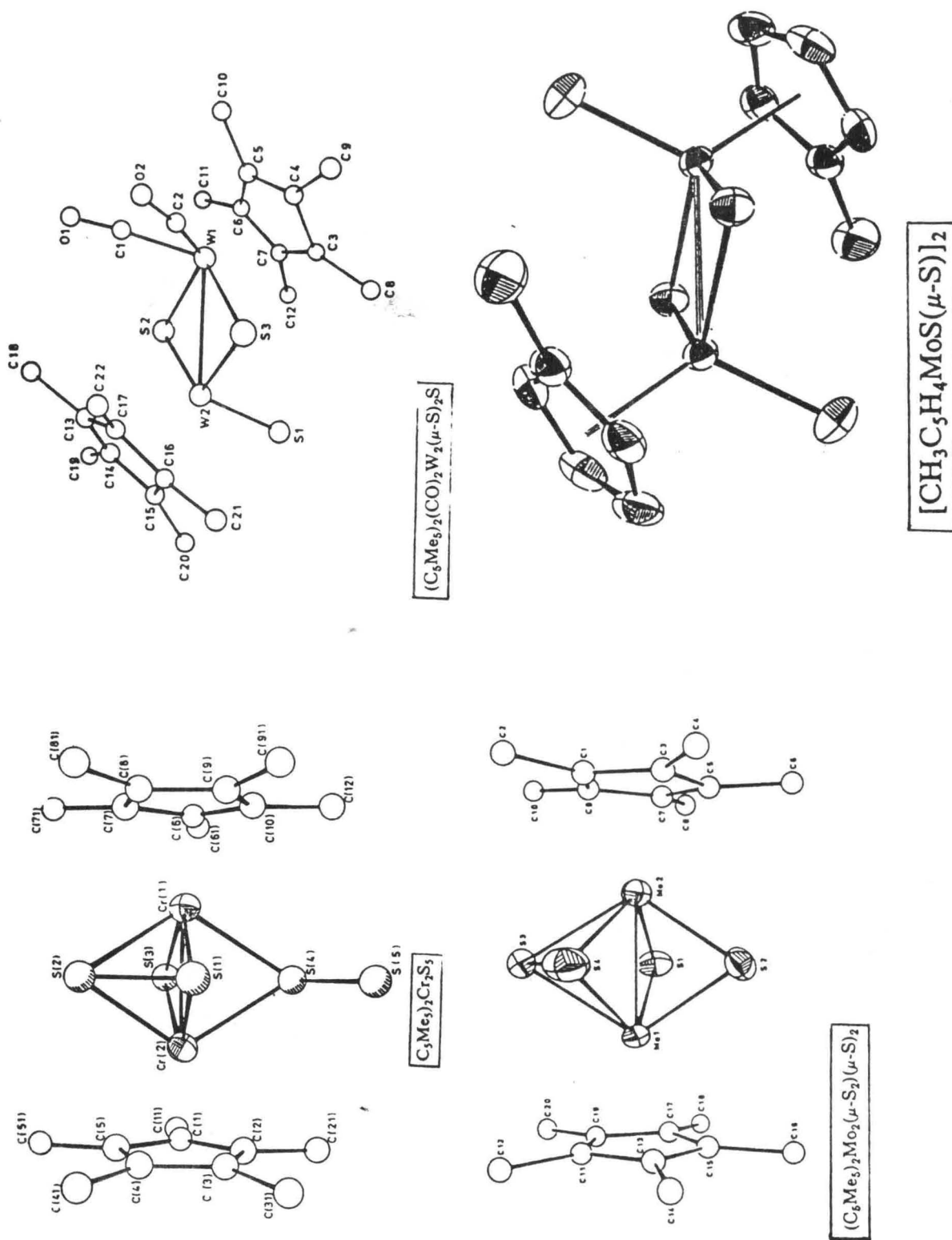


FIG. 3: MOLECULAR STRUCTURES OF SOME SULPHUR COMPLEXES OF GROUP VI METALS.

CONCLUSION

The new complexes described above reemphasise the versatile manner in which sulphur can bond to transition metals, resulting often in complexes with novel interesting structural features and indicate again the often-demonstrated potential of sulphur in the generation of high nuclearity clusters,¹⁷ particularly of mixed metals, which promise to be of both biological and catalytic importance. Apart from this, the unusually facile reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ with S_8 shows considerable potential for application in desulphurisation reactions.

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A NEW METHOD OF REDUCTIVE DEHALOGENATION OF ARYL AND ALKYL HALIDES BY LITHIUM ALUMINIUM HYDRIDE

Goh Swee Hock

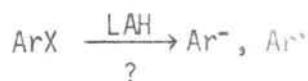
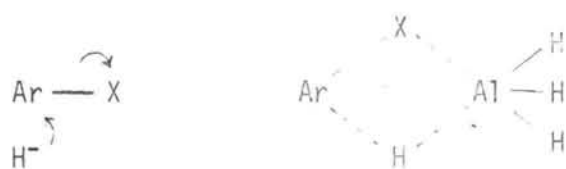
University of Malaya, Malaysia.

The reduction of aryl halides by lithium aluminium hydride proceeds via formation of radical and/or carbanion intermediates. A photochemical procedure is developed for the reduction of various halo compounds including aryl chlorides and fluorides, vinyl bromides, neophyl chloride and 7,7-dichloronorcaradiene, all of which are normally difficult to be reduced by other methods.

Among the complex hydrides, lithium aluminium hydride (LAH) is one of the most versatile of reducing agents capable of reducing a variety of functional types. The reagent is known to reduce some organic halides and recently this was reappraised by Krishnamurthy and Brown (1). Although the reactivity pattern for aliphatic halides ($RI > RBr > RCl$; allylic $> 1^\circ > 2^\circ > 3^\circ$; sec-butyl $>>$ neopentyl; cyclopentyl $>$ cycloheptyl $>$ cyclohexyl) appears to favour a simple SN_2 -type of reaction, the substantial reactivity of aryl, vinyl and cyclopropyl halides (which are normally resistant to SN_2 attack) is very surprising. Despite previous reports (2,3) that aryl bromides undergo uncatalysed reduction conveniently, the reaction should more appropriately be described as erratic. For example, p-bromotoluene has been reported (2) to be only 7% reduced by LAH in tetrahydrofuran at 65° after 24 h but Bondjonk (4) found a 20% reaction at 25° after 24 h. Curiously however, the reduction can be accelerated by ultrasound irradiation.

Brown (1,3) who first explored the reaction extensively considered broadside SN_2 and four-centre mechanisms (Scheme 1). Chung (5) detected carbanion and radical formation while Singh (6) also found radical cyclization products. The detection of radicals is one thing but the overall significance of radicals in the reaction may be a different matter. LAH reductions may give inconsistent results, e.g. the reduction of o-allyloxybromobenzene gave variable amounts of radical cyclization product.

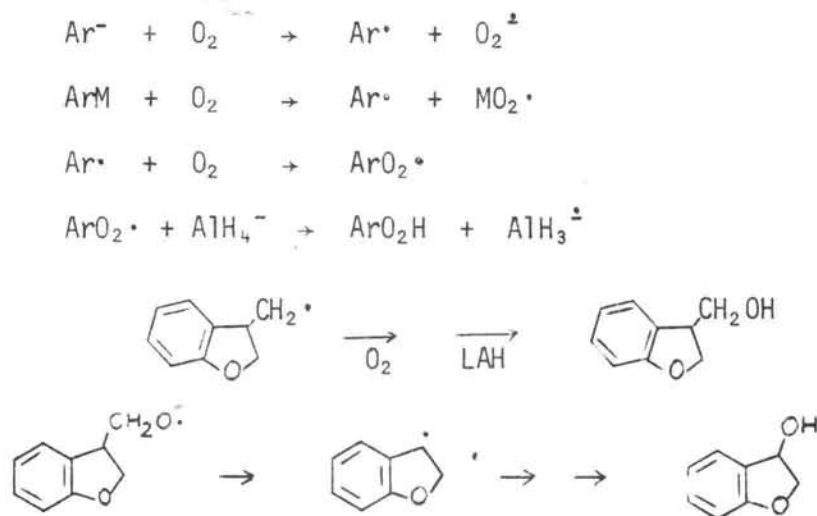
SCHEME 1. PREVIOUSLY POSTULATED MECHANISMS



A careful examination into the mechanism of the reduction was carried out especially to monitor carbanion and radical formation and the

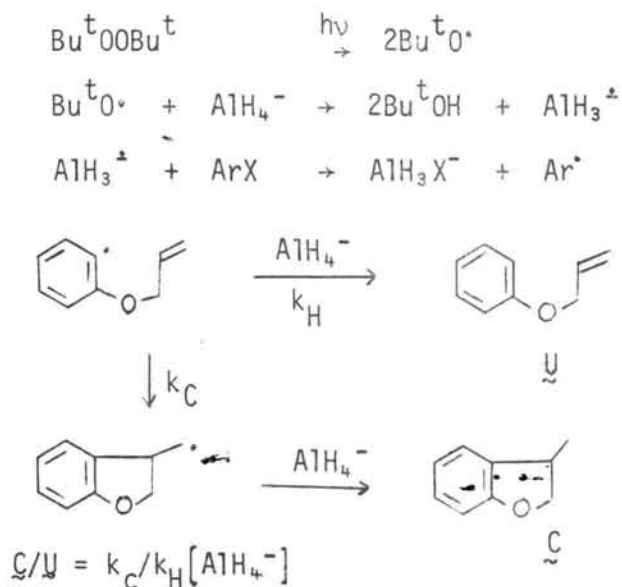
results are summarised in Table 1. Under nitrogen, the amount of cyclization (radical formation) was small but the large amount of deuterium incorporation indicates anion (or arylmetal species) formation. The presence of oxygen (or air) causes the rate to increase and the radical cyclization product also increases considerably (Table 2). The participation of oxygen as illustrated in Scheme 2 shows the generation of aryl radical and alane radical ion $\text{AlH}_3^{\cdot-}$. The presence of oxygen also gives rise to O_2 -trapped products which are as shown.

SCHEME 2. INITIATION BY OXYGEN AND OXYGENATED PRODUCTS



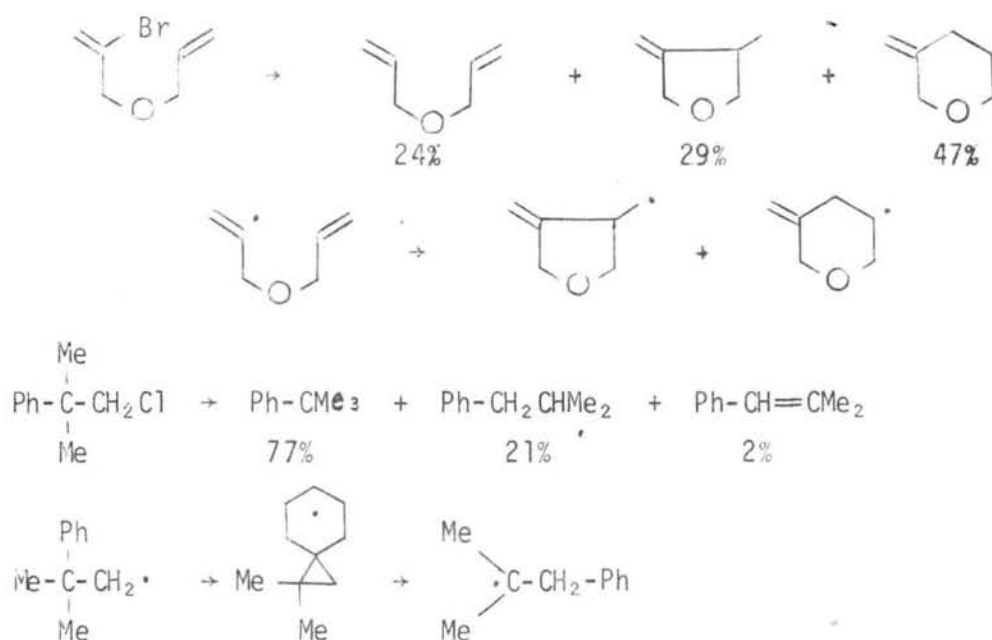
Having clarified the problems associated with the LAH reductions, an improvement can be incorporated into the reduction by the use of suitable radical initiators. This was carried out by the photolysis of di-tert-butyl peroxide in the reaction and results obtained are shown in Table 3. These are in good accord with the mechanism shown in Scheme 3. The expected increase in the ratio C/U with decreasing concentration of lithium aluminium hydride was observed.

SCHEME 3. MECHANISM OF REACTION



The photostimulated reduction was extended to a variety of organic halides and excellent results were obtained (Table 4). Aryl halides including fluorides were reduced in good yields and reactivity was of the expected order $\text{ArI} > \text{ArBr} > \text{ArCl} > \text{ArF}$. Nuclear substituent effects were small. Aliphatic halides including cyclopropyl halides were similarly reduced. The reduction of allyl 2-bromoallyl ether and neophyl chloride gave cyclisation and 1,2-rearrangement products respectively as illustrated in Scheme 4.

SCHEME 4. RADICAL CYCLISATION AND REARRANGEMENT



The results presented in this paper resolves most of the controversies (7) surrounding lithium aluminium hydride reductions of organic halides and the procedure developed paves the way for the convenient dehalogenation of most organic halides encountered in organic synthesis (8).

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TABLE 1. REDUCTIONS OF O-ALLYLOXYBROMOBENZENE AND 4(O-BROMOPHENYL) BUTENE-1.

X	[LAH]/M	Time/h	Yield/%	C/U*	Quench	U-d ₁	C-d ₁
O	1.2	28	18	0.03	D ₂ O	91%	-
O	0.95	64	34	0.3	D ₂ O	69%	0%
O	0.5(LAD)	64	17	0.1	H ₂ O	19	71
					D ₂ O	91	76
CH ₂	0.4(LAD)	67	47	0.2			

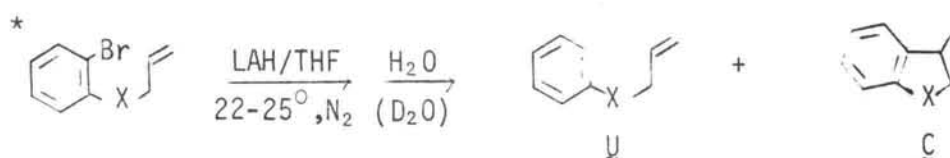


TABLE 2. EFFECT OF OXYGEN

X	[LAH]/M	Conditions	Time/h	% Reaction	C/U*
O	0.95	N ₂ , air	26	33	0.02
		admitted after 26h	28	40	0.2
O	0.95	limited air	21	100	2.5
O	1.0	1 equiv. O ₂	0.5	23	1.5
			2.0	56	1.8
			22	100	2.6
CH ₂	0.26(LAD)	limited air	8	47	1.4

* Reactions as shown in footnote of Table 1.

TABLE 3. PHOTOLYSIS OF O-ALLYLOXYBROMOBENZENE WITH DI-TERT-BUTYL PEROXIDE IN TETRAHYDROFURAN.

[LAH]/M	Time/h	Reaction/%	C/U ^a	Quench	U-d ₁	C-d ₁
1.0	1.6	100	2.2	D ₂ O	8	1
(1.0) ^b	1.0	14	0.7			
0.85	1.5	78	3.1			
0.09	1.5	23	5.7(8.1) ^c	D ₂ O	30	0
0.6(LAD)	1.3	65	4.3	D ₂ O	81	80
				H ₂ O	n.d. ^d	80

^a Cyclised and uncyclised products as in footnote of Table 1.

^b Without di-tert-butyl peroxide

^c Corrected for 30% U-d₁

^d Not determined

TABLE 4. PHOTOSTIMULATED REDUCTIONS BY LITHIUM ALUMINIUM HYDRIDE^a

Halide	Time/h	Product	Yield/%
p-Iodoanisole	1.5	Anisole	100
o-Bromoanisole	1.5	Anisole	86
o-Allyloxybromobenzene	2.3	Mixture ^b	96
p-Bromochlorobenzene	1.0	Chlorobenzene	92
p-Bromo-N,N-dimethylaniline	3.0	N,N-Dimethylaniline	93
p-Fluoroanisole	1.9	Anisole	93
p-Fluorotoluene	1.9	Toluene	90
7,7-Dichloronorcarane	0.5	Mixture ^c	93
Chlorocyclohexane	2.5	Cyclohexane	72
Allyl 2-bromoallyl ether	2.0	Mixture ^d	53
Neophyl chloride	3.0	Mixture ^d	91

^a Reactions were carried out with the halides dissolved in clear 1M solutions of LAH in tetrahydrofuran containing di-tert-butyl peroxide and irradiated by a high pressure Hg lamp.

^b Refer Table 3 for product distribution.

^c Mixture of norcarane (10%), *syn*-7-chloronorcarane (65%), and *anti*-7-chloronorcarane (25%); yield of norcarane increased for longer reaction times.

^d Refer Scheme 4 for product ratios.

STRUCTURAL ASPECTS OF PHOTOINDUCED CHARGE SEPARATION
IN MICROHETEROGENEOUS MEDIA: AN ESR STUDY

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ABSTRACT

The relative location of the photoelectron in micelles was probed with various types of electron scavengers. It is observed that in the presence of Ag(I), Cu(II) and Eu(III) the lifetime of TMB cation in SDS anionic micelles increased up to 20 times. In the presence of organic additives which has been determined to reside in the organic non-polar region of the micelle, decrease the yield of the TMB cation in SDS anionic micelles.

The yield of TMB cation was observed to be much less in the vesicle systems than in the micelles. This is probably due to the further distance of TMB solubilization site to bulk aqueous phase. Dimerization of photoionized products was observed in vesicles but not in micelles. This also decreases the yield. Both factors are evaluated for optimum charge separation.

Introduction

Photoredox reactions in microheterogeneous media has been undergone intensive research in the recent years.¹⁻⁶ This mainly stem from the fact that it could be used to harvest solar energy. The best known such system, probably the least understood, is the photosynthetic process from our nature. The initial step of photosynthesis is photoionization leading to net charge separation and thus stored the captured quanta.⁷ Rapid charge recombination after photoionization is not a practical way to store energy. Recently, it has been established that an oil/water boundary is necessary to maintain charge separation.⁸⁻⁹ The interpretation is that the excited photoelectron once transferred through the oil-water interface was captured (or hydrated) on the other side and could not return. Though the exact mechanistic step is not known, the exact rearrangement of the chromophores in the region of the oil-water phase boundary is responsible for the vectorial electron transfer. In other words, one wants to know more about the relative location, the local environment of the photoionized species, or the site where photoionization takes place. Unfortunately, very little is understood in this aspect.¹⁰

The electron spin resonance (ESR) and electron spin echo spectroscopy (ESE) are well-known for studying paramagnetic species. They are particularly adapted to the study of disordered system as exemplified by micelles, microemulsions and synthetic vesicles. We have recently shown how ESR and ESE can be successfully used to deduce the relative location of the cation of a chromophore N,N,N',N'-tetramethylbenzidine (TMB) in organized molecular assemblies.¹¹⁻¹⁵ In this paper we study the effect of various electron scavengers and monitored the yield of the TMB cation as a function of time. From the kinetics, the solubilization sites of various electron scavengers and their reduced species, we obtained structural information about the relative location of the photoelectrons. We also extend our studies into the synthetic vesicles, both anionic and cationic. We find interesting contrasts with micellar systems that give new information about the structural requirements for optimum photogenerated charge separation in microheterogeneous media.

Experimental

Micelle solutions were prepared by dissolving the surfactants in triply distilled water. The micelle concentrations were typically 0.1 M. The TMB solution was prepared by adding TMB to the micelle solution and stirring the mixture at 60 °C to help solubilizing the TMB. The TMB concentration was determined to be 0.3 mM by optical absorption with a Cary 14. The wavelength scale was calibrated with a holmium oxide filter and is accurate to ± 0.3 nm. Inorganic electron scavengers used were silver perchlorate, silver nitrate, silver sulfate, europium(III) nitrate and copper(II) sulfate. They were added to the freshly prepared TMB/micellar solutions. Organic electron scavengers used were iodomethane, acetone, benzene, dimethyl sulfoxide (DMSO), dichloromethane and iodoethane. The electron scavengers added were typically 1 mM. Deuterium oxide and deuterated compounds were used for

ESE measurements.

The vesicle solutions were prepared by dissolving the synthetic surfactants in triply distilled water, heated to 80 °C followed by sonication at 80 °C for 1 hr with a Fisher Model 300 Sonic dismembrator which was operated at 30 W with a 4 mm o.d. microtip. Typical concentrations used were 9 mg of DODAC, 6 mg of DODAB, and 6 mg of DHP, each in 1.5 mL of water.

Optical and ESR samples were prepared in a glovebag flushed with dry nitrogen. The ESR samples for room temperature measurements were contained in 75 μ pipettes, and the ESR samples for 77 K and 4 K experiments were prepared in 2 mm i.d. by 3 mm o.d. Suprasil quartz tubing. The samples were frozen in 2-3 s by plunging the sample tubes directly into liquid nitrogen. This is rapid enough that the water at a micellar surface retains a disordered, noncrystalline structure,¹¹⁻¹⁵ so it is assumed that micelle and vesicle shapes in the frozen solutions are similar to those in liquid solutions.

Photoirradiations were carried out with a 900 W high-pressure mercury lamp (Philips Model SP). A narrow band-pass filter (Corning no. 760) was used to pass light of predominantly 350 nm. The total light flux was 1.0×10^2 W/m² as measured by a radiometer. Typical irradiation times were 200 s. The ESR spectra were recorded at room temperature and at 77 K on a Varian-E4 ESR spectrometer. The ESE data were recorded at 4.2 K on a home-built pulsed ESR spectrometer that has been described.¹⁶ Most of the surfactants and the TMB were obtained from Eastman Chemicals. Dihexadecylphosphate (DHP) was obtained from Sigma Chemicals. Dioctadecyldimethylammonium bromide (DODAB) was exchanged by chloride ion to produce dioctadecyldimethylammonium chloride (DODAC).¹⁵

Results

TMB in micelles

TMB dissolves in micelles has an optical absorption maximum at 307 nm and is quite similar to TMB in ethanol.¹⁷ TMB in micelle does not exhibit any ESR spectrum. After photoirradiation for 250 s at room temperature the characteristic ESR spectrum of the TMB cation is observed. The decay of the intensity of the ESR signal is monitored as a function of time. A linear semilog plot gives a first order rate constant of $135 \times 10^{-5} \text{ s}^{-1}$. This is the initial decay rate of the TMB cation in anionic SDS micelle at room temperature, i.e. the decay rate right after the light is turned off. In the presence of Ag(I), Cu(II), and Eu(III) the initial decay rate becomes 3, 7 and $7 \times 10^{-5} \text{ s}^{-1}$ respectively. In the case of Ag(I), the rate is measured with light off since silver chemically reacts with TMB. The maximum intensity observed from these samples also differ from plain TMB sample. In the presence of Ag(I), Cu(II) and Eu(III) the maximum yield becomes 5.6, 0.60 and 4.0 times of the plain TMB sample. The halflife changes from 0.3 hr of the plain TMB sample to 8.3 hours and 2.3 hours in the presence of Ag(I) and Eu(III). TMB cation is the only paramagnetic species observed in the above samples. The expected reduced species of Ag(I) and Eu(II) are not observed. Due to the broad signal of the Cu(II), it has not been able

to determine whether the Cu(II) signal has changed.

In the presence of the organic electron scavengers, acetone, iodomethane, benzene and duroquinone, the maximum yield of the TMB cation is reduced. The maximum yield of TMB cations are 90, 80, 80, 80, and 60 % of plain TMB samples in the presence of acetone, iodomethane, benzene and duroquinone respectively. Again, TMB cation is the only radical observed.

A sample with added iodomethane froze at 77 K into a white polycrystalline solid and no ESR signal was observed before irradiation. After irradiation the sample exhibited strong green yellow phosphorescence and turned into a bright yellow polycrystalline matrix. The dominant specie is a quartet with an isotropic hyperfine splitting of 23 G and an intensity distribution of 1:3:3:1. This is identified as the methyl radical. The ESR signal of the TMB cation, though heavily masked by the methyl radical, was indicated by the yellow color of the sample.¹³ Proton spin flip lines¹⁸ were observed on the methyl radical spectra at both low field and high field of the methyl peaks in both protiated and deuterated water samples. The nearest protons to the TMB cation thus from the organic chain of the surfactant molecules rather than from the aqueous protons. This indicated that the methyl radical is residing in the organic apolar region of the micelle. This is consistent with the fact that methyl radical is nonpolar, and thus is expected to prefer the nonpolar micelle core. The ESE decay envelopes of the methyl radicals in deuterated water samples did not show deuterium modulation. This suggested that the methyl radicals is far away from the bulk aqueous surrounding.¹¹⁻¹⁴

Deuterated iodomethane added samples after irradiation displayed the characteristic spectrum of a deuterated methyl radical, a septet with an intensity distribution of 1:3:6:7:6:3:1. Here the TMB cation is clearly observed since the deuterated methyl radical is too narrow to mask the broad TMB cation signal. When iodoethane was added, the corresponding ethyl radical was produced after irradiation.

The experiment is repeated with TMB in cationic DTAC micelle. The yield of the TMB cation at room temperature is approximately 33 times weaker than in the anionic SDS micelle. This goes to the detection limit of the spectrometer and thus no experiment with the added electron scavengers were attempted.

TMB in vesicles

TMB dissolves in vesicle solutions has an optical absorption maximum at 313 nm which is more close to TMB in benzene. TMB in vesicles do not exhibit any ESR signal before irradiation. After photoirradiation at 350 nm at room temperature, the colorless solution turns pale yellow. This color fades away in a couple of hours in both cationic and anionic vesicle solutions. Thus the yellow color after photoirradiation denotes a relatively stable product. No such color changes were observed in the absence of TMB. The same color changes occur in micellar solutions where the oxidation product was confirmed by optical absorption and by ESR to be the TMB radical cation.¹¹⁻¹³ Optical absorption spectrum is slightly different from the usual TMB cation spectrum. The cationic DODAC vesicle shows the characteristic TMB cation spectrum overlapping with a broad peak at 385 nm. The assignment of the TMB radical cation was later confirmed with ESR. At shorter

photoirradiation times the 385 nm peak decreases relative to the TMB cation peaks. The anionic DHP vesicle solution behaves similarly except the intensity was only 30 % as intense as in the cationic DODAC vesicles.

The vesicle solutions containing TMB rapidly frozen to 77 K formed a white polycrystalline matrix. After photoirradiation, it gives strong phosphorescence in green and changes to a yellow matrix. These characteristics are the same as observed for frozen micellar solutions containing TMB. ESR spectrum again displays the familiar TMB cation radical. The yield of the TMB cation was approximately 2 times more for the cationic DODAC than the anionic DHP vesicles.

ESE studies at 4.2 K observed that the TMB cation-water interaction is much weaker in the vesicle when compared to the micelle. It is approximately 25 % weaker than the micelle.

Discussion

We first look at the effect of added inorganic electron scavengers in the TMB/micelle systems. The kinetic studies clearly show the effect of these added ions. In the presence of these ions, the initial decay rate decreases from 135 to $3 \times 10^{-5} \text{ s}^{-1}$. The decay rate decreases a factor of 20 times. The maximum yield of TMB cation is also increased to roughly 4 and 6 times. This suggests that the photoejected electron is scavenged by the metal ions to prevent some back reaction with the TMB cation. This agrees well with previous workers.¹⁹⁻²⁰ The interpretation is that the photoionization takes place in the organic core of the micelle. The photoelectron is ejected from the apolar core to the polar bulk aqueous phase and is rapidly hydrated. Some recombination reaction of the hydrated electron with the parent cation inside the micelle core is prevented by the negative micellar surface potential of the anionic micelle. Our ESR studies at room temperature gives physical supporting evidence for this model. The expected paramagnetic products, $\text{Ag}(0)$ and $\text{Eu}(\text{II})$, are not stable at room temperature and so can only be inferred by ESR. The black precipitates observed indicated the formation of clusters of reduced $\text{Ag}(\text{I})$.²¹ The kinetic study and maximum yield also inferred competing process of the $\text{Eu}(\text{II})$ with the photoelectron.

The sample with added $\text{Cu}(\text{II})$ shows a slight decrease in the maximum yield of the TMB cation. This could be due to the fact that $\text{Cu}(\text{II})$ has a high degree of being solubilized on the micelle surface.²² The adsorbed $\text{Cu}(\text{II})$ ions are at a much closer distance to the TMB cation than when in the bulk aqueous phase. Thus the $\text{Cu}(\text{II})$ ions that captured the photoelectrons are capable of back donating the electrons to the TMB cations. It has been reported that the back donation of the photoelectron from $\text{Eu}(\text{II})$ to TMB cation is observed in methanoic solution.²⁰ Similar reaction may take place in the micelle. Thus $\text{Cu}(\text{II})$ acts as a mediator for the back donation thus enhancing the back reaction rather than blocking it. Therefore the observed maximum yield of the TMB cation is lowered in the presence of $\text{Cu}(\text{II})$.

Proton spin flip lines arise from dipolar interactions with neighboring protons.¹⁸ Since it is observed on methyl radicals in deuterated water samples, the protons are from the organic chain of the micelle rather than from protons of the bulk aqueous phase. This

suggests that the location of the iodomethane is in the organic region of the micelle. ESE decay envelopes do not show deuteron modulation in deuterated water samples again confirms this. The lack of linewidth change of the methyl radical lines on going from protiated to deuterated water samples further strengthened this assignment. Back donation from the reduced organic scavengers to the TMB cations is thus enhanced by the close distance of the organic scavengers to the TMB. This is actually what is observed. All added organic scavengers lower the yield of the TMB cation.

The two types of electron scavengers form a self consistent picture. Both provides physical evidence to support the model that the photoelectrons leave the micelle core after photoionization.

Photoionization of TMB in the vesicle solutions at room temperature generates a low concentration of the stable TMB cation radical based on the optical and ESR spectra. But, in addition, another species with $\lambda(\text{max})=385 \text{ nm}$ appears to be formed. Based on recent reports, these other species are probably the nonparamagnetic diamine-diimine charge-transfer complex which formed from two TMB cation radicals.^{2,3} Because of the large number of TMB molecules per vesicle, it seems possible that two TMB cations may be formed in some vesicles. This is supported by the decrease of the 385 nm peak relative to the TMB cation peaks at shorter irradiation times. In other vesicles only one TMB cation is formed and so is stabilized as such. In frozen solutions TMB cation is localized at its formation site and formation of the charge-transfer complex does not occur.

The average environment of TMB in micelle and vesicle systems is different as suggested by the ESE spectroscopy. The weaker cation-water interaction in vesicles when compared to micelles suggests that the average interaction distance between TMB cation and the nearest solvent water molecule is greater in the vesicle systems. This indicates that there is less water penetration into the vesicle surface than into the micellar surface. Therefore TMB is in a worse environment for hydrogen bonding in the vesicle system as compared to the micellar system. This explains the observation that the absorption maximum of TMB in vesicle is at shorter wavelength than in the micelles. A semiquantitative evaluation of the cation-water interaction indicates a TMB cation to solvent water interaction distance of 0.5-0.6 nm.

Finally we look at the yield of the TMB cation. The yield of the TMB cation is the net permanent chemical change, i.e. the net charge separation maintained. The yield is much lower in the vesicle systems than the micelles. Base on the structural information obtained from this studies, the reason is two fold. Firstly the TMB solubilizing site is approximately 20 % further away from the bulk aqueous phase in the case of vesicles as compares to micelles. This lowers the chance of photoionization. It is partly due to the 20 % more distance required from the photoejected electron, in order to transport accross the oil/water interface and get hydrated in the other side. Secondly dimerization of the photoionized species also brings the yield down. The micelle systems is slightly superior in this aspect. The small size of the micelle shortened the travel distance of the photoelectrons. The compartmentalization of the micelles limit the number of chromophores per micelle and thus reduce the chance of dimerization.

Structural Aspects Of Photoinduced Charge Separation In Microheterogeneous Media: An ESR Study

Conclusion

The present study provides physical evidence for supporting the model that photoelectrons leave the micelle after photoionization. From the point of view of charge separation, the micelle systems are structurally superior than the vesicles. A travel distance of 0.4-0.5nm from site of photoionization to oil/water interface is probably the limit for efficient charge separation in these organized molecular assemblies.

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OCCURRENCE OF UNUSUALLY HIGH LEVELS OF
SQUALENE IN THE LIVER OF THE SHARK
CENTROPHORUS ARMATUS

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A variety of shark *Centrophorus armatus* living in the deep-sea off Sri Lanka has been found to be a good source of squalene. The liver of this species forms almost a quarter of its body weight and contains more than 80% (w/w) oil. The liver oil is made up of as much as 70-98% (w/w) squalene. The oil contains significant quantities of glyceryl ethers as well. Squalene is important commercially as it is used as an aviation lubricant and also as a cosmetic ingredient. The paper describes a rapid and reliable gas chromatographic method for the quantitative determination of squalene in shark liver oils. Isolation and identification of alkyl glyceryl ethers in *C. armatus* liver oil are also discussed.

1. INTRODUCTION

Although hydrocarbons are widely distributed in marine organisms they are generally found only as minor constituents. However, some species of shark, especially those living in deep-sea are known to contain relatively large amounts of hydrocarbons with squalene as the dominant component (1-10). For example, the sharks *Centrophorus granulosus* (1), *Centrophorus uyato* (2) and *Centroscymnus fuscus* (3) have been reported to contain as much as 80-90% of squalene in their liver lipids.

Altogether about 250 varieties of sharks are known, out of which 22 species, distributed among the four families *Orectolobidae*, *Lamnidae*, *Scyliorhinidae* and *Carcharinidae*, are found in Sri Lankan waters (11). The species *Centrophorus armatus* lives near the sea-bed, 300-475 metres deep, where the temperature of the water is about 10°C. In size, it is smaller than the common shark varieties, the average length and weight of a fully grown individual being 85cm and 1kg respectively. It has fins at the first and second dorsals, and rather large, protruding eyes.

Squalene is commercially important as it is useful as a cosmetic ingredient as well as an aviation lubricant. This paper reports on the presence of unusually high contents of squalene in the liver oil of the shark *Centrophorus armatus*, which is being commercially exploited.

2. EXPERIMENTAL

2.1 Source of Materials

Two male sharks, one mature and the other immature, of length 59.5 and 52.5 cm, and weighing 1030 and 685g respectively were used for the experiment. They were taken in the deep-sea, about 3 kilometers from the Trincomalee harbour, which is on the northeastern coast of Sri Lanka. The sharks were caught by employing the long-line technique and transported to the laboratory in ice boxes. The tissues were stored at -20°C under methanol containing 2,6-di-~~tert~~-butyl-*p*-cresol (BHT) and the lipids extracted with chloroform/methanol according to the method of Bligh and Dyer (12).

Commercial *C.armatus* liver oil obtained from two local exporters were also examined.

2.2 Thin Layer Chromatography

Analytical thin layer chromatography was carried out on plates (20x5cm) coated with silica gel G (0.1mm). The developing solvent was a mixture of petroleum ether (b.p. $40-60^{\circ}\text{C}$), diethyl ether and acetic acid (80:10:1). The components were detected by heating the plate at 105°C for 5 minutes after spraying with an ethanolic solution of phosphobolybdc acid (10%) when they appeared as brown spots in a green background.

2.3 Separation of Lipid Classes

Commercial *C.armatus* liver oil (40g) was partially separated into its component lipids by chromatography on silica gel (1kg) using petroleum ether (b.p. $40-60^{\circ}\text{C}$) containing increasing quantities of diethyl ether as the eluting solvent. Pure squalene (87.3%) was obtained with petroleum ether, but diacylglyceryl ethers ^{and} triacylglycerols eluted as mixtures (12.6%) with petroleum ether containing 10% of diethyl ether.

The diacylglyceryl ethers and triacylglycerols were separated from each other by preparative thin layer chromatography on plates (20x20cm) coated with silica gel G (0.5mm) using upto 50mg of mixture per plate. Petroleum ether containing 10% diethyl ether was used as the developing solvent, and the components were detected by viewing under ultraviolet light after spraying with an ethanolic solution of 2',7'-dichlorofluorein (0.2%). The separated components were extracted with diethyl ether.

2.4 Gas Liquid Chromatography

Gas liquid chromatography was carried out on a Varian model 2440 chromatograph equipped with a flame ionization detector. Glass columns (1.5m x 4 mm i.d.) packed with 10% SP-2340 coated on 100/120 chromosorb W AW or 3% OV-1 coated on Gas-chrom Q 100/120 ^{were used}. The two columns were operated at 190°C and 240°C respectively, using Argon as the carrier gas.

3. RESULTS AND DISCUSSION

3.1 Size of the Liver and Oil Content

The weights of the fresh livers of the mature and immature individuals were 247g and 147g respectively, and represented 24% and 21% respectively of their body weights. The content of oil in the respective livers were 82% and 81% (w/w) as determined by the method of Bligh and Dyer. The livers were virtually bags of oil and near quantitative oil extraction could be obtained by merely cutting them up.

3.2 Chracteristics of *C.armatus* Oil

Shark liver oils rich in squalene are easily distinguished from other fish oils by their rather low saponification values and extraordinarily high unsaponifiable matter content (Table I). For example, ordinary shark liver oil produced for use as a Vitamin A supplement for animals has a saponification value of 191 and unsaponifiable matter content of only 1.6%, whereas the values for *C.armatus* liver oils were 26.3-19.6 and 70.3-98.7% respectively. Low specific gravity and high iodine value are also chracteristic of squalene-rich oils.

TABLE 1 : PHYSICAL AND CHEMICAL PROPERTIES OF C.ARMATUS LIVER OIL

	Mature ^a	Immature ^a	Commer- ^b cial 1	Commer- ^b cial 2	Ordinary ^c Shark liver oil
Specific Gravity, 30°C	0.863	0.858	0.857	0.855	0.918
Refractive Index, 30°C	1.492	1.488	1.481	1.489	1.480
Iodine Value	237	230	214	235	144
Saponification Value	20.7	21.9	26.3	19.6	191
Unsaponifiable Matter	98.7	87.3	70.3	91.6	1.6
Squalene	98.0	84.2	68.5	89.7	--

^a *C.armatus* liver oils from individual sharks

^b Bulk *C.armatus* liver oil produced for export

^c Ordinary shark liver oil produced by the
Fisheries Corporation of Sri Lanka.

3.3 Composition of *C.armatus* Oil

Thin layer chromatography of the *C.armatus* lipid showed the presence of three main components the least polar of which had mobility similar to that of hydrocarbons. The other two had mobilities indicative of diacylglyceryl ether and triacylglycerol respectively.

3.3.1 Identification of the Hydrocarbon as Squalene. Gas chromatographic analysis of the hydrocarbon fraction isolated by column chromatography showed the presence of a single component with retention times of 14.2 and 8.9 relative to n-eicosane on liquid phases SP-2340 and OV-1 respectively. On hydrogenation, it was converted quantitatively to squalane.

The infrared spectrum of the hydrocarbon showed the pattern expected of a long-chain alkene including the presence of $C=C$ stretching vibration at 1650 cm^{-1} . Its PMR spectrum was identical with that of authentic squalene.

It has been reported that high levels of squalene in fish livers are usually accompanied by small amounts of other hydrocarbons, notably pristane (6). Careful glc analysis of *C.armatus* oil, however, failed to show any hydrocarbons other than squalene.

3.3.2 Quantification of squalene. Quantitative analysis of squalene in the oil samples was carried out by subjecting the oil directly to gas chromatography in the presence of squalane as an internal standard. 3% OV-1 was preferred as the column material as it gave sharp, fast eluting peaks for both squalane and squalene. It afforded a rapid and reliable method for quantitative determination of squalene in the oils; a glc run being complete in about 20 minutes.

The liver oils from the mature and immature *C.armatus* specimens comprised as much as 98.0% and 84.2% squalene. The two commercial samples examined had squalene contents of 68.5% and 89.7%.

3.3.3 Other component lipids. Removal of squalene from commercial *C.armatus* oil by column chromatography furnished a mixture of two components (12.6%) which were then separated from each other by preparative tlc. The more polar of the two (5.5%) was identified as triacylglycerol on the basis of its tlc mobility and infrared spectrum.

The infrared spectrum of the less polar component (7.1%) also had absorption peaks characteristic of long-chain esters (2900 cm^{-1} and 1740 cm^{-1}), but in addition displayed a sharp peak at 1110 cm^{-1} showing the presence of C-O-C groupings. Treatment with alcoholic potassium hydroxide followed by ether extraction yielded a product whose infrared spectrum did not show absorption at 1740 cm^{-1} (ester $C=O$), but displayed a new strong peak at 3300 cm^{-1} (O-H). On this evidence and on the basis of its tlc mobility, the component was identified as alkyl diacylglyceryl ether.

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3.4 The Component Acids *C.armatus* Lipids

The fatty acid composition of *C.armatus* liver oil as well as that of its flesh lipids were examined by gas liquid chromatography on 10% SP 2340 after conversion into methyl esters (Table 2).

TABLE 2 : FATTY ACID COMPOSITION (% wt) OF *C.armatus* LIVER
AND FLESH LIPIDS

Acid	Liver	Flesh	Ordinary Shark liver oil
Saturated	(29.4)	(13.8)	(33.7)
14:0	2.0	0.7	3.3
16:0	23.8	7.1	22.3
18:0	3.6	6.0	8.1
Monoenes	(53.4)	(11.8)	(16.4)
16:1	7.8	-	1.6
18:1	40.7	11.1	11.7
20:1	3.2	0.7	1.8
22:1	1.7	-	1.3
24:1	-	-	-
n-6 Polyenes	(9.8)	(14.6)	(11.1)
18:2	1.6	1.0	1.0
18:3	0.3	0.1	0.9
20:3	0.6	-	0.2
20:4	2.7	10.6	3.0
22:4	1.0	2.2	0.2
22:5	3.6	0.7	5.8
n-3 Polyenes	(5.5)	(56.5)	(35.8)
18:4	0.2	0.1	0.3
20:4	-	-	0.4
20:5	1.3	1.6	3.8
22:5	0.9	0.8	2.8
22:6	3.1	54.0	28.5
Others	1.9	3.3	3.0

The liver oil of *C.armatus* contains much less polyunsaturated acids (15.3%) than that of ordinary shark (46.9%). Its flesh lipid (3.0% w/w), on the other hand, is rich in polyunsaturated acids (71.1%) with 22:6 n-3 (54.0%) dominating.

3.5 Significance of High Contents of Squalene

It appears that the presence of high levels of hepatic squalene is peculiar to sharks living in the deep-sea. The basking shark, which is caught at the surface is known to contain squalene; however, there is evidence that it may winter in deep water. The reason for the presence of such high contents of squalene is not clear, but it seems probable that it provides buoyancy as well as cold and pressure resistance to the fish living in deep-sea.

Squalene is an intermediate in the biosynthesis of cholesterol, and so it would be of great significance to know how deep-sea sharks accumulate large amounts of squalene while maintaining only slightly elevated cholesterol levels. It is conceivable that in the deep-sea sharks cholesterologenesis is blocked just beyond the step of squalene synthesis because of the lack of oxygen or other factors including co-enzymes required for cyclization.

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NEW NATURAL PRODUCTS FROM MALAYSIAN TERMITES

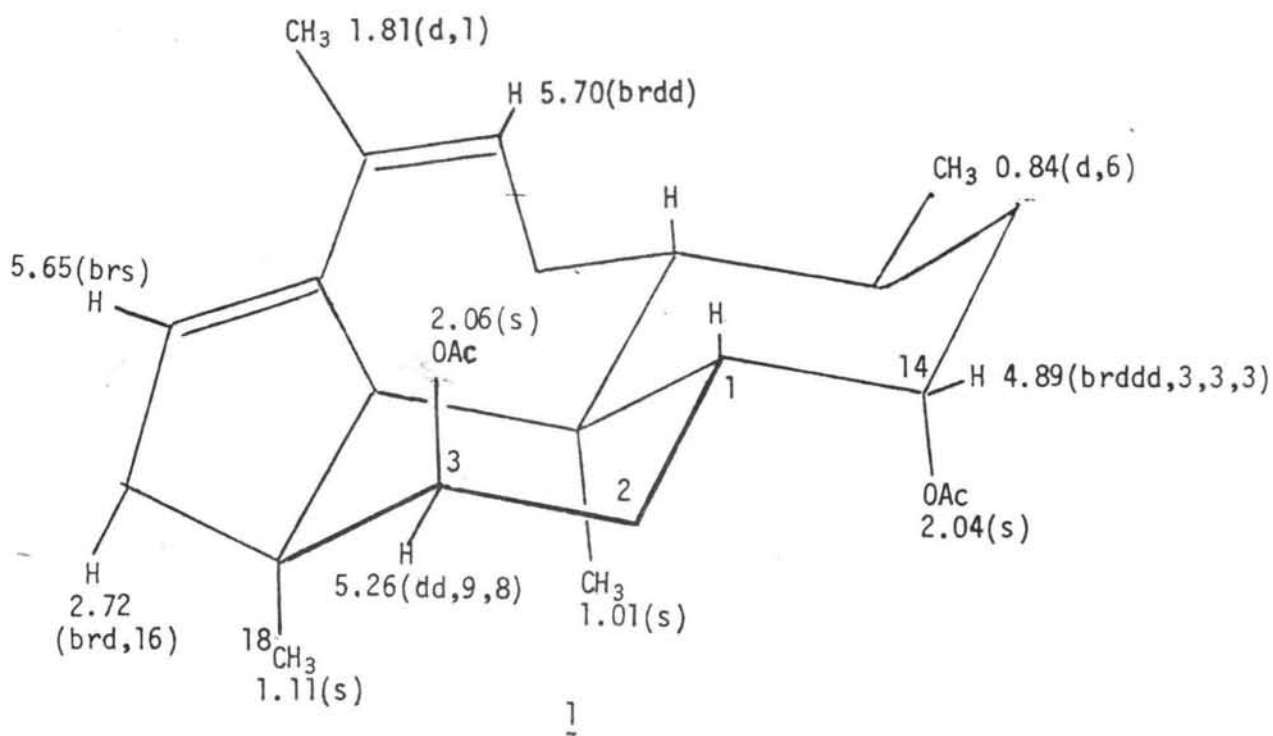
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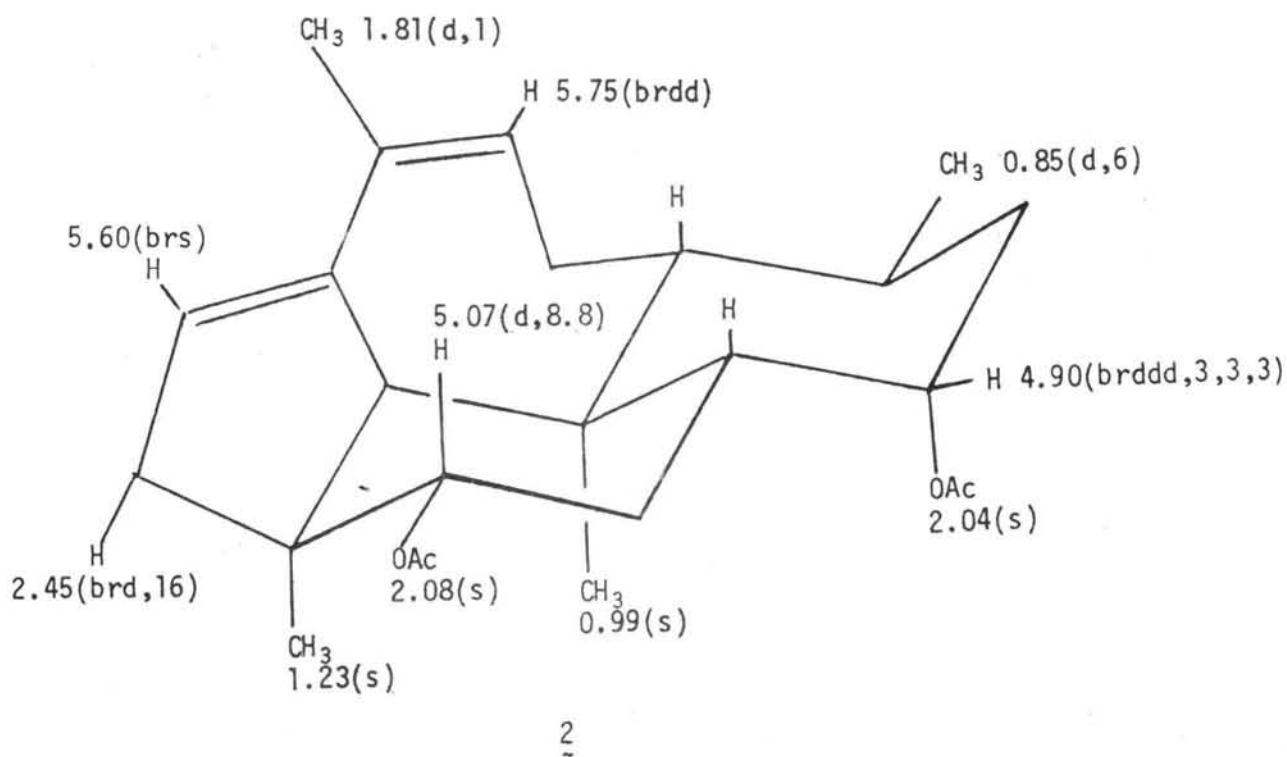
The chemical defence secretions of Malaysian termites (Nasutitermitinae, Isoptera) were analysed chromatographically and spectrometrically. New diterpenes discovered have novel bicyclic secotrinervitane, tricyclic trinervitane, tetracyclic kempene and spirotetracyclic longipane skeletons, which are of considerable significance in the understanding of the biosynthesis of these dome-shaped diterpenes by the termites.

Termites (Isoptera) are social insects and are ubiquitous in this part of the world. To protect the colony and the individuals that forage for food, most species have developed soldier castes having a vast array of defensive behaviour. In general, termites can depend on mechanical mode of defense (e.g. biting, flicking or snapping with mandibles), chemical defense (brushing or squirting secretions) or a combination of these modes. Termites of the subfamily Nasutitermitinae are entirely dependent on chemicals for defense and have developed a most elaborate chemical defense mechanism. The secretion is delivered via a nozzle-shaped projection on the top of the head and is 'shot' out at predators.

The defence secretion of Nasutitermitinae soldiers consists mainly of a mixture of mono- and di-terpenoids, sometimes accompanied by trace amounts of sesquiterpenes. Two compounds isolated from extracts of *Bulbitermes singaporensis*¹ were spectrometrically identified as kempa-6,8-dien-3 β ,14 α -diol 3,14-O-diacetate (1) and kempa-6,8-dien-3 α ,14 α -diol 3,14-O-diacetate (2) as shown in Figure 1. EI-MS spectral of kempene 1 (m/e 386, $C_{24}H_{34}O_4$) and 2 (m/e 386, $C_{24}H_{34}O_4$) show similar fragmentation pattern while ¹H-NMR exhibited four methyl, two acetate methyl and two olefinic proton signals. The configuration at C-14 was assigned as 3 β -acetoxy in compound 1 and 3 α -acetoxy in compound 2 on the basis of the following observations. Firstly, the chemical shift of equatorial H-3 α is more downfield than the axial H-3 β . Secondly, H-3 α bisects the angle of

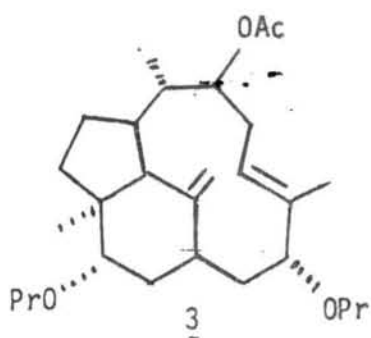


Kempa-6,8-dien-3 β ,14 α -diol 3,14-O-diacetate

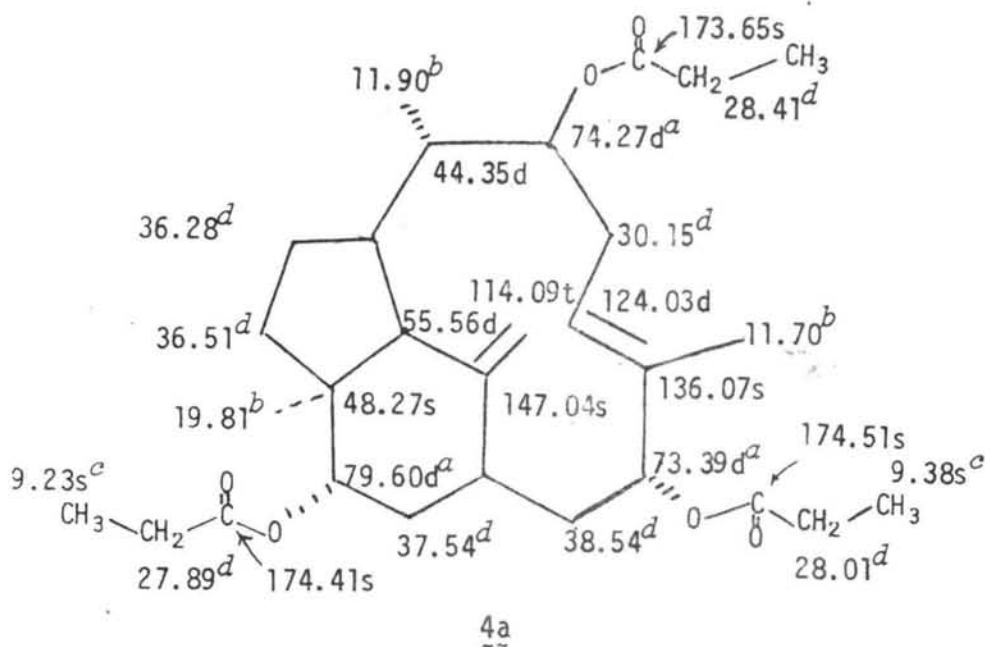
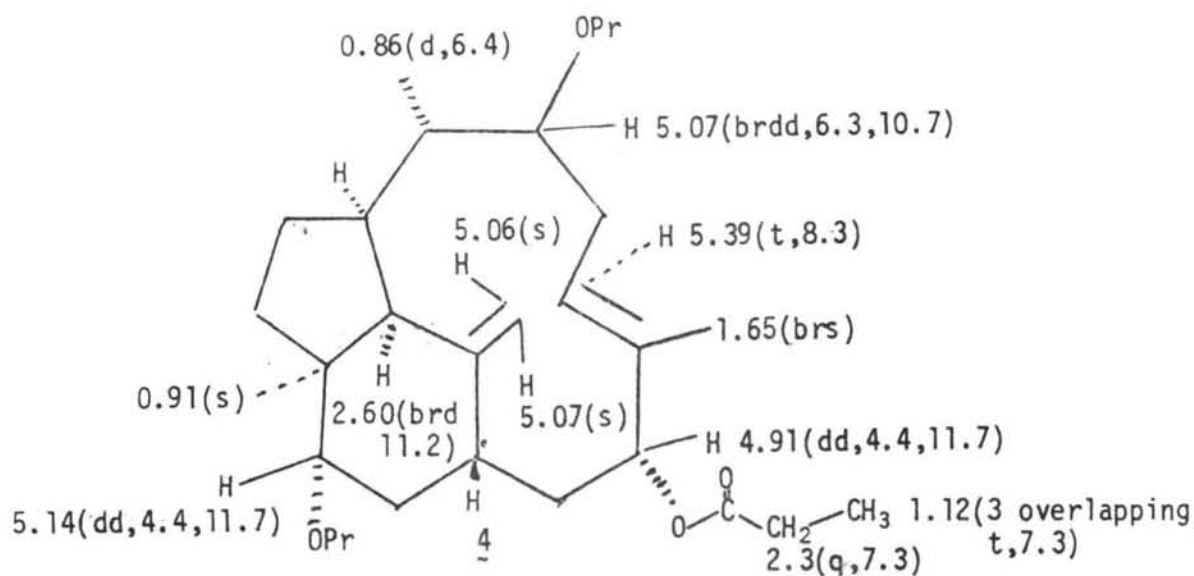


Kempa-6,8-dien-3 α ,14 α -diol 3,14-O-diacetate

FIGURE 1: KAMPANE STRUCTURE



Trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol 9-O-acetoxy-3,13-dipropionate



Trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol tripropionate.

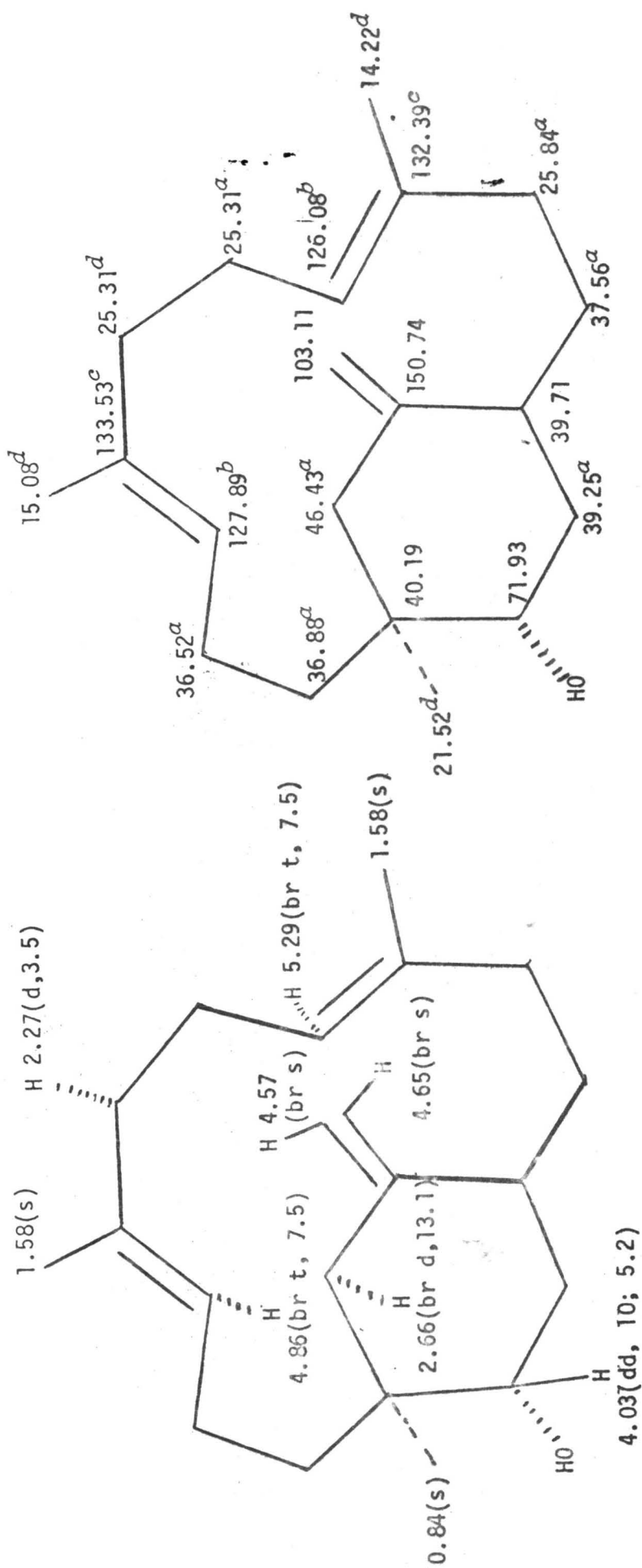
FIGURE 2: TRICYCLIC DITERPENES.

H-2 α and H-2 β to give virtually equal coupling constants, while axial H-3 β is nearly orthogonal to H-2 β and couples only to H-2 α with a reduced axial-axial coupling. Finally, the axial nature of the 3 β -acetate is sterically permissible while maintaining the chair conformation for that 6-membered ring. In this configuration, the axial acetate does not deshield the H-1 β methyl protons (1.11 ppm in 1) while the equatorial acetate does affect the shift of that methyl (1.23 ppm in 2). Reduction of the known 3-oxo-kempa-6,8-dien-14 α -ol 14-O-acetate² (structure established by X-ray crystallography) with excess LiAlH₄ gave two isomeric diols which on acetylation gave compounds 1 and 2, thus verifying the correct assignment.

Trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol tripropionate (4), isolated from *Nasutitermes matagensis*³ had mass spectrum m/e 488 (M⁺, C₂₉H₄₄O₆) and IR (CCl₄) 1732 cm⁻¹ (ester C=O). In its ¹H-NMR spectrum, tripropionate 4 showed three methyl, three propionate and two terminal olefinic protons as summarised in Figure 2. In the ¹³C-NMR spectrum, one quaternary, seven methine, eight methylene and four olefinic carbons were present. The 360 MHz ¹H-NMR of trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol 9-O-acetoxy-3,13-dipropionate (3) showed the same resonances as tripropionate 4, with the following exceptions: δ 4.90 (s, H-9), 2.30(q, 7.3Hz, propionate methylenes), 2.03(s, acetate methyl), and 1.21(t, 7.3Hz, propionate methyls). The structural assignment was proved by X-ray diffraction. Dipropionate monoacetate 3 had mass spectrum m/e 474 (M⁺, C₂₈H₄₂O₆) and had fragmentation pattern analogous to that of tripropionate 4.

The bicyclic secotrinervita-7(8),11(12),15(17)-trien-3 α -ol (5) (Figure 3) and secotrinervita-7(8),11(12),15(17)-trien-2 β ,3 α -diol (6) (Figure 4) isolated from *Longipeditermes longipes*⁴ showed 6 olefinic carbons from ¹³C-NMR spectrum and also showed three methyl (two overlapping), allylic and vinylic protons from 90 MHz ¹H-NMR. Secotrinervitatriene mono- α -cohol 5 and diol 6 have mass spectra m/e 288 (M⁺, C₂₀H₃₂O) and m/e 304 (M⁺, C₂₀H₃₂O₂) respectively and both show similar fragmentation patterns. The bicyclic secotrinervitane structural type was discovered at the same time by Braekman in the defence secretion of a Papua-New Guinea species *Nasutitermes priceps*,⁵ and the structural skeleton was established by X-ray crystallography.

The new compound trinervita-1(15),8(19)-dien-2 β ,3 α -diol 2-O-acetate (7) which was secreted in relatively large quantities in *Hospitalitermes umbrinus*⁶ was identified on the basis of its proton NMR, IR, and mass spectral data; hydrolysis with methanolic sodium hydroxide gave the known trinervita-1(15),8(19)-dien-2 β ,3 α -diol. In its ¹H-NMR, diol monoacetate 7 shows four methyl signals (two s, one d, one acetate methyl), two terminal olefinic protons and a hydroxymethine as shown in Figure 5. The C-2 proton appeared as a



5a

FIGURE 3: Secotrinervita-7(8),11(12),15(17)-trien-3 α -ol

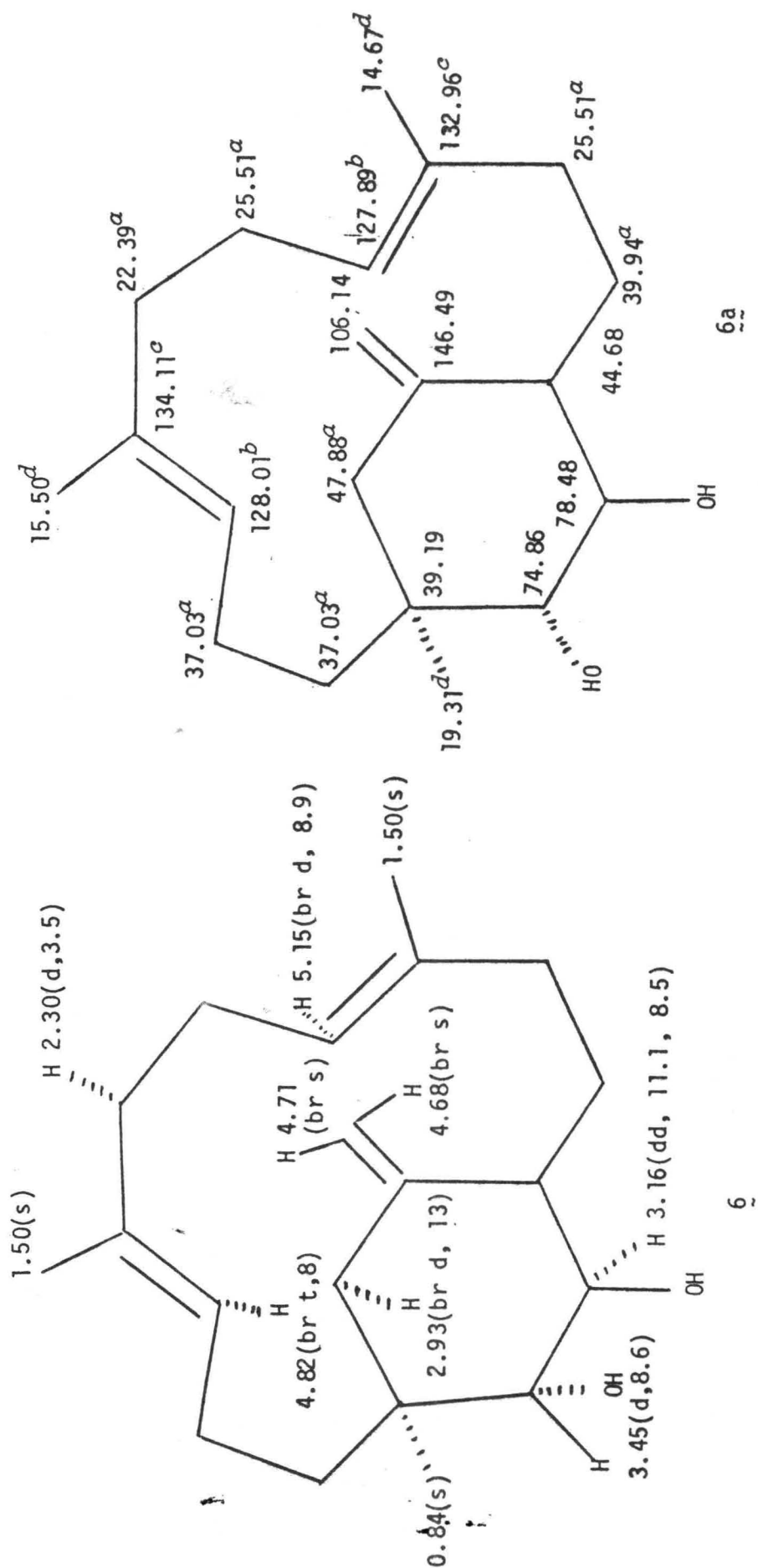
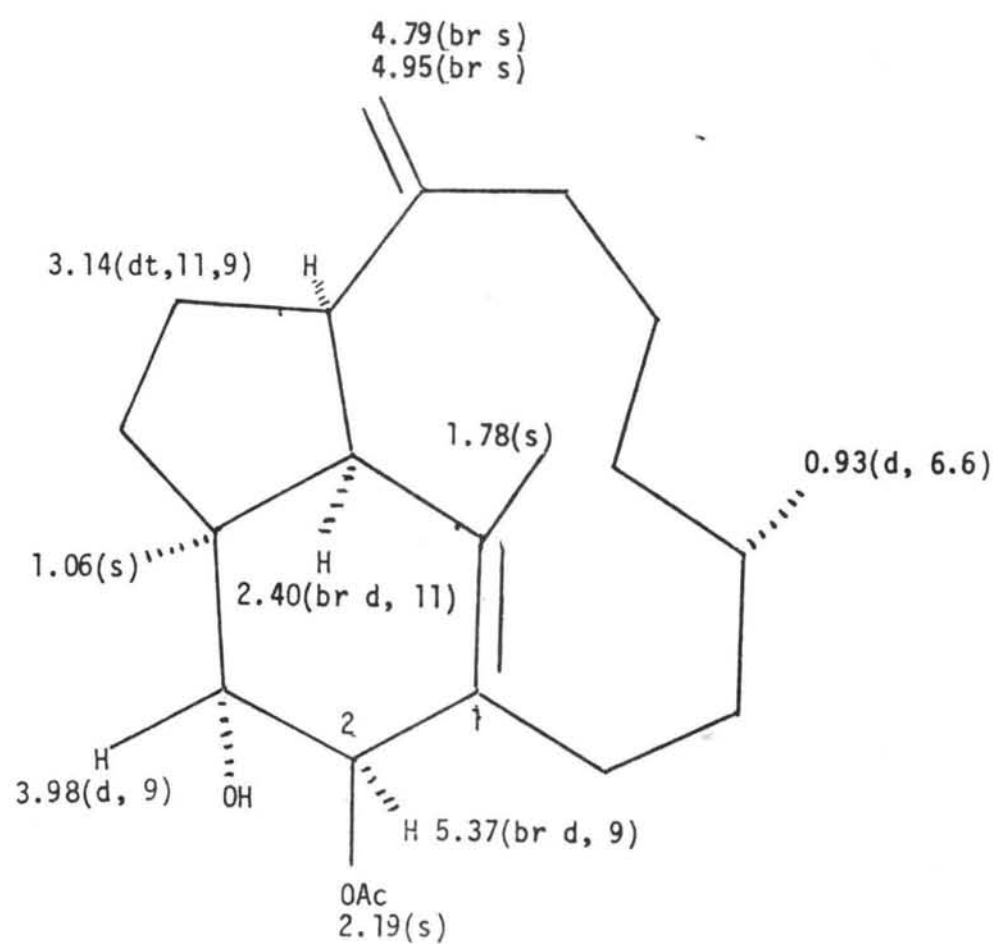


FIGURE 4: Secotrinervita-7(8),11(12),15(17)-trien-2 β ,3 α -diol



7

FIGURE 5: Trinervita-1(15),8(19)-dien-2 β ,3 α -diol 2-O-acetate

broad 9 Hz doublet at δ 5.37. The IR (CCl_4) shows absorptions at 3500 (O-H), 1735 ($\text{C}=\text{O}$) and 905 cm^{-1} ($\text{C}=\text{CH}_2$). The EI-mass spectrum of this diol monoacetate 7 did not show the molecular ion but only the M-AcOH ion. However, the trimethylsilyl derivative gave the correct molecular ion and an expected fragmentation pattern, including a retro-Diels Alder fragment $[\text{Me}_3\text{SiOCH}=\text{CMeCH}_2\text{CH}_2\text{CH}=\text{C}=\text{CH}_2]^+$ at m/e 196 (13%).

A novel compound longipenol (8) with new spiro-tetracyclic skeleton isolated from *Longipeditermes longipes*^{4,9} shows three CH_3 signals (two d, one s), a hydroxymethine coupled to two non-equivalent hydrogens, and two terminal olefinic protons as shown in Figure 6. In its ^{13}C -NMR spectrum, two quaternary, six methine, seven methylene, three methyl carbons, and a characteristic pair of 1,1-disubstituted olefinic carbons were present. Longipenol (8) had mass spectrum m/e 288 (M^+ , $\text{C}_{20}\text{H}_{32}\text{O}$) with a strong peak at m/e 255 (85%) while the trimethylsilyl derivative gave strong peak at m/e 360 (M^+ , 57%) and a RDA fragment at m/e 196 $[\text{Me}_3\text{SiOCH}=\text{CMeCH}_2\text{CH}_2\text{CH}=\text{C}=\text{CH}_2]^+$.

The diterpenes presently isolated from nasute termites are of interest in relation to earlier postulated biogenetic schemes. These compounds are known to be biosynthesized by nasute termites independently of the dietary source. Cembrene A, previously isolated from *Nasutitermes exitiosus*⁷ and from *Cubitermes*,⁸ or its 3,4-epoxide (12) would be an obvious choice as a precursor to the observed diterpenoids. As shown in Figure 7, a one-step cyclization of (R)-cembrene-*trans*-3,4-epoxide (12) would yield directly the secotrinervita-7(8),11(12),15(17)- 3α -ol (5). Interestingly, after isomerisation 5 has the double bonds positioned for further cyclisations to give longipenol (8), trinervitane- 3α -ol (11) and Kempene- 3α -ol (10). The methyl-shifted rippertenol (9) would arise similarly via step-wise cyclisation using bicyclic secotrinervitatrienol and tricyclic trinervitadienol as intermediates.

The new diterpene skeletal types found in Malaysian termites^{4,10} have provided a better understanding of the biosynthesis of these dome-shaped diterpenes produced by nasute termite soldiers. Besides interest in a new class of compounds, perhaps continuing research would show forth new uses for these and related compounds.

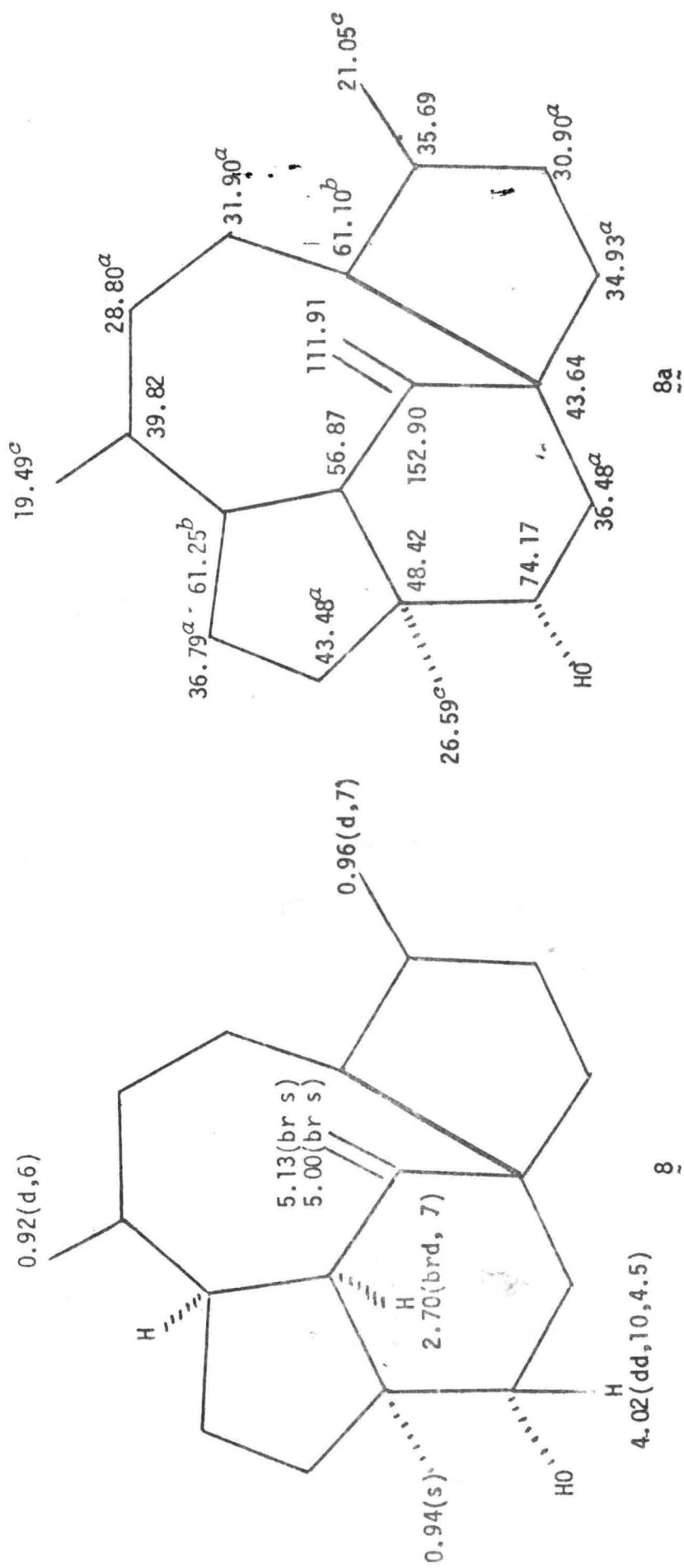


FIGURE 6: Longipenol

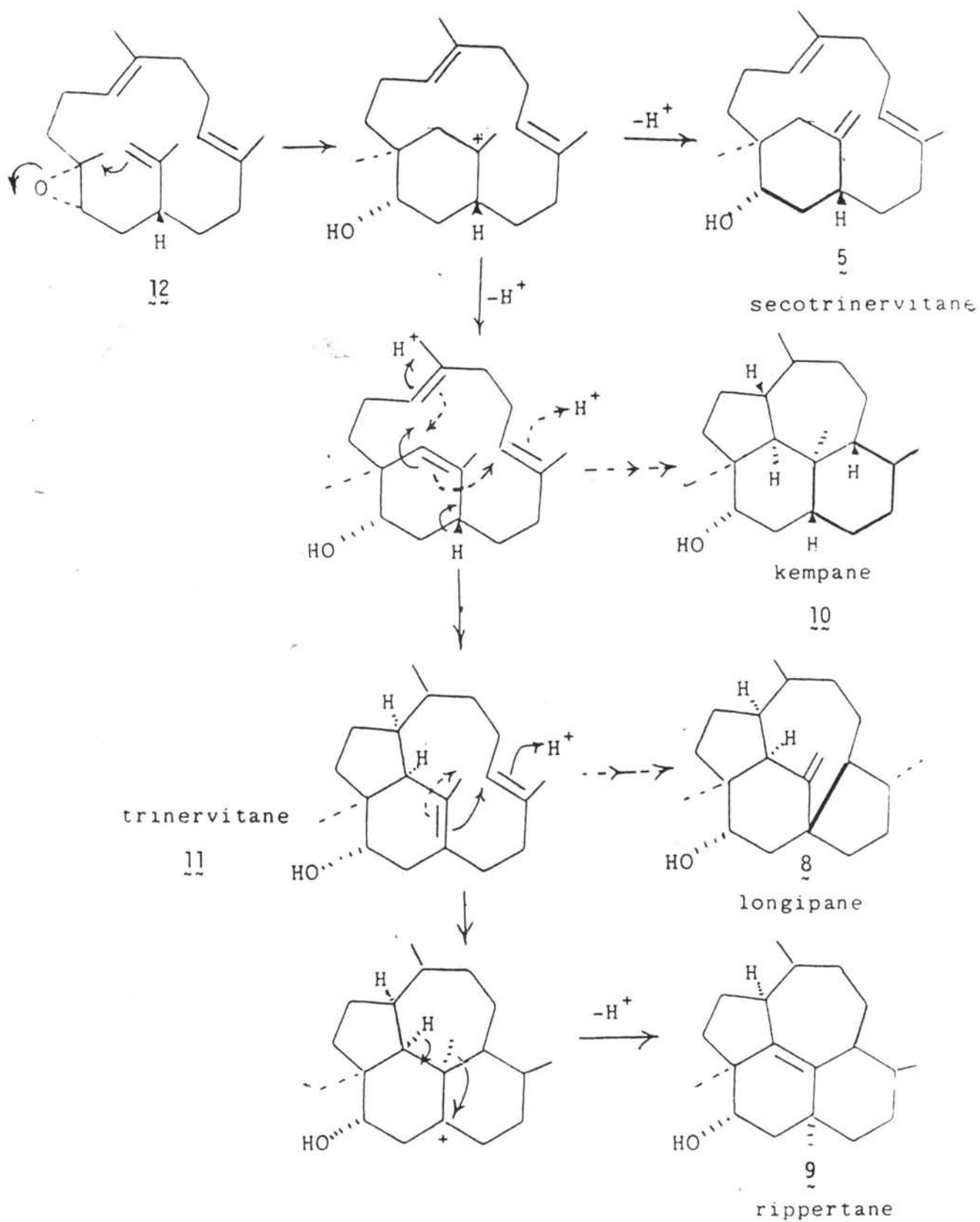


Figure 7: Possible Biogenesis Pathways

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UNREPORTED CONSTITUENTS FROM *ELAEIS GUINEENSIS*

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Chromatographic and spectroscopic techniques were used for the structure elucidation for newly isolated constituents from Elaeis guineensis. Aliphatic and terpenoid hydrocarbons, and methyl ketone homologs were isolated and characterised. Hydrocarbons, terpenoids and esters were isolated and identified from the exocarp of the palm fruits. Estragole was found to be the major component of the volatiles isolated from the male inflorescence of the oil palm.

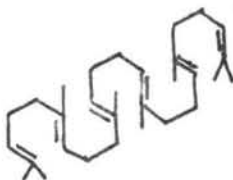
INTRODUCTION

Despite the preeminent position of palm oil in this country, most of the composition of palm oil is very much based on earlier work, principally of Jacobsberg (1). Recently reviews have appeared from PORIM on minor components in palm oil in view of their values (eg. carotene and vitamin E) and their roles in affecting oil quality (2). In this paper, a preliminary account of a study of selected minor and trace components from palm oil is presented.

RESULTS AND DISCUSSION

In the search for non-carotenoid hydrocarbons in palm oil it was found that hydrocarbons (ca. 2-3%) could be readily isolated from PFAD. High performance liquid chromatography (HPLC) and gas liquid chromatography (GLC) revealed that the major component of the hydrocarbons is squalene, a common acyclic triterpene.

FIG. I: SQUALENE



Squalene constitutes ca. 60% of the total hydrocarbons and was identified by HPLC and GLC and further confirmed by gas chromatography-mass spectroscopy (GCMS) and nuclear magnetic resonance (NMR) spectroscopy. Also identified were ionene and dimethylnaphthalene. These two compounds as well as toluene and xylene are known to form from the thermal decomposition of β -carotene.

The hydrocarbons occur as a complex mixture and had to be further purified by repeated chromatography before spectroscopic analysis. Results obtained are summarised in Table I.

TABLE I: HYDROCARBONS

Formulae	Relative amounts ^a	Assignments
C ₁₅ H ₃₂	T	n-pentadecane
C ₁₇ H ₃₆	T	n-heptadecane
C ₁₅ H ₃₀	S	pentadecene
C ₁₆ H ₃₂	T	hexadecene
C ₁₇ H ₃₄	T	heptadecene
C ₁₈ H ₃₆	M	octadecene
C ₁₉ H ₃₈	T	nonadecene
C ₂₁ H ₄₂	S	heneicosene
C ₂₄ H ₄₈	M	tetracosene
C ₂₆ H ₅₂	S	hexacosene
C ₂₃ H ₄₄	S	tricosadiene ^b
C ₂₆ H ₅₀	M	hexacosadiene ^b
C ₂₄ H ₅₀	T	branched alkane ^b
C ₂₇ H ₅₆	S	branched alkane ^b
C ₂₆ H ₄₈	S	hexacosatriene ^b
C ₂₀ H ₃₂	L	diterpene hydrocarbon ^b
C ₃₀ H ₅₀	VL	squalene
C ₁₃ H ₁₈	M	ionene
C ₁₂ H ₁₂	S	dimethylnaphthalene

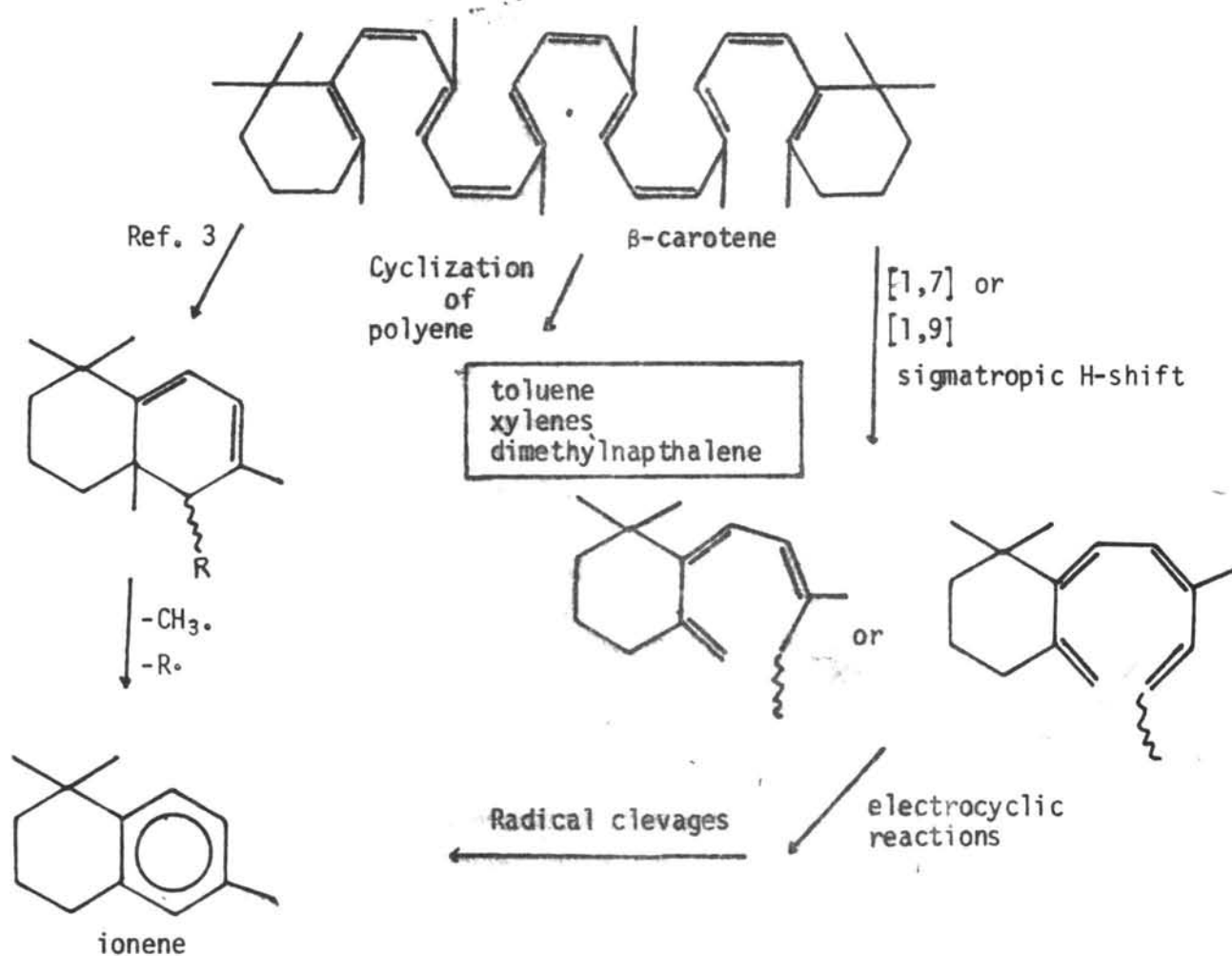
^aT = trace quantity, S = small, M = medium, L = large and VL = very large

^bTentative assignment.

Typically, only traces of n-alkanes were present. Monoenes were present in fairly substantial amounts consisting mainly of C15, C18, C21, C24 and C26. A few cyclic or polyene hydrocarbons (relatively small to trace amounts) remained unidentified; so were some diterpenoid hydrocarbons.

Among the more volatile components of PFAD, toluene, xylene, ionene and dimethylnaphthalene were readily detectable by GCMS. The formation of these have been the subject of much speculation. A reasonable scheme depicting their formation from thermal degradation of β -carotene is given in Fig. 2.

FIG. 2: DEGRADATION OF β -CAROTENE



Methyl ketones were isolated by silica gel column chromatography on the unsaponifiables of PFAD. The structures were deduced from the GCMS studies, being further supported by proton NMR spectroscopy. GCMS of methyl ketones showed pronounced McLafferty rearrangement and α -cleavage giving characteristic fragment with of m/e 58 and m/e 43 respectively.

These methyl ketones were rather unusual differing from the expected 2-pentadecanone (4) which could arise from microbiological action of C16 fatty acid (5). The composition of methyl ketone homologs found were summarised in Table II.

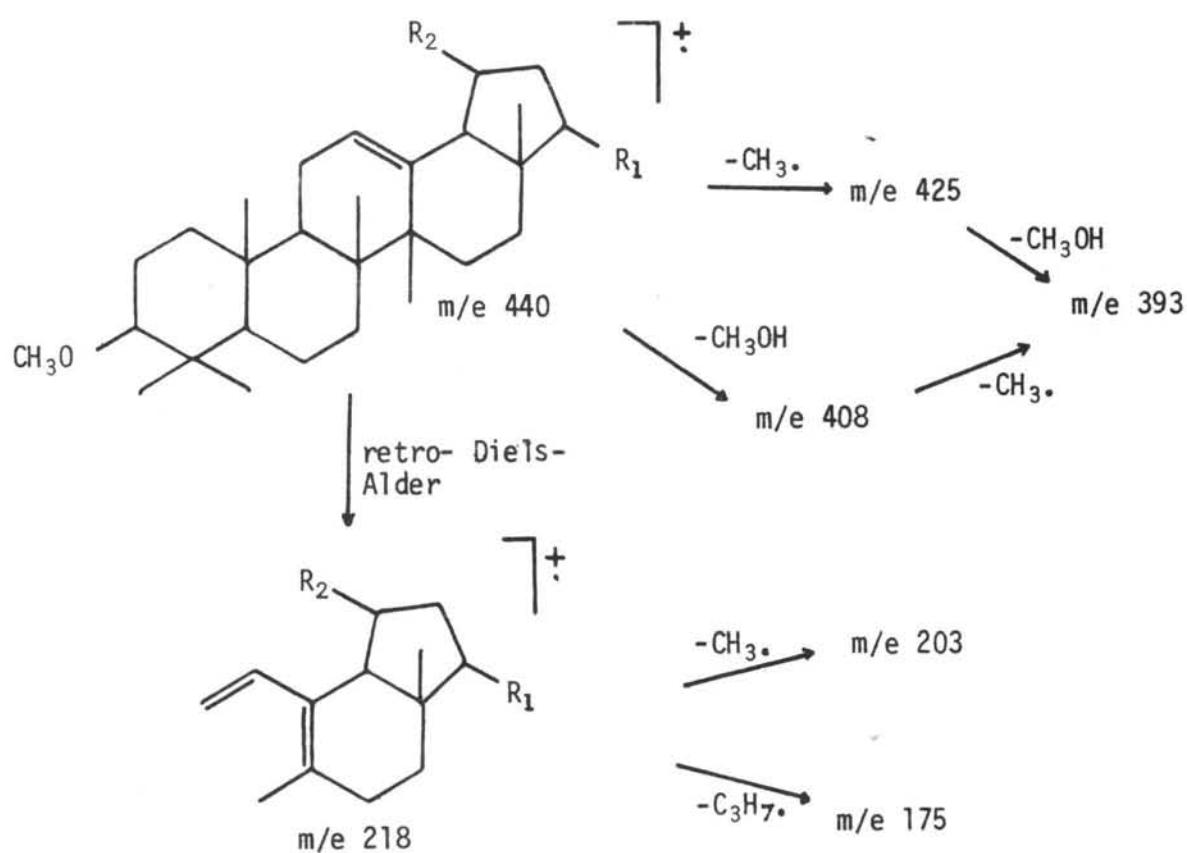
TABLE II: METHYL KETONES

Methyl ketones	Formulae	Relative amounts
2-pentadecanone	$C_{15}H_{30}O$	small
2-heptadecanone	$C_{17}H_{34}O$	large
2-nonadecanone	$C_{19}H_{38}O$	large
2-heneicosanone	$C_{21}H_{42}O$	medium
2-tricosanone	$C_{23}H_{46}O$	small

Extracts of palm fruit exocarp were examined by column and TLC. Apart from glycerides, hydrocarbons, esters, terpenoids and sterols were found. GLC again revealed that the major hydrocarbon component is squalene. Methyl esters identified were methyl myristate, methyl palmitate and methyl oleate (major). Methyl esters have characteristic m/e 74 fragment in GCMS and sharp singlet at ca. 3.7 ppm in 1H NMR spectrum.

Two triterpene methyl ethers were also isolated and tentatively assigned as arundoin and neomotiol methyl ether (I) or 12,13-dehydro-20,30-dihydrolupeol methyl ether (II). Isomers (I) and (II) cannot be distinguished by mass spectroscopy, as the spectra of these two isomers may not show any difference. The mass spectrum shows characteristic fragment ions at m/e 440 (M^+), 408 (M^+-OMe), 218 and 175. These fragment ions reveal that a double bond is at C-12 position giving the retro-Diels-Alder rearrangement ion at m/e 218 followed by loss of an isopropyl group (m/e 175).

FIG. 3: MASS SPECTRAL FRAGMENTATION OF ISOMER (I)/(II)

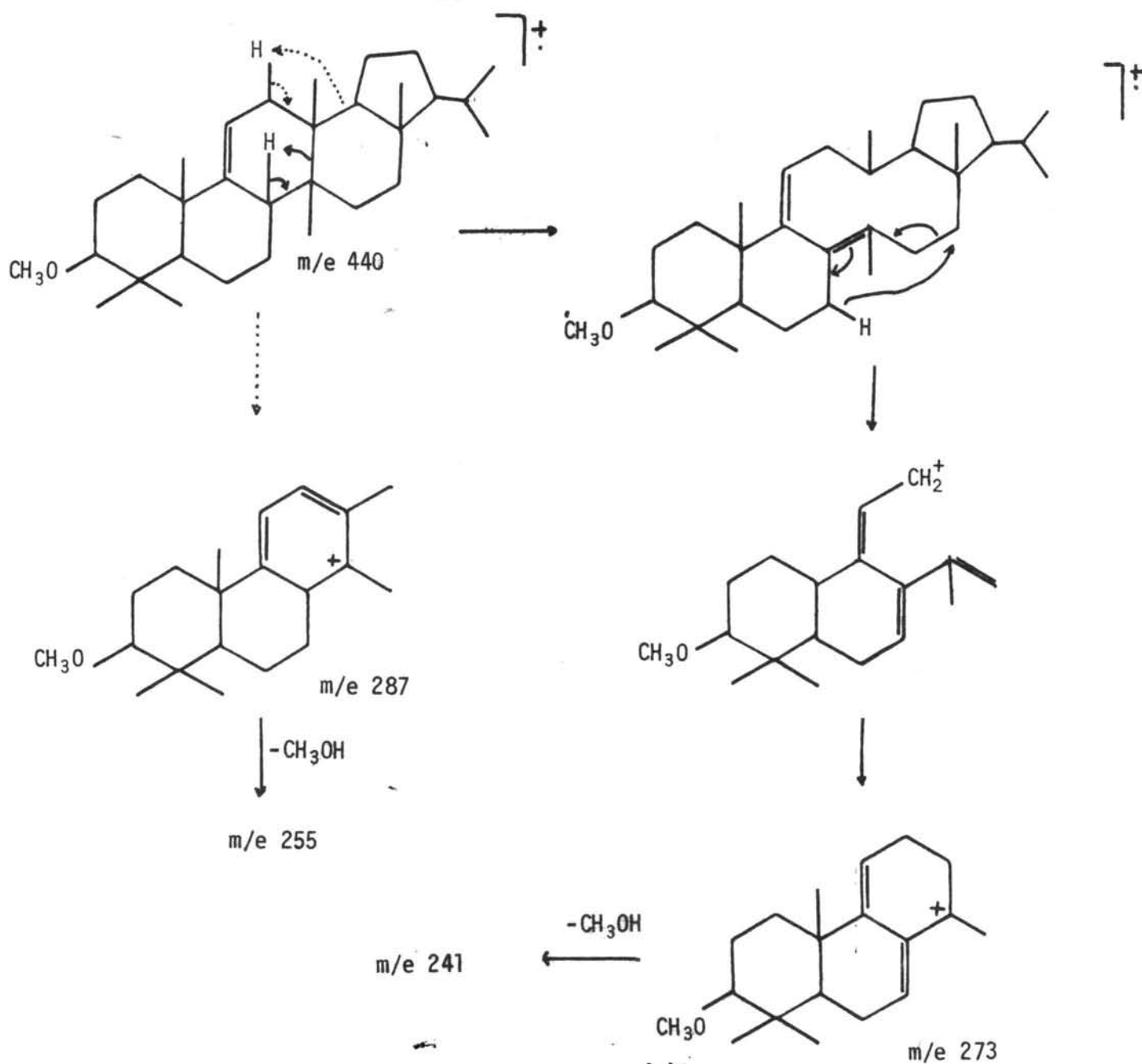


(I) $R_1 = C_3H_7$, $R_2 = H$: neomotiol methyl ether

(II) $R_1 = H$, $R_2 = C_3H_7$: 12,13-dehydro-20,30-dihydrolupeol methyl ether

Arundoin shows a different fragmentation pattern. Retro-Diels-Alder reaction is not significant due to the presence of methyl groups at positions 13 and 14, which enhance the fragmentation to occur at the C/D ring juncture giving a characteristic m/e 273 ion.

FIG. 4: FRAGMENTATION OF ARUNDOIN



Finally, a simple compound was easily isolated from the male inflorescence by vacuum distillation. GLC and NMR revealed that estragole, $4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$, is the major component (>90%). The structure was verified by proton NMR. Estragole is responsible for the characteristic odour of the palm flowers.

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THE ALKALOIDS OF LEUCONOTIS GRIFFITHII (APOCYNACEAE)

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A study of the Malaysian woody climber, Leuconotis griffithii (Apocynaceae), provided five alkaloids of which three have been positively identified by spectroscopy. Two of them, norfluorocurarine (II) and eburnamine (IV) are known whilst the third, norfluorocurarine N-oxide (III) is new. The other two alkaloids were given tentative structural assignments.

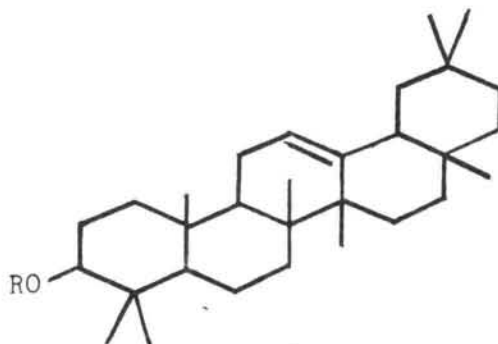
INTRODUCTION

The chemistry of alkaloids has always been an active and important part of organic chemistry and has provided many of the most challenging and subtle of all chemical problems, both of structural deductions and synthesis. By definition, "alkaloids occur characteristically in plants, and are frequently distinguished by their remarkable physiological activity. They contain carbon, hydrogen and nitrogen, and in most cases oxygen as well; in many respects they resemble the alkalis (hence the name)". This definition was given by Meyer in 1896 (1) and is still generally applicable today but needs some modifications. Initially, alkaloids are found only in the plant kingdom, but recently, they have also been discovered in the animals as well. For example, castoramine, samandrine and tetrodotoxin are some of the animal alkaloids that have so far been isolated (1). Secondly, it is true that most of the alkaloids are considered as strong bases. For example, strychnine has a pKa value of 8.26. However, colchicine is almost neutral in its properties (1).

There are over 6000 alkaloids that have so far been isolated from both plants and animals. During the last 40 years, research in the field of alkaloids has focussed its attention on the search of compounds of pharmacological interest. More recently, the work has been geared to finding alkaloids with anti-cancer activity.

The genus Leuconotis (family Apocynaceae) contains 10 species altogether (2), but in Peninsular Malaysia, it is represented by three species only. They are L. eugenifolia, L. griffithii and L. maingayi. All of them are woody climbers. The latex produced has been used in folk medicine for the treatment of yaws (3). Alkaloid tests have shown that the leaves, bark and wood of the first two species contain alkaloids, but in L. maingayi only the bark contains alkaloids.

Not much chemical work has been done on any of the Leuconotis species. However, some work was done on the species L. eugenifolia where some Indian workers reported the isolation of a few triterpenes (4,5). Among the triterpenes isolated were two new triterpenoid esters β -amrenyl behenate (Ia) and β -amrenyl eicosanoate (Ib) (6).



Ia: R= $\text{CH}_3(\text{CH}_2)_{20}\text{CO}-$

Ib; R= $\text{CH}_3(\text{CH}_2)_{18}\text{CO}-$

RESULT AND DISCUSSION

The air dried, powdered bark and wood of *L. griffithii* were extracted and purified to give 0.15% of crude alkaloid extract. The alkaloids were further separated using column chromatography and preparative thin layer chromatography. Five different alkaloids were isolated and subjected to spectroscopic analysis.

Norfluorocurarine

The first alkaloid identified was norfluorocurarine (II). The alkaloid has a molecular weight of 292 and a molecular formula of $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$. The mass spectrum shows characteristic indole fragmentation pattern by having peaks at m/e 130, 143 and 144. The base peak at m/e 121 is a characteristic feature of all akuammicine type of alkaloids.

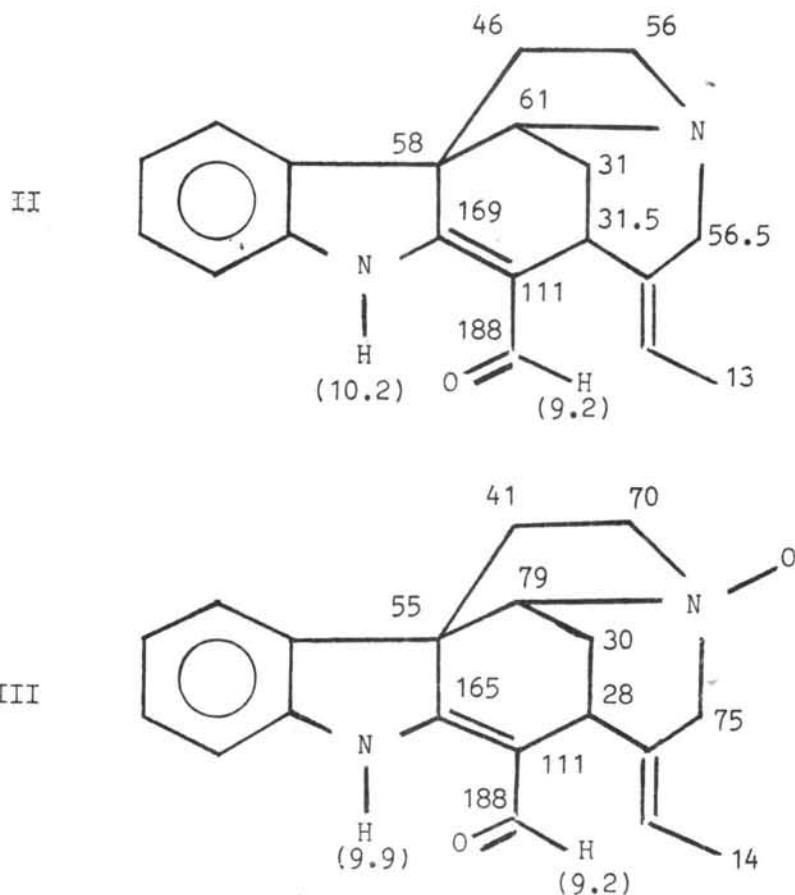
The infra-red spectrum shows absorption at 3320 and 1605 cm^{-1} , due to the presence of secondary NH. It also shows the absorption at 1645 cm^{-1} , showing the presence of a hydrogen bonded carbonyl group. The presence of the olefinic bond in conjugation with a carbonyl group is shown by the presence of an absorption at 1610 cm^{-1} . The U.V. spectrum shows absorption at 202, 228 and 360 nm.

The proton spectrum shows an exchangeable proton at 10.2 δ . This peak which integrates for one proton is assigned to the hydrogen on the secondary nitrogen. A sharp singlet at 9.2 δ also integrates for one proton. This is assigned to the aldehyde proton. The spectrum also shows the presence of aromatic protons at 7 to 7.2 δ .

The completely decoupled C-13 spectrum accounted for all the 19 carbons. It clearly shows the presence of a carbonyl carbon with a peak at 188 ppm. There are 11 carbons in the lower field and 8 carbons in the higher field. The high field carbons at 61, 56.5 and 56 ppm are assigned to carbons attached to the tertiary nitrogen. The carbon at 58 ppm is assigned to the aliphatic quaternary carbon.

A partially decoupled spectrum of the alkaloid clearly differentiates the types of carbons present in the molecule. The spectrum shows a quartet (CH_3) at 13 ppm, triplets (CH_2) at 31, 46, 56 and 56.5 ppm, doublets (CH) at 31.5, 61 and 188 ppm and singlets (C) at 58, 111, 137, 139 and 169 ppm. The doublet at 188 ppm indicates the presence of an aldehyde carbonyl carbon. The five peaks at 120 to 127 ppm represent the five aromatic and olefinic CH carbons present in the molecule.

Spectral information confirms the structure of norfluorocurarine which was also previously isolated from several *Vinca* species (7).



Norfluorocurarine N-oxide

The second alkaloid identified was norfluorocurarine N-oxide (III). The alkaloid has a molecular weight of 308 and a molecular formula of $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$. The mass spectrum shows a major fragment at m/e 292, corresponding to a loss of an oxygen. It also shows fragments at m/e 130, 143, 144 and 156, and the base peak at m/e 121.

The infrared spectrum shows absorption at 3320 cm^{-1} due to the secondary NH , at 1660 cm^{-1} due to the carbonyl group and at 1615 cm^{-1} due to the olefinic group. The U.V. spectrum shows similar absorptions to that of norfluorocurarine, i.e. at 202, 228 and 360 nm.

The proton spectrum also shows distinct similarities to that of norfluorocurarine. It shows the presence of an exchangeable proton at 9.9 δ and the one proton singlet at 9.2 δ . Similarities in the completely decoupled C-13 spectra of the two alkaloids are also distinct. All the carbon chemical shifts are quite unchanged except for the chemical shifts of three carbons. They are the carbons at 61, 56.5 and 56 ppm in the norfluorocurarine spectrum which are shifted to 79, 75 and 70 ppm respectively in the N-oxide spectrum. These three carbons are the carbons that are attached to the tertiary nitrogen.

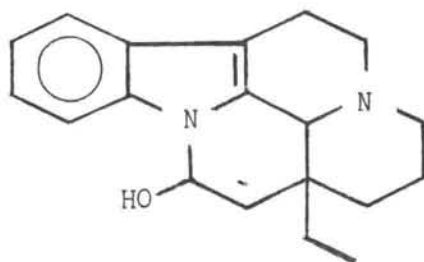
Since the alkaloid has only one oxygen more than norfluorocurarine, and the presence of this oxygen affects only the chemical shifts of the three carbons attached to the nitrogen, it is concluded that the oxygen is bonded to the nitrogen as an N-oxide.

Eburnamine

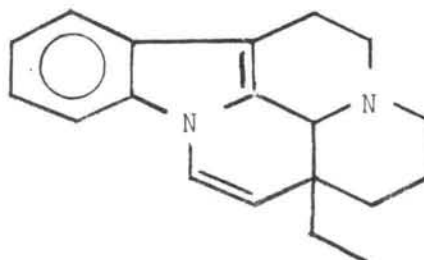
Eburnamine (IV) has a molecular weight of 296 and a molecular formula of $C_{19}H_{24}N_2O$. The alkaloid has previously been isolated from *Hunteria eburnea* (7). The identification of this alkaloid was based mainly on the interpretation of the mass spectrum.

The completely decoupled C-13 spectrum shows the presence of 11 carbons in the high field region. The carbon at 77 ppm is assigned to the carbon attached to an oxygen. The carbons at 59, 51, 44 and 43 ppm are the four carbons adjacent to the nitrogens. The proton spectrum shows the presence of an exchangeable proton at 1.9 δ due to the presence of a hydroxy group.

The mass spectrum of that alkaloid shows similar fragmentation pattern with that of eburnamenine (V), a known alkaloid of molecular weight 278 mass units. It was earlier reported (8) that eburnamine is very sensitive to dehydration. As a result of the loss of a water molecule, the mass spectrum of eburnamine looks similar to that of eburnamenine.



IV



V

Alkaloid 326 and Alkaloid 376

The other two alkaloids that have been isolated are Alkaloid 326 and Alkaloid 376. They are tentatively named according to their molecular weights. Alkaloid 326 is a major alkaloid of this plant. From the mass spectrum, the alkaloid has a molecular formula of $C_{19}H_{22}N_2O_3$. The proton n.m.r spectrum shows the presence of an NH and OH by the presence of exchangeable peaks at 8.2 and 5.4 δ respectively. It also shows a sharp singlet integrating for one proton at 5.9 δ . The triplet at 0.5 δ shows the presence of a methyl group adjacent to a CH_2 group.

The infrared spectrum shows the presence of a carbonyl group and confirms the presence of the OH and NH groups. The completely decoupled C-13 spectrum of the alkaloid confirms the presence of a carbonyl group. The spectrum also shows the presence of 7 quaternary carbons, 5 CH , 6 CH_2 and one methyl group. Structural elucidation of these compounds is in progress.

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ANALYSIS OF OILY COMPONENT OF THE SAP OF LACQUER TREE IN BURMA AND THAILAND

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Oily component of sap of the lacquer tree originating in Burma and Thailand, Melanorrhoea usitate is analyzed by using high performance liquid chromatography. Novel phenolic lipids, ω -phenylalkyl-phenols, are found in addition to previously known homologues of thitsiol, urushiol and laccol.

INTRODUCTION

In 1922 (1), Majima reported that 4-substituted catechols having a C_{17} n-alkyl side chain is the main constituent of sap of the lac tree, Melanorrhoea usitate grown in Burma, and he named this compound thitsiol (isourushiol). In the report, he also pointed out that other saturated substances were included in the sap besides thitsiol in a considerably great amount, though their nature and chemical structures could not be elucidated.

We have recently developed a general method to separate and analyze oily component of sap of lac trees based on high performance liquid chromatography (hplc) (2-4). Urushiol of the lac tree, Rhus vernicifera (China and Japan) was separated into more than ten congeners as dimethyl ethers and the structure of olefinic side chains was exactly determined by ozonolysis accompanied with hplc-identification of dinitrophenylhydrazones derived from ozonolysis products (4). More recently, high-resolution l.c. separation of intact urushiol has been achieved by reversed-phase l.c. using weakly acidic eluent (5).

In a preliminary report (6), sap of the lac tree, Melanorrhoea usitate (Burma) was examined after methylation and hydrogenation to simplify analytical procedure, as it was found to be a highly complicated mixture of many constituents. As a result, it was revealed to contain congeners of laccol and urushiol as well as those of thitsiol. A more significant fact is that in addition to these classical substances, it includes 3- or 4-substituted catechols with 10'-phenyldecyl or 12'-phenyldodecyl groups and 5-substituted resorcinols with similar substituents.

To determine exact structures of these novel compounds, or in order to clarify whether they have olefinic groups in the side chain or not, we executed separation of oily component of sap of Burmese lac as the intact form. This was succeeded by using the

recently developed reversed-phase l.c. method, which was applied to the analysis of sap of Rhus vernicifera (5).

In this paper we report the result of extensive analysis of sap of Burmese lac, presenting complete structures of novel dihydric phenols with -phenylalkyl substituents and some new constituents, monohydric phenols with a variety of substituents. We also wish to emphasize that a highly complicated substance as the present subject can be readily analyzed by a modern chromatographic technique.

EXPERIMENTAL

Material

Sap of the lacquer tree, Melanorrhoea usitata originating in Burma was obtained by the courtesy of The Burmese Embassy in Tokyo and The South Sea Association (Tokyo). It was mixed with 3-fold amount of acetone and the mixture was filtered. The filtrate was evaporated and the obtained residue was subjected to gel permeation chromatography (g.p.c.) to remove polymeric material. G.p.c. technique is adequate to pre-treatment of the air-sensitive sap as it is executed under mild conditions compared with classical distillation. The obtained monomeric preparation was separated by hplc.

Instruments

Hplc was carried out with a hand-made apparatus comprising a mini pump (Nihon Seimitsu Co., Tokyo), a pressure gauge, a syringe-loading sample injection valve (Rheodyne Inc., CA). Effluent was monitored with a UV-detector (Oyobunko, Co., Tokyo) at 254 nm. A 2.2 x 30 cm stainless steel column packed with 5 μ m ODS-silica (Hitachi #3053) and a 0.8 x 25 cm column packed with ODS-silica (TSK-gel LS-410, 5 μ m) were used. G.p.c. was done with the hand-made apparatus equipped with an RI monitor (RI-2, Japan Analytical Industries, Tokyo) on Hitachi A-120 and A-110 columns (0.8 x 50 cm) using chloroform as eluent. G.l.c. was done with a Hewlett-Packard 3790 instrument equipped with a flame ionization detector on a fused-silica WCOT column (ULTRA#2, 0.2mm x 25 m) coated with methylsilicone (the thickness of liquid phase, 0.33 μ m). I.r. spectra was recorded on a JASCO IRA-2 instrument. ¹H-N.m.r. spectra were measured with a JEOL GX-400 spectrometer (resonance frequency, 400 MHz). E.i.-m.s. diagrams were obtained with a Hitachi RMU-6E mass spectrometer (ionization voltage, 70 eV). G.l.c.-m.s. measurement was executed with a Hewlett-Packard 5996A g.c.-m.s. system.

RESULTS AND DISCUSSION

Fig. 1 is a chromatogram of intact oily component of sap of Burmese lac on a 0.8x25-cm ODS-silica column using acetonitrile/water/acetic acid (80/20/2, v/v) as eluent. Each peak was extensively separated on a 2.2x30-cm ODS-silica column; if an obtained fraction was composed of more than one component as revealed by high-resolution g.l.c., it was again subjected to second l.c. separation on a 0.8x25-cm column. Each fraction was

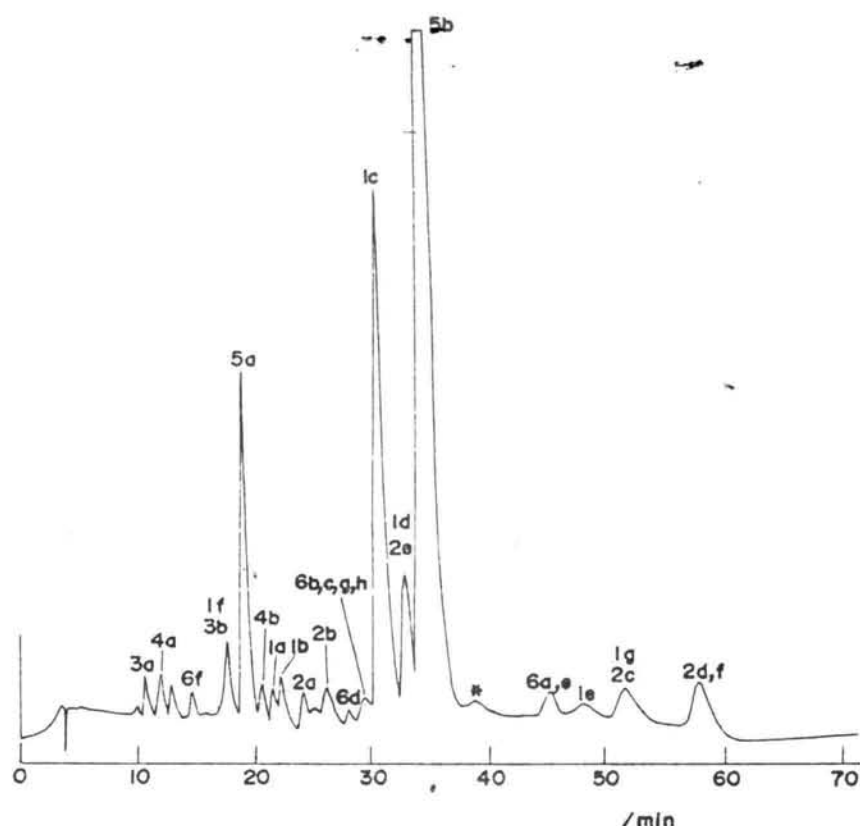


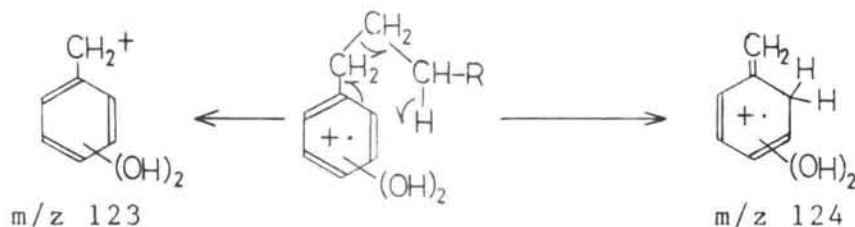
Fig. 1. CHROMATOGRAM OF INTACT OILY COMPONENT OF SAP OF *Melanorrhoea usitata*. CONDITIONS: COLUMN, TSK-GEL LS-410, 0.8x25cm; ELUENT, CH₃CN/H₂O/CH₃COOH (80/20/2, v/v); FLOW RATE, 2.5 ml/min; DETECTOR, 254 nm.

evaporated at 30 C to remove most of acetonitrile and the remained dispersion was extracted with n-hexane. The hexane solution was evaporated to give separated constituents of sap of *Melanorrhoea usitata*. Some fractions containing several components were subjected to g.l.c.-m.s. analysis.

Isolated constituents were identified by measuring i.r., ¹H-n.m.r. and mass spectra to give results summarized in Table I. Symbols attached to peaks in Fig. 1 are corresponding to identified compounds in this Table.

Dihydric phenols with alkyl or alkenyl side chains

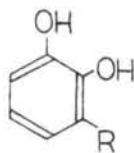
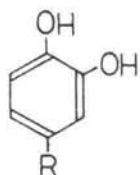
In m.s. diagrams of compounds 1a-1c, 1e, 1g, 2a-2c and 2f appeared a intense molecular ion peak and peaks of fragment ions given by cleavage of the bond beta to the aromatic ring (m/z 123) and by the McLafferty rearrangement (m/z 124) of the molecular ion (7):



Compounds **1a-1c**, **1e** and **1g** exhibited out-of-plane bending deformation bands of 1,2,4-trisubstituted benzene (810, 850 cm^{-1}), and were identified with congeners of thitsiol. The numbers of carbon atoms and double bonds in the side chain were determined from the M^+ value; **1b** and **1e** include isolated trans olefin groups as they have an i.r. band at 960 cm^{-1} .

In i.r. spectra of **2a-2c** and **2f**, out-of-plane bending deformation bands of 1,2,3-trisubstituted benzene were observed at 730 and 770 cm^{-1} . From M^+ values, **2a-2c** were identified with congeners of laccol and **2f** with saturated urushiol.

Compounds **1d**, **1f**, **2d** and **2e** were obtained as mixtures with other compounds and characterized by g.l.c.-m.s. measurement. They also showed molecular ion peaks and peaks due to dihydrobenzyl ion (m/z 123) and cyclohexadiene ion (m/z 124). Substituted position could not be determined from these m.s. data, but were suspected based on their retention time in the l.c. chart.



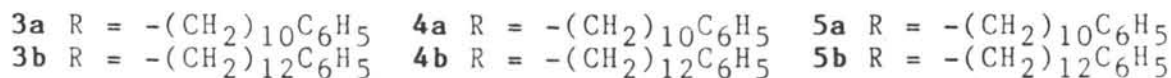
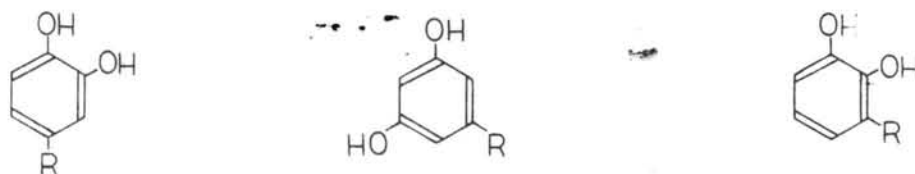
1a R = C_{17:3}
1b R = C_{17:2(t)}
1c R = C_{17:2}
1d R = C_{17:2(t)}
1e R = C_{17:1(t)}
1f R = C_{15:1}
1g R = C_{15:0}

2a R = C_{17:3}
2b R = C_{17:3(t)}
2c R = C_{17:1}
2d R = C_{17:1(t)}
2e R = C_{15:1}
2f R = C_{15:0}

The complete side chain structure of each homologue of thitsiol, laccol and urushiol found in this study should be determined in due time.

Dihydric phenols with ω -phenylalkyl side chains

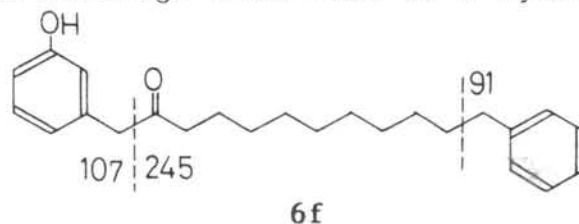
Compounds **3a**, **3b**, **4a**, **4b**, **5a** and **5b** showed very simple mass spectra, where only a molecular ion peak, peaks due to the m/z 123 and 124 ions and the m/z 91 ion were prominent. The presence of m/z 123 and 124 ions indicates that they are derivatives of dihydric phenol. As the m/z 91 ion stands for tropyllum ion derived from monoalkylbenzene, an alkylphenyl group is included in these compounds. This was confirmed by the existence of an intense i.r. band of monosubstituted benzene (700 cm^{-1}). The substituted position of phenolic nucleus in these compounds was determined from characteristic i.r. bands of out-of-plane bending deformation of the benzene ring. Consequently, it is established that **3a** and **3b** are 4-(10'-phenyldecyl)- and 4-(12'-phenyldodecyl)catechol, respectively, **4a** and **4b** are 5-(10'-phenyldecyl)- and 5-(12'-phenyldodecyl)resorcinol, and **5a** and **5b**, 3-(10'-phenyldecyl)- and 3-(12'-phenyldodecyl)catechol.



In the ^1H -n.m.r. spectra of 5a and 5b appeared superimposed triplets due to methylene protons at the 1' and 10' (12') positions (δ 2.59), quintets from methylene protons at the 2' and 9' (11') positions (δ 1.60), two singlets of hydroxyl protons (δ 4.95, 5.08), a multiplet due to monosubstituted phenyl protons (δ 7.17, 7.18), an apparent singlet of protons of 1,2,3-trisubstituted phenyl group (δ 6.71), and intense multiplets of methylene protons of the remaining portion of the molecule (δ 1.27, 1.30).

3-Substituted monohydric phenols

Compounds 6d-6f showed simple mass spectra with a distinct molecular ion peak, peaks of m/z 107 and 108 and the m/z 91 peak. The m/z 107 and 108 ions were derived by cleavage of the bond beta to the aromatic ring and the MacLafferty rearrangement of the molecular ion, respectively. This means that these compounds are monohydric phenols substituted with a long alkyl side chain. They also include a monoalkylphenyl group as a peak due to tropylium ion (m/z 91) was detected. In their i.r. spectra, absorption bands due to out-of-plane bending deformation of 1,3-disubstituted benzene (750 , 790 cm^{-1}) and that of monosubstituted benzene (700 cm^{-1}) were observed. Then these compounds are 3-substituted phenols with an -phenylalkyl side chain. From the M^+ value, 6d was revealed to be 3-(10'-phenyldecyl)phenol and 6e, 3-(12'-phenyldodecyl)phenol, 6f showed an i.r. band due to a keto function at 1700 cm^{-1} , and a fragment ion of m/z 245 was found in the m.s. diagram which was given through α -cleavage with loss of a hydroxybenzyl group;



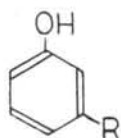
In the ^1H -n.m.r. spectrum were observed a singlet of methylene protons at the 1' position (δ 3.51) and two triplets due to methylene protons at the 3' (δ 2.42) and 12' positions (δ 2.60). From these data, the unique structure of 6f has been established.

Compounds 6a-6c, 6g and 6h were obtained in a very small amount as mixtures with other compounds and characterized by g.l.c.-m.s. measurement. The m/z 107 and 108 ions were common for all of their m.s. diagrams, leading that these compounds are

monohydric alkylphenols. **6a** showed series of fragment ions characteristic of n-alkenes and was revealed to be substituted with a C₁₇ n-alkenyl group with two double bonds from the M⁺ value (328). Compounds **6b** and **6c** showed relatively weak molecular ion peaks (m/z 372 and 373) and peaks of m/z 265 and 263, each of which was accompanied with a peak due to a fragment ion given by elimination of water. It was then revealed that they have a hydroxyl group at C-2' in the side chain. The number of carbon atoms and double bonds in the side chain were elucidated from the M⁺ value.

6g exhibited in the m.s. diagram a molecular ion peak (m/z 380) and a fragment ion of m/z 273 and no peak derived by dehydration as found in compounds **6d** and **6e**, and was concluded to contain a keto function at the 2' position. In the m.s. diagram of **6h**, the molecular ion (m/z 382) and the fragment ion (m/z 275) were associated with peaks derived by loss of water from these ions, indicating that this compound has a hydroxyl group at the 2' position.

The substituted position of these minor constituents was tentatively assigned to meta considering the biosynthetic route proposed for formation of phenolic lipids (8, 9).



- 6a** R = C_{17:2}
- 6b** R = -CH₂CH(OH)C_{17:2}
- 6c** R = -CH₂CH(OH)C_{17:3}
- 6d** R = -(CH₂)₁₀C₆H₅
- 6e** R = -(CH₂)₁₂C₆H₅
- 6f** R = -CH₂CO(CH₂)₁₀C₆H₅
- 6g** R = -CH₂CO(CH₂)₁₂C₆H₅
- 6h** R = -CH₂CH(OH)(CH₂)₁₂C₆H₅

CONCLUDING REMARKS

Content of each constituent was listed in Table I. One should notice that these values may not represent the exact composition of oily component of native sap as it exudates from lac tree, since the sample used in this investigation included only 50% of monomeric fraction presumably due to the polymerization during the storage and the transportation.

Nevertheless, it has been clarified that sap of Melanorrhoea usitate contains several types of phenolic lipids, i.e., thitsiol, laccol, urushiol, 3- and 4-(ω-phenylalkyl)catechols, 5-(ω-phenylalkyl)resorcinols and 3-substituted phenols with unique side chains. Latter novel compounds with ω-phenylalkyl side chains may be the substance which Majima suggested to exist in sap of Burmese lac in addition to thitsiol about 60 years ago.

An unusual phenolic lipid having a keto function at C-2', campnospermanol (3-(2'-oxo-9'(Z)-nonadecyl)phenol), has previously been isolated from Campnospermum auriculate (8). In the present study, have been found some compounds with a keto or hydroxyl function specifically attached to C-2'. This

specificity relates to the biosynthetic "polyketide" pathway which has been proposed as the general mechanism of formation of phenolic lipids (8, 9).

The analytical procedure presented here may be effectively applied to the quality control of natural products from plants grown in Southeast Asian countries. The more easier method based on modern capillary g.l.c. technique will be presented in a separate report.

Acknowledgment The authors would like to express their sincere gratitude to Dr. K. Hatanaka for measurement of 400 MHz ¹H-n.m.r. spectra, Mr. T. Takayama for m.s. measurement and Mr. S. Yamashita for g.l.c.-m.s. operation.

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TABLE I. CHARACTERISTICS OF CONSTITUENTS OF SAP OF Melanorrhoea usitate

compound	apparent content	m.s. (m/z)		i.r. (cm ⁻¹)
		M ⁺	others	
	wt%			
1a	2.0	342	123, 124	810, 850
1b	2.1	342	123, 124	810, 860, 960
1c	12.4	344	123, 124	810, 860
1d	ud*	344	123, 124	
1e	1.4	346	123, 124	810, 860, 960
1f	tr**	318	123, 124	
1g	1.0	320	123, 124	810, 860
2a	0.8	342	123, 124	730, 770
2b	0.9	342	123, 124	730, 770, 970
2c	tr	346	123, 124	730, 770
2d	tr	346	123, 124	
2e	tr	318	123, 124	
2f	2.7	320	123, 124	730, 770
3a	0.5	326	123, 124, 91	
3b	1.8	354	123, 124, 91	810, 850, 700
4a	0.4	326	123, 124, 91	830, 700
4b	0.3	354	123, 124, 91	830, 700
5a	8.6	326	123, 124, 91	730, 770, 700
5b	45.4	354	123, 124, 91	730, 770, 700
6a	tr	328	107, 108	
6b	tr	372	107, 108, 354, 265	
6c	tr	370	107, 108, 352, 263, 245	
6d	0.6	310	107, 108, 91	750, 790, 700
6e	0.7	338	107, 108, 91	750, 790, 700
6f	0.5	352	107, 108, 91, 245	750, 790, 700, 1700
6g	tr	380	107, 108, 91, 273	
6h	tr	382	107, 108, 91, 364, 275, 257	

* undetermined.

** trace.

THE DEVELOPMENT OF A SIMPLE METHOD
FOR TREATMENT OF TIMBER I PERMEABILITY MEASUREMENTS

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A simple idealized model for treatment of timber is a single step immersion process in a preservative bath. The first stage in developing such a method is to obtain precise permeability data. An experimental study has been made to identify the factors involved in acquiring reliable and reproducible permeability data of wood.

INTRODUCTION

The volume flow rate per unit area through porous media is given by Darcy's law:

$$\frac{dQ}{dt} = \frac{KA\Delta P}{\eta l}$$

where $\frac{dQ}{dt}$ is the volume flow rate of a fluid of viscosity η through a medium of cross-sectional area A and length l under a pressure differential ΔP . K is the permeability constant, characteristic of the penetrated medium and independent of the penetrating fluid.

While wood scientists generally assume that fluid flow in wood obeys Darcy's law, there is considerable evidence in the literature to indicate that this can be a questionable assumption. Several investigators of liquid flow in wood (1,2,3) found that, contrary to Darcy's law, liquid flow rate through wood decreased with time. Subsequently, it was shown (4,5,6) that the decreasing rate of flow was caused by blockage of submicroscopic pit pores by extraneous materials and gas bubbles, and that filtered, gas-free water could be passed through wood at a constant flow rate. Bailey (7) found that liquid flow rate increased more than expected with increased applied pressure and attributed this to the compression and flushing out of gas bubbles restricting critical passages. A deviation in the opposite direction was observed by Sucoff (8), who found that in passing water in the axial direction through northern white cedar sapwood increases in flow rate with increased pressure differential were substantially below those predicted by Darcy's law. They considered that air blockage and pit closure were not the causes of deviation and attributed it rather to turbulence and non-linear laminar flow.

It is evident from literature that there is some uncertainty in the application of Darcy's law to all wood specimens. The present investigation was therefore designed to ascertain whether Darcy's law could be used to determine longitudinal permeability of the sapwood of Kempas (*Koompassia Malaccensis*).

EXPERIMENTAL

The apparatus constructed was identical to that detailed by Kininmonth (9), but the level of the hydrostatic pressure was automatically maintained by a carburettor float. The flow rate through the specimen was measured with a Tri-Flat flowmeter which takes ten seconds to give a reliable reading after a steady flow is established. The liquid inlet and outlet sections to the specimen were sealed between the flanges by two neoprene O-rings of 14.5 mm in diameter. The O-rings were aligned with respect to the grain in order to prevent water spillage. The specimen cell assembly was then clamped between two perspex sheets, machined to accept the glass flanges, by bolts and nuts.

All specimens were cut from the sapwood of Kempas (*Koompassia Malaccensis*), microtomed and outgassed prior to permeability measurements. To remove air from the specimens, a beaker containing the submerged specimens was placed in a dessicator and evacuated by a water-suction pump. The vacuum was released and the specimens were allowed to soak in the water. This cycle was repeated over a period of two days. Finally the specimens were left for 12 hours under vacuum. The method adopted for the deaeration of water was by ultrasonic cavitation under reduced pressure, the ultrasonic generator used being a Soniprobe, made by Dawe Instruments Ltd.

RESULTS AND DISCUSSION

It is generally considered by wood scientists that Darcy's law is obeyed with respect to length of the wood specimen. The effect of specimen length on wood permeability is shown in Fig. 1. It is apparent from the

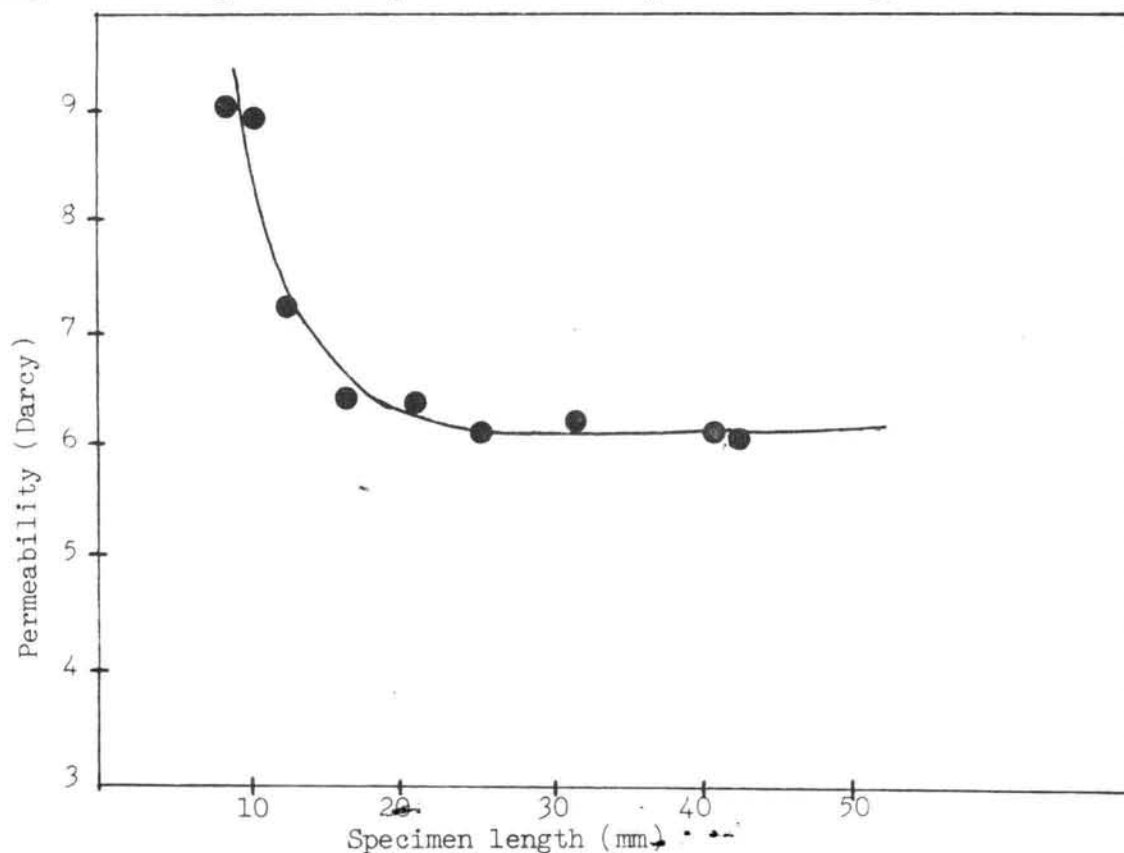


FIG. 1 PERMEABILITY AS A FUNCTION OF SPECIMEN LENGTH

curve that only specimens greater than 20 mm obey Darcy's law. Because all specimens were microtomed, water has unimpeded access to the lumens at the end faces, so that the effective permeation length is slightly less than the measured length. If the specimen is long this effect will be negligible. But, it is reasonable to assume that with shorter specimens, some of conducting paths will now offer very little resistance to flow. Consequently, in such cases, the permeability will be abnormally high as observed suggesting a deviation from Darcy's law.

Fig. 2 shows the variation in flow rate with time for a specimen whose length was 22 mm. The flow rate decreases very rapidly during the first 3 min. of flow after which the decrease continues at a much slower rate. If the direction of flow is reversed, flow would start at a rate considerably

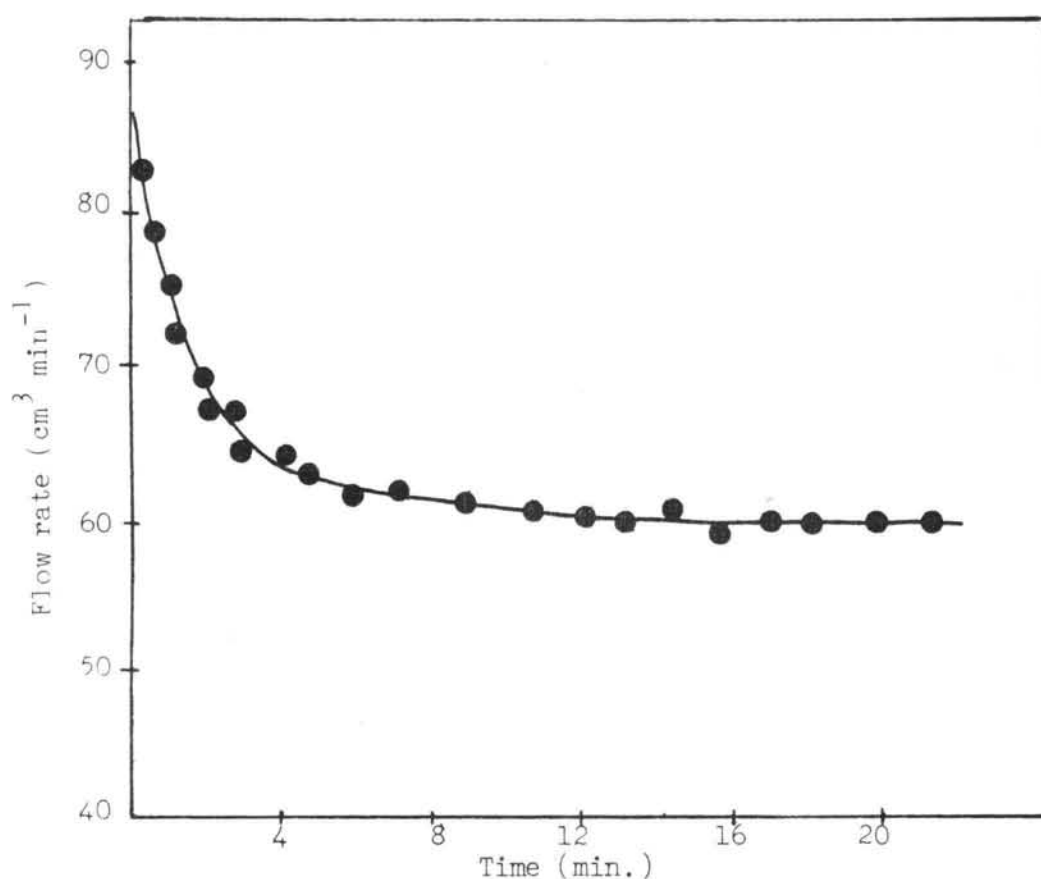


FIG. 2 FLOW RATE AS A FUNCTION OF TIME WITH DOUBLE-DISTILLED FILTERED WATER.

higher than that which prevailed just prior to reversal and then decrease in the same manner as before. These observations could be accounted for by the presence of minute particles in the water. These particles would become trapped in the pores and progressively reduce the permeability of the specimen. Reversal of the direction of the flow would remove some of the obstructions thus increasing the flow rate as observed. However when flow was temporarily interrupted, the flow rate recovered to a similar extent as when the direction of flow was reversed indicating that the decrease in flow rate with time was not due to obstructions in the flow paths caused by particles in the water.

Kelso (8) attributed the decrease in flow rate with time to the formation of air bubbles. Wood is composed of a complex series-parallel arrangement of conducting vessels with constrictions. If under conditions of constant mass flow, a constriction is placed in an uniform cylindrical conductor, the linear velocity must increase at the point of constriction. It follows from Bernoulli's principle that when the linear velocity of a fluid in a conductor is increased, the pressure is decreased accordingly. When a fluid is passed through wood, the size and distribution of the constrictions in the path of flow would similarly influence the linear velocity and pressure distribution. If the liquid contained dissolved gas, then the gas may evolve from the liquid at a constriction where the pressure is below the original saturation pressure for the gas. The resulting bubbles could then be trapped at the next downstream constriction thereby progressively reducing the wood's permeability. This explanation is

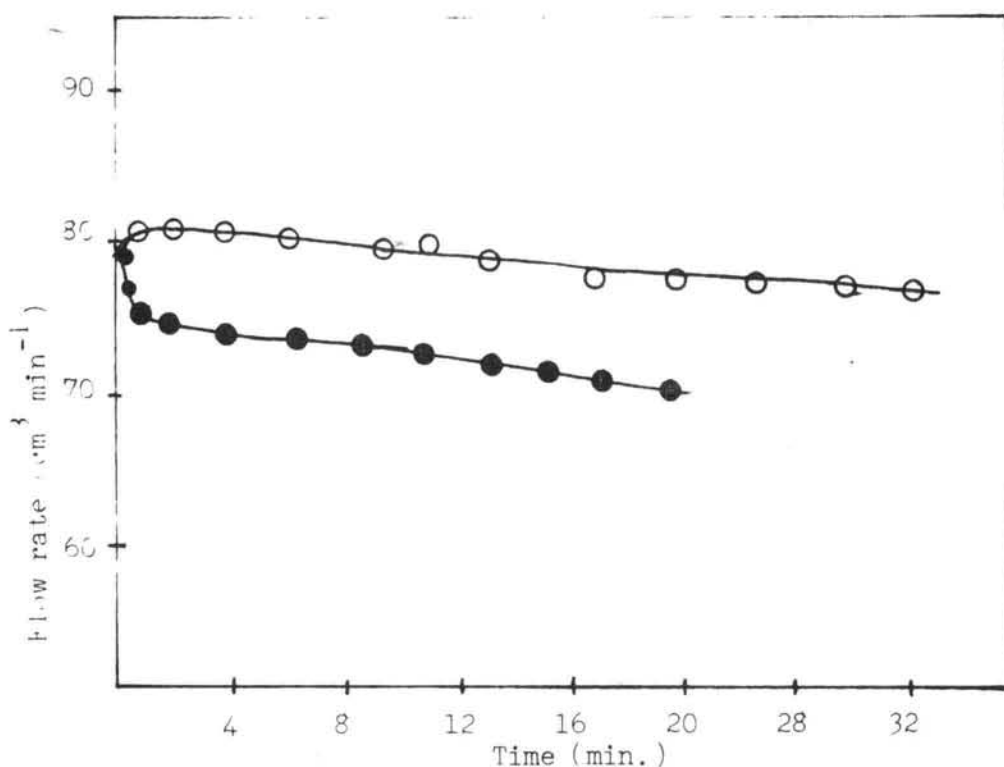


FIG. 3 COMPARISON OF THE RATES OF FLOW OF DEAERATED WATER WHICH WAS NOT DEAERATED THROUGH TWO OUTGASSED MATCHED SPECIMENS.
○ DEAERATED WATER; ● NON-DEAERATED WATER.

consistent with the results shown in Fig. 3 where the flow rates with time of deaerated water and water which had not been deaerated for two matched specimens are compared. Almost constant flow was obtained with deaerated water over a period of 30 min. The slight decrease in flow rate can be attributed to re-aeration of water during the measurements. However no explanation can currently be offered for the increase in flow rate observed in the initial region of the deaerated water plot.

Fig. 4 shows the variation in flow rate with time for a specimen that was not outgassed but where deaerated filtered water was used for permeation. The specimen was end-matched to the specimens in Fig. 3. The expected initial rapid decrease in flow rate is observed but this is followed by an increase in the permeability of the specimen. The increase in flow rate suggests that the air bubbles causing blockage of pit pores are being removed probably because of its solubility in deaerated water. However, in all cases the initial flow rate of end-matched deaerated and non-deaerated water were similar.

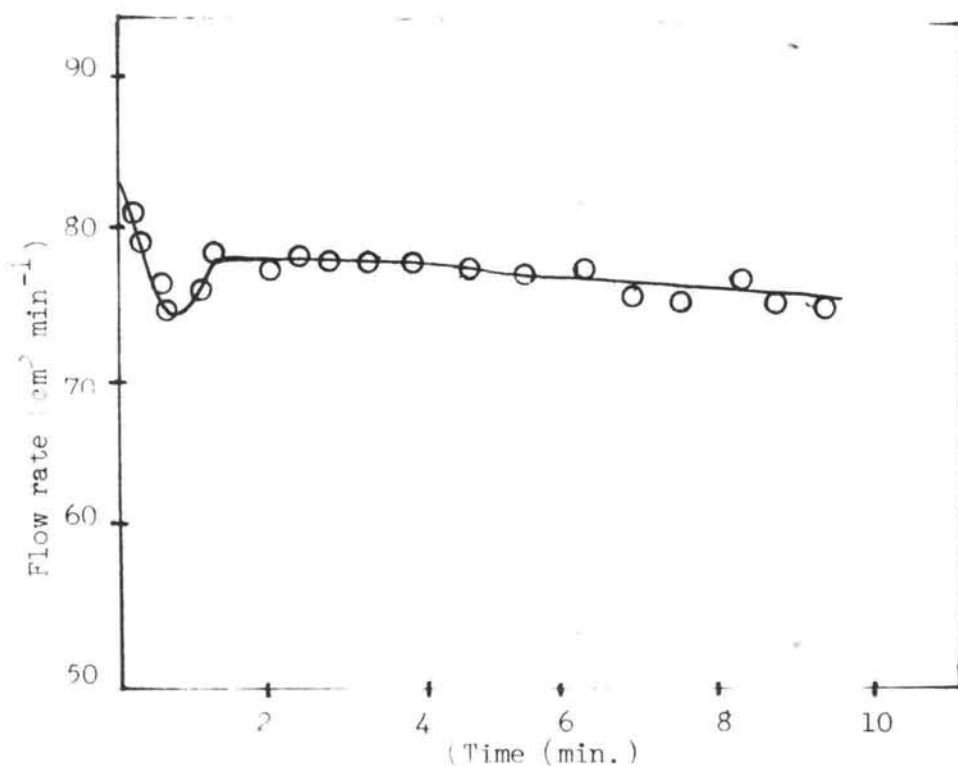


FIG. 4 FLOW RATE AS A FUNCTION OF TIME OF DEAERATED FILTERED WATER THROUGH A SPECIMEN THAT WAS NOT OUTGASSED.

The rates of flow with filtered (100 nm) and unfiltered deaerated tapwater are shown for two matched specimens in Fig. 5. The constant flow rate with filtered tapwater was similar to that obtained with double-distilled filtered water, an indication that the pore size of the pits in the specimen was in excess of 100 nm. With unfiltered tapwater the flow rate dropped to half its value in about 12 min.

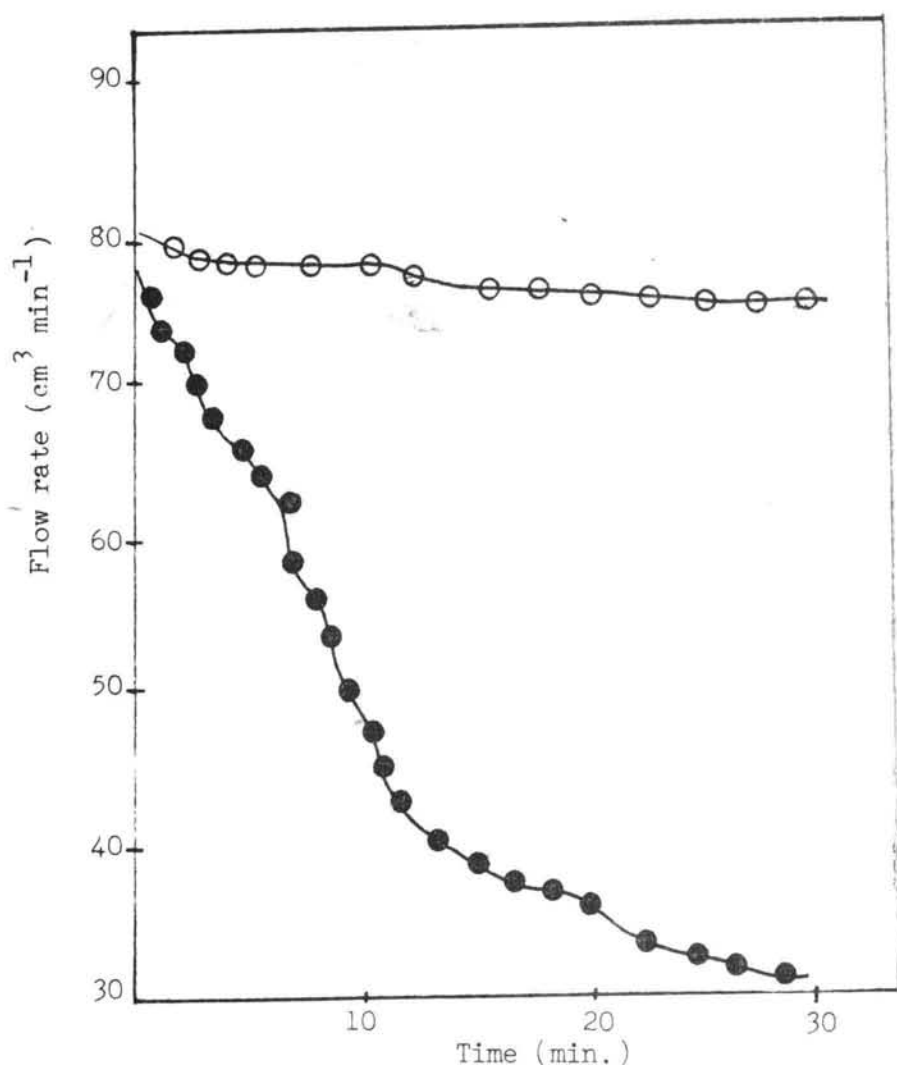


FIG. 5 COMPARISON OF THE RATES OF FILTERED AND UNFILTERED TAPWATER THROUGH TWO MATCHED SPECIMENS. ○ FILTERED TAPWATER; ● UNFILTERED TAPWATER.

CONCLUSIONS

- i. The specimens of length greater than 22 mm were found to obey Darcy's law.
- ii. With extreme care constant flow can be achieved through a degassed sample with deaerated double-distilled water.
- iii. The flow rate decreased sharply for specimens that have not been degassed or when non-deaerated water is used. However, if the degree of aeration is small, the initial flow rate is the same as it would have been if complete deaeration had occurred.
- iv. Reliable permeability values can be calculated for specimens using the initial flow rate, even if deaeration was not complete in wood or water.

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THE STUDY OF AMMONIUM BIFLUORIDE AS A FLUORINATING AGENT

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ABSTRACT

The utilization of ammonium bifluoride as fluorinating agent is relatively inexpensive and easy to handle hence worthwhile to be investigated extensively. Reactions of organochloro-silanes, -phosphorus compounds and organosulfonyl chlorides with ammonium bifluoride have been studied and the proposed mechanisms discussed.

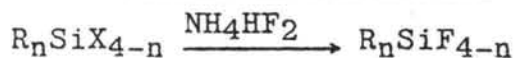
INTRODUCTION

The various applications of organic fluoro-compounds and rising demand for them stimulated the interest in searching for more versatile fluorinating agents. Ammonium bifluoride, NH_4HF_2 , readily obtainable by reacting ammonium hydroxide with hydrofluoric acid, seems to be a potential fluorinating agent though its capability in this respect has not been often reported.¹⁻⁵

Fluorination using NH_4HF_2 showed the advantages of relative low cost and simple handling of the reactions. In this work, fluorination of organochloro-silanes, -phosphorus compounds as well as organosulfonyl chlorides were investigated.

RESULTS AND DISCUSSION

Organic Silicon Fluorides

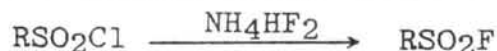


For X was a chlorine and R were some alkyl groups, the reaction gave 91-98% yield of fluorinated products under room temperature. While X was a chlorine and R were several different aryl groups, yields of 60-87% were obtained. For X was alkoxy or amino groups and the reaction was carried out in refluxing CCl_4 , 82-85% yield of products were obtained.

The less satisfactory yield of arylfluorosilanes was owing to the splitting of C-Si bonding by hydrogen chloride generated from the reaction of ammonium bifluoride and chlorosilanes. Bott⁶ had proposed a mechanism of electrophilic aromatic substitution to explain the cleavage of C-Si bond.

Carbon tetrachloride played an important role to form a complex with phenyldichlorophosphine. This complex was then reacted with NH_4HF_2 to produce phenyltrichlorofluorophosphorane¹⁰, which was further fluorinated to $\text{C}_6\text{H}_5\text{PF}_4$. Consequently, $\text{C}_6\text{H}_5\text{-P(O)F}_2$ was produced by hydrolysis of $\text{C}_6\text{H}_5\text{PF}_4$.

Organic Sulfonyl Fluorides



For this kind of compounds the rate of halogen exchange reaction was quite depending on solvent system. Sulfonyl chlorides could readily be converted to the corresponding fluorides by ammonium bifluoride in H_2O , DMSO or DMF under ambient temperature. When acetonitrile or o-dichlorobenzene was used as solvent, this conversion proceeded under reflux. Acid-binder (i.e. triethyl amine) was required to promote this fluorination reaction, in case of the solvent used was toluene or petroleum ether.

EXPERIMENTAL

Fluorination was carried out in the usual way using Pyrex flask fitted with reflux condenser on the magnetic stirrer. The analytical instruments used were

H^1 NMR: Bruker WP 80, internal TMS

F^{19} NMR: Jeol FX90Q, internal CFCl_3 or CF_3COOH (TFA)
negative chemical shifts refer to high field.

The experimental results are list on the table I - III.

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TABLE I. SYNTHESIS OF ORGANIC SILICON FLUORIDES

Reactants	Products	Solvent	Condi- tion	Rxn. Time (hr)	Yield %	^1H NMR δ_{TMS} ppm (CD_3) $_2$ CO	^{19}F NMR δ_{TFA} ppm (CD_3) $_2$ CO
CH_3SiCl_3	CH_3SiF_3	CCl_4	r. t.	0.5	98	0.66(q) $J_{\text{HF}}=4.0\text{Hz}$	-57.1(q) $J_{\text{HF}}=4.0\text{Hz}$
$(\text{CH}_3)_2\text{SiCl}_2$	$(\text{CH}_3)_2\text{SiF}_2$	CCl_4	r. t.	0.5	95	0.35(t) $J_{\text{HF}}=5.9\text{Hz}$	-55.1(heptet) $J_{\text{HF}}=5.9\text{Hz}$
$(\text{CH}_3)_3\text{SiCl}$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	r. t.	2	98	0.24(d) $J_{\text{HF}}=7.2\text{Hz}$	-80.9(decet) $J_{\text{HF}}=7.2\text{Hz}$
$(\text{CH}_3)_3\text{SiOMe}$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	reflux	2	91	"	"
$(\text{CH}_3)_3\text{SiNHPH}$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	reflux	2	85	"	"
$(\text{CH}_3)_3\text{SiNEt}_2$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	reflux	2	83	"	"
$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$	$(\text{CH}_3)_2\text{SiF}_2$	CCl_4	reflux	4	82	"	"
PhSiCl_3	PhSiF_3	CH_2Cl_2	r. t.	2	60	7.6(m), 3H 7.4(m), 2H	-66.3(S)
Ph_2SiCl_2	Ph_2SiF_2	$\text{O}-\text{C}_6\text{H}_4\text{Cl}_2$	r. t.	2	81	7.70(m)	-66.2(S)
Ph_3SiCl	Ph_3SiF	C_6H_6	r. t.	4	62	7.54(m)	-92.9(S)
Et_3SiCl	Et_3SiF	$\text{C}_6\text{H}_5\text{NO}_2$	r. t.	2	85	0.6-1.0(m)	-99.4(m)
$(\text{CH}_3)_2\text{PhSiCl}$	$(\text{CH}_3)_2\text{PhSiF}$	CCl_4	r. t.	2	87	0.45(d), 6H $J_{\text{HF}}=8.0\text{Hz}$ 7.5(m), 5H	-84.8(heptet) $J_{\text{HF}}=8.0\text{Hz}$
$\text{CH}_2=\text{CHSiCl}_3$	$\text{CH}_2=\text{CHSiF}_3$	CCl_4	r. t.	2	94	6.0-6.8(m)	-65.2(S)

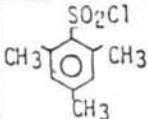
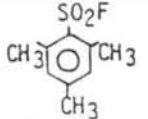
TABLE II. SYNTHESIS OF ORGANIC PHOSPHORUS FLUORIDES

Reactants	Products	Rxn. Time	Rxn. Solvent	Condi- tion	Yield %	B.P. of Products	F^{19} NMR δ_{CCl_3} ppm
$(EtO)_2\overset{O}{\parallel}PCl$	$(EtO)_2\overset{O}{\parallel}PF$	2 hr	CCl_4	r.t.	51	$78^\circ C/20mm$	$-81.55, J_{P-F}=975Hz$
$(i-PrO)_2\overset{O}{\parallel}PCl$	$(i-PrO)_2\overset{O}{\parallel}PF$	2 hr	CCl_4	r.t.	69	$82-3^\circ C/20mm$	$-78.7, J_{P-F}=973Hz$
$Ph\overset{O}{\parallel}PCl_2$	$Ph\overset{O}{\parallel}PF_2$	2 hr	CCl_4	r.t.	50	$86-7^\circ C/20mm$	$-65.7, J_{P-F}=1105Hz$
$CH_3\overset{S}{\parallel}PCl_2$	$CH_3\overset{S}{\parallel}PF_2$	2 hr	CCl_4	r.t.	40	$59-60^\circ C$	$-42.75, J_{P-F}=1142Hz$
$PhPCl_2$	$PhPF_4$	2 hr	CCl_4	r.t.	42	$132-4^\circ C$	$-55.4, J_{P-F}=966Hz$
$PhOPCl_2$	$PhOPF_2^{(1)}$	2 hr	CCl_4	r.t.	40	$124-5^\circ C$	$-44.5, J_{P-F}=1327Hz$
$EtOPCl_2$	$EtOPF_2^{(2)}$	2 hr	CCl_4	r.t.	20<	$16^\circ C$	$-49.3, J_{P-F}=1288Hz$

(1) Other trace amount of impurities were $PhOPClF$ (^{19}F δ -53.3,d), PF_3 (^{19}F δ -32.9,d), $FHP(O)OH$ (^{19}F δ -61.2,dd).

(2) Other trace amount of impurities were PF_3 (^{19}F δ -33.4,d), $FHP(O)OH$ (^{19}F δ -60.7,dd).

TABLE III. SYNTHESIS OF ORGANIC SULFONYL FLUORIDES

Reactants	Products	Solvent (Et) ₃ N	Rxn. Temp. (hr)	Rxn. Temp. (°C)	Yield (%)	¹⁹ F NMR δCCl ₃ F ppm
CCl ₃ SO ₂ Cl	CCl ₃ SO ₂ F ^{#1}	xylene	4	reflux	no	
		ether ✓	24	r.t.	no	
		H ₂ O	18	r.t.	no	
		H ₂ O+ acetone	18	r.t.	no	
CH ₃ SO ₂ Cl	CH ₃ SO ₂ F	DCB	4	r.t.	no	61.1(q)
		DCB	8	reflux	57	
		CH ₃ CN	4	r.t.	no	
		CH ₃ CN	72	reflux	64	
		H ₂ O	6	r.t.	50	
		DMSO	0.2	r.t.	89	
		DMF	0.2	r.t.	64	
o-NO ₂ C ₆ H ₄ SO ₂ Cl	o-NO ₂ C ₆ H ₄ SO ₂ F	toluene	4	reflux	trace	64.6(S)
		toluene ✓	4	reflux	75	
		H ₂ O	18	r.t.	95.3	
		H ₂ O+ acetone	18	r.t.	93.8	
p-NO ₂ C ₆ H ₄ SO ₂ Cl	p-NO ₂ C ₆ H ₄ SO ₂ F	xylene	4	r.t.	no	65.7(S)
		xylene	5	reflux	trace	
		toluene ✓	3	reflux	75	
		H ₂ O	24	40	87	
p-CH ₃ C ₆ H ₄ SO ₂ Cl	p-CH ₃ C ₆ H ₄ SO ₂ F	toluene	5	reflux	trace	65.8(S)
		toluene ✓	3	reflux	73	
		H ₂ O	24	r.t.	22	
		Benzene	14	r.t.	85	
PhSO ₂ Cl	PhSO ₂ F	xylene	5	reflux	43	65.4(S)
		xylene	4	r.t.	no	
		CH ₃ CN	4	r.t.	no	
		CH ₃ CN	72	reflux	60	
		H ₂ O	48	r.t.	73	
		DMSO	0.2	r.t.	74	
p-BrC ₆ H ₄ SO ₂ Cl	p-BrC ₆ H ₄ SO ₂ F	toluene	5	reflux	trace	65.9(S)
		toluene ✓	4	reflux	80	
		H ₂ O	20	40	94	
		xylene	5	reflux	no	67.8(S)
		Petroleum ether ✓	3	reflux	60	
		H ₂ O	20	40	89	

OCCURRENCE OF UNUSUALLY HIGH LEVELS OF
SQUALENE IN THE LIVER OF THE SHARK
CENTROPHORUS ARMATUS

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A variety of shark *Centrophorus armatus* living in the deep-sea off Sri Lanka has been found to be a good source of squalene. The liver of this species forms almost a quarter of its body weight and contains more than 80% (w/w) oil. The liver oil is made up of as much as 70-98% (w/w) squalene. The oil contains significant quantities of glyceryl ethers as well. Squalene is important commercially as it is used as an aviation lubricant and also as a cosmetic ingredient. The paper describes a rapid and reliable gas chromatographic method for the quantitative determination of squalene in shark liver oils. Isolation and identification of alkyl glyceryl ethers in *C. armatus* liver oil are also discussed.

1. INTRODUCTION

Although hydrocarbons are widely distributed in marine organisms they are generally found only as minor constituents. However, some species of shark, especially those living in deep-sea are known to contain relatively large amounts of hydrocarbons with squalene as the dominant component (1-10). For example, the sharks *Centrophorus granulosus* (1), *Centrophorus uyato* (2) and *Centroscymnus fuscus* (3) have been reported to contain as much as 80-90% of squalene in their liver lipids.

Altogether about 250 varieties of sharks are known, out of which 22 species, distributed among the four families *Orectolobidae*, *Lamnidae*, *Scyliorhinidae* and *Carcharinidae*, are found in Sri Lankan waters (11). The species *Centrophorus armatus* lives near the sea-bed, 300-475 metres deep, where the temperature of the water is about 10°C. In size, it is smaller than the common shark varieties, the average length and weight of a fully grown individual being 85cm and 1kg respectively. It has fins at the first and second dorsals, and rather large, protruding eyes.

Squalene is commercially important as it is useful as a cosmetic ingredient as well as an aviation lubricant. This paper reports on the presence of unusually high contents of squalene in the liver oil of the shark *Centrophorus armatus*, which is being commercially exploited.

2. EXPERIMENTAL

2.1 Source of Materials

Two male sharks, one mature and the other immature, of length 59.5 and 52.5 cm, and weighing 1030 and 685g respectively were used for the experiment. They were taken in the deep-sea, about 3 kilometers from the Trincomalee harbour, which is on the northeastern coast of Sri Lanka. The sharks were caught by employing the long-line technique and transported to the laboratory in ice boxes. The tissues were stored at -20°C under methanol containing 2,6-di-~~tert~~-butyl-*p*-cresol (BHT) and the lipids extracted with chloroform/methanol according to the method of Bligh and Dyer (12).

Commercial *C.armatus* liver oil obtained from two local exporters were also examined.

2.2 Thin Layer Chromatography

Analytical thin layer chromatography was carried out on plates (20x5cm) coated with silica gel G (0.1mm). The developing solvent was a mixture of petroleum ether (b.p. $40-60^{\circ}\text{C}$), diethyl ether and acetic acid (80:10:1). The components were detected by heating the plate at 105°C for 5 minutes after spraying with an ethanolic solution of phosphobolybdic acid (10%) when they appeared as brown spots in a green background.

2.3 Separation of Lipid Classes

Commercial *C.armatus* liver oil (40g) was partially separated into its component lipids by chromatography on silica gel (1kg) using petroleum ether (b.p. $40-60^{\circ}\text{C}$) containing increasing quantities of diethyl ether as the eluting solvent. Pure squalene (87.3%) was obtained with petroleum ether, but diacylglyceryl ethers ^{and} triacylglycerols eluted as mixtures (12.6%) with petroleum ether containing 10% of diethyl ether.

The diacylglyceryl ethers and triacylglycerols were separated from each other by preparative thin layer chromatography on plates (20x20cm) coated with silica gel G (0.5mm) using upto 50mg of mixture per plate. Petroleum ether containing 10% diethyl ether was used as the developing solvent, and the components were detected by viewing under ultraviolet light after spraying with an ethanolic solution of 2',7'-dichlorofluorescein (0.2%). The separated components were extracted with diethyl ether.

2.4 Gas Liquid Chromatography

Gas liquid chromatography was carried out on a Varian model 2440 chromatograph equipped with a flame ionization detector. Glass columns (1.5m x 4 mm i.d.) packed with 10% SP-2340 coated on 100/120 chromosorb W AW or 3% OV-1 coated on Gas-chrom Q 100/120 ^{were used.} The two columns were operated at 190°C and 240°C respectively, using Argon as the carrier gas.

3. RESULTS AND DISCUSSION

3.1 Size of the Liver and Oil Content

The weights of the fresh livers of the mature and immature individuals were 247g and 147g respectively, and represented 24% and 21% respectively of their body weights. The content of oil in the respective livers were 82% and 81% (w/w) as determined by the method of Bligh and Dyer. The livers were virtually bags of oil and near quantitative oil extraction could be obtained by merely cutting them up.

3.2 Characteristics of *C.armatus* Oil

Shark liver oils rich in squalene are easily distinguished from other fish oils by their rather low saponification values and extraordinarily high unsaponifiable matter content (Table I). For example, ordinary shark liver oil produced for use as a Vitamin A supplement for animals has a saponification value of 191 and unsaponifiable matter content of only 1.6%, whereas the values for *C.armatus* liver oils were 26.3-19.6 and 70.3-98.7% respectively. Low specific gravity and high iodine value are also characteristic of squalene-rich oils.

TABLE 1 : PHYSICAL AND CHEMICAL PROPERTIES OF *C.ARMATUS* LIVER OIL

	Mature ^a	Immature ^a	Commer- ^b cial 1	Commer- ^b cial 2	Ordinary ^c Shark liver oil
Specific Gravity, 30°C	0.863	0.858	0.857	0.855	0.918
Refractive Index, 30°C	1.492	1.488	1.481	1.489	1.480
Iodine Value	237	230	214	235	144
Saponification Value	20.7	21.9	26.3	19.6	191
Unsaponifiable Matter	98.7	87.3	70.3	91.6	1.6
Squalene	98.0	84.2	68.5	89.7	--

^a *C.armatus* liver oils from individual sharks

^b Bulk *C.armatus* liver oil produced for export

^c Ordinary shark liver oil produced by the
Fisheries Corporation of Sri Lanka.

3.3 Composition of *C.armatus* Oil

Thin layer chromatography of the *C.armatus* lipid showed the presence of three main components the least polar of which had mobility similar to that of hydrocarbons. The other two had mobilities indicative of diacylglyceryl ether and triacylglycerol respectively.

3.3.1 Identification of the Hydrocarbon as Squalene. Gas chromatographic analysis of the hydrocarbon fraction isolated by column chromatography showed the presence of a single component with retention times of 14.2 and 8.9 relative to n-eicosane on liquid phases SP-2340 and OV-1 respectively. On hydrogenation, it was converted quantitatively to squalane.

The infrared spectrum of the hydrocarbon showed the pattern expected of a long-chain alkene including the presence of c=c stretching vibration at 1650 cm^{-1} . Its PMR spectrum was identical with that of authentic squalene.

It has been reported that high levels of squalene in fish livers are usually accompanied by small amounts of other hydrocarbons, notably pristane (6). Careful glc analysis of *C.armatus* oil, however, failed to show any hydrocarbons other than squalene.

3.3.2 Quantification of squalene. Quantitative analysis of squalene in the oil samples was carried out by subjecting the oil directly to gas chromatography in the presence of squalane as an internal standard. 3% OV-1 was preferred as the column material as it gave sharp, fast eluting peaks for both squalane and squalene. It afforded a rapid and reliable method for quantitative determination of squalene in the oils; a glc run being complete in about 20 minutes.

The liver oils from the mature and immature *C.armatus* specimens comprised as much as 98.0% and 84.2% squalene. The two commercial samples examined had squalene contents of 68.5% and 89.7%.

3.3.3 Other component lipids. Removal of squalene from commercial *C.armatus* oil by column chromatography furnished a mixture of two components (12.6%) which were then separated from each other by preparative tlc. The more polar of the two (5.5%) was identified as triacylglycerol on the basis of its tlc mobility and infrared spectrum.

The infrared spectrum of the less polar component (7.1%) also had absorption peaks characteristic of long-chain esters (2900 cm^{-1} and 1740 cm^{-1}), but in addition displayed a sharp peak at 1110 cm^{-1} showing the presence of C-O-C groupings. Treatment with alcoholic potassium hydroxide followed by ether extraction yielded a product whose infrared spectrum did not show absorption at 1740 cm^{-1} (ester C=O), but displayed a new strong peak at 3300 cm^{-1} (O-H). On this evidence and on the basis of its tlc mobility, the component was identified as alkyl diacylglyceryl ether.

3.4 The Component Acids *C.armatus* Lipids

The fatty acid composition of *C.armatus* liver oil as well as that of its flesh lipids were examined by gas liquid chromatography on 10% SP 2340 after conversion into methyl esters (Table 2).

TABLE 2 : FATTY ACID COMPOSITION (% wt) OF *C.armatus* LIVER
AND FLESH LIPIDS

Acid	Liver	Flesh	Ordinary Shark liver oil
Saturated	(29.4)	(13.8)	(33.7)
14:0	2.0	0.7	3.3
16:0	23.8	7.1	22.3
18:0	3.6	6.0	8.1
Monoenes	(53.4)	(11.8)	(16.4)
16:1	7.8	-	1.6
18:1	40.7	11.1	11.7
20:1	3.2	0.7	1.8
22:1	1.7	-	1.3
24:1	-	-	-
<i>n</i> -6 Polyenes	(9.8)	(14.6)	(11.1)
18:2	1.6	1.0	1.0
18:3	0.3	0.1	0.9
20:3	0.6	-	0.2
20:4	2.7	10.6	3.0
22:4	1.0	2.2	0.2
22:5	3.6	0.7	5.8
<i>n</i> -3 Polyenes	(5.5)	(56.5)	(35.8)
18:4	0.2	0.1	0.3
20:4	-	-	0.4
20:5	1.3	1.6	3.8
22:5	0.9	0.8	2.8
22:6	3.1	54.0	28.5
Others	1.9	3.3	3.0

The liver oil of *C.armatus* contains much less polyunsaturated acids (15.3%) than that of ordinary shark (46.9%). Its flesh lipid (3.0% w/w), on the other hand, is rich in polyunsaturated acids (71.1%) with 22:6 *n*-3 (54.0%) dominating.

3.5 Significance of High Contents of Squalene

It appears that the presence of high levels of hepatic squalene is peculiar to sharks living in the deep-sea. The basking shark, which is caught at the surface is known to contain squalene; however, there is evidence that it may winter in deep water. The reason for the presence of such high contents of squalene is not clear, but it seems probable that it provides buoyancy as well as cold and pressure resistance to the fish living in deep-sea.

Squalene is an intermediate in the biosynthesis of cholesterol, and so it would be of great significance to know how deep-sea sharks accumulate large amounts of squalene while maintaining only slightly elevated cholesterol levels. It is conceivable that in the deep-sea sharks cholesterologenesis is blocked just beyond the step of squalene synthesis because of the lack of oxygen or other factors including co-enzymes required for cyclization.

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STRUCTURAL ASPECTS OF PHOTOINDUCED CHARGE SEPARATION
IN MICROHETEROGENEOUS MEDIA: AN ESR STUDY

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ABSTRACT

The relative location of the photoelectron in micelles was probed with various types of electron scavengers. It is observed that in the presence of Ag(I), Cu(II) and Eu(III) the lifetime of TMB cation in SDS anionic micelles increased up to 20 times. In the presence of organic additives which has been determined to reside in the organic non-polar region of the micelle, decrease the yield of the TMB cation in SDS anionic micelles.

The yield of TMB cation was observed to be much less in the vesicle systems than in the micelles. This is probably due to the further in distance of TMB solubilization site to bulk aqueous phase. Dimerization of photoionized products was observed in vesicles but not in micelles. This also decreases the yield. Both factors are evaluated for optimum charge separation.

Introduction

Photoredox reactions in microheterogeneous media has been undergone intensive research in the recent years.¹⁻⁶ This mainly stems from the fact that it could be used to harvest solar energy. The best known such system, probably the least understood, is the photosynthetic process from our nature. The initial step of photosynthesis is photoionization leading to net charge separation and thus stored the captured quanta.⁷ Rapid charge recombination after photoionization is not a practical way to store energy. Recently, it has been established that an oil/water boundary is necessary to maintain charge separation.⁸⁻⁹ The interpretation is that the excited photoelectron once transferred through the oil-water interface was captured (or hydrated) on the other side and could not return. Though the exact mechanistic step is not known, the exact rearrangement of the chromophores in the region of the oil-water phase boundary is responsible for the vectorial electron transfer. In other words, one wants to know more about the relative location, the local environment of the photoionized species, or the site where photoionization takes place. Unfortunately, very little is understood in this aspect.¹⁰

The electron spin resonance (ESR) and electron spin echo spectroscopy (ESE) are well-known for studying paramagnetic species. They are particularly adapted to the study of disordered system as exemplified by micelles, microemulsions and synthetic vesicles. We have recently shown how ESR and ESE can be successfully used to deduce the relative location of the cation of a chromophore N,N,N',N'-tetramethylbenzidine (TMB) in organized molecular assemblies.¹¹⁻¹⁵ In this paper we study the effect of various electron scavengers and monitored the yield of the TMB cation as a function of time. From the kinetics, the solubilization sites of various electron scavengers and their reduced species, we obtained structural information about the relative location of the photoelectrons. We also extend our studies into the synthetic vesicles, both anionic and cationic. We find interesting contrasts with micellar systems that give new information about the structural requirements for optimum photogenerated charge separation in microheterogeneous media.

Experimental

Micelle solutions were prepared by dissolving the surfactants in triply distilled water. The micelle concentrations were typically 0.1 M. The TMB solution was prepared by adding TMB to the micelle solution and stirring the mixture at 60 °C to help solubilizing the TMB. The TMB concentration was determined to be 0.3 mM by optical absorption with a Cary 14. The wavelength scale was calibrated with a holmium oxide filter and is accurate to ± 0.3 nm. Inorganic electron scavengers used were silver perchlorate, silver nitrate, silver sulfate, europium(III) nitrate and copper(II) sulfate. They were added to the freshly prepared TMB/micellar solutions. Organic electron scavengers used were iodomethane, acetone, benzene, dimethyl sulfoxide (DMSO), dichloromethane and iodoethane. The electron scavengers added were typically 1 mM. Deuterium oxide and deuterated compounds were used for

ESE measurements.

The vesicle solutions were prepared by dissolving the synthetic surfactants in triply distilled water, heated to 80 °C followed by sonication at 80 °C for 1 hr with a Fisher Model 300 Sonic dismembrator which was operated at 30 W with a 4 mm o.d. microtip. Typical concentrations used were 9 mg of DODAC, 6 mg of DODAB, and 6 mg of DHP, each in 1.5 mL of water.

Optical and ESR samples were prepared in a glovebag flushed with dry nitrogen. The ESR samples for room temperature measurements were contained in 75 λ pipettes, and the ESR samples for 77 K and 4 K experiments were prepared in 2 mm i.d. by 3 mm o.d. Suprasil quartz tubing. The samples were frozen in 2-3 s by plunging the sample tubes directly into liquid nitrogen. This is rapid enough that the water at a micellar surface retains a disordered, noncrystalline structure,¹¹⁻¹⁵ so it is assumed that micelle and vesicle shapes in the frozen solutions are similar to those in liquid solutions.

Photoirradiations were carried out with a 900 W high-pressure mercury lamp (Philips Model SP). A narrow band-pass filter (Corning no. 760) was used to pass light of predominantly 350 nm. The total light flux was 1.0×10^2 W/m² as measured by a radiometer. Typical irradiation times were 200 s. The ESR spectra were recorded at room temperature and at 77 K on a Varian-E4 ESR spectrometer. The ESE data were recorded at 4.2 K on a home-built pulsed ESR spectrometer that has been described.¹⁶ Most of the surfactants and the TMB were obtained from Eastman Chemicals. Dihexadecylphosphate (DHP) was obtained from Sigma Chemicals. Dioctadecyldimethylammonium bromide (DODAB) was exchanged by chloride ion to produce dioctadecyldimethylammonium chloride (DODAC).¹⁵

Results

TMB in micelles

TMB dissolves in micelles has an optical absorption maximum at 307 nm and is quite similar to TMB in ethanol.¹⁷ TMB in micelle does not exhibit any ESR spectrum. After photoirradiation for 250 s at room temperature the characteristic ESR spectrum of the TMB cation is observed. The decay of the intensity of the ESR signal is monitored as a function of time. A linear semilog plot gives a first order rate constant of $135 \times 10^{-5} \text{ s}^{-1}$. This is the initial decay rate of the TMB cation in anionic SDS micelle at room temperature, i.e. the decay rate right after the light is turned off. In the presence of Ag(I), Cu(II), and Eu(III) the initial decay rate becomes 3, 7 and $7 \times 10^{-5} \text{ s}^{-1}$ respectively. In the case of Ag(I), the rate is measured with light off since silver chemically reacts with TMB. The maximum intensity observed from these samples also differ from plain TMB sample. In the presence of Ag(I), Cu(II) and Eu(III) the maximum yield becomes 5.6, 0.60 and 4.0 times of the plain TMB sample. The halflife changes from 0.3 hr of the plain TMB sample to 8.3 hours and 2.3 hours in the presence of Ag(I) and Eu(III). TMB cation is the only paramagnetic species observed in the above samples. The expected reduced species of Ag(I) and Eu(II) are not observed. Due to the broad signal of the Cu(II), it has not been able

to determine whether the Cu(II) signal has changed.

In the presence of the organic electron scavengers, acetone, iodomethane, benzene and duroquinone, the maximum yield of the TMB cation is reduced. The maximum yield of TMB cations are 90, 80, 80, 80, and 60 % of plain TMB samples in the presence of acetone, iodomethane, benzene and duroquinone respectively. Again, TMB cation is the only radical observed.

A sample with added iodomethane froze at 77 K into a white polycrystalline solid and no ESR signal was observed before irradiation. After irradiation the sample exhibited strong green yellow phosphorescence and turned into a bright yellow polycrystalline matrix. The dominant specie is a quartet with an isotropic hyperfine splitting of 23 G and an intensity distribution of 1:3:3:1. This is identified as the methyl radical. The ESR signal of the TMB cation, though heavily masked by the methyl radical, was indicated by the yellow color of the sample.¹³ Proton spin flip lines¹⁸ were observed on the methyl radical spectra at both low field and high field of the methyl peaks in both protiated and deuterated water samples. The nearest protons to the TMB cation thus from the organic chain of the surfactant molecules rather than from the aqueous protons. This indicated that the methyl radical is residing in the organic apolar region of the micelle. This is consistent with the fact that methyl radical is nonpolar, and thus is expected to prefer the nonpolar micelle core. The ESE decay envelopes of the methyl radicals in deuterated water samples did not show deuteron modulation. This suggested that the methyl radicals is far away from the bulk aqueous surrounding.¹¹⁻¹⁴

Deuterated iodomethane added samples after irradiation displayed the characteristic spectrum of a deuterated methyl radical, a septet with an intensity distribution of 1:3:6:7:6:3:1. Here the TMB cation is clearly observed since the deuterated methyl radical is too narrow to mask the broad TMB cation signal. When iodoethane was added, the corresponding ethyl radical was produced after irradiation.

The experiment is repeated with TMB in cationic DTAC micelle. The yield of the TMB cation at room temperature is approximately 33 times weaker than in the anionic SDS micelle. This goes to the detection limit of the spectrometer and thus no experiment with the added electron scavengers were attempted.

TMB in vesicles

TMB dissolved in vesicle solutions has an optical absorption maximum at 313 nm which is more close to TMB in benzene. TMB in vesicles do not exhibit any ESR signal before irradiation. After photoirradiation at 350 nm at room temperature, the colorless solution turns pale yellow. This color fades away in a couple of hours in both cationic and anionic vesicle solutions. Thus the yellow color after photoirradiation denotes a relatively stable product. No such color changes were observed in the absence of TMB. The same color changes occur in micellar solutions where the oxidation product was confirmed by optical absorption and by ESR to be the TMB radical cation.¹¹⁻¹³ Optical absorption spectrum is slightly different from the usual TMB cation spectrum. The cationic DODAC vesicle shows the characteristic TMB cation spectrum overlapping with a broad peak at 385 nm. The assignment of the TMB radical cation was later confirmed with ESR. At shorter

photoirradiation times the 385 nm peak decreases relative to the TMB cation peaks. The anionic DHP vesicle solution behaves similarly except the intensity was only 30 % as intense as in the cationic DODAC vesicles.

The vesicle solutions containing TMB rapidly frozen to 77 K formed a white polycrystalline matrix. After photoirradiation, it gives strong phosphorescence in green and changes to a yellow matrix. These characteristics are the same as observed for frozen micellar solutions containing TMB. ESR spectrum again displays the familiar TMB cation radical. The yield of the TMB cation was approximately 2 times more for the cationic DODAC than the anionic DHP vesicles.

ESE studies at 4.2 K observed that the TMB cation-water interaction is much weaker in the vesicle when compared to the micelle. It is approximately 25 % weaker than the micelle.

Discussion

We first look at the effect of added inorganic electron scavengers in the TMB/micelle systems. The kinetic studies clearly show the effect of these added ions. In the presence of these ions, the initial decay rate decreases from 135 to $3 \times 10^{-5} \text{ s}^{-1}$. The decay rate decreases a factor of 20 times. The maximum yield of TMB cation is also increased to roughly 4 and 6 times. This suggests that the photoejected electron is scavenged by the metal ions to prevent some back reaction with the TMB cation. This agrees well with previous workers.¹⁹⁻²⁰ The interpretation is that the photoionization takes place in the organic core of the micelle. The photoelectron is ejected from the apolar core to the polar bulk aqueous phase and is rapidly hydrated. Some recombination reaction of the hydrated electron with the parent cation inside the micelle core is prevented by the negative micellar surface potential of the anionic micelle. Our ESR studies at room temperature gives physical supporting evidence for this model. The expected paramagnetic products, $\text{Ag}(0)$ and Eu(II) , are not stable at room temperature and so can only be inferred by ESR. The black precipitates observed indicated the formation of clusters of reduced Ag(I) .²¹ The kinetic study and maximum yield also inferred competing process of the Eu(II) with the photoelectron.

The sample with added Cu(II) shows a slight decrease in the maximum yield of the TMB cation. This could be due to the fact that Cu(II) has a high degree of being solubilized on the micelle surface.²² The adsorbed Cu(II) ions are at a much closer distance to the TMB cation than when in the bulk aqueous phase. Thus the Cu(II) ions that captured the photoelectrons are capable of back donating the electrons to the TMB cations. It has been reported that the back donation of the photoelectron from Eu(II) to TMB cation is observed in methanoic solution.²⁰ Similar reaction may take place in the micelle. Thus Cu(II) acts as a mediator for the back donation thus enhancing the back reaction rather than blocking it. Therefore the observed maximum yield of the TMB cation is lowered in the presence of Cu(II) .

Proton spin flip lines arise from dipolar interactions with neighboring protons.¹⁸ Since it is observed on methyl radicals in deuterated water samples, the protons are from the organic chain of the micelle rather than from protons of the bulk aqueous phase. This

suggests that the location of the iodomethane is in the organic region of the micelle. ESE decay envelopes do not show deuteron modulation in deuterated water samples again confirms this. The lack of linewidth change of the methyl radical lines on going from protiated to deuterated water samples further strengthened this assignment. Back donation from the reduced organic scavengers to the TMB cations is thus enhanced by the close distance of the organic scavengers to the TMB. This is actually what is observed. All added organic scavengers lower the yield of the TMB cation.

The two types of electron scavengers form a self consistent picture. Both provides physical evidence to support the model that the photoelectrons leave the micelle core after photoionization.

Photoionization of TMB in the vesicle solutions at room temperature generates a low concentration of the stable TMB cation radical based on the optical and ESR spectra. But, in addition, another species with $\lambda(\text{max})=385 \text{ nm}$ appears to be formed. Based on recent reports, these other species are probably the nonparamagnetic diamine-diimine charge-transfer complex which formed from two TMB cation radicals.²³ Because of the large number of TMB molecules per vesicle, it seems possible that two TMB cations may be formed in some vesicles. This is supported by the decrease of the 385 nm peak relative to the TMB cation peaks at shorter irradiation times. In other vesicles only one TMB cation is formed and so is stabilized as such. In frozen solutions TMB cation is localized at its formation site and formation of the charge-transfer complex does not occur.

The average environment of TMB in micelle and vesicle systems is different as suggested by the ESE spectroscopy. The weaker cation-water interaction in vesicles when compared to micelles suggests that the average interaction distance between TMB cation and the nearest solvent water molecule is greater in the vesicle systems. This indicates that there is less water penetration into the vesicle surface than into the micellar surface. Therefore TMB is in a worse environment for hydrogen bonding in the vesicle system as compared to the micellar system. This explains the observation that the absorption maximum of TMB in vesicle is at shorter wavelength than in the micelles. A semiquantitative evaluation of the cation-water interaction indicates a TMB cation to solvent water interaction distance of 0.5-0.6 nm.

Finally we look at the yield of the TMB cation. The yield of the TMB cation is the net permanent chemical change, i.e. the net charge separation maintained. The yield is much lower in the vesicle systems than the micelles. Base on the structural information obtained from this studies, the reason is two fold. Firstly the TMB solubilizing site is approximately 20 % further away from the bulk aqueous phase in the case of vesicles as compares to micelles. This lowers the chance of photoionization. It is partly due to the 20 % more distance required from the photoejected electron, in order to transport accross the oil/water interface and get hydrated in the other side. Secondly dimerization of the photoionized species also brings the yield down. The micelle systems is slightly superior in this aspect. The small size of the micelle shortened the travel distance of the photoelectrons. The compartmentalization of the micelles limit the number of chromophores per micelle and thus reduce the chance of dimerization.

Structural Aspects Of Photoinduced Charge Separation In Microheterogeneous Media: An ESR Study

Conclusion

The present study provides physical evidence for supporting the model that photoelectrons leave the micelle after photoionization. From the point of view of charge separation, the micelle systems are structurally superior than the vesicles. A travel distance of 0.4-0.5nm from site of photoionization to oil/water interface is probably the limit for efficient charge separation in these organized molecular assemblies.

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A NEW METHOD OF REDUCTIVE DEHALOGENATION OF ARYL AND ALKYL HALIDES BY LITHIUM ALUMINIUM HYDRIDE

Goh Swee Hock

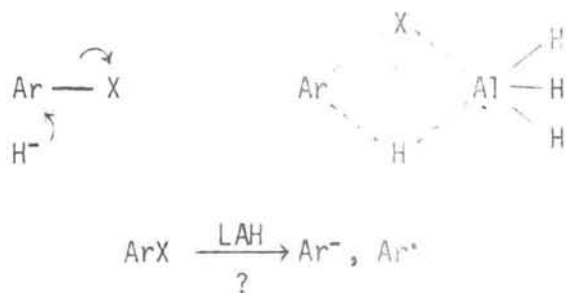
University of Malaya, Malaysia.

The reduction of aryl halides by lithium aluminium hydride proceeds via formation of radical and/or carbanion intermediates. A photochemical procedure is developed for the reduction of various halo compounds including aryl chlorides and fluorides, vinyl bromides, neophyl chloride and 2,7-dichloronorcaradiene, all of which are normally difficult to be reduced by other methods.

Among the complex hydrides, lithium aluminium hydride (LAH) is one of the most versatile of reducing agents capable of reducing a variety of functional types. The reagent is known to reduce some organic halides and recently this was reappraised by Krishnamurthy and Brown (1). Although the reactivity pattern for aliphatic halides ($RI > RBr > RCl$; allylic $> 1^\circ > 2^\circ > 3^\circ$; sec-butyl $\gg$ neopentyl; cyclopentyl $>$ cycloheptyl $>$ cyclohexyl) appears to favour a simple SN_2 -type of reaction, the substantial reactivity of aryl, vinyl and cyclopropyl halides (which are normally resistant to SN_2 attack) is very surprising. Despite previous reports (2,3) that aryl bromides undergo uncatalysed reduction conveniently, the reaction should more appropriately be described as erratic. For example, p-bromotoluene has been reported (2) to be only 7% reduced by LAH in tetrahydrofuran at 65° after 24 h but Bondjonk (4) found a 20% reaction at 25° after 24 h. Curiously however, the reduction can be accelerated by ultrasound irradiation.

Brown (1,3) who first explored the reaction extensively considered broadside SN_2 and four-centre mechanisms (Scheme 1). Chung (5) detected carbanion and radical formation while Singh (6) also found radical cyclization products. The detection of radicals is one thing but the overall significance of radicals in the reaction may be a different matter. LAH reductions may give inconsistent results, e.g. the reduction of o-allyloxybromobenzene gave variable amounts of radical cyclization product.

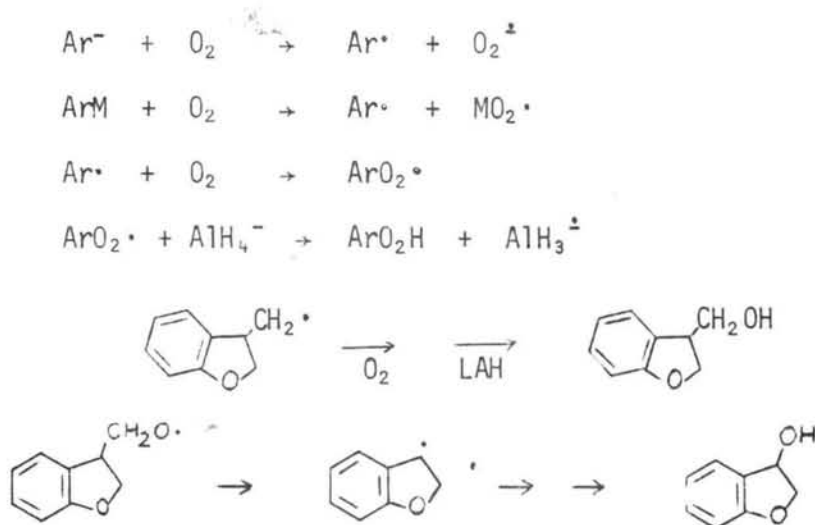
SCHEME 1. PREVIOUSLY POSTULATED MECHANISMS



A careful examination into the mechanism of the reduction was carried out especially to monitor carbanion and radical formation and the

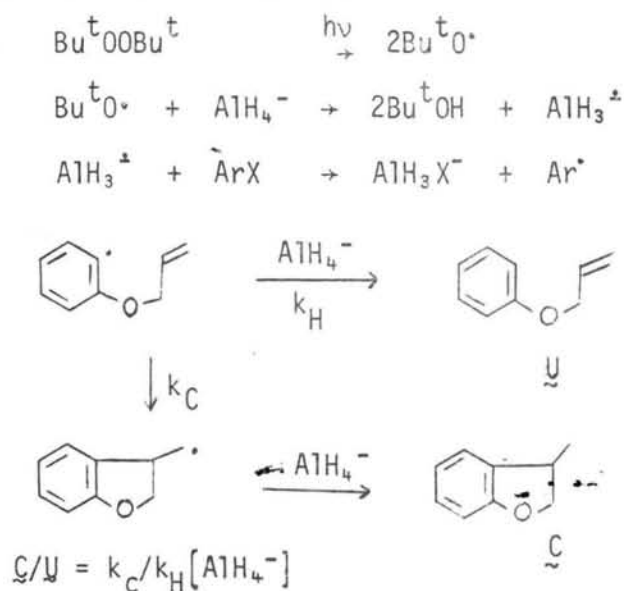
results are summarised in Table 1. Under nitrogen, the amount of cyclization (radical formation) was small but the large amount of deuterium incorporation indicates anion (or arylmetal species) formation. The presence of oxygen (or air) causes the rate to increase and the radical cyclization product also increases considerably (Table 2). The participation of oxygen as illustrated in Scheme 2 shows the generation of aryl radical and alane radical ion $\text{AlH}_3^\pm$. The presence of oxygen also gives rise to O_2 -trapped products which are as shown.

SCHEME 2. INITIATION BY OXYGEN AND OXYGENATED PRODUCTS



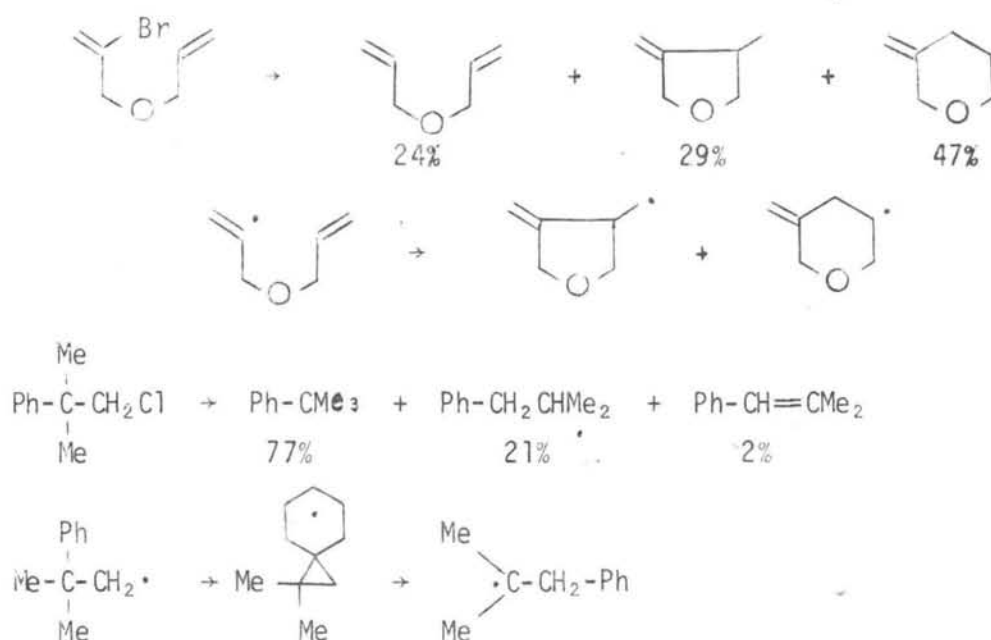
Having clarified the problems associated with the LAH reductions, an improvement can be incorporated into the reduction by the use of suitable radical initiators. This was carried out by the photolysis of di-tert-butyl peroxide in the reaction and results obtained are shown in Table 3. These are in good accord with the mechanism shown in Scheme 3. The expected increase in the ratio C/U with decreasing concentration of lithium aluminium hydride was observed.

SCHEME 3. MECHANISM OF REACTION



The photostimulated reduction was extended to a variety of organic halides and excellent results were obtained (Table 4). Aryl halides including fluorides were reduced in good yields and reactivity was of the expected order $\text{ArI} > \text{ArBr} > \text{ArCl} > \text{ArF}$. Nuclear substituent effects were small. Aliphatic halides including cyclopropyl halides were similarly reduced. The reduction of allyl 2-bromoallyl ether and neophyl chloride gave cyclisation and 1,2-rearrangement products respectively as illustrated in Scheme 4.

SCHEME 4. RADICAL CYCLISATION AND REARRANGEMENT



The results presented in this paper resolves most of the controversies (7) surrounding lithium aluminium hydride reductions of organic halides and the procedure developed paves the way for the convenient dehalogenation of most organic halides encountered in organic synthesis (8).

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TABLE 1. REDUCTIONS OF O-ALLYLOXYBROMOBENZENE AND 4(O-BROMOPHENYL) BUTENE-1.

X	[LAH]/M	Time/h	Yield/%	C/U*	Quench	U-d ₁	C-d ₁
O	1.2	28	18	0.03	D ₂ O	91%	-
O	0.95	64	34	0.3	D ₂ O	69%	0%
O	0.5(LAD)	64	17	0.1	H ₂ O	19	71
					D ₂ O	91	76
CH ₂	0.4(LAD)	67	47	0.2			

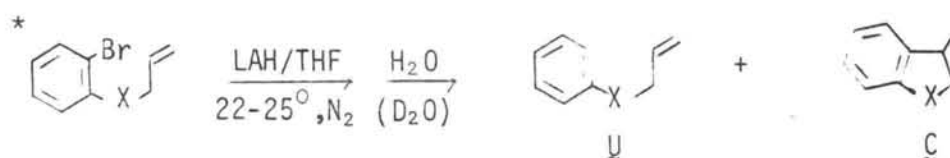


TABLE 2. EFFECT OF OXYGEN

X	[LAH]/M	Conditions	Time/h	% Reaction	C/U*
O	0.95	N ₂ , air	26	33	0.02
		admitted after 26h	28	40	0.2
O	0.95	limited air	21	100	2.5
O	1.0	1 equiv. O ₂	0.5	23	1.5
			2.0	56	1.8
			22	100	2.6
CH ₂	0.26(LAD)	limited air	8	47	1.4

* Reactions as shown in footnote of Table 1.

TABLE 3. PHOTOLYSIS OF O-ALLYLOXYBROMOBENZENE WITH DI-TERT-BUTYL PEROXIDE IN TETRAHYDROFURAN.

[LAH]/M	Time/h	Reaction/%	C/U ^a	Quench	U-d ₁	C-d ₁
1.0	1.6	100	2.2	D ₂ O	8	1
(1.0) ^b	1.0	14	0.7			
0.85	1.5	78	3.1			
0.09	1.5	23	5.7(8.1) ^c	D ₂ O	30	0
0.6(LAD)	1.3	65	4.3	D ₂ O	81	80
				H ₂ O	n.d. ^d	80

^a Cyclised and uncyclised products as in footnote of Table 1.

^b Without di-tert-butyl peroxide

^c Corrected for 30% U-d₁

^d Not determined

TABLE 4. PHOTOSTIMULATED REDUCTIONS BY LITHIUM ALUMINIUM HYDRIDE^a

Halide	Time/h	Product	Yield/%
p-Iodoanisole	1.5	Anisole	100
o-Bromoanisole	1.5	Anisole	86
o-Allyloxybromobenzene	2.3	Mixture ^b	96
p-Bromochlorobenzene	1.0	Chlorobenzene	92
p-Bromo-N,N-dimethylaniline	3.0	N,N-Dimethylaniline	93
p-Fluoroanisole	1.9	Anisole	93
p-Fluorotoluene	1.9	Toluene	90
7,7-Dichloronorcarane	0.5	Mixture ^c	93
Chlorocyclohexane	2.5	Cyclohexane	72
Allyl 2-bromoallyl ether	2.0	Mixture ^d	53
Neophyl chloride	3.0	Mixture ^d	91

^a Reactions were carried out with the halides dissolved in clear 1M solutions of LAH in tetrahydrofuran containing di-tert-butyl peroxide and irradiated by a high pressure Hg lamp.

^b Refer Table 3 for product distribution.

^c Mixture of norcarane (10%), *syn*-7-chloronorcarane (65%), and *anti*-7-chloronorcarane (25%); yield of norcarane increased for longer reaction times.

^d Refer Scheme 4 for product ratios.

SULPHUR COMPLEXES OF THE TRANSITION METALS WITH SPECIAL REFERENCE TO CHROMIUM

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ABSTRACT

The preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ (1) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5(\text{S}_2)$ (2) from the facile reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ with elemental sulphur, together with their structural features, will be discussed, against a brief background review of available synthetic methods and known structural types of transition metal sulphur complexes. The significance and implications of this area of sulphur research will be noted.

INTRODUCTION

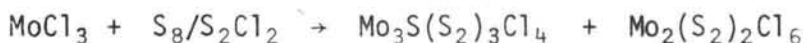
Complexation of diatomic molecules eg. O_2 , N_2 , CO , NO , CN^- , is a subject of continuing research interest, because of its biological and catalytic implications. In the last decade, this area has been extended to cover the S_2 ligand, which shows a remarkable versatility in bonding modes and thus demonstrates a great potential in the synthesis of new metal cluster complexes.¹ So far most of the work has been focussed on Fe, Mo and Mn, for obvious biochemical reasons. Thus the interest in Fe-S clusters lies in their potential applications as models for the active site in non-heme iron proteins such as the ferredoxins. In fact the Fe_4S_4 -cubane geometry of $[(\text{C}_5\text{H}_5)\text{FeS}]_4$ and $[(\text{RS})\text{FeS}]_4^{2-}$ are found in the $[(\text{RS})\text{FeS}]_4$ units in the ferredoxin from *peptococcus aerogenes*.² Likewise a lot of Fe-S and Mo-S chemistry is aimed at unravelling the nature of the enzyme nitrogenase which converts N_2 to NH_3 under normal conditions and is now known to contain 2 proteins, one of which is an Fe protein (the electron carrier) containing subunits of 4Fe-4S clusters and the other a MoFe protein (the reaction carrier) with 2 Mo, about 32-33 Fe and 27-32 "labile" S atoms.³

Sulphur complexes of the rest of the transition elements, other than Fe and Mo, are only occasionally reported.¹ Here in our laboratories, I have chosen to investigate the reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ with elemental S_8 for two main reasons. First, despite much work on Mo-S₂ systems (for reasons mentioned above) sulphur complexes of Cr and W, the lighter congeners of Mo in Group VIA are unknown.* Secondly, by virtue of its very long Cr-Cr bond as shown by Cotton's X-ray structural analysis,⁶ $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ is much more reactive than $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$, as demonstrated by its reaction with $\text{P}(\text{OMe})_3$.⁷ The reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with S_8 in refluxing C_6H_6 for 16h., has been reported to give only an unidentified insoluble polymeric material.⁸ It would be interesting therefore to study the reactivity of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ towards S_8 .

SYNTHESES OF SULPHUR COMPLEXES

Disulphur complexes can be prepared by various methods, which can be grouped together under five main classes of reactions,¹ namely, via.

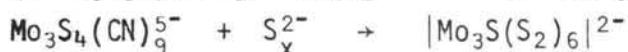
- a) a positive S₂ group (agent: $\text{S}_2^{2+}\text{Cl}_2$ or $\text{S}_8/\text{S}_2\text{Cl}_2$), e.g.



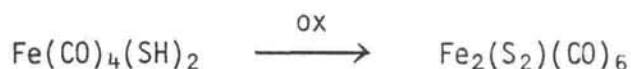
- b) a neutral S₂ group (agent: S_8), e.g.



- c) a negative S₂²⁻ group (agent: S₂²⁻ in polysulphide) e.g.



- d) oxidation of S-containing ligands, e.g.



* During the course of this work the W analogues of some Mo-S₂ complexes⁴ and the first Cr-S₂ complex⁵ were reported.

e) other S-containing reagents e.g.

H_2S , P_4S_{10} , COS , Na_2S_4 or Na_2S , R_2S_x and Na_2SO_3 .

In recent years, method (b) has been found to lead to many new S_2 complexes.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr(CO)}_3]_2$ with S_8

Unlike most reactions of cyclooctasulphur with transition metal complexes, which require either thermal or photochemical activation for prolonged periods,^{4,9} it is found that $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3]_2$ reacts instantaneously with S_8 at ambient temperature. A deep green solution of $[\eta^5\text{-C}_5\text{H}_5\text{Cr(CO)}_3]_2$ in THF or toluene under nitrogen with 1/8 equivalent of S_8 turned immediately to a greenish brown solution from which was isolated $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ (1), as air-stable dark green needle-shaped crystals (m.p. 111-112°) in 100% of isolated yield. With 2/8 equivalent or more of S_8 , a deep reddish brown solution resulted, from which was isolated $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5(\text{S}_2)$ (2), as fine dark brown air-stable crystals in 90% yield. The product crystallised as dark-brown rectangular prisms with curved faces from THF/pentane after ca. 20 days at -78°. Both complexes have been characterised by total elemental, complete spectral and X-ray diffraction analyses.¹⁰

STRUCTURES OF S_2 COMPLEXES

Structural Variety

The remarkable versatility of S as a ligand has resulted in a variety of bonding modes and hence a variety of structures, conventionally classified by Muller¹ as types Ia, IIa and IIb, III and IV, illustrated in Table I below. Modifications of these structures arise from the ability of the remaining one pair of electrons on S to coordinate to additional metal atoms.

TABLE I: STRUCTURAL TYPES OF S_2 COMPLEXES¹

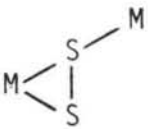
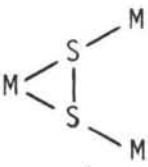
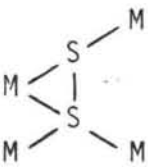
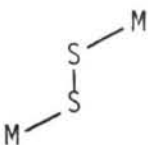
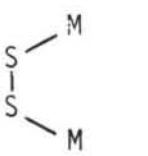
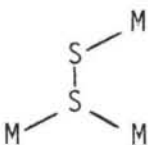
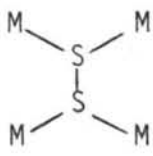
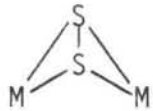
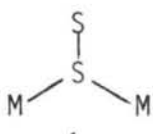
Type	Structure	Example
Ia		$[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$
Ib		$[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$ $\text{Cp}_2\text{Fe}_2(\text{S}_2)_2(\text{CO})$
Ic		$\text{Mn}_4(\text{S}_2)_2(\text{CO})_{16}$
Id		$\text{Mn}_4(\text{S}_2)_2(\text{CO})_{16}$
IIa		$[(\text{NH}_3)_5\text{Ru}(\text{S}_2)\text{Ru}(\text{NH}_3)_5]^+$
IIb		$\text{Cp}_2\text{Fe}_2(\text{S}_2)(\text{SEt})$
IIc		$\text{Cp}_4\text{Co}_4(\text{S}_2)_4\text{S}_2$

TABLE 1 (continued)

Type	Structure	Example
IIId		$\{\text{SCo}_3(\text{CO})_7\}_2(\text{S}_2)$
III		$[\text{Mo}_2(\text{S}_2)_6]^{2-}$, $\text{Fe}_2(\text{CO})_6(\text{S}_2)$
IV		$\text{Cp}_2\text{Cr}_2(\text{S}_2)_2\text{S}$

Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$ (2)

The complex (2) with a structure as shown in Fig. 1, is the first example of a Cr-S complex based on the Cr_2S_2 unit. The most outstanding feature is the simultaneous end-on and side-on bonding of the S_2 ligand, i.e. S_2 functions as an unsymmetrical bridge between the two Cr atoms, S1 being bound to both Cr1 and Cr2 [Cr-S = 2.348(2) and 2.466(2) Å respectively] while S2 is bound only to Cr1 [Cr-S = 2.399(2) Å]. This bonding feature, of type Ib in Müller's classification is the first of its kind for a Cr complex and the third of its kind among the transition metals. The two previous examples were $[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$ which possesses four such (S_2) groups. [S-S = 2.048(7) Å av., Mo-S = 2.465(5)-2.492(5) Å]¹¹ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{S}_2)_2(\text{CO})$ [S-S = 1.993(8) Å av., Fe-S = 2.230(6)-2.293(6) Å]⁹. The S-S distance in (2) [2.009 Å] is close to the above values and to that in octasulphur S_8 [2.060 Å]¹². The coordination geometry around Cr2 is of the 4-legged piano stool type with the metal atom having an $18e^-$ configuration completed via one $6e^-$ and four 2-electron donor ligands. In contrast, Cr1 is electron deficient ($16e^-$) and is best envisaged as having a 3-legged piano-stool coordination geometry as found in $(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$ ¹³ with a single $\pi(\text{L})\text{-d}(\text{M})$ σ -bond to the η^2 -bonded S_2 group.

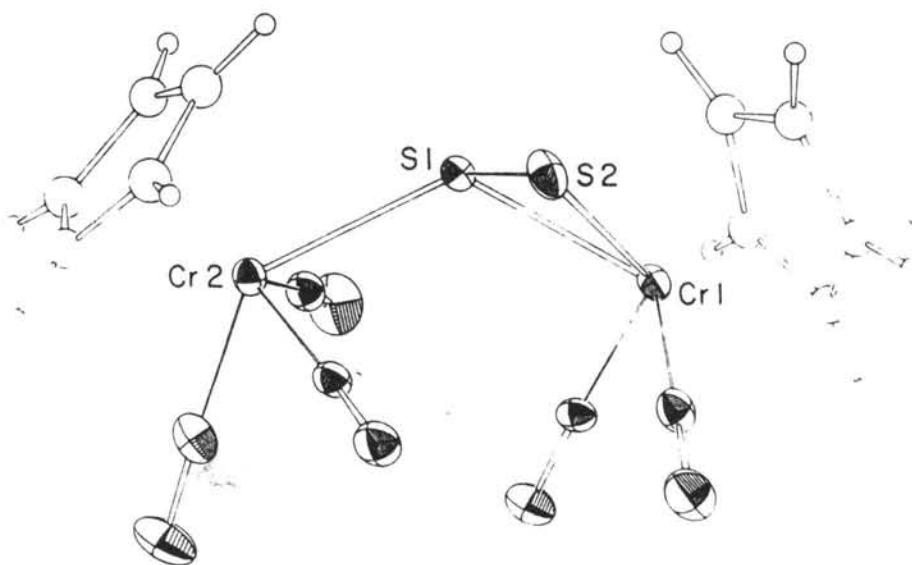


FIG. 1: Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$, (2). Bond angles at sulphur are: $\text{Cr1-S1-Cr2} = 125.8(1)^\circ$, $\text{Cr1-S1-S2} = 66.3(1)^\circ$, $\text{Cr1-S2-S1} = 63.7(1)^\circ$, $\text{S1-S2-Cr1} = 50.1(1)^\circ$, $\text{Cr2-S1-S2} = 115.5(1)^\circ$.

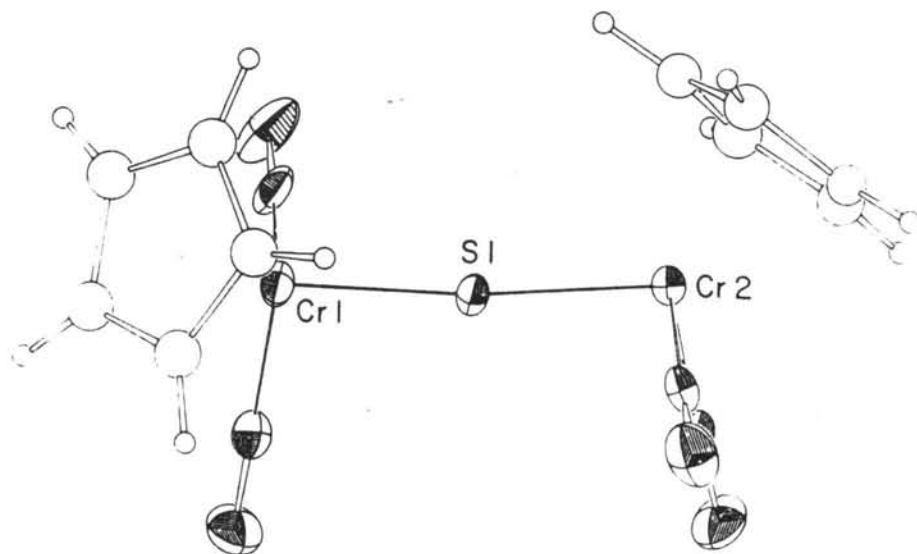


FIG. 2: Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$, (1). Bond angle at sulphur: $\text{Cr1-S1-Cr2} = 174.4(1)^\circ$.

Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ (1)

In (1), as shown in Fig. 2, the two Cr atoms are linked by a single $\mu\text{-S}$ bridge, the ligand arrangement about each metal atom being of the 3-legged piano-stool type.¹³ This is the first example of a binuclear Cr complex based on the Cr_2S unit, i.e. a *single* bridging S. The Cr- μS distances [2.067-2.076Å] are noticeably shorter than those in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$ [av. 2.238Å]⁵. Indeed, the Cr_2S unit [Cr-S = 2.072Å av., Cr-S-Cr = 174.4° av.] is structurally very similar to the Mo_2S unit in $[(\text{CN})_6\text{MoSMo}(\text{CN})_6]^{6-}$ ¹⁴ [Mo-S = 2.173Å & Mo-S-Mo = 169.50°], and as in the Mo complex, the unusually short Cr-S bonds are probably due to the presence of S $\rightarrow$ M π -bonding interactions.¹⁵ The parallel-antiparallel dispositions of the carbonyl groups are also consistent with the presence of Cr-S double-bonding. The observation of a single ^{13}C (CO) resonance in both the 25° and 183°K NMR suggests that the barrier to rotation about the Cr-S-Cr axis is small.

It is of interest to compare the metal-sulphur bonding features of these Cr-S complexes with those of other S complexes of Group VIA elements (Fig. 3). It will be noted that the bonding mode of S in (2) is not observed at all in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$, the only other reported S complex of Cr,⁵ nor in any of the other Mo or W complexes in Fig. 3. Instead, there is a strong structural resemblance between $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2\text{S}_4$.⁴ Both molecules contain a planar arrangement of S atoms perpendicular to the metal-metal bond and parallel to the two $(\eta^5\text{-C}_5\text{Me}_5)$ planes, and both contain S in similar bonding modes, namely, a $\mu\text{-}\eta^2\text{-S}_2$ bonding mode (side-on bonded disulphur bridging two metal atoms) and a $\mu\text{-S}$ bonding mode (bridging two metal atoms). The Cr complex, however, has an additional novel $\eta^1(\mu\text{-S},\text{S})$ ligand with one uncoordinated S atom. The other two complexes in Fig. 3, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}_2\text{S}_3$ ⁴ and $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{MoS}_2]_2$,¹ which possess very similar structures, again show very little resemblance to (1), other than the presence of $\mu\text{-S}$ bridging ligands and the anti-parallel disposition of the M-CO and/or M-S groupings in all of them.

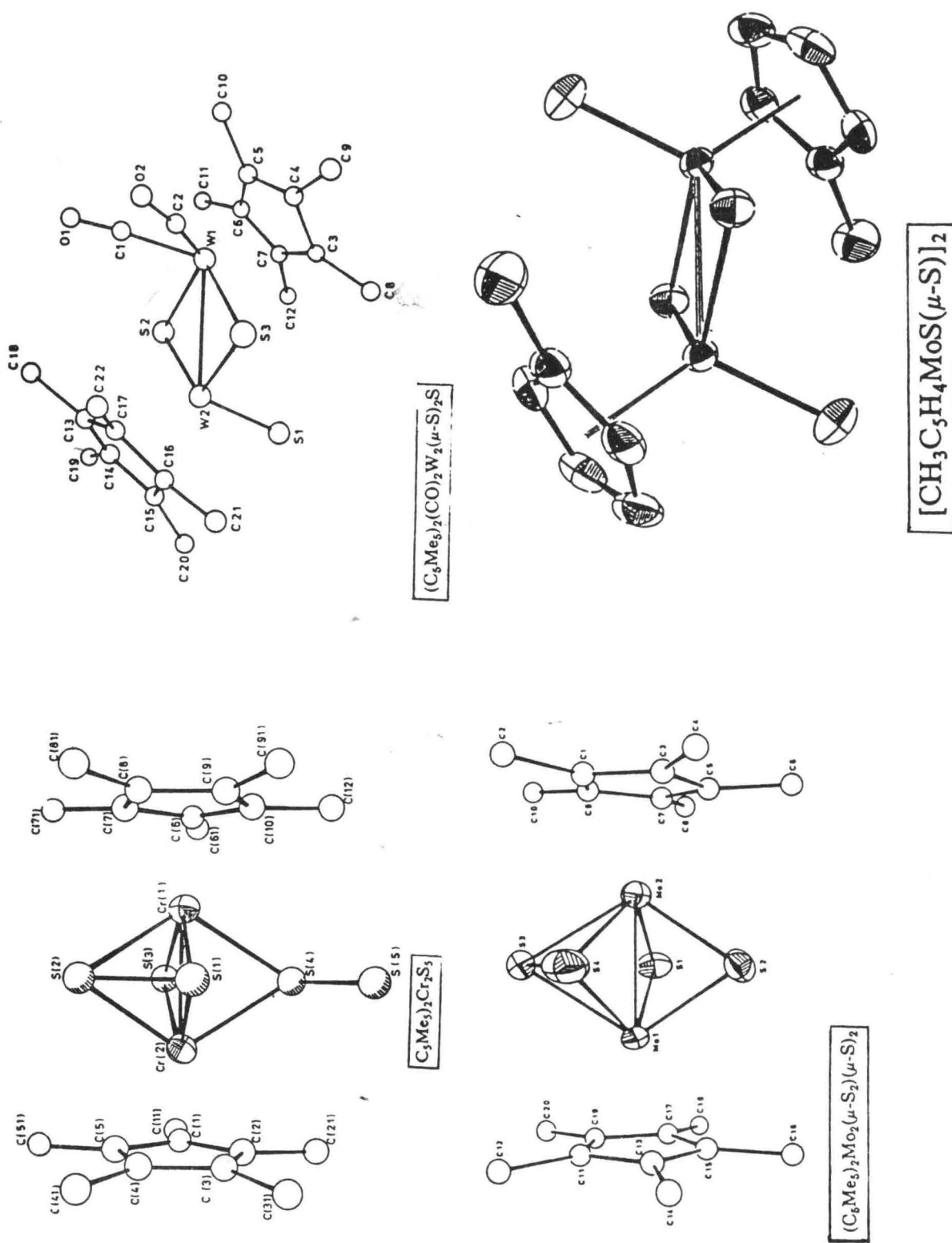


FIG. 3: MOLECULAR STRUCTURES OF SOME SULPHUR COMPLEXES OF GROUP VI METALS.

CONCLUSION

The new complexes described above reemphasise the versatile manner in which sulphur can bond to transition metals, resulting often in complexes with novel interesting structural features and indicate again the often-demonstrated potential of sulphur in the generation of high nuclearity clusters,¹⁷ particularly of mixed metals, which promise to be of both biological and catalytic importance. Apart from this, the unusually facile reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ with S_8 shows considerable potential for application in desulphurisation reactions.

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NEW NATURAL PRODUCTS FROM MALAYSIAN TERMITES

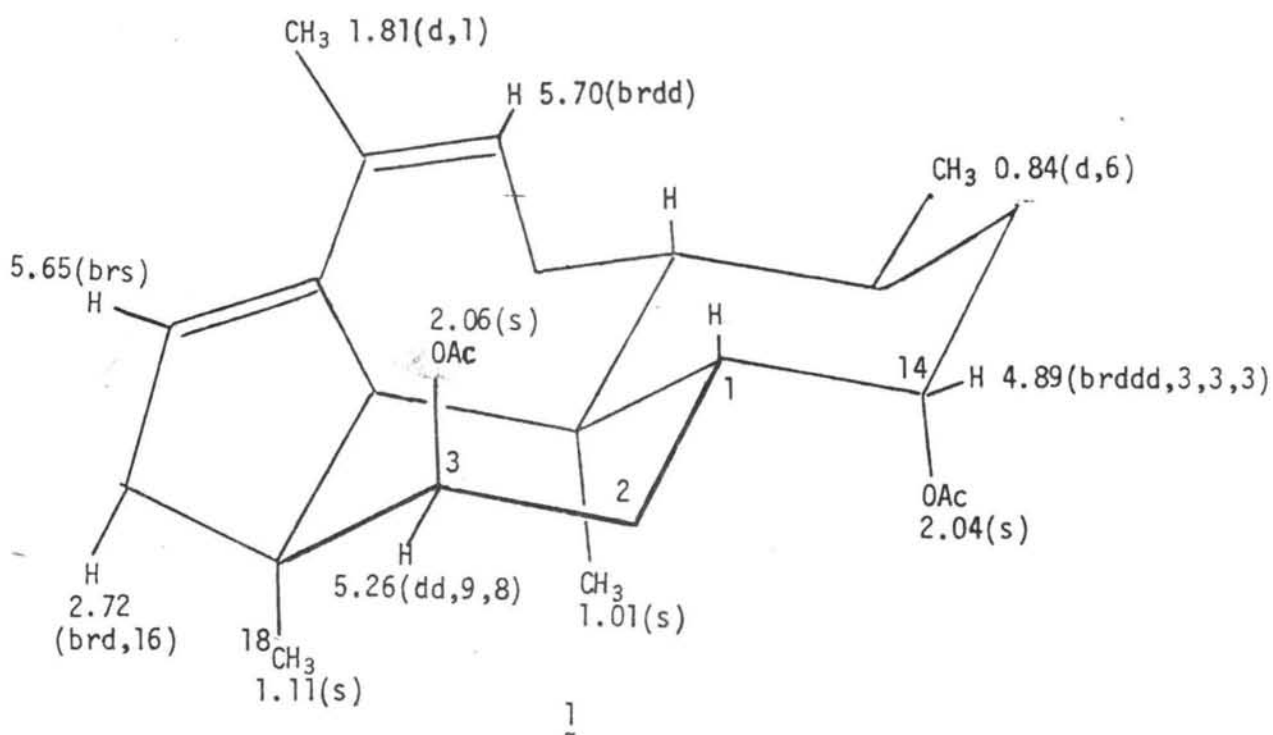
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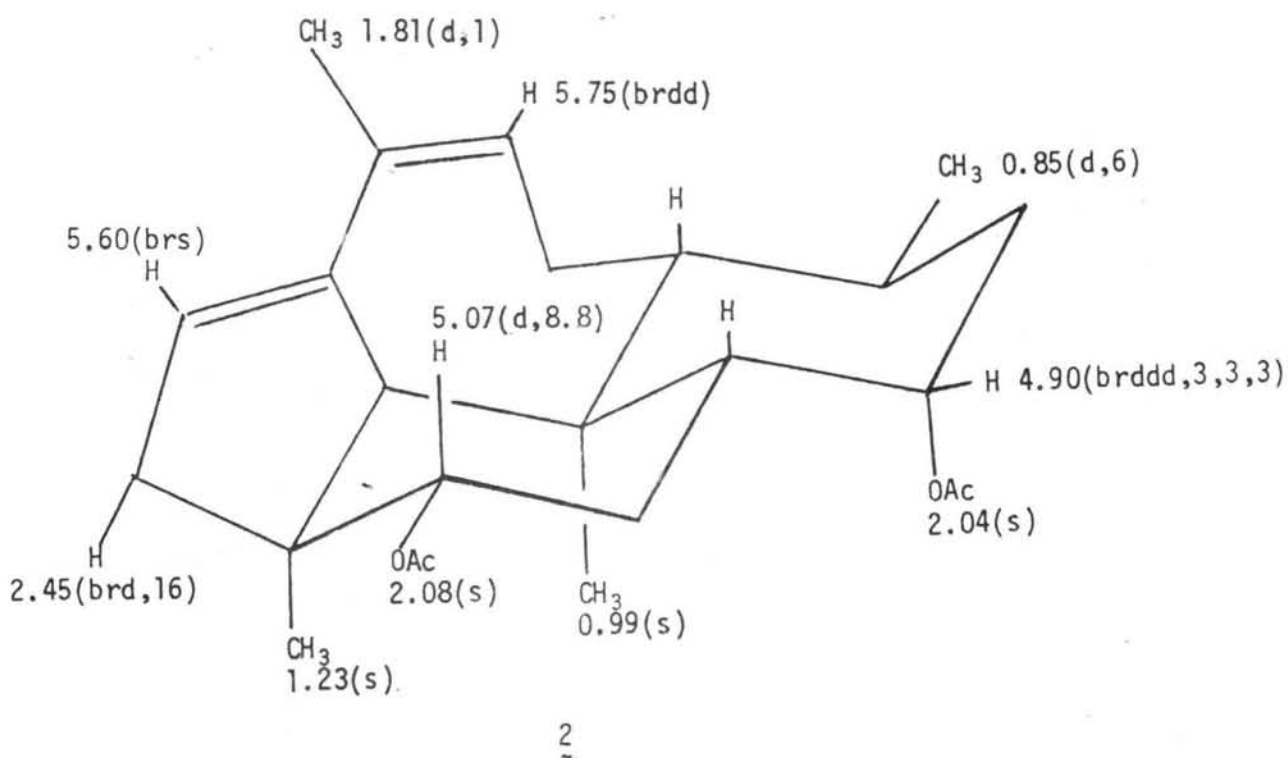
The chemical defence secretions of Malaysian termites (Nasutitermitinae, Isoptera) were analysed chromatographically and spectrometrically. New diterpenes discovered have novel bicyclic secotrinervitane, tricyclic trinervitane, tetracyclic kempene and spiro-tetracyclic longipene skeletons, which are of considerable significance in the understanding of the biosynthesis of these dome-shaped diterpenes by the termites.

Termites (Isoptera) are social insects and are ubiquitous in this part of the world. To protect the colony and the individuals that forage for food, most species have developed soldier castes having a vast array of defensive behaviour. In general, termites can depend on mechanical mode of defense (e.g. biting, flicking or snapping with mandibles), chemical defense (brushing or squirting secretions) or a combination of these modes. Termites of the subfamily Nasutitermitinae are entirely dependent on chemicals for defense and have developed a most elaborate chemical defense mechanism. The secretion is delivered via a nozzle-shaped projection on the top of the head and is 'shot' out at predators.

The defence secretion of Nasutitermitinae soldiers consists mainly of a mixture of mono- and di-terpenoids, sometimes accompanied by trace amounts of sesquiterpenes. Two compounds isolated from extracts of *Bulbitermes singaporensis*¹ were spectrometrically identified as kempa-6,8-dien-3 β ,14 α -diol 3,14-O-diacetate (1) and kempa-6,8-dien-3 α ,14 α -diol 3,14-O-diacetate (2) as shown in Figure 1. EI-MS spectral of kempene 1 (m/e 386, C₂₄H₃₄O₄) and 2 (m/e 386, C₂₄H₃₄O₄) show similar fragmentation pattern while ¹H-NMR exhibited four methyl, two acetate methyl and two olefinic proton signals. The configuration at C-14 was assigned as 3 β -acetoxy in compound 1 and 3 α -acetoxy in compound 2 on the basis of the following observations. Firstly, the chemical shift of equatorial H-3 α is more downfield than the axial H-3 β . Secondly, H-3 α bisects the angle of

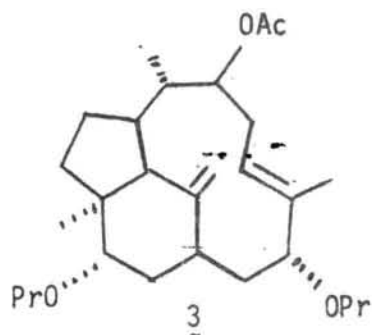


Kempa-6,8-dien-3 β ,14 α -diol 3,14-O-diacetate

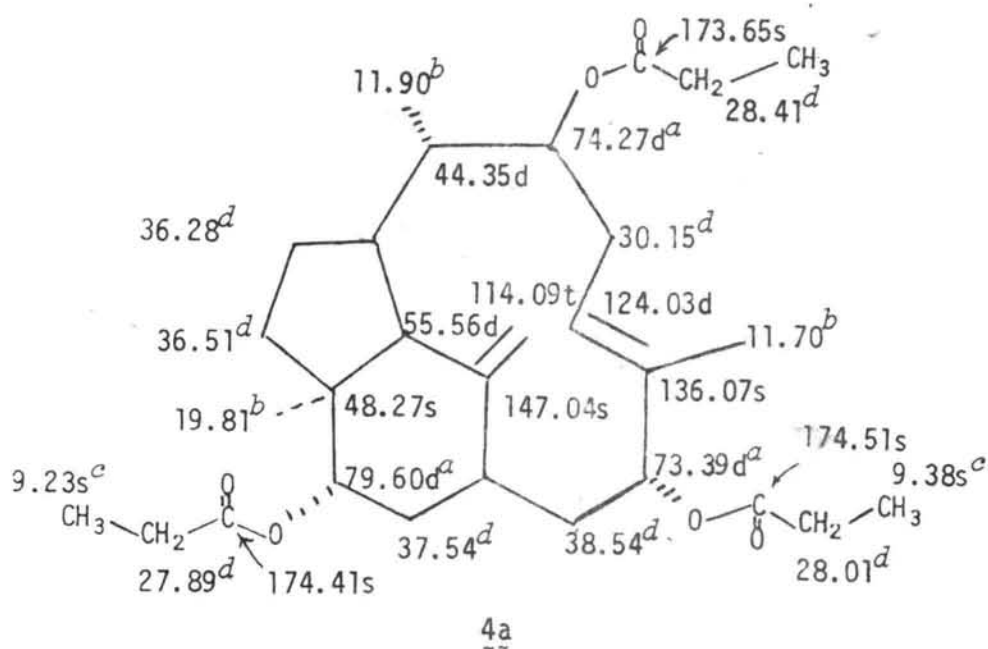
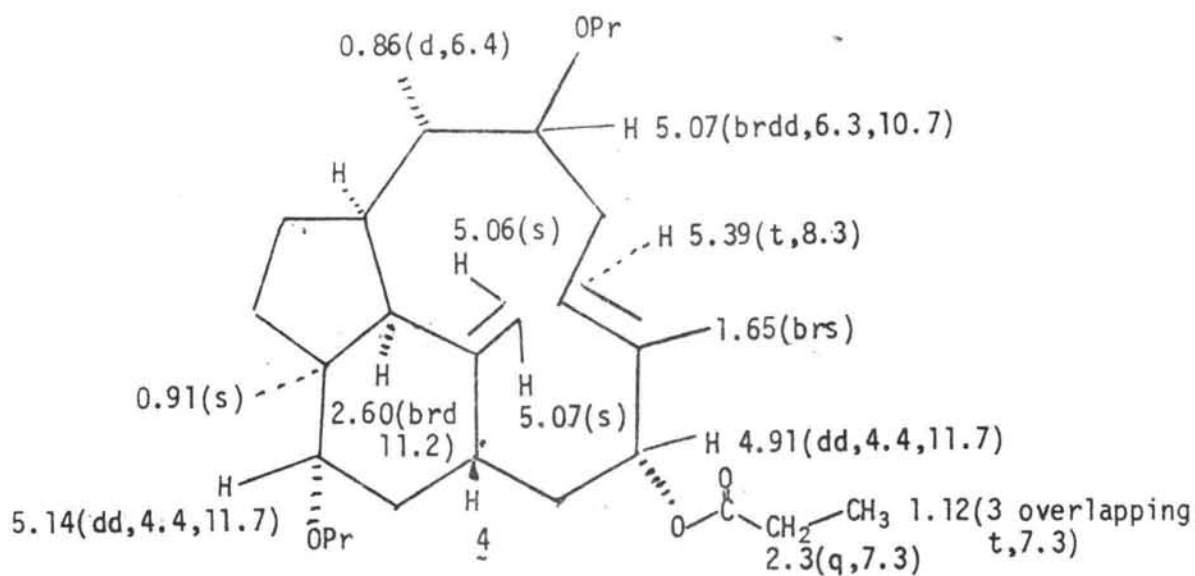


Kempa-6,8-dien-3 α ,14 α -diol 3,14-O-diacetate

FIGURE 1: KAMPANE STRUCTURE



Trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol 9-O-acetoxy-3,13-dipropionate



Trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol tripropionate.

FIGURE 2: TRICYCLIC DITERPENES.

H-2 α and H-2 β to give virtually equal coupling constants, while axial H-3 β is nearly orthogonal to H-2 β and couples only to H-2 α with a reduced axial-axial coupling. Finally, the axial nature of the 3 β -acetate is sterically permissible while maintaining the chair conformation for that 6-membered ring. In this configuration, the axial acetate does not deshield the H-18 methyl protons (1.11 ppm in **1**) while the equatorial acetate does affect the shift of that methyl (1.23 ppm in **2**). Reduction of the known 3-oxo-kempa-6,8-dien-14 α -ol 14-O-acetate² (structure established by X-ray crystallography) with excess LiAlH₄ gave two isomeric diols which on acetylation gave compounds **1** and **2**, thus verifying the correct assignment.

Trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol tripropionate (**4**), isolated from *Nasutitermes matagensis*³ had mass spectrum m/e 488 (M⁺, C₂₉H₄₄O₆) and IR (CCl₄) 1732 cm⁻¹ (ester C=O). In its ¹H-NMR spectrum, tripropionate **4** showed three methyl, three propionate and two terminal olefinic protons as summarised in Figure 2. In the ¹³C-NMR spectrum, one quaternary, seven methine, eight methylene and four olefinic carbons were present. The 360 MHz ¹H-NMR of trinervita-11(12),15(17)-dien-3 α ,9 β ,13 α -triol 9-O-acetoxy-3,13-dipropionate (**3**) showed the same resonances as tripropionate **4**, with the following exceptions: δ 4.90 (s, H-9), 2.30(q, 7.3Hz, propionate methylenes), 2.03(s, acetate methyl), and 1.21(t, 7.3Hz, propionate methyls). The structural assignment was proved by X-ray diffraction. Dipropionate monoacetate **3** had mass spectrum m/e 474 (M⁺, C₂₈H₄₂O₆) and had fragmentation pattern analogous to that of tripropionate **4**.

The bicyclic secotrinervita-7(8),11(12),15(17)-trien-3 α -ol (**5**) (Figure 3) and secotrinervita-7(8),11(12),15(17)-trien-2 β ,3 α -diol (**6**) (Figure 4) isolated from *Longipeditermes longipes*⁴ showed 6 olefinic carbons from ¹³C-NMR spectrum and also showed three methyl (two overlapping), allylic and vinylic protons from 90 MHz ¹H-NMR. Secotrinervitatriene mono-cohol **5** and diol **6** have mass spectra m/e 288 (M⁺, C₂₀H₃₂O) and m/e 304 (M⁺, C₂₀H₃₂O₂) respectively and both show similar fragmentation patterns. The bicyclic secotrinervitane structural type was discovered at the same time by Braekman in the defence secretion of a Papua-New Guinea species *Nasutitermes priceps*,⁵ and the structural skeleton was established by X-ray crystallography.

The new compound trinervita-1(15),8(19)-dien-2 β ,3 α -diol 2-O-acetate (**7**) which was secreted in relatively large quantities in *Hospitalitermes umbrinus*⁶ was identified on the basis of its proton NMR, IR, and mass spectral data; hydrolysis with methanolic sodium hydroxide gave the known trinervita-1(15),8(19)-dien-2 β ,3 α -diol. In its ¹H-NMR, diol monoacetate **7** shows four methyl signals (two s, one d, one acetate methyl), two terminal olefinic protons and a hydroxymethine as shown in Figure 5. The C-2 proton appeared as a

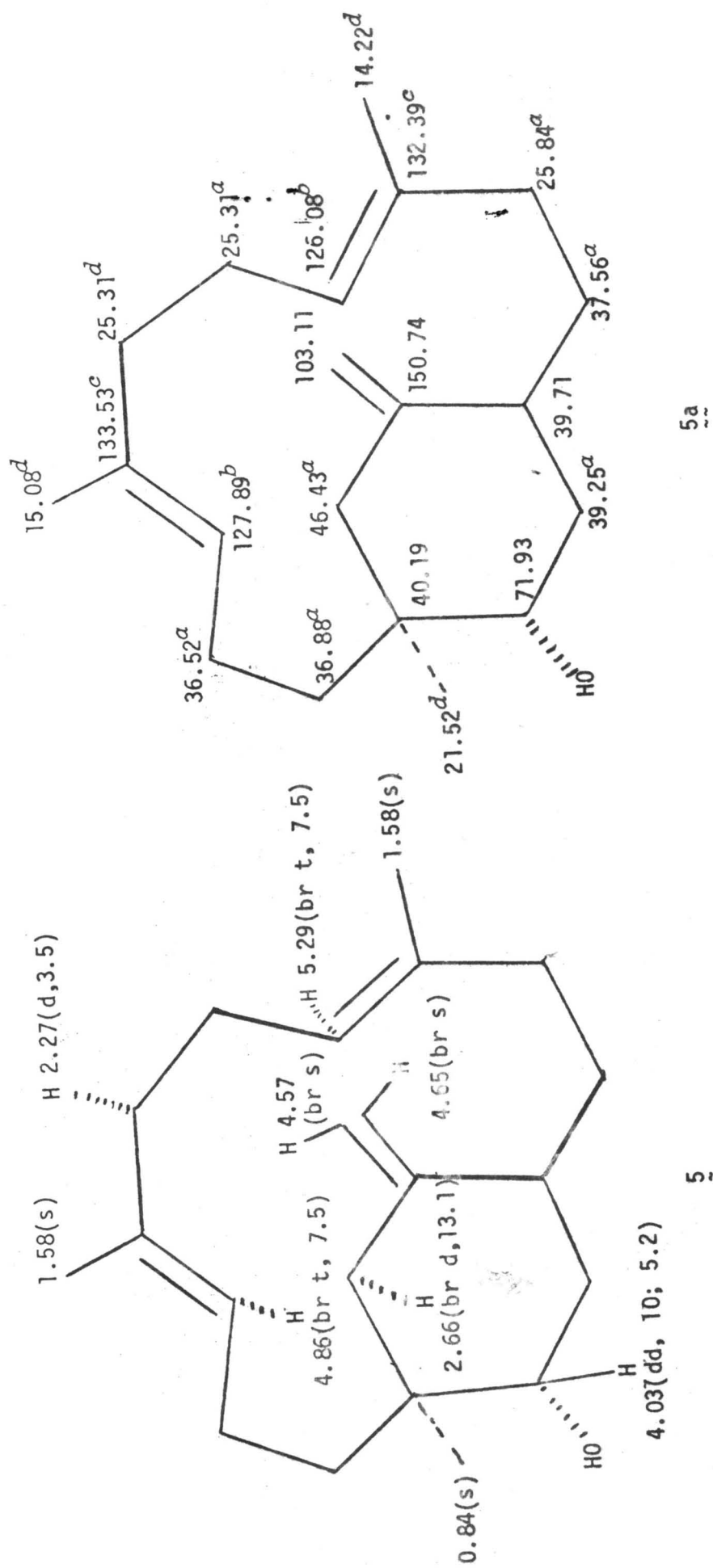


FIGURE 3: Secotrinervita-7(8),11(12),15(17)-trien-3 α -ol

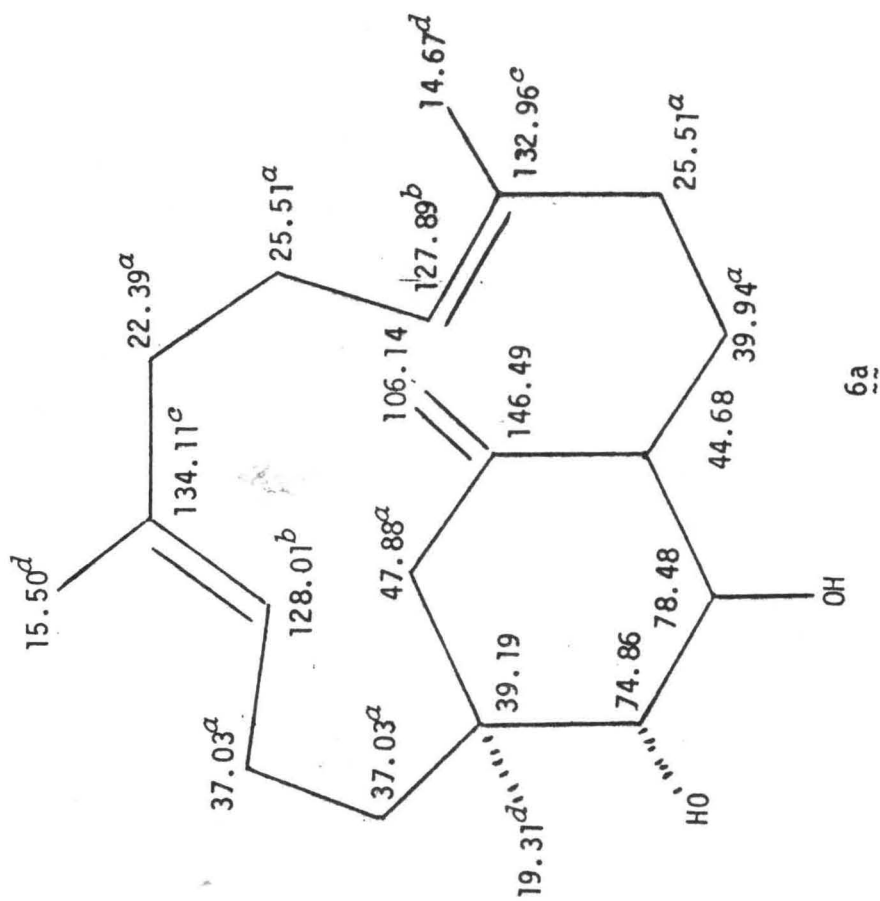
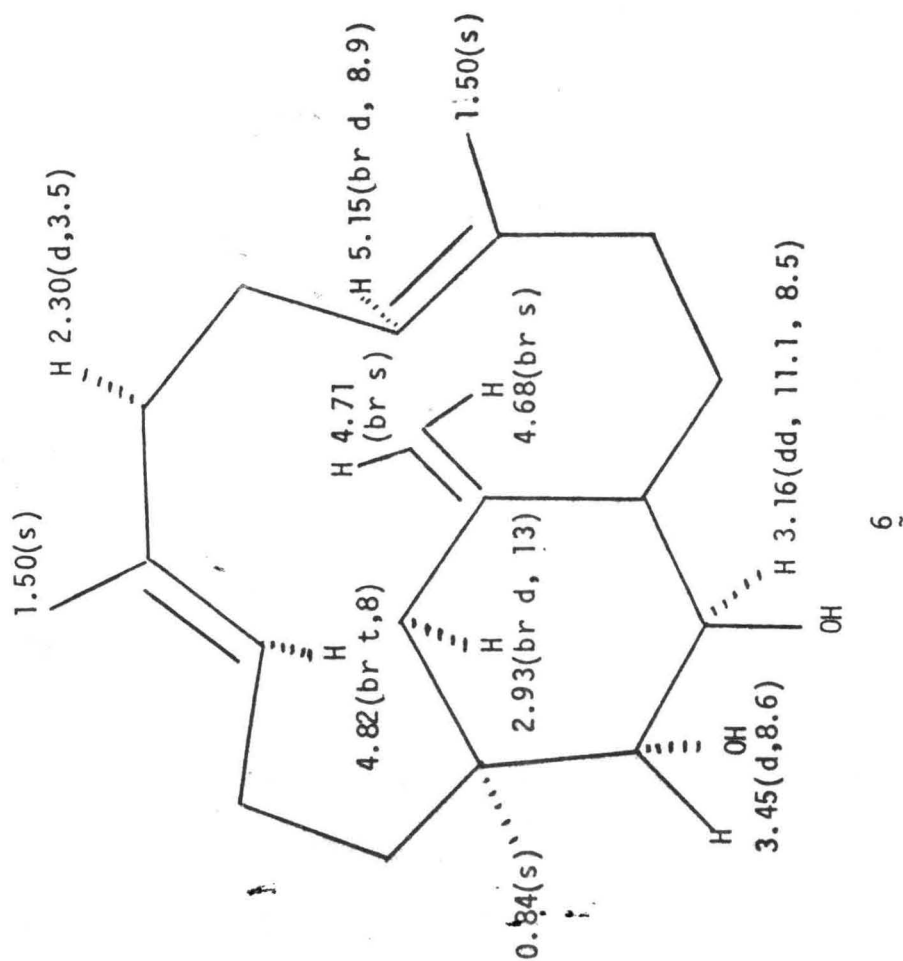
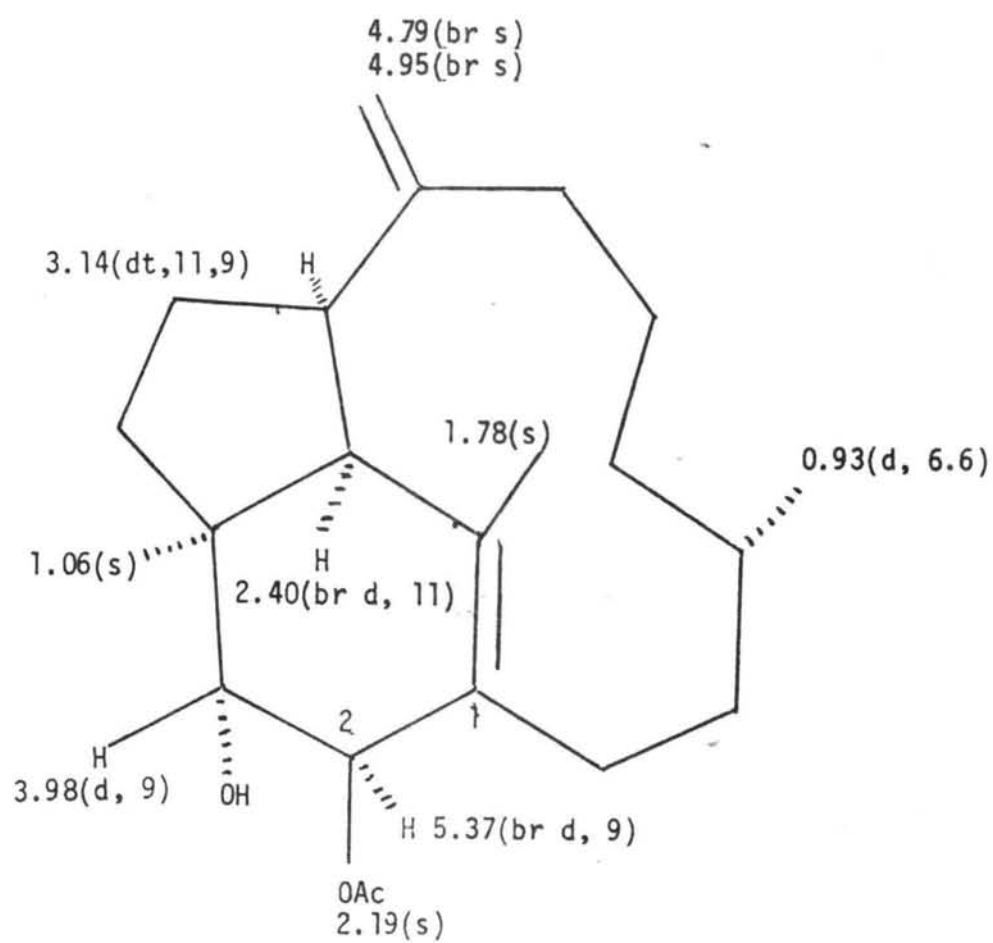


FIGURE 4: Secotrinervita-7(8),11(12),15(17)-trien-2β,3α-diol



7

FIGURE 5: Trinervita-1(15),8(19)-dien-2 β ,3 α -diol 2-O-acetate

broad 9 Hz doublet at δ 5.37. -The IR (CCl_4) shows absorptions at 3500 (O-H), 1735 (C=O) and 905 cm^{-1} (C=CH₂). The EI-mass spectrum of this diol monoacetate 7 did not show the molecular ion but only the M-AcOH ion. However, the trimethylsilyl derivative gave the correct molecular ion and an expected fragmentation pattern, including a retro-Diels Alder fragment $[\text{Me}_3\text{SiOCH}=\text{CMeCH}_2\text{CH}_2\text{CH}=\text{C}=\text{CH}_2]^+$ at m/e 196 (13%).

A novel compound longipenol (8) with new spirotetracyclic skeleton isolated from *Longipeditermes longipes*^{4,9} shows three CH₃ signals (two d, one s), a hydroxymethine coupled to two non-equivalent hydrogens, and two terminal olefinic protons as shown in Figure 6. In its ¹³C-NMR spectrum, two quaternary, six methine, seven methylene, three methyl carbons, and a characteristic pair of 1,1-disubstituted olefinic carbons were present. Longipenol (8) had mass spectrum m/e 288 (M⁺, C₂₀H₃₂O) with a strong peak at m/e 255 (85%) while the trimethylsilyl derivative gave strong peak at m/e 360 (M⁺, 57%) and a RDA fragment at m/e 196 $[\text{Me}_3\text{SiOCH}=\text{CMeCH}_2\text{CH}_2\text{CH}=\text{C}=\text{CH}_2]^+$.

The diterpenes presently isolated from nasute termites are of interest in relation to earlier postulated biogenetic schemes. These compounds are known to be biosynthesized by nasute termites independently of the dietary source. Cembrene A, previously isolated from *Nasutitermes exitiosus*⁷ and from *Cubitermes*⁸ or its 3,4-epoxide (12) would be an obvious choice as a precursor to the observed diterpenoids. As shown in Figure 7, a one-step cyclization of (R)-cembrene-*trans*-3,4-epoxide (12) would yield directly the secotrinervita-7(8),11(12),15(17)-3 α -ol (5). Interestingly, after isomerisation 5 has the double bonds positioned for further cyclisations to give longipenol (8), trinervitane-3 α -ol (11) and Kempane-3 α -ol (10). The methyl-shifted rippertenol (9) would arise similarly via step-wise cyclisation using bicyclic secotrinervitatrienol and tricyclic trinervitadienol as intermediates.

The new diterpene skeletal types found in Malaysian termites^{4,10} have provided a better understanding of the biosynthesis of these dome-shaped diterpenes produced by nasute termite soldiers. Besides interest in a new class of compounds, perhaps continuing research would show forth new uses for these and related compounds.

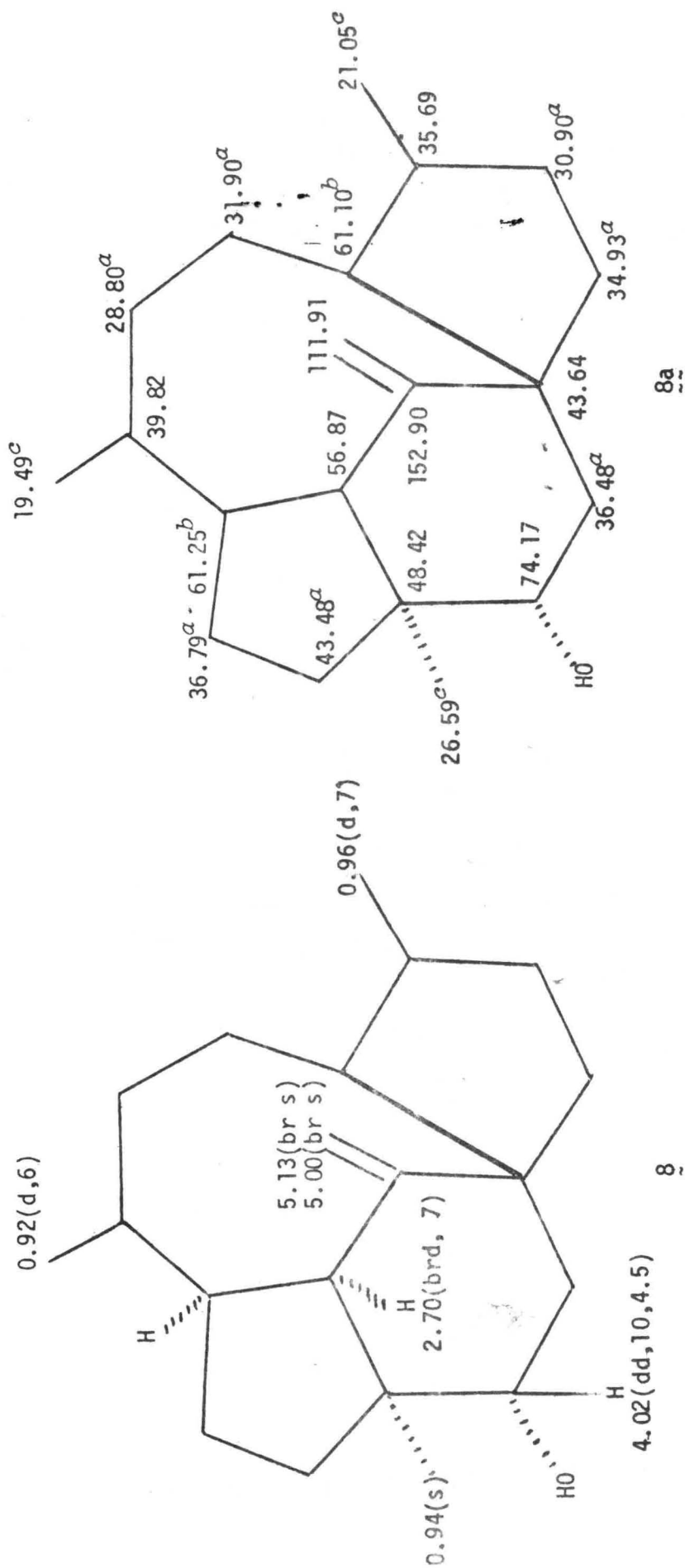


FIGURE 6: Longipenol

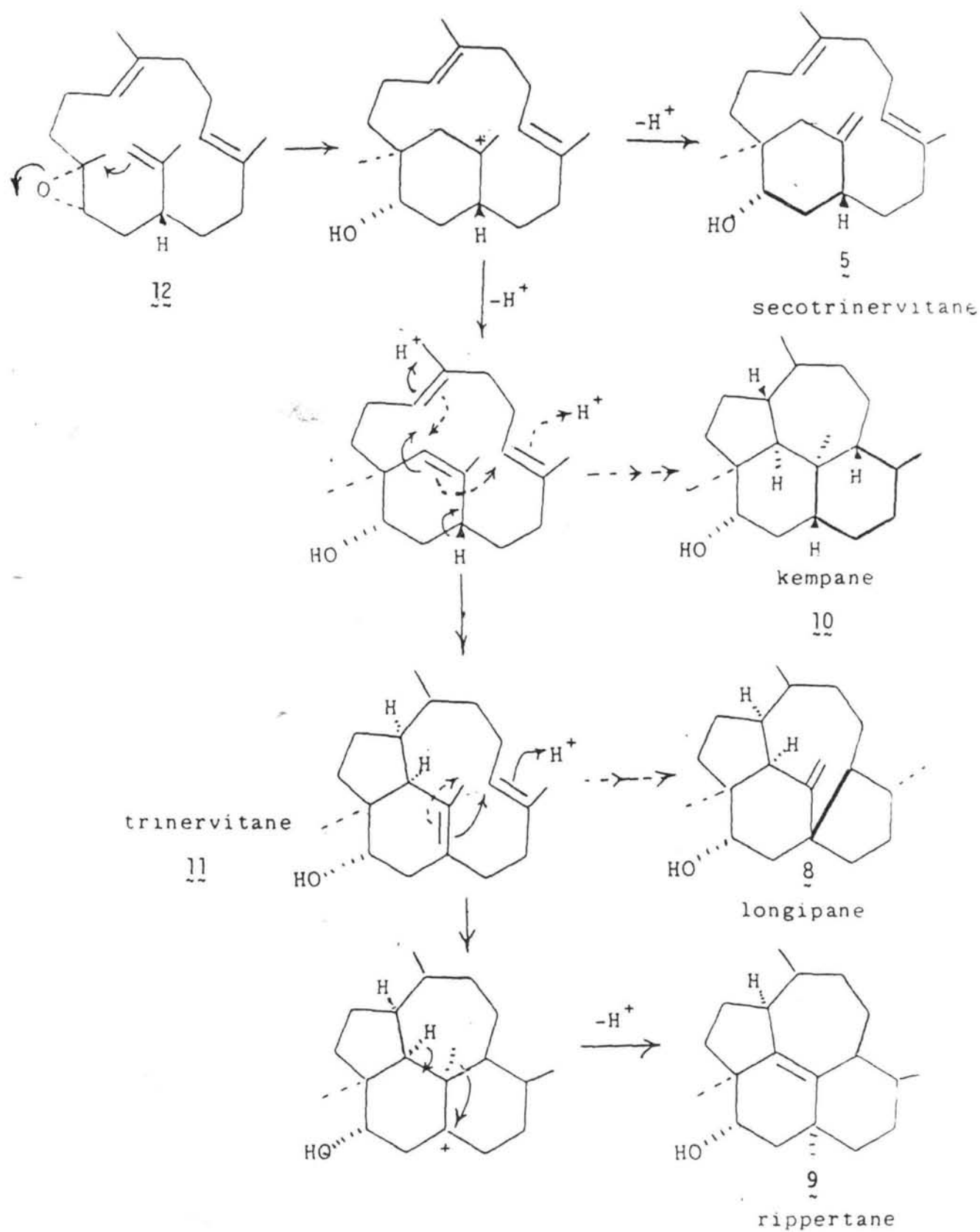


Figure 7: Possible Biogenesis Pathways

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UNREPORTED CONSTITUENTS FROM *ELAEIS GUINEENSIS*

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Chromatographic and spectroscopic techniques were used for the structure elucidation for newly isolated constituents from Elaeis guineensis. Aliphatic and terpenoid hydrocarbons, and methyl ketone homologs were isolated and characterised. Hydrocarbons, terpenoids and esters were isolated and identified from the exocarp of the palm fruits. Estragole was found to be the major component of the volatiles isolated from the male inflorescence of the oil palm.

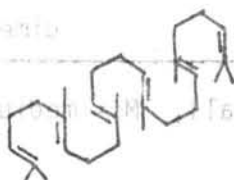
INTRODUCTION

Despite the preeminent position of palm oil in this country, most of the composition of palm oil is very much based on earlier work, principally of Jacobsberg (1). Recently reviews have appeared from PORIM on minor components in palm oil in view of their values (eg. carotene and vitamin E) and their roles in affecting oil quality (2). In this paper, a preliminary account of a study of selected minor and trace components from palm oil is presented.

RESULTS AND DISCUSSION

In the search for non-carotenoid hydrocarbons in palm oil it was found that hydrocarbons (ca. 2-3%) could be readily isolated from PFAD. High performance liquid chromatography (HPLC) and gas liquid chromatography (GLC) revealed that the major component of the hydrocarbons is squalene, a common acyclic triterpene.

FIG. 1: SQUALENE



Squalene constitutes ca. 60% of the total hydrocarbons and was identified by HPLC and GLC and further confirmed by gas chromatography-mass spectroscopy (GCMS) and nuclear magnetic resonance (NMR) spectroscopy. Also identified were ionene and dimethylnaphthalene. These two compounds as well as toluene and xylene are known to form from the thermal decomposition of β -carotene.

The hydrocarbons occur as a complex mixture and had to be further purified by repeated chromatography before spectroscopic analysis. Results obtained are summarised in Table I.

TABLE I: HYDROCARBONS

Formulae	Relative amounts ^a	Assignments
$C_{15}H_{32}$	T	n-pentadecane
$C_{17}H_{36}$	T	n-heptadecane
$C_{15}H_{30}$	S	pentadecene
$C_{16}H_{32}$	T	hexadecene
$C_{17}H_{34}$	T	heptadecene
$C_{18}H_{36}$	M	octadecene
$C_{19}H_{38}$	T	nonadecene
$C_{21}H_{42}$	S	heneicosene
$C_{24}H_{48}$	M	tetracosene
$C_{26}H_{52}$	S	hexacosene
$C_{23}H_{44}$	S	tricosadiene ^b
$C_{26}H_{50}$	M	hexacosadiene ^b
$C_{24}H_{50}$	T	branched alkane ^b
$C_{27}H_{56}$	S	branched alkane ^b
$C_{26}H_{48}$	S	hexacosatriene ^b
$C_{20}H_{32}$	L	diterpene hydrocarbon ^b
$C_{30}H_{50}$	VL	squalene
$C_{13}H_{18}$	M	ionene
$C_{12}H_{12}$	S	dimethylnaphthalene

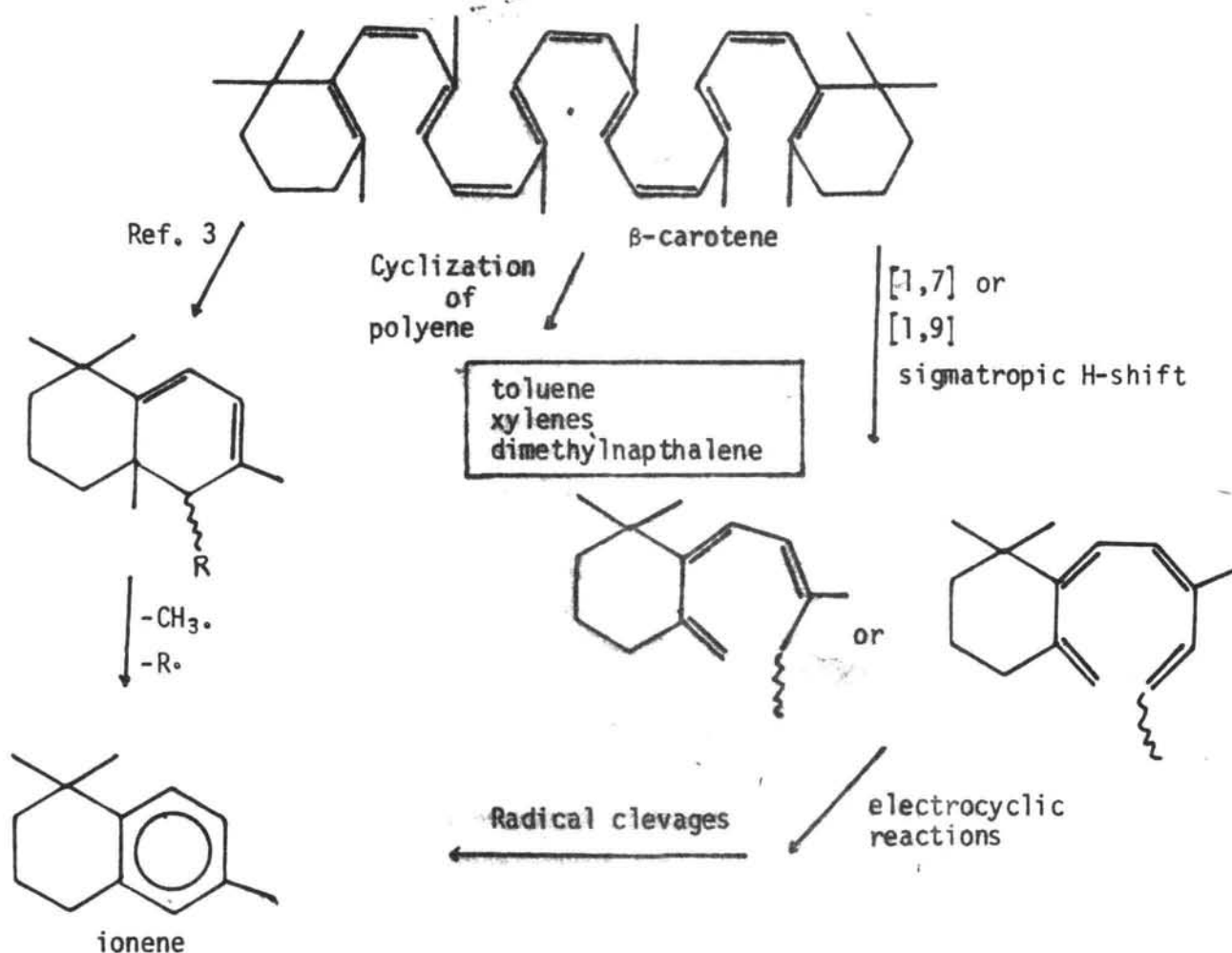
^aT = trace quantity, S = small, M = medium, L = large and VL = very large

^bTentative assignment.

Typically, only traces of n-alkanes were present. Monoenes were present in fairly substantial amounts consisting mainly of C15, C18, C21, C24 and C26. A few cyclic or polyene hydrocarbons (relatively small to trace amounts) remained unidentified; so were some diterpenoid hydrocarbons.

Among the more volatile components of PFAD, toluene, xylene, ionene and dimethylnaphthalene were readily detectable by GCMS. The formation of these have been the subject of much speculation. A reasonable scheme depicting their formation from thermal degradation of β -carotene is given in Fig. 2.

FIG. 2: DEGRADATION OF β -CAROTENE



Methyl ketones were isolated by silica gel column chromatography on the unsaponifiables of PFAD. The structures were deduced from the GCMS studies, being further supported by proton NMR spectroscopy. GCMS of methyl ketones showed pronounced McLafferty rearrangement and α -cleavage giving characteristic fragment with of m/e 58 and m/e 43 respectively.

These methyl ketones were rather unusual differing from the expected 2-pentadecanone (4) which could arise from microbiological action of C16 fatty acid (5). The composition of methyl ketone homologs found were summarised in Table II.

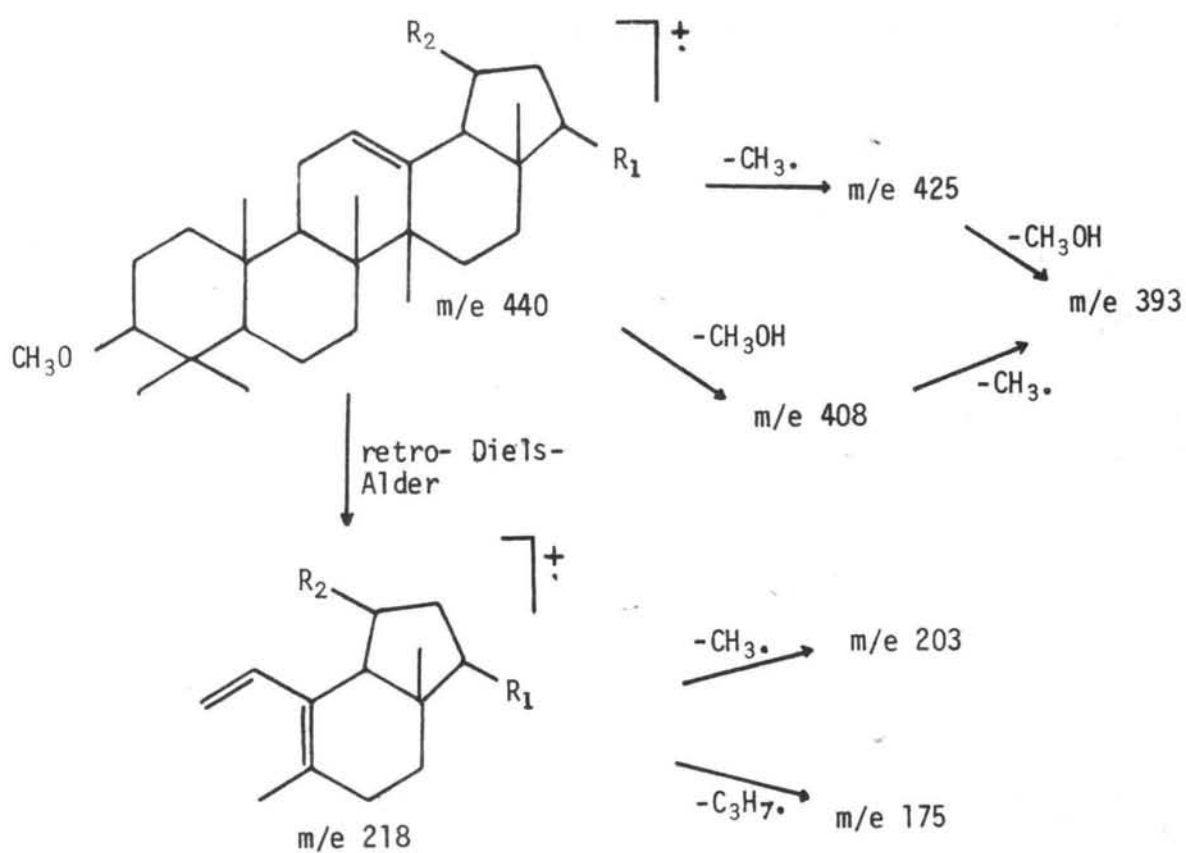
TABLE II: METHYL KETONES

Methyl ketones	Formulae	Relative amounts
2-pentadecanone	$C_{15}H_{30}O$	small
2-heptadecanone	$C_{17}H_{34}O$	large
2-nonadecanone	$C_{19}H_{38}O$	large
2-heneicosanone	$C_{21}H_{42}O$	medium
2-tricosanone	$C_{23}H_{46}O$	small

Extracts of palm fruit exocarp were examined by column and TLC. Apart from glycerides, hydrocarbons, esters, terpenoids and sterols were found. GLC again revealed that the major hydrocarbon component is squalene. Methyl esters identified were methyl myristate, methyl palmitate and methyl oleate (major). Methyl esters have characteristic m/e 74 fragment in GCMS and sharp singlet at ca. 3.7 ppm in 1H NMR spectrum.

Two triterpene methyl ethers were also isolated and tentatively assigned as arundoin and neomotioli methyl ether (I) or 12,13-dehydro-20,30-dihydrolupeol methyl ether (II). Isomers (I) and (II) cannot be distinguished by mass spectroscopy, as the spectra of these two isomers may not show any difference. The mass spectrum shows characteristic fragment ions at m/e 440 (M^+), 408 (M^+-OMe), 218 and 175. These fragment ions reveal that a double bond is at C-12 position giving the retro-Diels-Alder rearrangement ion at m/e 218 followed by loss of an isopropyl group (m/e 175).

FIG. 3: MASS SPECTRAL FRAGMENTATION OF ISOMER (I)/(II)

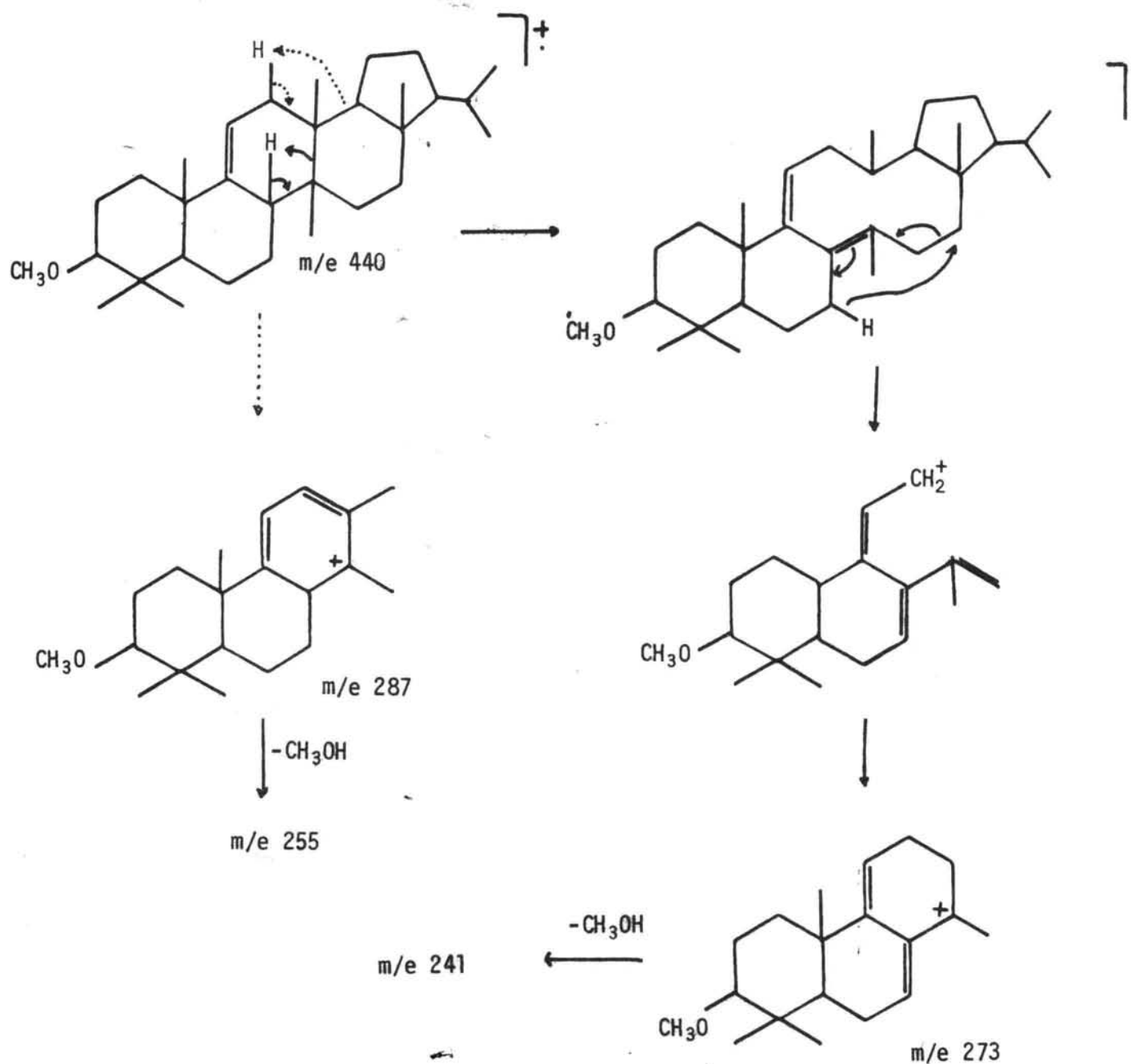


(I) $R_1 = C_3H_7$, $R_2 = H$: neomotiol methyl ether

(II) $R_1 = H$, $R_2 = C_3H_7$: 12,13-dehydro-20,30-dihydrolupeol methyl ether

Arundoin shows a different fragmentation pattern. Retro-Diels-Alder reaction is not significant due to the presence of methyl groups at positions 13 and 14, which enhance the fragmentation to occur at the C/D ring juncture giving a characteristic m/e 273 ion.

FIG. 4: FRAGMENTATION OF ARUNDOIN



Finally, a simple compound was easily isolated from the male inflorescence by vacuum distillation. GLC and NMR revealed that estragole, $4\text{-MeOC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$, is the major component (>90%). The structure was verified by proton NMR. Estragole is responsible for the characteristic odour of the palm flowers.

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THE ALKALOIDS OF LEUCONOTIS GRIFFITHII (APOCYNACEAE)

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A study of the Malaysian woody climber, Leuconotis griffithii (Apocynaceae), provided five alkaloids of which three have been positively identified by spectroscopy. Two of them, norfluorocurarine (II) and eburnamine (IV) are known whilst the third, norfluorocurarine N-oxide (III) is new. The other two alkaloids were given tentative structural assignments.

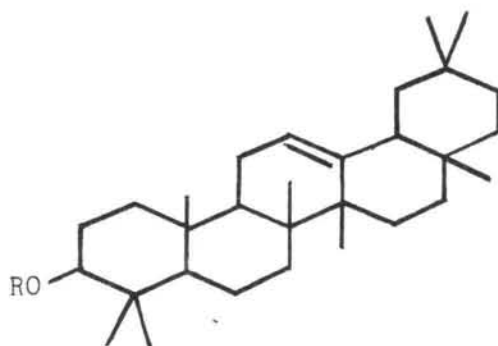
INTRODUCTION

The chemistry of alkaloids has always been an active and important part of organic chemistry and has provided many of the most challenging and subtle of all chemical problems, both of structural deductions and synthesis. By definition, "alkaloids occur characteristically in plants, and are frequently distinguished by their remarkable physiological activity. They contain carbon, hydrogen and nitrogen, and in most cases oxygen as well; in many respects they resemble the alkalis (hence the name)". This definition was given by Meyer in 1896 (1) and is still generally applicable today but needs some modifications. Initially, alkaloids are found only in the plant kingdom, but recently, they have also been discovered in the animals as well. For example, castoramine, samandrine and tetrodotoxin are some of the animal alkaloids that have so far been isolated (1). Secondly, it is true that most of the alkaloids are considered as strong bases. For example, strychnine has a pK_a value of 8.26. However, colchicine is almost neutral in its properties (1).

There are over 6000 alkaloids that have so far been isolated from both plants and animals. During the last 40 years, research in the field of alkaloids has focussed its attention on the search of compounds of pharmacological interest. More recently, the work has been geared to finding alkaloids with anti-cancer activity.

The genus Leuconotis (family Apocynaceae) contains 10 species altogether (2), but in Peninsula Malaysia, it is represented by three species only. They are L. eugenifolia, L. griffithii and L. maingayi. All of them are woody climbers. The latex produced has been used in folk medicine for the treatment of yaws (3). Alkaloid tests have shown that the leaves, bark and wood of the first two species contain alkaloids, but in L. maingayi only the bark contains alkaloids.

Not much chemical work has been done on any of the Leuconotis species. However, some work was done on the species L. eugenifolia where some Indian workers reported the isolation of a few triterpenes (4,5). Among the triterpenes isolated were two new triterpenoid esters β -amrenyl behenate (Ia) and β -amrenyl eicosanoate (Ib) (6).



Ia: R = $\text{CH}_3(\text{CH}_2)_{20}\text{CO}-$

Ib; R = $\text{CH}_3(\text{CH}_2)_{18}\text{CO}-$

RESULT AND DISCUSSION

The air dried, powdered bark and wood of *L. griffithii* were extracted and purified to give 0.15% of crude alkaloid extract. The alkaloids were further separated using column chromatography and preparative thin layer chromatography. Five different alkaloids were isolated and subjected to spectroscopic analysis.

Norfluorocurarine

The first alkaloid identified was norfluorocurarine (II). The alkaloid has a molecular weight of 292 and a molecular formula of $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$. The mass spectrum shows characteristic indole fragmentation pattern by having peaks at m/e 130, 143 and 144. The base peak at m/e 121 is a characteristic feature of all akuammicine type of alkaloids.

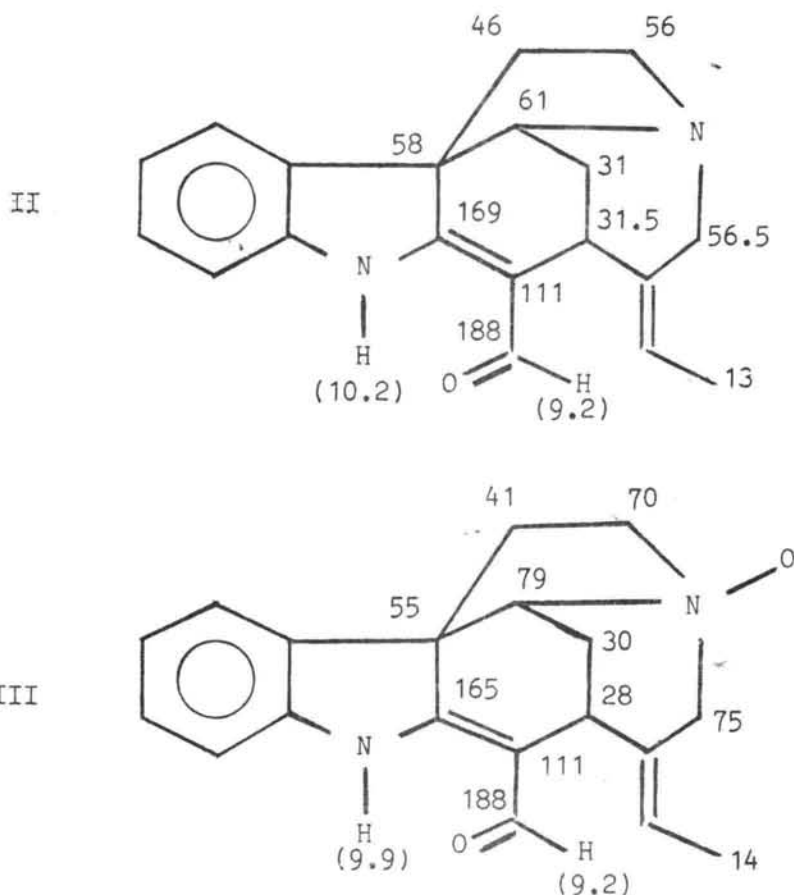
The infra-red spectrum shows absorption at 3320 and 1605 cm^{-1} , due to the presence of secondary NH. It also shows the absorption at 1645 cm^{-1} , showing the presence of a hydrogen bonded carbonyl group. The presence of the olefinic bond in conjugation with a carbonyl group is shown by the presence of an absorption at 1610 cm^{-1} . The U.V. spectrum shows absorption at 202, 228 and 360 nm.

The proton spectrum shows an exchangeable proton at 10.2 δ . This peak which integrates for one proton is assigned to the hydrogen on the secondary nitrogen. A sharp singlet at 9.2 δ also integrates for one proton. This is assigned to the aldehyde proton. The spectrum also shows the presence of aromatic protons at 7 to 7.2 δ .

The completely decoupled C-13 spectrum accounted for all the 19 carbons. It clearly shows the presence of a carbonyl carbon with a peak at 188 ppm. There are 11 carbons in the lower field and 8 carbons in the higher field. The high field carbons at 61, 56.5 and 56 ppm are assigned to carbons attached to the tertiary nitrogen. The carbon at 58 ppm is assigned to the aliphatic quaternary carbon.

A partially decoupled spectrum of the alkaloid clearly differentiates the types of carbons present in the molecule. The spectrum shows a quartet (CH_3) at 13 ppm, triplets (CH_2) at 31, 46, 56 and 56.5 ppm, doublets (CH) at 31.5, 61 and 188 ppm and singlets (C) at 58, 111, 137, 139 and 169 ppm. The doublet at 188 ppm indicates the presence of an aldehyde carbonyl carbon. The five peaks at 120 to 127 ppm represent the five aromatic and olefinic CH carbons present in the molecule.

Spectral information confirms the structure of norfluorocurarine which was also previously isolated from several *Vinca* species (7).



Norfluorocurarine N-oxide

The second alkaloid identified was norfluorocurarine N-oxide (III). The alkaloid has a molecular weight of 308 and a molecular formula of $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$. The mass spectrum shows a major fragment at m/e 292, corresponding to a loss of an oxygen. It also shows fragments at m/e 130, 143, 144 and 156, and the base peak at m/e 121.

The infrared spectrum shows absorption at 3320 cm^{-1} due to the secondary NH, at 1660 cm^{-1} due to the carbonyl group and at 1615 cm^{-1} due to the olefinic group. The U.V. spectrum shows similar absorptions to that of norfluorocurarine, i.e. at 202, 228 and 360 nm.

The proton spectrum also shows distinct similarities to that of norfluorocurarine. It shows the presence of an exchangeable proton at 9.9 δ and the one proton singlet at 9.2 δ . Similarities in the completely decoupled C-13 spectra of the two alkaloids are also distinct. All the carbon chemical shifts are quite unchanged except for the chemical shifts of three carbons. They are the carbons at 61, 56.5 and 56 ppm in the norfluorocurarine spectrum which are shifted to 79, 75 and 70 ppm respectively in the N-oxide spectrum. These three carbons are the carbons that are attached to the tertiary nitrogen.

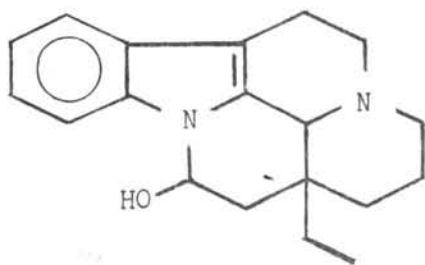
Since the alkaloid has only one oxygen more than norfluorocurarine, and the presence of this oxygen affects only the chemical shifts of the three carbons attached to the nitrogen, it is concluded that the oxygen is bonded to the nitrogen as an N-oxide.

Eburnamine

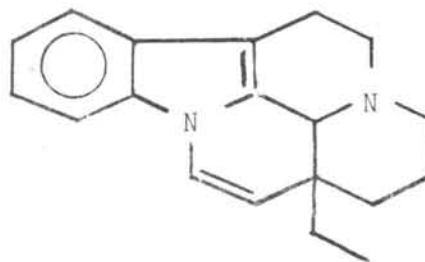
Eburnamine (IV) has a molecular weight of 296 and a molecular formula of $C_{19}H_{24}N_2O$. The alkaloid has previously been isolated from *Hunteria eburnea* (7). The identification of this alkaloid was based mainly on the interpretation of the mass spectrum.

The completely decoupled C-13 spectrum shows the presence of 11 carbons in the high field region. The carbon at 77 ppm is assigned to the carbon attached to an oxygen. The carbons at 59, 51, 44 and 43 ppm are the four carbons adjacent to the nitrogens. The proton spectrum shows the presence of an exchangeable proton at 1.9 δ due to the presence of a hydroxy group.

The mass spectrum of that alkaloid shows similar fragmentation pattern with that of eburnamenine (V), a known alkaloid of molecular weight 278 mass units. It was earlier reported (8) that eburnamine is very sensitive to dehydration. As a result of the loss of a water molecule, the mass spectrum of eburnamine looks similar to that of eburnamenine.



IV



V

Alkaloid 326 and Alkaloid 376

The other two alkaloids that have been isolated are Alkaloid 326 and Alkaloid 376. They are tentatively named according to their molecular weights. Alkaloid 326 is a major alkaloid of this plant. From the mass spectrum, the alkaloid has a molecular formula of $C_{19}H_{22}N_2O_3$. The proton n.m.r spectrum shows the presence of an NH and OH by the presence of exchangeable peaks at 8.2 and 5.4 δ respectively. It also shows a sharp singlet integrating for one proton at 5.9 δ . The triplet at 0.5 δ shows the presence of a methyl group adjacent to a CH_2 group.

The infrared spectrum shows the presence of a carbonyl group and confirms the presence of the OH and NH groups. The completely decoupled C-13 spectrum of the alkaloid confirms the presence of a carbonyl group. The spectrum also shows the presence of 7 quaternary carbons, 5 CH , 6 CH_2 and one methyl group. Structural elucidation of these compounds is in progress.

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ANALYSIS OF OILY COMPONENT OF THE SAP OF LACQUER TREE IN BURMA AND THAILAND

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Oily component of sap of the lacquer tree originating in Burma and Thailand, Melanorrhoea usitate is analyzed by using high performance liquid chromatography. Novel phenolic lipids, ω -phenylalkyl-phenols, are found in addition to previously known homologues of thitsiol, urushiol and laccol.

INTRODUCTION

In 1922 (1), Majima reported that 4-substituted catechols having a C_{17} n-alkyl side chain is the main constituent of sap of the lac tree, Melanorrhoea usitate grown in Burma, and he named this compound thitsiol (isourushiol). In the report, he also pointed out that other saturated substances were included in the sap besides thitsiol in a considerably great amount, though their nature and chemical structures could not be elucidated.

We have recently developed a general method to separate and analyze oily component of sap of lac trees based on high performance liquid chromatography (hplc) (2-4). Urushiol of the lac tree, Rhus vernicifera (China and Japan) was separated into more than ten congeners as dimethyl ethers and the structure of olefinic side chains was exactly determined by ozonolysis accompanied with hplc-identification of dinitrophenylhydrazones derived from ozonolysis products (4). More recently, high-resolution l.c. separation of intact urushiol has been achieved by reversed-phase l.c. using weakly acidic eluent (5).

In a preliminary report (6), sap of the lac tree, Melanorrhoea usitate (Burma) was examined after methylation and hydrogenation to simplify analytical procedure, as it was found to be a highly complicated mixture of many constituents. As a result, it was revealed to contain congeners of laccol and urushiol as well as those of thitsiol. A more significant fact is that in addition to these classical substances, it includes 3- or 4-substituted catechols with 10'-phenyldecyl or 12'-phenyldodecyl groups and 5-substituted resorcinols with similar substituents.

To determine exact structures of these novel compounds, or in order to clarify whether they have olefinic groups in the side chain or not, we executed separation of oily component of sap of Burmese lac as the intact form. This was succeeded by using the

recently developed reversed-phase l.c. method, which was applied to the analysis of sap of Rhus vernicifera (5).

In this paper we report the result of extensive analysis of sap of Burmese lac, presenting complete structures of novel dihydric phenols with -phenylalkyl substituents and some new constituents, monohydric phenols with a variety of substituents. We also wish to emphasize that a highly complicated substance as the present subject can be readily analyzed by a modern chromatographic technique.

EXPERIMENTAL

Material

Sap of the lacquer tree, Melanorrhoea usitate originating in Burma was obtained by the courtesy of The Burmese Embassy in Tokyo and The South Sea Association (Tokyo). It was mixed with 3-fold amount of acetone and the mixture was filtered. The filtrate was evaporated and the obtained residue was subjected to gel permeation chromatography (g.p.c.) to remove polymeric material. G.p.c. technique is adequate to pre-treatment of the air-sensitive sap as it is executed under mild conditions compared with classical distillation. The obtained monomeric preparation was separated by hplc.

Instruments

Hplc was carried out with a hand-made apparatus comprising a mini pump (Nihon Seimitsu Co., Tokyo), a pressure gauge, a syringe-loading sample injection valve (Rheodyne Inc., CA). Effluent was monitored with a UV-detector (Oyobunko, Co., Tokyo) at 254 nm. A 2.2 x 30 cm stainless steel column packed with 5 μ m ODS-silica (Hitachi #3053) and a 0.8 x 25 cm column packed with ODS-silica (TSK-gel LS-410, 5 μ m) were used. G.p.c. was done with the hand-made apparatus equipped with an RI monitor (RI-2, Japan Analytical Industries, Tokyo) on Hitachi A-120 and A-110 columns (0.8 x 50 cm) using chloroform as eluent. G.l.c. was done with a Hewlett-Packard 3790 instrument equipped with a flame ionization detector on a fused-silica WCOT column (ULTRA#2, 0.2mm x 25 m) coated with methylsilicone (the thickness of liquid phase, 0.33 μ m). I.r. spectra was recorded on a JASCO IRA-2 instrument. ¹H-N.m.r. spectra were measured with a JEOL GX-400 spectrometer (resonance frequency, 400 MHz). E.i.-m.s. diagrams were obtained with a Hitachi RMU-6E mass spectrometer (ionization voltage, 70 eV). G.l.c.-m.s. measurement was executed with a Hewlett-Packard 5996A g.c.-m.s. system.

RESULTS AND DISCUSSION

Fig. 1 is a chromatogram of intact oily component of sap of Burmese lac on a 0.8x25-cm ODS-silica column using acetonitrile/water/acetic acid (80/20/2, v/v) as eluent. Each peak was extensively separated on a 2.2x30-cm ODS-silica column; if an obtained fraction was composed of more than one component as revealed by high-resolution g.l.c., it was again subjected to second l.c. separation on a 0.8x25-cm column. Each fraction was

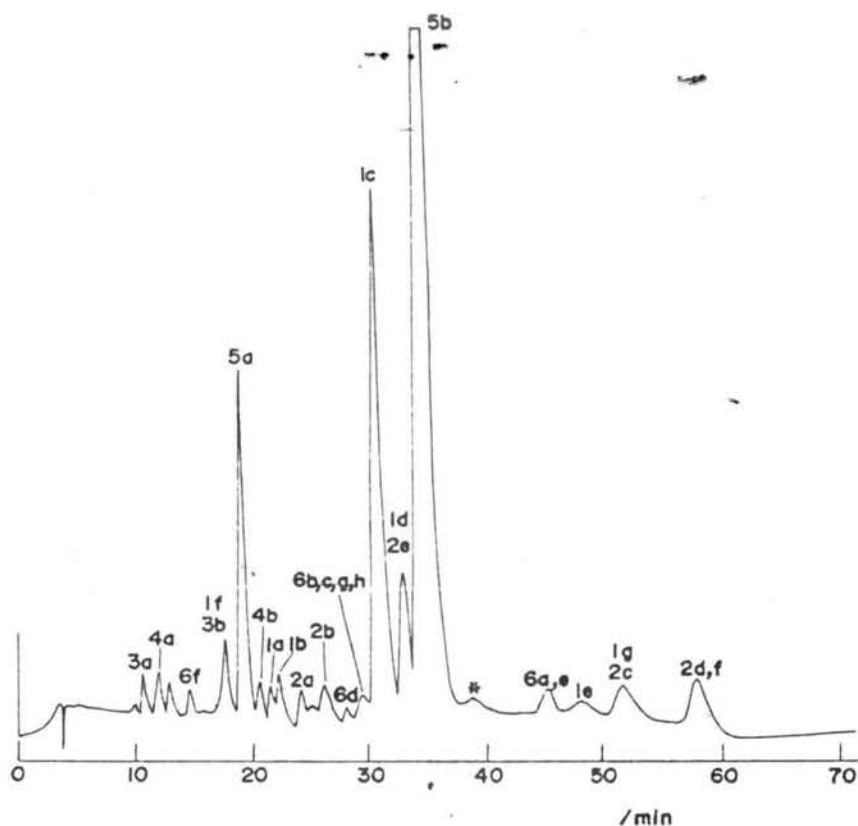


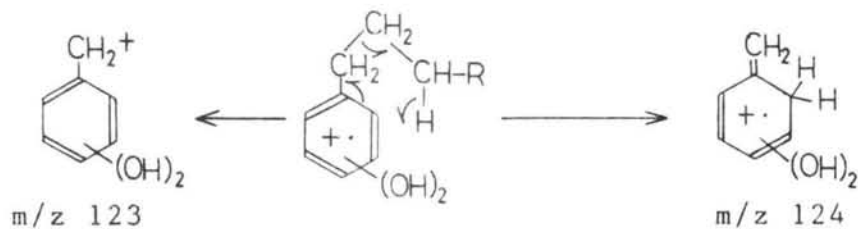
Fig. 1. CHROMATOGRAM OF INTACT OILY COMPONENT OF SAP OF *Melanorrhoea usitata*. CONDITIONS: COLUMN, TSK-GEL LS-410, 0.8x25cm; ELUENT, $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ (80/20/2, v/v); FLOW RATE, 2.5 ml/min; DETECTOR, 254 nm.

evaporated at 30 C to remove most of acetonitrile and the remained dispersion was extracted with n-hexane. The hexane solution was evaporated to give separated constituents of sap of *Melanorrhoea usitata*. Some fractions containing several components were subjected to g.l.c.-m.s. analysis.

Isolated constituents were identified by measuring i.r., ¹H n.m.r. and mass spectra to give results summarized in Table I. Symbols attached to peaks in Fig. 1 are corresponding to identified compounds in this Table.

Dihydric phenols with alkyl or alkenyl side chains

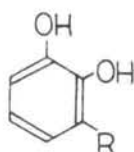
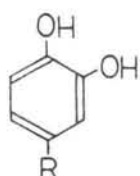
In m.s. diagrams of compounds 1a-1c, 1e, 1g, 2a-2c and 2f appeared a intense molecular ion peak and peaks of fragment ions given by cleavage of the bond beta to the aromatic ring (m/z 123) and by the McLafferty rearrangement (m/z 124) of the molecular ion (7):



Compounds **1a-1c**, **1e** and **1g** exhibited out-of-plane bending deformation bands of 1,2,4-trisubstituted benzene (810, 850 cm^{-1}), and were identified with congeners of thitsiol. The numbers of carbon atoms and double bonds in the side chain were determined from the M^+ value; **1b** and **1e** include isolated trans olefin groups as they have an i.r. band at 960 cm^{-1} .

In i.r. spectra of **2a-2c** and **2f**, out-of-plane bending deformation bands of 1,2,3-trisubstituted benzene were observed at 730 and 770 cm^{-1} . From M^+ values, **2a-2c** were identified with congeners of laccol and **2f** with saturated urushiol.

Compounds **1d**, **1f**, **2d** and **2e** were obtained as mixtures with other compounds and characterized by g.l.c.-m.s. measurement. They also showed molecular ion peaks and peaks due to dihydrobenzyl ion (m/z 123) and cyclohexadiene ion (m/z 124). Substituted position could not be determined from these m.s. data, but were suspected based on their retention time in the l.c. chart.



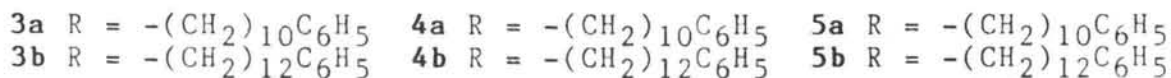
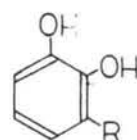
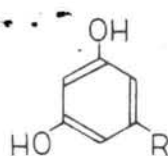
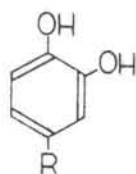
1a R = $\text{C}_{17:3}$
1b R = $\text{C}_{17:2(t)}$
1c R = $\text{C}_{17:2}$
1d R = $\text{C}_{17:2(t)}$
1e R = $\text{C}_{17:1(t)}$
1f R = $\text{C}_{15:1}$
1g R = $\text{C}_{15:0}$

2a R = $\text{C}_{17:3}$
2b R = $\text{C}_{17:3(t)}$
2c R = $\text{C}_{17:1}$
2d R = $\text{C}_{17:1(t)}$
2e R = $\text{C}_{15:1}$
2f R = $\text{C}_{15:0}$

The complete side chain structure of each homologue of thitsiol, laccol and urushiol found in this study should be determined in due time.

Dihydric phenols with ω -phenylalkyl side chains

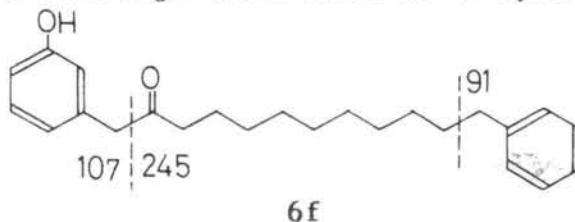
Compounds **3a**, **3b**, **4a**, **4b**, **5a** and **5b** showed very simple mass spectra, where only a molecular ion peak, peaks due to the m/z 123 and 124 ions and the m/z 91 ion were prominent. The presence of m/z 123 and 124 ions indicates that they are derivatives of dihydric phenol. As the m/z 91 ion stands for tropyllum ion derived from monoalkylbenzene, an alkylphenyl group is included in these compounds. This was confirmed by the existence of an intense i.r. band of monosubstituted benzene (700 cm^{-1}). The substituted position of phenolic nucleus in these compounds was determined from characteristic i.r. bands of out-of-plane bending deformation of the benzene ring. Consequently, it is established that **3a** and **3b** are 4-(10'-phenyldecyl)- and 4-(12'-phenyldodecyl)catechol, respectively, **4a** and **4b** are 5-(10'-phenyldecyl)- and 5-(12'-phenyldodecyl)resorcinol, and **5a** and **5b**, 3-(10'-phenyldecyl)- and 3-(12'-phenyldodecyl)catechol.



In the ^1H -n.m.r. spectra of **5a** and **5b** appeared superimposed triplets due to methylene protons at the 1' and 10' (12') positions (δ 2.59), quintets from methylene protons at the 2' and 9' (11') positions (δ 1.60), two singlets of hydroxyl protons (δ 4.95, 5.08), a multiplet due to monosubstituted phenyl protons (δ 7.17, 7.18), an apparent singlet of protons of 1,2,3-trisubstituted phenyl group (δ 6.71), and intense multiplets of methylene protons of the remaining portion of the molecule (δ 1.27, 1.30).

3-Substituted monohydric phenols

Compounds **6d-6f** showed simple mass spectra with a distinct molecular ion peak, peaks of m/z 107 and 108 and the m/z 91 peak. The m/z 107 and 108 ions were derived by cleavage of the bond beta to the aromatic ring and the McLafferty rearrangement of the molecular ion, respectively. This means that these compounds are monohydric phenols substituted with a long alkyl side chain. They also include a monoalkylphenyl group as a peak due to tropylium ion (m/z 91) was detected. In their i.r. spectra, absorption bands due to out-of-plane bending deformation of 1,3-disubstituted benzene (750 , 790 cm^{-1}) and that of monosubstituted benzene (700 cm^{-1}) were observed. Then these compounds are 3-substituted phenols with an -phenylalkyl side chain. From the M^+ value, **6d** was revealed to be 3-(10'-phenyldecyl)phenol and **6e**, 3-(12'-phenyldodecyl)phenol, **6f** showed an i.r. band due to a keto function at 1700 cm^{-1} , and a fragment ion of m/z 245 was found in the m.s. diagram which was given through α -cleavage with loss of a hydroxybenzyl group;



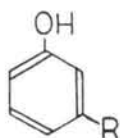
In the ^1H -n.m.r. spectrum were observed a singlet of methylene protons at the 1' position (δ 3.51) and two triplets due to methylene protons at the 3' (δ 2.42) and 12' positions (δ 2.60). From these data, the unique structure of **6f** has been established.

Compounds **6a-6c**, **6g** and **6h** were obtained in a very small amount as mixtures with other compounds and characterized by g.l.c.-m.s. measurement. The m/z 107 and 108 ions were common for all of their m.s. diagrams, leading that these compounds are

monohydric alkylphenols. **6a** showed series of fragment ions characteristic of n-alkenes and was revealed to be substituted with a C₁₇ n-alkenyl group with two double bonds from the M⁺ value (328). Compounds **6b** and **6c** showed relatively weak molecular ion peaks (m/z 372 and 373) and peaks of m/z 265 and 263, each of which was accompanied with a peak due to a fragment ion given by elimination of water. It was then revealed that they have a hydroxyl group at C-2' in the side chain. The number of carbon atoms and double bonds in the side chain were elucidated from the M⁺ value.

6g exhibited in the m.s. diagram a molecular ion peak (m/z 380) and a fragment ion of m/z 273 and no peak derived by dehydration as found in compounds **6d** and **6e**, and was concluded to contain a keto function at the 2' position. In the m.s. diagram of **6h**, the molecular ion (m/z 382) and the fragment ion (m/z 275) were associated with peaks derived by loss of water from these ions, indicating that this compound has a hydroxyl group at the 2' position.

The substituted position of these minor constituents was tentatively assigned to meta considering the biosynthetic route proposed for formation of phenolic lipids (8, 9).



- 6a** R = C_{17:2}
- 6b** R = -CH₂CH(OH)C_{17:2}
- 6c** R = -CH₂CH(OH)C_{17:3}
- 6d** R = -(CH₂)₁₀C₆H₅
- 6e** R = -(CH₂)₁₂C₆H₅
- 6f** R = -CH₂CO(CH₂)₁₀C₆H₅
- 6g** R = -CH₂CO(CH₂)₁₂C₆H₅
- 6h** R = -CH₂CH(OH)(CH₂)₁₂C₆H₅

CONCLUDING REMARKS

Content of each constituent was listed in Table I. One should notice that these values may not represent the exact composition of oily component of native sap as it exudates from lac tree, since the sample used in this investigation included only 50% of monomeric fraction presumably due to the polymerization during the storage and the transportation.

Nevertheless, it has been clarified that sap of Melanorrhoea usitate contains several types of phenolic lipids, i.e., thitsiol, laccol, urushiol, 3- and 4-(ω-phenylalkyl)catechols, 5-(ω-phenylalkyl)resorcinols and 3-substituted phenols with unique side chains. Latter novel compounds with ω-phenylalkyl side chains may be the substance which Majima suggested to exist in sap of Burmese lac in addition to thitsiol about 60 years ago.

An unusual phenolic lipid having a keto function at C-2', camnospermanol (3-(2'-oxo-9'(Z)-nonadecyl)phenol), has previously been isolated from Camnospermum auriculate (8). In the present study, have been found some compounds with a keto or hydroxyl function specifically attached to C-2'. This

specificity relates to the biosynthetic "polyketide" pathway which has been proposed as the general mechanism of formation of phenolic lipids (8, 9).

The analytical procedure presented here may be effectively applied to the quality control of natural products from plants grown in Southeast Asian countries. The more easier method based on modern capillary g.l.c. technique will be presented in a separate report.

Acknowledgment The authors would like to express their sincere gratitude to Dr. K. Hatanaka for measurement of 400 MHz ¹H-n.m.r. spectra, Mr. T. Takayama for m.s. measurement and Mr. S. Yamashita for g.l.c.-m.s. operation.

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TABLE I. CHARACTERISTICS OF CONSTITUENTS OF SAP OF Melanorrhoea usitate

compound	apparent content	m.s. (m/z)		i.r. (cm ⁻¹)
		M ⁺	others	
	wt%			
1a	2.0	342	123, 124	810, 850
1b	2.1	342	123, 124	810, 860, 960
1c	12.4	344	123, 124	810, 860
1d	ud*	344	123, 124	
1e	1.4	346	123, 124	810, 860, 960
1f	tr**	318	123, 124	
1g	1.0	320	123, 124	810, 860
2a	0.8	342	123, 124	730, 770
2b	0.9	342	123, 124	730, 770, 970
2c	tr	346	123, 124	730, 770
2d	tr	346	123, 124	
2e	tr	318	123, 124	
2f	2.7	320	123, 124	730, 770
3a	0.5	326	123, 124, 91	
3b	1.8	354	123, 124, 91	810, 850, 700
4a	0.4	326	123, 124, 91	830, 700
4b	0.3	354	123, 124, 91	830, 700
5a	8.6	326	123, 124, 91	730, 770, 700
5b	45.4	354	123, 124, 91	730, 770, 700
6a	tr	328	107, 108	
6b	tr	372	107, 108, 354, 265	
6c	tr	370	107, 108, 352, 263, 245	
6d	0.6	310	107, 108, 91	750, 790, 700
6e	0.7	338	107, 108, 91	750, 790, 700
6f	0.5	352	107, 108, 91, 245	750, 790, 700, 1700
6g	tr	380	107, 108, 91, 273	
6h	tr	382	107, 108, 91, 364, 275, 257	

* undetermined.

** trace.

THE DEVELOPMENT OF A SIMPLE METHOD
FOR TREATMENT OF TIMBER I PERMEABILITY MEASUREMENTS

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A simple idealized model for treatment of timber is a single step immersion process in a preservative bath. The first stage in developing such a method is to obtain precise permeability data. An experimental study has been made to identify the factors involved in acquiring reliable and reproducible permeability data of wood.

INTRODUCTION

The volume flow rate per unit area through porous media is given by Darcy's law:

$$\frac{dQ}{dt} = \frac{KA\Delta P}{\eta l}$$

where $\frac{dQ}{dt}$ is the volume flow rate of a fluid of viscosity η through a medium of cross-sectional area A and length l under a pressure differential ΔP . K is the permeability constant, characteristic of the penetrated medium and independent of the penetrating fluid.

While wood scientists generally assume that fluid flow in wood obeys Darcy's law, there is considerable evidence in the literature to indicate that this can be a questionable assumption. Several investigators of liquid flow in wood (1,2,3) found that, contrary to Darcy's law, liquid flow rate through wood decreased with time. Subsequently, it was shown (4,5,6) that the decreasing rate of flow was caused by blockage of submicroscopic pit pores by extraneous materials and gas bubbles, and that filtered, gas-free water could be passed through wood at a constant flow rate. Bailey (7) found that liquid flow rate increased more than expected with increased applied pressure and attributed this to the compression and flushing out of gas bubbles restricting critical passages. A deviation in the opposite direction was observed by Sucoff (8), who found that in passing water in the axial direction through northern white cedar sapwood increases in flow rate with increased pressure differential were substantially below those predicted by Darcy's law. They considered that air blockage and pit closure were not the causes of deviation and attributed it rather to turbulence and non-linear laminar flow.

It is evident from literature that there is some uncertainty in the application of Darcy's law to all wood specimens. The present investigation was therefore designed to ascertain whether Darcy's law could be used to determine longitudinal permeability of the sapwood of Kempas (*Koompassia Malaccensis*).

EXPERIMENTAL

The apparatus constructed was identical to that detailed by Kininmonth (9), but the level of the hydrostatic pressure was automatically maintained by a carburettor float. The flow rate through the specimen was measured with a Tri-Flat flowmeter which takes ten seconds to give a reliable reading after a steady flow is established. The liquid inlet and outlet sections to the specimen were sealed between the flanges by two neoprene O-rings of 14.5 mm in diameter. The O-rings were aligned with respect to the grain in order to prevent water spillage. The specimen cell assembly was then clamped between two perspex sheets, machined to accept the glass flanges, by bolts and nuts.

All specimens were cut from the sapwood of Kempas (*Koompassia Malaccensis*), microtomed and outgassed prior to permeability measurements. To remove air from the specimens, a beaker containing the submerged specimens was placed in a dessicator and evacuated by a water-suction pump. The vacuum was released and the specimens were allowed to soak in the water. This cycle was repeated over a period of two days. Finally the specimens were left for 12 hours under vacuum. The method adopted for the deaeration of water was by ultrasonic cavitation under reduced pressure, the ultrasonic generator used being a Soniprobe, made by Dawe Instruments Ltd.

RESULTS AND DISCUSSION

It is generally considered by wood scientists that Darcy's law is obeyed with respect to length of the wood specimen. The effect of specimen length on wood permeability is shown in Fig. 1. It is apparent from the

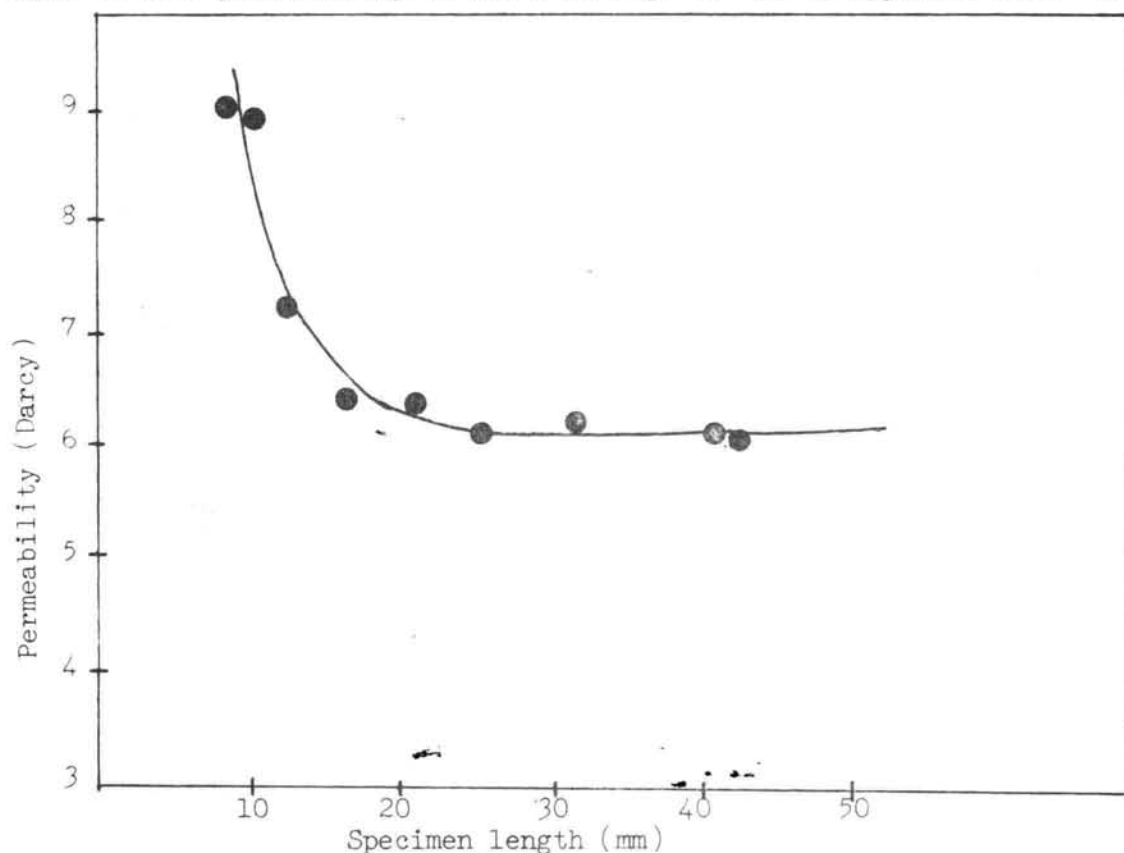


FIG. 1 PERMEABILITY AS A FUNCTION OF SPECIMEN LENGTH

curve that only specimens greater than 20 mm obey Darcy's law. Because all specimens were microtomed, water has unimpeded access to the lumens at the end faces, so that the effective permeation length is slightly less than the measured length. If the specimen is long this effect will be negligible. But, it is reasonable to assume that with shorter specimens, some of conducting paths will now offer very little resistance to flow. Consequently, in such cases, the permeability will be abnormally high as observed suggesting a deviation from Darcy's law.

Fig. 2 shows the variation in flow rate with time for a specimen whose length was 22 mm. The flow rate decreases very rapidly during the first 3 min. of flow after which the decrease continues at a much slower rate. If the direction of flow is reversed, flow would start at a rate considerably

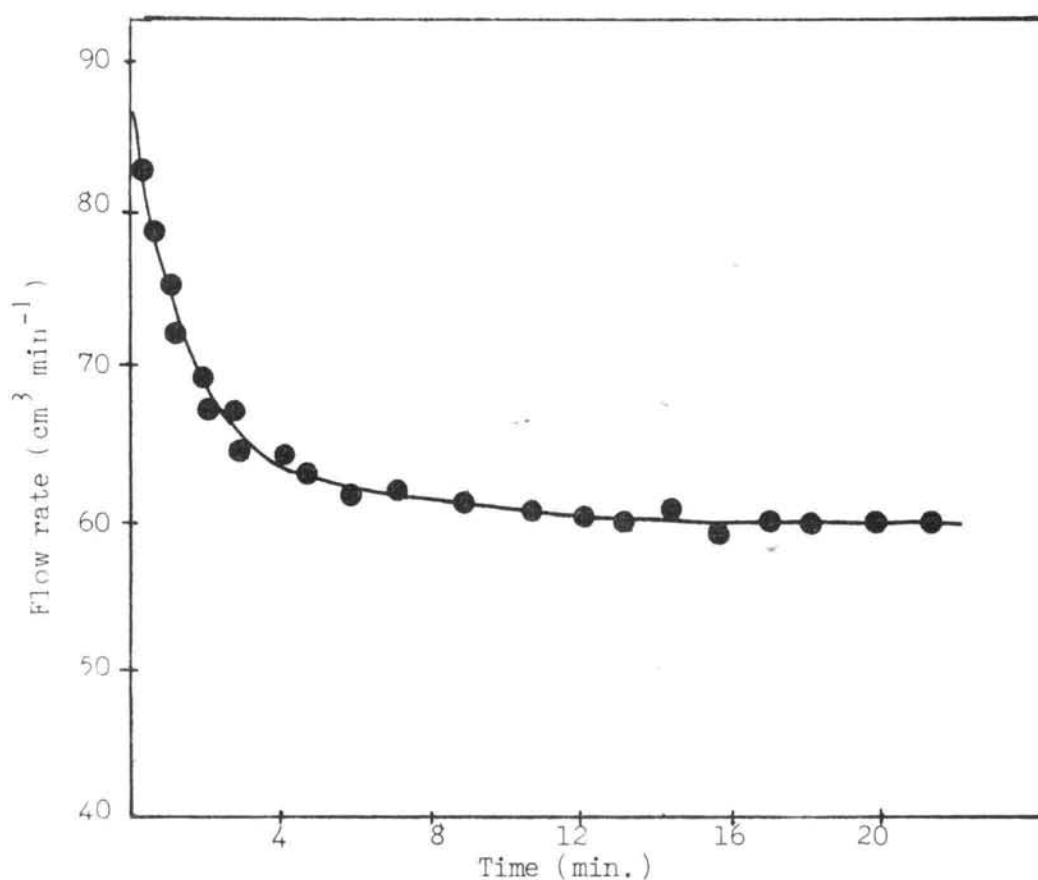


FIG. 2 FLOW RATE AS A FUNCTION OF TIME WITH DOUBLE-DISTILLED FILTERED WATER.

higher than that which prevailed just prior to reversal and then decrease in the same manner as before. These observations could be accounted for by the presence of minute particles in the water. These particles would become trapped in the pores and progressively reduce the permeability of the specimen. Reversal of the direction of the flow would remove some of the obstructions thus increasing the flow rate as observed. However when flow was temporarily interrupted, the flow rate recovered to a similar extent as when the direction of flow was reversed indicating that the decrease in flow rate with time was not due to obstructions in the flow paths caused by particles in the water.

Kelso (8) attributed the decrease in flow rate with time to the formation of air bubbles. Wood is composed of a complex series-parallel arrangement of conducting vessels with constrictions. If under conditions of constant mass flow, a constriction is placed in an uniform cylindrical conductor, the linear velocity must increase at the point of constriction. It follows from Bernoulli's principle that when the linear velocity of a fluid in a conductor is increased, the pressure is decreased accordingly. When a fluid is passed through wood, the size and distribution of the constrictions in the path of flow would similarly influence the linear velocity and pressure distribution. If the liquid contained dissolved gas, then the gas may evolve from the liquid at a constriction where the pressure is below the original saturation pressure for the gas. The resulting bubbles could then be trapped at the next downstream constriction thereby progressively reducing the wood's permeability. This explanation is

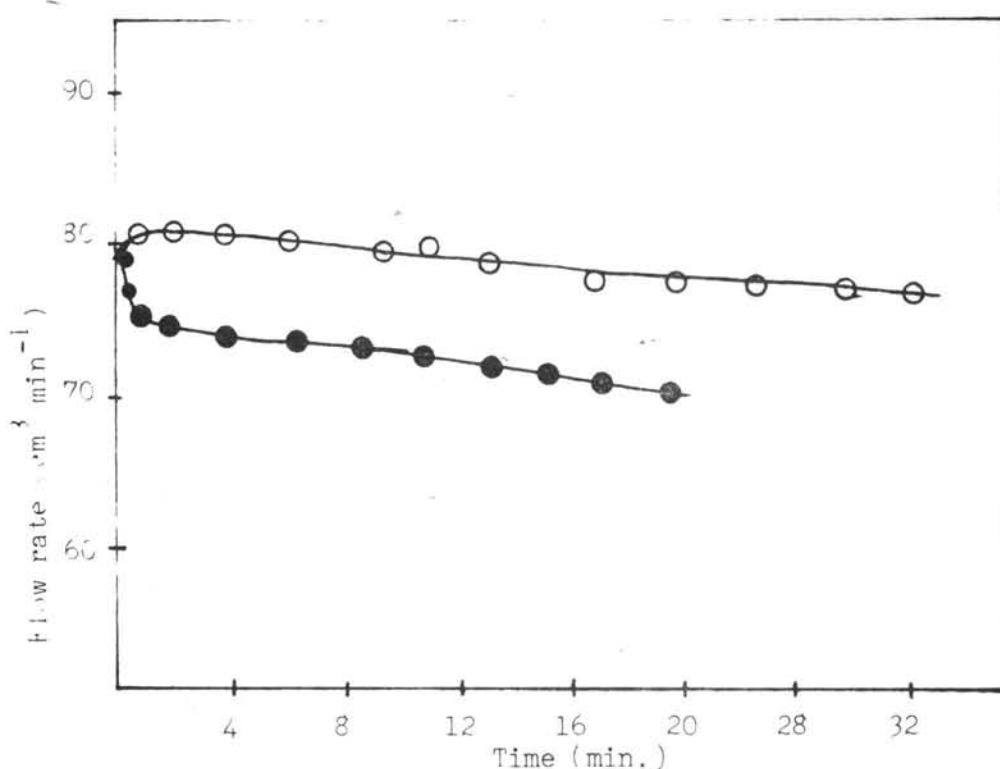


FIG. 3 COMPARISON OF THE RATES OF FLOW OF DEAERATED WATER WHICH WAS NOT DEAERATED THROUGH TWO OUTGASSED MATCHED SPECIMENS.
○ DEAERATED WATER; ● NON-DEAERATED WATER.

consistent with the results shown in Fig. 3 where the flow rates with time of deaerated water and water which had not been deaerated for two matched specimens are compared. Almost constant flow was obtained with deaerated water over a period of 30 min. The slight decrease in flow rate can be attributed to re-aeration of water during the measurements. However no explanation can currently be offered for the increase in flow rate observed in the initial region of the deaerated water plot.

Fig. 4 shows the variation in flow rate with time for a specimen that was not outgassed but where deaerated filtered water was used for permeation. The specimen was end-matched to the specimens in Fig. 3. The expected initial rapid decrease in flow rate is observed but this is followed by an increase in the permeability of the specimen. The increase in flow rate suggests that the air bubbles causing blockage of pit pores are being removed probably because of its solubility in deaerated water. However, in all cases the initial flow rate of end-matched deaerated and non-deaerated water were similar.

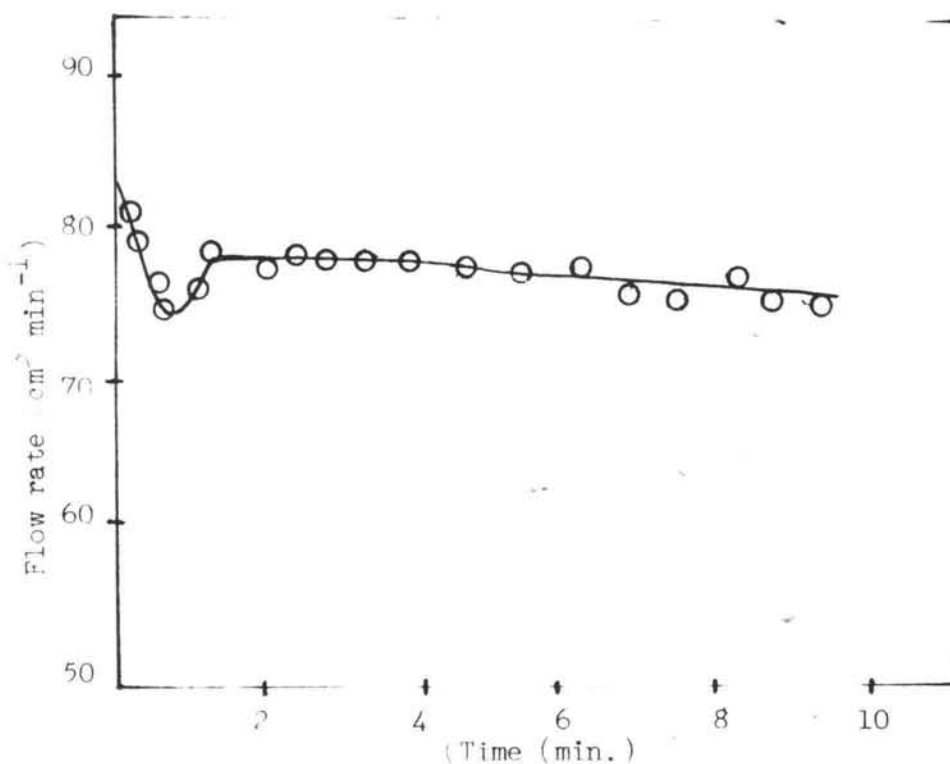


FIG. 4 FLOW RATE AS A FUNCTION OF TIME OF DEAERATED FILTERED WATER THROUGH A SPECIMEN THAT WAS NOT OUTGASSED.

The rates of flow with filtered (100 nm) and unfiltered deaerated tapwater are shown for two matched specimens in Fig. 5. The constant flow rate with filtered tapwater was similar to that obtained with double-distilled filtered water, an indication that the pore size of the pits in the specimen was in excess of 100 nm. With unfiltered tapwater the flow rate dropped to half its value in about 12 min.

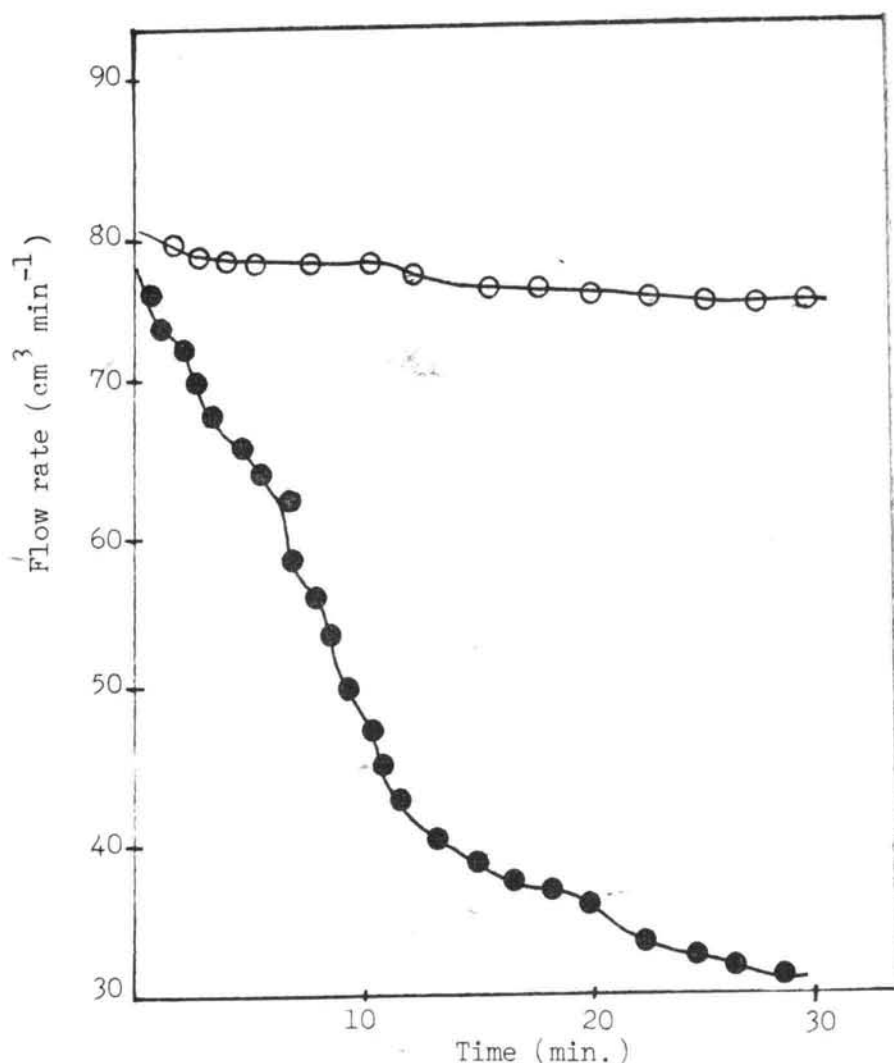


FIG. 5 COMPARISON OF THE RATES OF FILTERED AND UNFILTERED TAPWATER THROUGH TWO MATCHED SPECIMENS. ○ FILTERED TAPWATER; ● UNFILTERED TAPWATER.

CONCLUSIONS

- i. The specimens of length greater than 22 mm were found to obey Darcy's law.
- ii. With extreme care constant flow can be achieved through a degassed sample with deaerated double-distilled water.
- iii. The flow rate decreased sharply for specimens that have not been degassed or when non-deaerated water is used. However, if the degree of aeration is small, the initial flow rate is the same as it would have been if complete deaeration had occurred.
- iv. Reliable permeability values can be calculated for specimens using the initial flow rate, even if deaeration was not complete in wood or water.

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THE STUDY OF AMMONIUM BIFLUORIDE AS A FLUORINATING AGENT

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ABSTRACT

The utilization of ammonium bifluoride as fluorinating agent is relatively inexpensive and easy to handle hence worthwhile to be investigated extensively. Reactions of organochloro-silanes, -phosphorus compounds and organosulfonyl chlorides with ammonium bifluoride have been studied and the proposed mechanisms discussed.

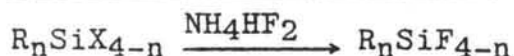
INTRODUCTION

The various applications of organic fluoro-compounds and rising demand for them stimulated the interest in searching for more versatile fluorinating agents. Ammonium bifluoride, NH_4HF_2 , readily obtainable by reacting ammonium hydroxide with hydrofluoric acid, seems to be a potential fluorinating agent though its capability in this respect has not been often reported.¹⁻⁵

Fluorination using NH_4HF_2 showed the advantages of relative low cost and simple handling of the reactions. In this work, fluorination of organochloro-silanes, -phosphorus compounds as well as organosulfonyl chlorides were investigated.

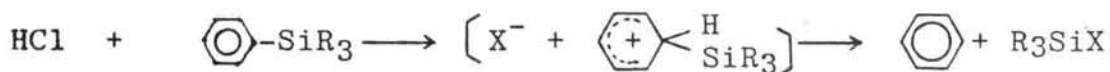
RESULTS AND DISCUSSION

Organic Silicon Fluorides



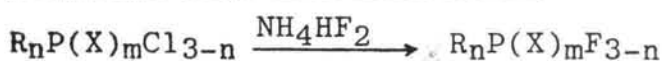
For X was a chlorine and R were some alkyl groups, the reaction gave 91-98% yield of fluorinated products under room temperature. While X was a chlorine and R were several different aryl groups, yields of 60-87% were obtained. For X was alkoxy or amino groups and the reaction was carried out in refluxing CCl_4 , 82-85% yield of products were obtained.

The less satisfactory yield of arylfluorosilanes was owing to the splitting of C-Si bonding by hydrogen chloride generated from the reaction of ammonium bifluoride and chlorosilanes. Bott⁶ had proposed a mechanism of electrophilic aromatic substitution to explain the cleavage of C-Si bond.

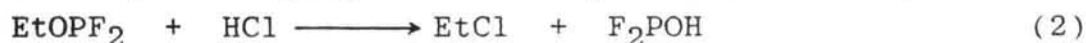


In consistence with this mechanism, we found the carbon-silicone bond splitted easily in the polar solvent, but much more sluggishly in the nonpolar solvent⁷.

Organic Phosphorus Fluorides

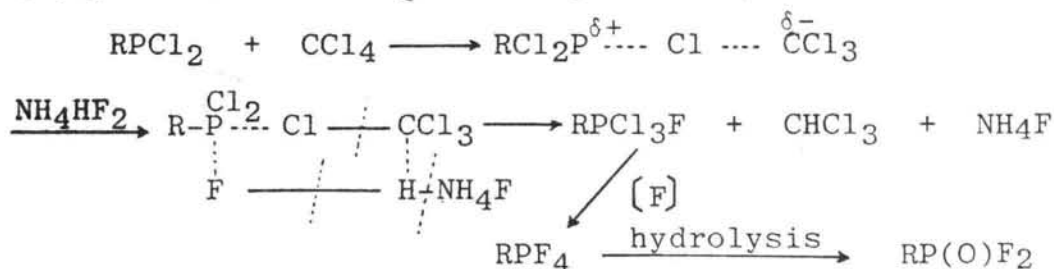


For the pentavalent phosphorus compounds, the corresponding fluorinated products have been prepared under mild conditions and the yields were relatively high. Whereas, in case of the trivalent phosphorus compounds only gave low yield of the desired halogen exchange products. When R was alkoxy group, the mixture of final products containing RCl, PF₃ as well as their corresponding fluorinated compounds were obtained. For instance, the reaction of (C₂H₅O)PCl₂ and ammonium bifluoride gave a reaction mixture which consists of EtOPF₂, EtCl, PF₃ and FHP(O)OH. The mechanism below was proposed to interpret the formation of these compounds.



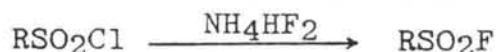
It has been known that hydrogen chloride can split the carbon-oxygen bond of alkyl phosphites (eq.(2)). The phosphinous acid, F₂POH, thus formed was converted readily to difluorophosphine oxide, F₂P(O)H (eq.(3)), which was then disproportionated to phosphorus trifluoride and phosphinic acid FHP(O)-OH⁸.

It was reported that C₆H₅PF₃H was the reaction product of C₆H₅PCl₂ and potassium hydrogen fluoride⁹. In our experiment, using carbon tetrachloride as solvent, fluorination of phenyldichlorophosphine by NH₄HF₂ yield C₆H₅PF₄ and trace of C₆H₅P(O)F₂. This result can be explained by the following scheme.



Carbon tetrachloride played an important role to form a complex with phenyldichlorophosphine. This complex was then reacted with NH_4HF_2 to produce phenyltrichlorofluorophosphorane¹⁰, which was further fluorinated to $\text{C}_6\text{H}_5\text{PF}_4$. Consequently, $\text{C}_6\text{H}_5\text{-P(O)F}_2$ was produced by hydrolysis of $\text{C}_6\text{H}_5\text{PF}_4$.

Organic Sulfonyl Fluorides



For this kind of compounds the rate of halogen exchange reaction was quite depending on solvent system. Sulfonyl chlorides could readily be converted to the corresponding fluorides by ammonium bifluoride in H_2O , DMSO or DMF under ambient temperature. When acetonitrile or o-dichlorobenzene was used as solvent, this conversion proceeded under reflux. Acid-binder (i.e. triethyl amine) was required to promote this fluorination reaction, in case of the solvent used was toluene or petroleum ether.

EXPERIMENTAL

Fluorination was carried out in the usual way using Pyrex flask fitted with reflux condenser on the magnetic stirrer. The analytical instruments used were

H^1 NMR: Bruker WP 80, internal TMS

F^{19} NMR: Jeol FX90Q, internal CFCl_3 or CF_3COOH (TFA)
negative chemical shifts refer to high field.

The experimental results are list on the table I - III.

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TABLE I. SYNTHESIS OF ORGANIC SILICON FLUORIDES

Reactants	Products	Solvent	Condi- tion	Rxn. Time (hr)	Yield %	^1H NMR δ_{TMS} ppm (CD_3) $_2\text{CO}$	^{19}F NMR δ_{TFA} ppm (CD_3) $_2\text{CO}$
CH_3SiCl_3	CH_3SiF_3	CCl_4	r.t.	0.5	98	0.66(q) $J_{\text{HF}}=4.0\text{Hz}$	-57.1(q) $J_{\text{HF}}=4.0\text{Hz}$
$(\text{CH}_3)_2\text{SiCl}_2$	$(\text{CH}_3)_2\text{SiF}_2$	CCl_4	r.t.	0.5	95	0.35(t) $J_{\text{HF}}=5.9\text{Hz}$	-55.1(heptet) $J_{\text{HF}}=5.9\text{Hz}$
$(\text{CH}_3)_3\text{SiCl}$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	r.t.	2	98	0.24(d) $J_{\text{HF}}=7.2\text{Hz}$	-80.9(decet) $J_{\text{HF}}=7.2\text{Hz}$
$(\text{CH}_3)_3\text{SiOMe}$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	reflux	2	91	"	"
$(\text{CH}_3)_3\text{SiNHPH}$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	reflux	2	85	"	"
$(\text{CH}_3)_3\text{SiNEt}_2$	$(\text{CH}_3)_3\text{SiF}$	CCl_4	reflux	2	83	"	"
$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$	$(\text{CH}_3)_2\text{SiF}_2$	CCl_4	reflux	4	82	"	"
PhSiCl_3	PhSiF_3	CH_2Cl_2	r.t.	2	60	7.6(m), 3H 7.4(m), 2H	-66.3(s)
Ph_2SiCl_2	Ph_2SiF_2	$\text{O}-\text{C}_6\text{H}_4\text{Cl}_2$	r.t.	2	81	7.70(m)	-66.2(s)
Ph_3SiCl	Ph_3SiF	C_6H_6	r.t.	4	62	7.54(m)	-92.9(s)
Et_3SiCl	Et_3SiF	$\text{C}_6\text{H}_5\text{NO}_2$	r.t.	2	85	0.6-1.0(m)	-99.4(m)
$(\text{CH}_3)_2\text{PhSiCl}$	$(\text{CH}_3)_2\text{PhSiF}$	CCl_4	r.t.	2	87	0.45(d), 6H $J_{\text{HF}}=8.0\text{Hz}$ 7.5(m), 5H	-84.8(heptet) $J_{\text{HF}}=8.0\text{Hz}$
$\text{CH}_2=\text{CHSiCl}_3$	$\text{CH}_2=\text{CHSiF}_3$	CCl_4	r.t.	2	94	6.0-6.8(m)	-65.2(s)

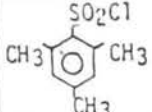
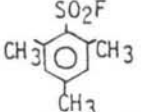
TABLE II. SYNTHESIS OF ORGANIC PHOSPHORUS FLUORIDES

Reactants	Products	Rxn. Time	Rxn. Solvent	Condi- tion	Yield %	B.P. of Products	^{19}F NMR $\delta\text{CCl}_3\text{F}$ ppm CDCl_3
$(\text{EtO})_2\text{P}(=\text{O})\text{Cl}$	$(\text{EtO})_2\text{P}(=\text{O})\text{F}$	2 hr	CCl_4	r.t.	51	$78^\circ\text{C}/20\text{mm}$	$-81.55, J_{\text{P-F}}=975\text{Hz}$
$(i\text{-PrO})_2\text{P}(=\text{O})\text{Cl}$	$(i\text{-PrO})_2\text{P}(=\text{O})\text{F}$	2 hr	CCl_4	r.t.	69	$82-3^\circ\text{C}/20\text{mm}$	$-78.7, J_{\text{P-F}}=973\text{Hz}$
$\text{PhP}(=\text{O})\text{Cl}_2$	$\text{PhP}(=\text{O})\text{F}_2$	2 hr	CCl_4	r.t.	50	$86-7^\circ\text{C}/20\text{mm}$	$-65.7, J_{\text{P-F}}=1105\text{Hz}$
$\text{CH}_3\text{P}(=\text{S})\text{Cl}_2$	$\text{CH}_3\text{P}(=\text{S})\text{F}_2$	2 hr	CCl_4	r.t.	40	$59-60^\circ\text{C}$	$-42.75, J_{\text{P-F}}=1142\text{Hz}$
PhPCl_2	PhPF_4	2 hr	CCl_4	r.t.	42	$132-4^\circ\text{C}$	$-55.4, J_{\text{P-F}}=966\text{Hz}$
PhOPCl_2	$\text{PhOPF}_2^{(1)}$	2 hr	CCl_4	r.t.	40	$124-5^\circ\text{C}$	$-44.5, J_{\text{P-F}}=1327\text{Hz}$
EtOPCl_2	$\text{EtOPF}_2^{(2)}$	2 hr	CCl_4	r.t.	20<	16°C	$-49.3, J_{\text{P-F}}=1288\text{Hz}$

(1) Other trace amount of impurities were PhOPClF (^{19}F δ -53.3,d), PF_3 (^{19}F δ -32.9,d), FHP(O)OH (^{19}F δ -61.2,dd).

(2) Other trace amount of impurities were PF_3 (^{19}F δ -33.4,d), FHP(O)OH (^{19}F δ -60.7,dd).

TABLE III. SYNTHESIS OF ORGANIC-SULFONYL FLUORIDES

Reactants	Products	Solvent (Et) ₃ N	Rxn. Temp. (hr)	Rxn. Temp. (°C)	Yield (%)	¹⁹ F NMR δCCl ₃ F ppm
CCl ₃ SO ₂ Cl	CCl ₃ SO ₂ F ⁷¹	xylene	4	reflux	no	
		ether ✓	24	r.t.	no	
		H ₂ O	18	r.t.	no	
		H ₂ O+ acetone	18	r.t.	no	
CH ₃ SO ₂ Cl	CH ₃ SO ₂ F	DCB	4	r.t.	no	61.1(q)
		DCB	8	reflux	57	
		CH ₃ CN	4	r.t.	no	
		CH ₃ CN	72	reflux	64	
		H ₂ O	6	r.t.	50	
		DMSO	0.2	r.t.	89	
		DMF	0.2	r.t.	64	
o-NO ₂ C ₆ H ₄ SO ₂ Cl	o-NO ₂ C ₆ H ₄ SO ₂ F	toluene	4	reflux	trace	64.6(S)
		toluene ✓	4	reflux	75	
		H ₂ O	18	r.t.	95.3	
		H ₂ O+ acetone	18	r.t.	93.8	
p-NO ₂ C ₆ H ₄ SO ₂ Cl	p-NO ₂ C ₆ H ₄ SO ₂ F	xylene	4	r.t.	no	65.7(S)
		xylene	5	reflux	trace	
		toluene ✓	3	reflux	75	
		H ₂ O	24	40	87	
p-CH ₃ C ₆ H ₄ SO ₂ Cl	p-CH ₃ C ₆ H ₄ SO ₂ F	toluene	5	reflux	trace	65.8(S)
		toluene ✓	3	reflux	73	
		H ₂ O	24	r.t.	22	
		Benzene	14	r.t.	85	
PhSO ₂ Cl	PhSO ₂ F	xylene	5	reflux	43	65.4(S)
		xylene	4	r.t.	no	
		CH ₃ CN	4	r.t.	no	
		CH ₃ CN	72	reflux	60	
		H ₂ O	48	r.t.	73	
		DMSO	0.2	r.t.	74	
p-BrC ₆ H ₄ SO ₂ Cl	p-BrC ₆ H ₄ SO ₂ F	toluene	5	reflux	trace	65.9(S)
		toluene ✓	4	reflux	80	
		H ₂ O	20	40	94	
		xylene	5	reflux	no	67.8(S)
		Petroleum ether ✓	3	reflux	60	
		H ₂ O	20	40	89	

