

# Journal of Scientific & Industrial Research



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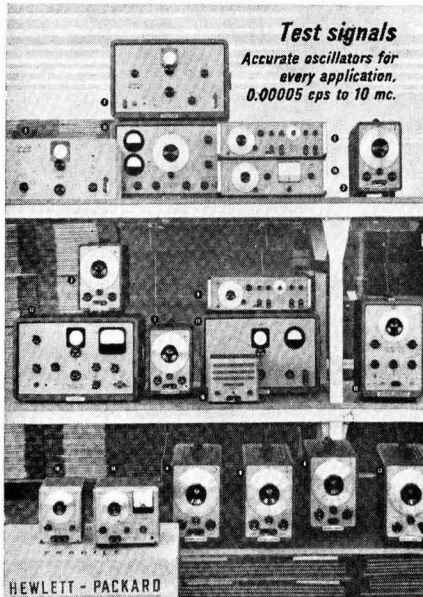
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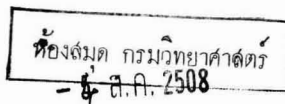
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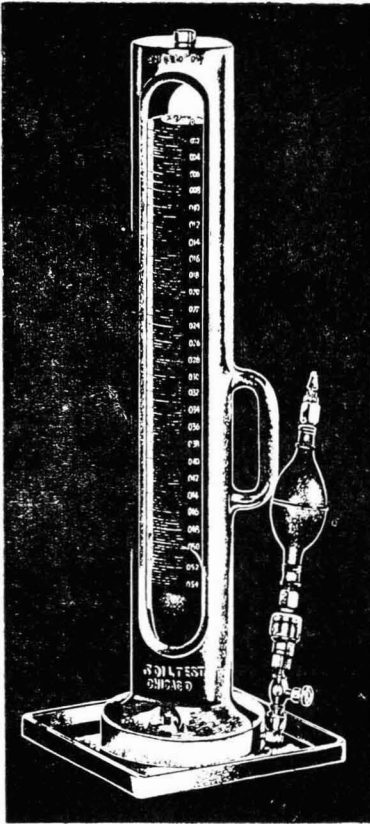
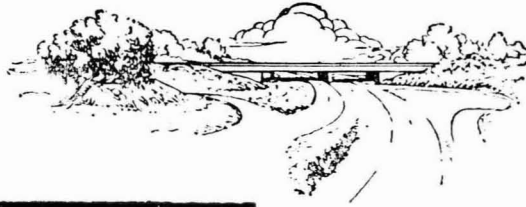
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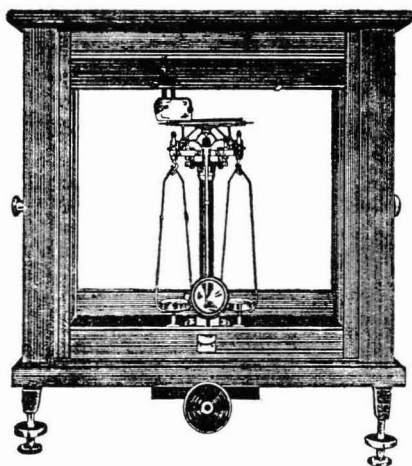


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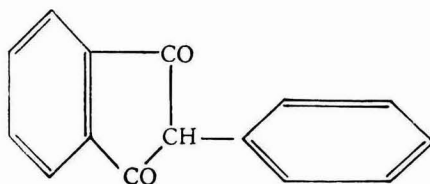
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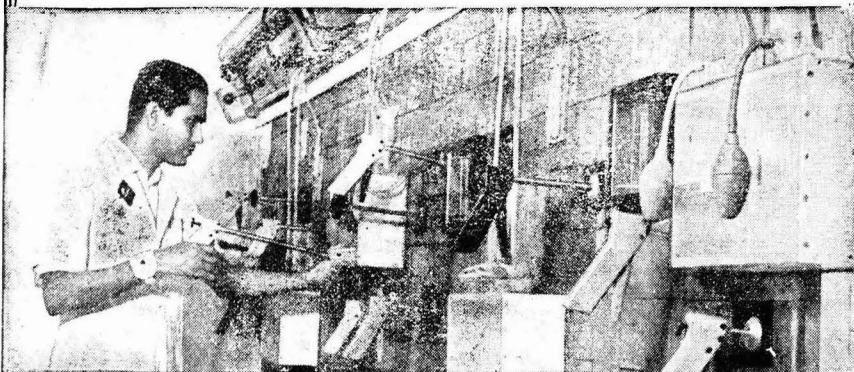
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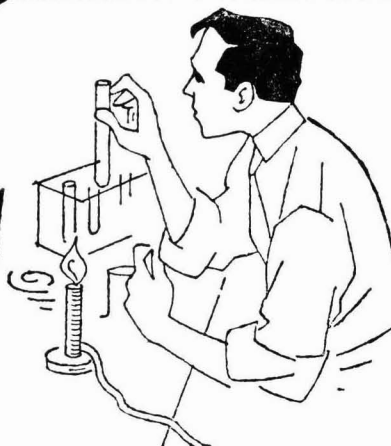
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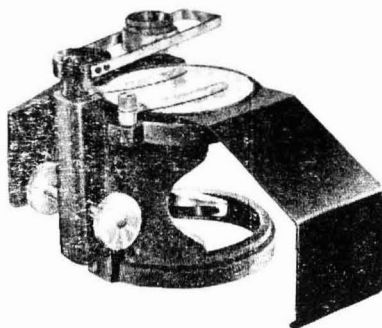
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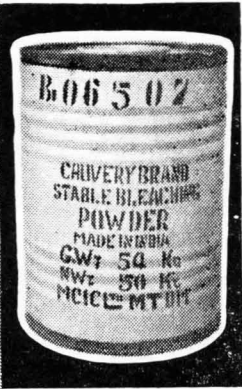
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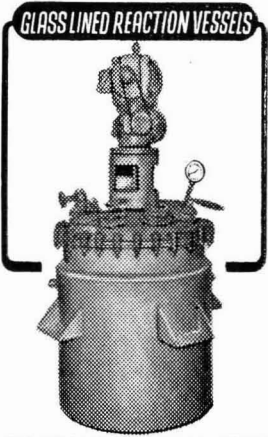


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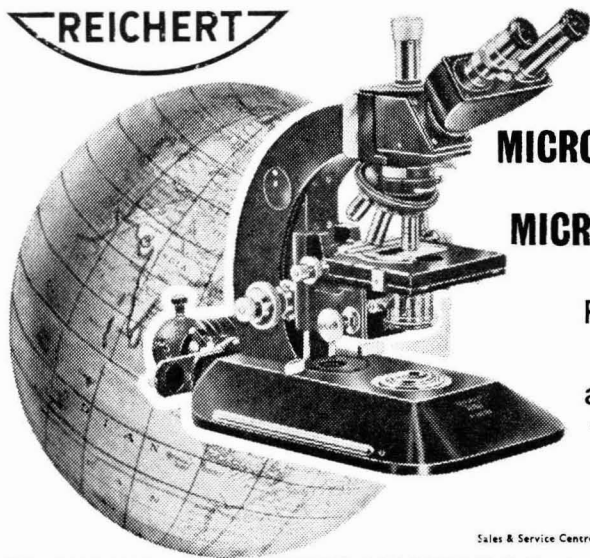
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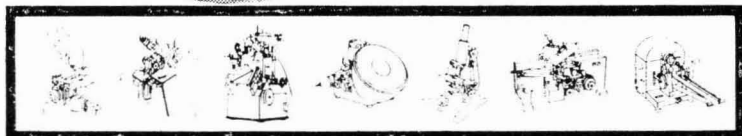
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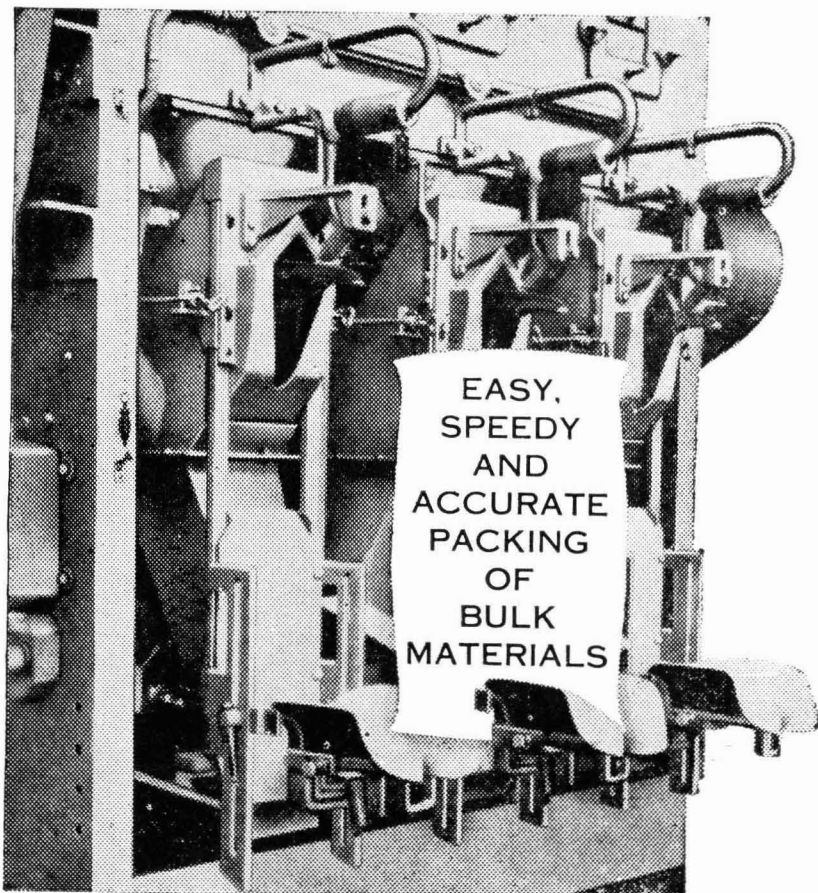
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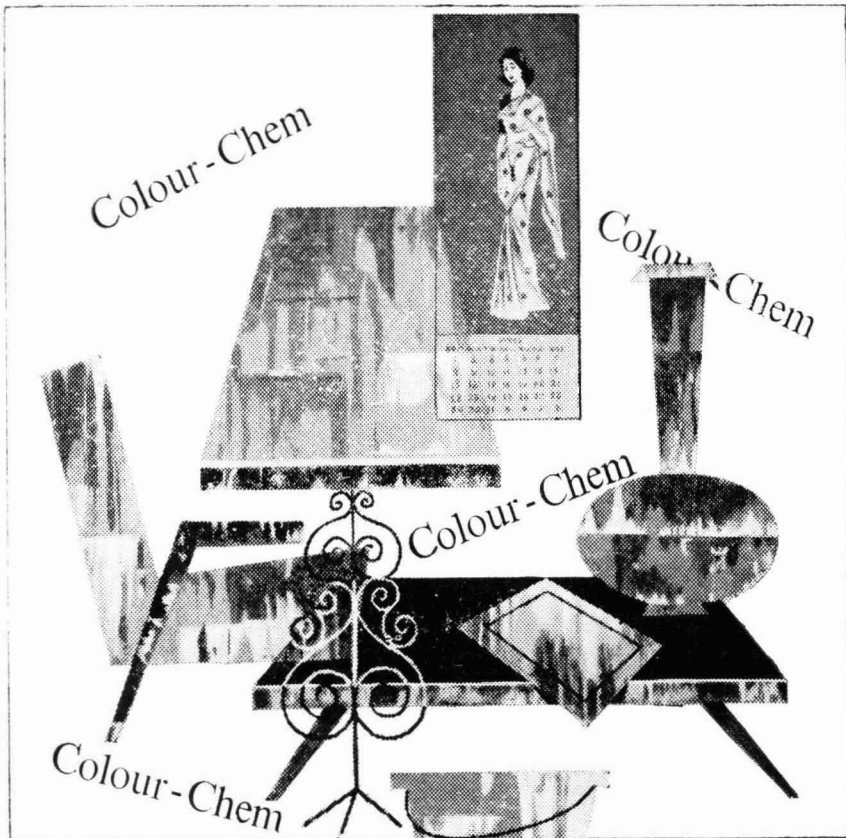
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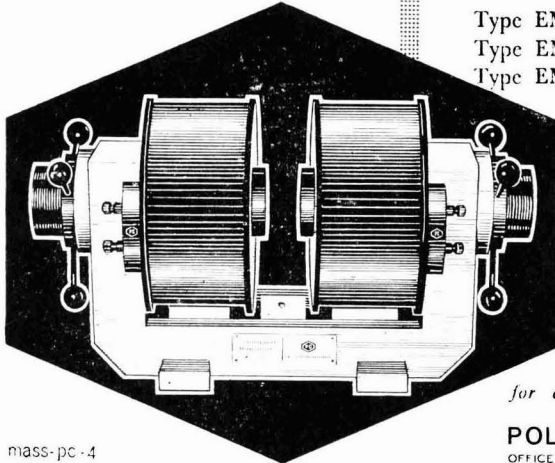
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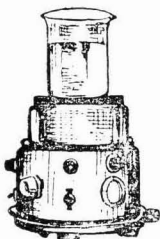
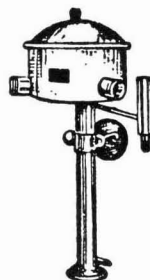
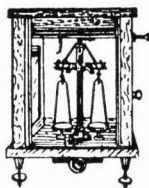
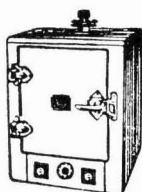
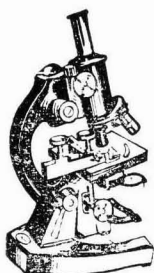
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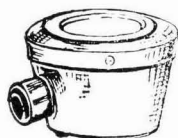
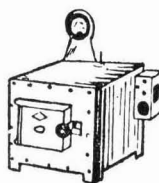
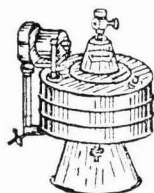
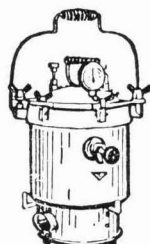
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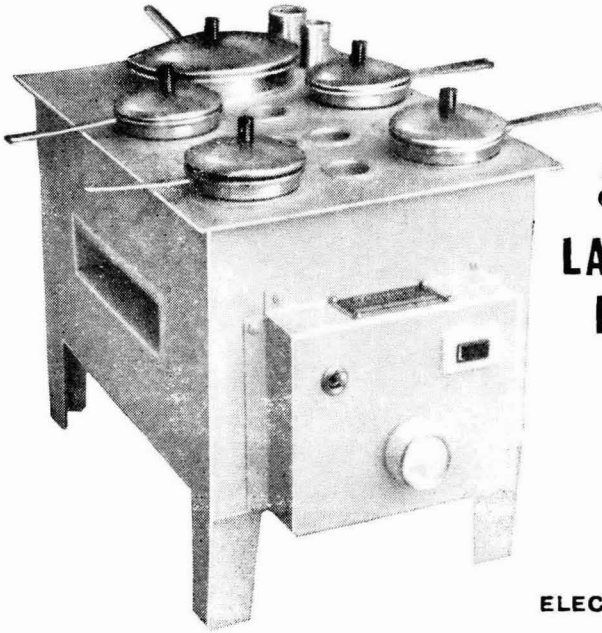
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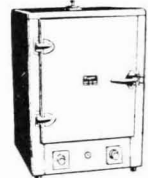
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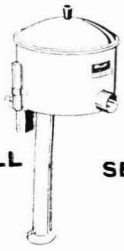
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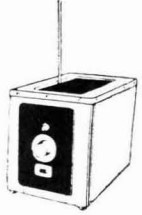
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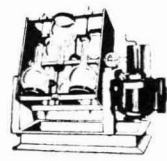


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# Current Topics

## Prevention of Malnutrition in the Pre-school Child

A FIVE-DAY International Conference on Prevention of Malnutrition in the Pre-school Child was held in Washington DC during 7-11 December 1964 under the sponsorship of the Food and Nutrition Board of the National Academy of Sciences and the National Research Council. Organized by the Board's Committees on Protein Malnutrition and Child Nutrition, the meeting brought together more than 100 leaders in medical and nutritional research programmes and alleviative operations from 20 countries. The conference is a sequel to an earlier conference held under the same auspices in 1960 to discuss the 'Progress in meeting the protein needs of infants and pre-school children'.

It is now being increasingly realized that the nutrition of the pre-school child is of paramount importance in the development of any country. Malnutrition in this group is widespread and has been recognized now as the cause of many diseases. The nutrition of the infant is fairly well cared for as long as it is on mother's milk, provided the mother is healthy and is able to supply adequate quantities of milk. But the post-weaning period, when the child is deprived of the mother's milk and is not provided with other nutritious food, is the most critical. Surveys in Africa, India, Burma and other countries have established that kwashiorkor and protein malnutrition are generally prevalent in this age group. As Dr W. H. Sebrell (Jr), Director, Institute of Nutritional Sciences, Columbia University and Chairman of the Committee on Protein Malnutrition, stated in his opening remarks, "from evidence gathered among under-privileged people in all parts of the world, it has been established that malnutrition in very young children is double-edged. It is responsible for physical and mental retardation that chains millions to poverty. It also is a primary contributory factor in countless deaths attributed to diseases that account for much lower death rates in protein-vitamin sufficient areas. Achievement of economic sufficiency by that half of the world termed underdeveloped or emerging is tragically impeded when so many of its populations are weakened throughout life and large segments of new generations die in immaturity from deficiencies in calories, proteins and vitamins. The costs of this situation to the world—in productive abilities, in health and well-being, and in its effect on peace—are incalculable."

The importance of this conference has to be viewed against this background. To us in India, it has a special significance, as nearly one-sixth of the total population of the country is in this age group. Due to lack of adequate supply of nutritious foods,

like milk or meat, and as a consequence of the general poverty of the people, the weaned infant is rarely provided with a food that can meet its protein requirements. Gruels made out of cereal grains or tubers, with very little (if at all any) milk supplement, form the main food of many children in this age group. More often they are fed on the highly starchy diets that are taken by their parents. Protein malnutrition, often associated with calorie and vitamin malnutrition, is a frequent occurrence in pre-school children, not only in India but also in many other developing countries, where similar conditions prevail.

During the last decade, considerable amount of work has been carried out in India to overcome this problem. Milk is not in sufficient supply to meet the requirements, nor is it available at a price within the purchasing power of the large majority. The fish wealth of the long coastline of India is still untapped, and processing and preservation units have yet to be established and developed. In this context, the obvious solution is proteins from vegetable sources, particularly oilseed meals. A conservative estimate has placed the available amount of protein from groundnut alone at 1 million tons per annum. This itself, if properly processed and used for the weaned child, would provide adequate amount of protein. In addition to this, large quantities of other seed cakes like cottonseed meal, sesame meal, etc., are available in the country.

The Central Food Technological Research Institute (CFTRI), Mysore, has pioneered research in this field and has evolved many foods suitable for the pre-school child. The Indian Multipurpose Food based on peanut flour and Bengal gram has now been established as a suitable food for pre-school children. The food is fortified with minerals and vitamins and has good nutritive value. Its use in the mid-day meal programme of the schools in Madras State has given encouraging results and this programme is being extended to other States. Another signal contribution of CFTRI in the field of protein-rich foods has been the standardization of the method of preparation of groundnut protein isolate and foods based on it. Spray dried protein foods which resemble milk powder have been prepared and tested by carrying out large-scale trials on infants and children. Blends of protein isolate with milk powder have been successfully used in the prevention and cure of kwashiorkor. The institute has also carried out considerable research work with malt food, fish meal and other similar foods.

The Nutrition Research Laboratories, Hyderabad, has carried out surveys and has established the wide prevalence of kwashiorkor in the country. Their work has thrown considerable light on the metabolic aspects of the disease.

Another active centre of research on problems of malnutrition and under-nourishment in pre-school children is the Institute of Central America and Panama (INCAP). This institute has evolved a number of foods under the name INCAPARINA based on vegetable proteins and one of the blends contains 40 per cent cottonseed cake. INCAPARINA has now been put out for sale through commercial channels and is very popular in that country.

The purpose of the recent Washington conference was to provide a forum for discussion of problems connected with malnutrition in the pre-school children. Representatives from countries most concerned with the problem, viz. Mexico, Peru, Central and Latin America, Africa and India, presented the problems of their respective countries and exchanged views on the methods of overcoming them. The discussions and proceedings of the conference when published will be of considerable importance to the research workers in the field.

The Committee on Protein Malnutrition which organized the conference deserves to be congratulated for holding the conference at a time when the problem has assumed a very critical stage, especially in the developing areas of the world.

M. R. CHANDRASEKHARA

### Puzzolanic Materials: Need for an Organized Industry

CHRONIC shortages of portland cement have led to a revival of interest in puzzolanic materials which had gone almost completely out of use with the advent of portland cement. Besides the natural puzzolanic materials such as trasses, tuffs and puzzolanic clays, a variety of industrial wastes, after suitable processing, are finding increasing use as substitutes for portland cement. Among these, the most important are fly ashes, blast furnace slags and *surkhi*. Though, to begin with, interest in puzzolanic materials rested mainly on considerations of conservation of portland cement, extensive researches during the past few years have shown them to be versatile materials capable of imparting many desired engineering properties to concrete, not possible with portland cement.

For India, the development of puzzolanic materials as partial substitutes for portland cement is of current importance, as she has ambitious irrigation, highway and building programmes. With an allocation of Rs 8000 crores for these projects in the Fourth Five Year Plan, the requirement of portland cement has been estimated to be of the order of 24 million tons per year. Against this, the present production is nearly 10.5 million tons a year. And with limited reserves of good quality limestone, the production of portland cement cannot be stepped up beyond a certain limit. Therefore, the bulk of the deficit has to be met by puzzolana-based cements.

In this context, the symposium\* on 'Puzzolanas — Their survey, manufacture and utilization' organized recently by the Central Road Research Institute

(CRRI), New Delhi, is timely. While providing an opportunity to the participants to exchange views on the various technological problems involved, the symposium emphasized the potentialities and versatility of the various puzzolanic materials. Concretes from puzzolana-metallurgical cements developed in France have been found to be superior to portland cement-based concretes and have been successfully used in every type of construction. Fly ash-based cements are extensively used in Japan in the construction of dams, harbour piers, water tanks, bridges and waterways, and for lining canals and tunnels. In USA, ready-to-use puzzolana mixtures are marketed in tonnage quantities. Compared to the developments elsewhere, India has made a rather modest beginning in this field. Notable among the developments are: (1) Use of locally available puzzolanic clays, after calcination, as partial substitutes for portland cement in the construction of dams; (2) investigations on the compositions and puzzolanic properties of fly ashes from different thermal power stations and slags from blast furnaces; and (3) survey of puzzolanic clay deposits of different regions. The estimated availability of fly ashes from the various existing thermal power stations in India is 1 million tons per year. About 3 million tons of blast furnace slag are available annually from the existing iron and steel plants. The survey of puzzolanic clay deposits, conducted by CRRI, has led to the location of more than 200 deposits of puzzolanic clay which can be commercially exploited. These data show that there are bright prospects for the production of puzzolanic materials on an industrial scale and that steps should be taken to organize such an industry.

Further work in several directions is necessary before puzzolana cement industry can be put on firm foundations. The survey on puzzolanic clays carried out by CRRI has indicated that some of the deposits located could be utilized by nearby cement factories for the manufacture of puzzolana cement. However, the fly ash available from power houses needs improvement in quality and it is necessary to install suitable processing units. Indian specifications for fly ashes should also be drawn up. Quick and reliable standard tests necessary for quality control and selection of puzzolanic materials have to be developed to encourage their wide use. Fundamental studies on the mechanism of puzzolanic reactions should be extended so that the right type of puzzolana could be selected for a desired end use.

As puzzolanic cements can be tailor-made to meet any specific requirement, there is need for close coordination between the producer and the consumer not only in quantitative terms but also as to the type of product needed for a specific use. A more important problem as far as India is concerned is that of educating the consumer with regard to the potentialities and applications of puzzolanas. The puzzolana industry is already well established even in countries which are better placed than India in respect of production and demand for portland cement. In India, where the shortage of portland cement is acute, it is high time that a beginning is made to evolve alternate materials for cement by developing the puzzolana industry.

\*A detailed technical report on the proceedings of the symposium has already been published [this *Journal*, 24 (No. 4) (1965), 158].



# Structure & Function in Biological Systems—A Symposium

T. RAMAKRISHNAN

Pharmacology Laboratory, Indian Institute of Science, Bangalore 12

**I**N recent years knowledge of protein structure has increased enormously. Complete sequences are known for one enzyme and a number of hormones. Shapes are being probed by many of the tools of the physical chemist and by X-ray diffraction technique of the physicist. Since the amino acid sequence of a particular protein is determined by a specific gene, the molecular biologist has studied the relationships existing between the gene and the protein, though he has not yet been able to determine the base sequences in the deoxyribonucleic acid which makes up the gene. Enough is now known about the relation of structure to function that serious experimentation can be carried out in this field. It was felt, therefore, that a symposium that would bring together workers in the diverse disciplines of physics, chemistry, biochemistry and molecular biology would lead to a productive exchange of information and ideas. Such a symposium was held at the Indian Institute of Science, Bangalore, on 28 and 29 January 1965. A brief report on the papers presented at the symposium is given below.

## Molecular Structure of Proteins and Polypeptides

G. N. Ramachandran of the Madras University spoke on molecular structure of proteins and polypeptides. Both proteins and polypeptides are polymers having a linear unbranched chain of amino acid residues. As there are some twenty different amino acids occurring in a protein chain, the first questions to be answered regarding the structure of a protein are chemical, namely its amino acid composition and sequence. While the composition is known in most cases, the sequence is known only for a few, like insulin and ribonuclease. However, even the sequence does not give the full story, for the biological activity of a protein depends vitally on the conformation of the polypeptide chain, or the way in which it is folded up. Even though the protein is chemically unaffected, if the conformation or the specific folding of the chain is disturbed (even by such mild alterations as a change in  $pH$ ) then its activity is lost. The study of conformation is made mainly by physical methods, the most useful of which is by X-ray diffraction. By its very nature, X-ray diffraction requires an ordered assemblage of molecules, so that proteins in solution cannot be studied so readily by this technique, as in the solid state. In this form two types of proteins can be studied, namely the crystalline (or globular) proteins and the fibrous proteins. The latter were the first to be studied as they contain a helical backbone. The helices, however, need not contain an integral number of residues per turn, as was first proposed by Pauling and Corey in 1951. The famous alpha helix, with 3.6 residues per turn built by them in

1951, has since then been shown to occur in the fibres of keratin, myosin and related proteins. A different type of helix occurs in collagen, namely a triple helix, each chain of which contains approximately 3.3 residues per turn and the three chains of which form coiled coils, being wound around a common central axis. This structure, put forward by workers at the Madras University in 1954-55, is now generally accepted. Related polypeptides like polyproline, polyhydroxyproline and polyglycine are found to have a similar triple chain. Of all the fibrous proteins, only feather keratin is still unsolved at the molecular level.

In crystalline proteins, the molecular chain takes a compact form, although it may have short helical segments, as has been found for myoglobin by the Cambridge group. Apart from the closely related protein, haemoglobin, the structure of no other globular protein has yet been solved.

This raises the question, namely whether any general principles can be formulated regarding the way in which the units in the chain are joined to each other. Such a study has been made at the Madras University. Although two neighbouring residues are joined together by single bonds  $NC\alpha$  and  $C\alpha C^1$  at an alpha carbon atom  $C\alpha$ , the rotations about these single bonds are not free but restricted because of possible short contacts between neighbouring residues. Denoting the rotation angles about the two bonds by angles  $\phi$  and  $\phi'$ , only about 25 per cent of the allowed range in the  $\phi$ - $\phi'$  plane is allowed. The limits of the allowed region have been worked out and tested in a number of simple peptides and the known types of conformations found in polypeptides and fibrous proteins. Recently, some work (unpublished) carried out in Cambridge University has shown that all the conformations observed in myoglobin fall within the allowed ranges. It appears that if the allowed and forbidden ranges for contact distances worked out at the Madras University are followed, the working out of conformations of the chains in many proteins can be greatly simplified.

## Chemical Modifications of Enzymes and Their Effects on Biological Function

P. J. Vithayathil of the Indian Institute of Science, Bangalore, dealt with the significant progress in our knowledge of the mechanism of action of proteins during their biologically important enzymic function which has, in the past few years, been achieved as a result of the increasing amount of information available regarding the chemical structure of enzymes and the chemical alterations in the enzyme structure that influence the catalytic activity. In this area of biochemical research two proteins, namely ribonuclease and  $\alpha$ -chymotrypsin, represent two enzymes with some particularly important features; the mechanism of

their catalytic action has been widely studied by kinetic methods, the amino acid sequences are known and the three-dimensional structures are being actively studied. Moreover, the enzymes are of low molecular weight and are sufficiently stable under mild chemical reaction conditions. Studies with these enzymes have, in a remarkable manner, brought out the primary role of some amino acid side chain groups in peptide interactions and in catalysis. In this context, investigation presently in progress at the Indian Institute of Science on the chemical modification of ribonuclease has revealed the functional nature of at least one carboxyl group in the enzyme molecule.

In the case of  $\alpha$ -chymotrypsin, clear experimental evidence has now been provided from a series of chemical modification studies to show the catalytically important function of a histidine in the B-chain and of one serine and of one methionine in the C-chain. The initial findings of Balls and coworkers, who found that the nerve gas diisopropyl fluorophosphate reacted stoichiometrically with  $\alpha$ -chymotrypsin to yield a phosphoryl protein, have recently been extended by similar stoichiometric reactions with diphenyl carbamyl *p*-nitrophenyl ester, diphenyl carbamyl chloride, L-1-tosylamido-2-phenylethyl chloromethyl ketone, N-bromoacetyl- $\alpha$ -aminoisobutyric acid, ethyl-5-iodopentyl phosphonofluoridate and *p*-nitrophenyl diazoacetate. These reagents, while participating in a pseudo-enzymic reaction, yielded chemically altered amino acid side chain residues making possible the identification of the above-mentioned 'active' amino acids in the sequences of the peptide chains. Further experimental evidence regarding the functional role of these amino acid residues has been obtained from photochemical and hydrogen peroxide oxidation studies of the enzyme. Analysis of the products of oxidation by the 'all or none assay' indicated the formation of a partially active enzyme by the oxidation of the methionine residue alone. This methionine residue as well as the 'active' serine and histidine residues have now been clearly identified in the amino acid sequence of  $\alpha$ -chymotrypsin.

In studies on ribonuclease, on the other hand, the method of utilizing reagents that have some structural similarity to the substrate of the enzyme has so far not been successfully attempted for lack of reagents. With this enzyme the approach has so far been to correlate alterations in catalytic activity of homogeneous protein derivatives, obtained by modification of specific amino acid residues, with the changes in charge or hydrophobic character of the side chain groups. Thus, by the use of simple reactions such as acetylation, guanidination, carboxy methylation and dinitrophenylation, the functional roles of histidine 12, histidine 119 and lysine 41 have been detected and clearly established.

As regards ribonuclease, little information is available on the question of the functional contribution, if any, of the eleven free carboxyl side chain groups in the protein chain. That some of the carboxyl groups have an important function

in the maintenance of the tertiary structure of the protein was indicated from the studies on the stability of the different forms of the protein under conditions of varying temperature and *pH*. In studies at the Indian Institute of Science it was observed that esterification of some of the carboxyl groups of ribonuclease resulted in the loss of the enzymic function of the protein. This loss in activity could be completely restored by releasing the carboxyl groups by careful hydrolysis of the ester. The location of the concerned 'active' carboxyl group in the protein chain has not yet been determined.

The overall picture of the mechanism of protein catalysis that has emerged from chemical modification studies is that of a series of enzyme-substrate complexes which in the simplest form is represented as a single complex by the classical Michaelis-Menton scheme of reaction. Once the enzyme and substrate are in close proximity, a chain of reactions takes place, determined by the specific chemical structure of the substrate and that of the protein. For maximum efficiency of catalysis these reactions involve essentially the entire forces of interaction of amino acid side chain groups in the protein. During the process the substrate as well as the product of the reaction, being in intimate contact with the side chain groups of the protein, markedly influence the course of the sequence of reactions taking place within the protein molecule.

#### Mucopolysaccharides — Structural Units of Living Cells

B. K. Bachhawat of the Christian Medical College and Hospital, Vellore, presented a review of the recent studies leading to the formation of various monosaccharide residues of mucopolysaccharides of connective tissue and described the studies on the sulphatation reaction with particular emphasis on the sulphatation at the polymer level of mucopolysaccharides. The recent work of Dorfmann and his coworkers on the enzymatic synthesis of the chondroitin sulphate and the transfer of sulphate after polymerization was also discussed. The studies at the laboratory in Vellore on the enzymic sulphatation of mucopolysaccharide in brain indicate that the enzyme activity varies with age; a change in the specificity towards acceptor mucopolysaccharides was also observed.

Some of the work on the isolation and characterization of mucopolysaccharides from brain was described by Bachhawat who also discussed the distribution and variation with age of mucopolysaccharides in brain. The role of mucopolysaccharides in maintaining the ion balance of the living tissue and its water binding capacity due to their polyanionic character were also discussed. The physiological role of protein-polysaccharide complexes as a structural component of connective tissue and the possible role of individual mucopolysaccharides due to their subtle structural differences in the binding with protein were also examined. The present concept of the role of mucopolysaccharide in calcification and in collagen fibrillation was outlined.

### Genetic Structure and Biologic Function

T. Ramakrishnan of the Indian Institute of Science, Bangalore, traced our knowledge of the genetic function from the earliest days to the present day and explained how fine structure analysis of the gene in bacteriophage and bacteria in modern times has led to a clear understanding of the various functions of the gene. In classical genetics each gene is considered capable of function, recombination and mutation. Molecular biology was born in the course of investigations whether these three units are really coterminous and, if not, how they are related to one another. Once it was known that the gene was composed of deoxyribonucleic acid (DNA), the next problem was to find out how many nucleotide units comprised the unit of mutation, recombination or function. Such fine structure analysis of the gene requires the examination of a very large number of mutant strains, since the random probability of two mutations arising independently at adjacent sites is 1 in 50,000. In order to carry out genetic analysis, all possible combinations of mutant pairs must be crossed to find the pair with the smallest recombination frequency, and thus the analysis of even 10,000 mutants would involve 50 million crosses. Hence, fine structure analysis had to wait till it became possible, in recent years, to carry it out in bacteria or bacteriophages where it is possible to analyse millions of organisms. S. Benzer of USA was the first to carry out the fine structure analysis of a gene. Benzer's brilliant and remarkable studies of the gene in the bacteriophage T4 showed that a number of distinct mutational sites, separable by recombination, might be found within the same functional region of a chromosome. These results have made it possible now to follow genetic events at the level of the DNA nucleotide and bridged the gap between chemistry and genetics. From Benzer's work it is now possible to calculate the number of nucleotide units which a functional unit of a particular gene contains. In recent years estimates of other genes which specify proteins of known composition have been made in bacteria. Assuming that the sequence of amino acids in such proteins is laid down by the base sequence in the DNA of the gene, the average number of base pairs which code for a single amino acid (coding ratio) can be calculated. For example, if a gene is estimated to constitute 900 nucleotide pairs of DNA and this gene carries the genetic information for the synthesis of a polypeptide composed of 300 amino acids, then each amino acid is specified by a sequence of 3 nucleotide pairs. Again, on the supposition that the average biological polypeptide contains some 300-350 amino acids, the average gene is about 1000 nucleotides long, which is the same as that derived from rather different data. Assuming that all of this DNA is genetically meaningful, this indicates that the DNA of an *Escherichia coli* chromosome, containing  $10^7$  base pairs, is sufficient to determine the synthesis of about 10,000 different proteins, and that of bacteriophage T4, with  $2 \times 10^5$  base pairs, to determine the synthesis of about 200 proteins.

### Functional Attributes of Subcellular Fractions

C. Bhubaneswaran of the Atomic Energy Establishment, Bombay, dealt with the subject with particular reference to the altered characteristics of particulate liver fractions in the carbon tetrachloride injured rat. The recognition, during recent years that the subcellular structures of the cell have among them, a level of organization above which can be ascertained from isolated enzyme system and that, therefore, they have a complexity which surpasses the sum of the activities and properties of the individual enzymatic mechanisms, together with the technical feasibility of the study of different particulate fractions *in vitro*, has enabled the biochemist to understand, increasingly, the function of the cell at molecular levels. Most of these organelles are, by necessity, extensively organized in relation to structure. With a view to correlating functional with structural aspects and also with the object of finding out a suitable index of mitochondrial damage, studies have been initiated both on enzyme functions as well as on some of the structural properties like swelling and contraction and the electrophoretic behaviour of this organelle and on their changes in a stress condition induced by carbon tetrachloride administration. Bhubaneswaran presented and discussed the results to show that in carbon tetrachloride liver injury, one of the properties correlating reversibility of mitochondrial damage with function may be the specific activity of the mitochondrial succinoxidase.

### Structure and Function of Flavoproteins

N. Appaji Rao of the Indian Institute of Science observed that the bright yellow colour and the yellowish green fluorescence of flavins were perhaps among the reasons for the early recognition of flavins in various tissues as components of enzyme. With a knowledge of the nucleotide forms of the flavin, as well as the vitamin precursor and the degradation products, it is not surprising that the attempts during the subsequent years resulted in the characterization and isolation of a large number of flavin enzymes.

Michaelis was the first to propose that flavins are reduced in two separate and distinct one-electron steps, with the intermediate formation of a semiquinone free radical. This was followed by the observation that a stable red colour is formed or the addition of TPNH to the old yellow enzyme. Although there is now some doubt as to the nature of the coloured intermediate, this has been generally accepted as the first demonstration of the occurrence of a semiquinone in flavoprotein catalysis. Beinert obtained unequivocal evidence for the formation of a semiquinone during the reoxidation of FMNH<sub>2</sub> by air. The semiquinone has absorption maxima at 570 and 900 m $\mu$  at pH 7.0. The maxima disappeared on complete reduction or oxidation. Massey and Gibson applied the technique of electron spin resonance spectrometry (ESR) to the study of flavoprotein catalysis and demonstrated that a semiquinone is formed during this enzymatic catalysis.

It has been established by several workers that oxidation of DPNH or TPNH proceeds via hydride ion mechanisms, whereas flavins are oxidized and reduced by free radical mechanisms. Thus, the transfer of reducing power from pyridine nucleotides to flavin nucleotides would be somewhat incompatible unless some intervening group is involved which is capable of participating in both hydride ion and free radical mechanisms. A vicinal dithiol has been demonstrated as the link in the case of lipoyl dehydrogenase. The possibility of a monothiol (thioketone) as a link in DPNH dehydrogenase and TPNH-glutathione reductase was discussed.

### Changing Concepts of the Functions of the Thyroid Cell

E. Raghupathy of the Medical College, Madras, dealt with the subject. In the thyroid follicle, the colloid has long been held to be the exclusive site of synthesis and subsequent proteolysis of thyroglobulin. Recent investigations on the properties of thyroid cells freed from follicular structure and extracellular colloid have, however, thrown considerable doubt on such a role for the colloid in thyroid function. Dispersed thyroid cells obtained by a continuous-flow trypsinization procedure retain in a good measure most of the characteristics of the intact thyroid gland. Thus, they concentrate iodide, form protein-bound iodotyrosines and iodothyronines and deiodinate iodotyrosines but not iodothyronines. Further, when these cells are cultivated as monolayers, they respond strikingly to the addition of TSH by undergoing a reorganization giving rise to a structural pattern resembling the cross-sections of the intact thyroid gland. Addition of TSH also results in an increased utilization and metabolism of iodide. From thyroid cells cultivated in monolayers, an iodoprotein resembling thyroglobulin in electrophoretic mobility behaviour on gel filtration and in reaction to anti-sheep thyroglobulin antibodies can be isolated. These results permit the conclusion that protein iodination occurs in the follicular cells and that if iodide secretion into extracellular colloid does occur, it is not an indispensable or essential aspect of thyroïdal iodine metabolism.

### Isolation and Characterization of Rat-liver Lysosomes

Lysosomes are cellular organelles whose density and size are intermediate between those of mitochondria and microsomes. P. L. Sawant of the

Atomic Energy Establishment, Bombay, reported that lysosomes, free from mitochondrial succinoxidase system activity but slightly contaminated with uricase particle and microsomal fraction, have been prepared from rat liver by differential and density-gradient centrifugation techniques. In batch operation, this method yields 60 mg. of lysosomal protein from 160 g. of liver and has permitted detailed studies on the interaction of lysosomes and other subcellular organelles and also the membrane properties and internal organization of lysosomes. This method can be adopted to isolate lysosomes from sheep liver with certain modifications.

Concentrated lysosomal preparations hydrolyse proteins and phosphate compounds from mitochondria and microsome and release cytochromes and other compounds from mitochondrial membranes; these results, according to Sawant, support the view that lysosomal enzymes may have a role in cellular catabolic hydrolysis. Respiring mitochondria when exposed to lysosomal enzyme show membrane damage, loss of oxidative phosphorylation and related functions. Variations of osmolarity and temperature of suspending medium result in significant changes in light scattering properties of the lysosomes—indicating their swelling or bursting. This phenomenon is accompanied by a release of lysosomal enzymes. Observations on the effects of large molecular weight compounds, ions and  $\beta\text{H}$  on lysosomal membrane show that under the influence of a single factor all the enzymes do not become available to the same extent. Binding of enzymes to different sites of membrane fraction is shown by their availability pattern of acid, alkaline and neutral  $\beta\text{H}$ , indicating that the lysosomal membrane has characteristics of a charged membrane.

Although lysosomal membrane peroxidizes at a comparatively slower rate than mitochondria or microsomes, reaction systems producing free radicals cause maximum damage to membranes and thus release lysosomal enzymes. The relationship between the availability of lysosomal enzymes and their internal organization was discussed.

Measurements of free and total specific activities of marker lysosomal enzymes from the liver of protein starved animals show increased structural freedom for lysosomal enzymes. This change parallels accumulation of hydrolytic end products of the tissue.

# Molecular Structure of Living Matter\*

THE riddle of life has always puzzled man from time immemorial. The ancient philosophers had imagined that life is an aspect of nature specially created by a divine force and that one should clearly distinguish between inanimate matter and living beings. Even with the great progress made in the physical and chemical sciences during the last century, it was still believed that the processes of life were beyond the domain of pure science. Thus, a whole group of compounds of carbon, which was found in the tissues of animals and plants, was called 'organic' compounds, signifying that they were essentially the products of life processes in organisms. However, in 1828 Wöhler synthetically prepared urea, a typical secretion of animals, from two compounds, cyanic acid and ammonia, which were at that time considered to be inorganic. This was followed soon after by the artificial preparation of acetic acid and a host of others. Today, the separation of organic and inorganic chemistry is purely formal.

Although it was thus possible to prepare artificially many of the chemical materials which occur in living beings, it was still believed that a vital force existed in all living organisms, which distinguished them from inanimate matter. This theory, known as the vitalistic theory, which was very much in vogue during the beginning of this century, was opposed more and more by scientists belonging to the mechanistic school, who believed that once we obtained more and more detailed information about the physics and chemistry of the matter in living beings, it would turn out that the phenomenon of life is only one of the manifestations of the physical and chemical processes characteristic of this matter. In fact, we have come in recent years very close indeed to this goal of the mechanistic school, as will be seen from what follows.

## Nature of Living Matter

If we should be able to properly understand all this exciting story, we must first of all be clear in our minds as to what constitutes life essentially. There are of course several well-known features of living beings, but the most essential of these are clearly growth and reproduction. A living being must have the capacity to grow when placed in the proper environment and must be capable of duplicating itself. This is true of all living organisms down to the microscopic bacteria and the still smaller viruses, which are probably the smallest beings, which can be classified under this category. However, it is an interesting fact that, when these viruses are taken out of the cells of the host and dried, many of them are crystalline and look exactly

like the crystals of any common chemical. On the other hand, when viruses are inside a host, they assimilate the body fluids of the host, convert them into a material similar to their own and thus duplicate themselves. So also, just like plants, flies and bacteria, whose hereditary characteristics can be modified by chemical agencies and by X-rays, the nature of a virus and its progeny can also be similarly modified and the genetics of this (that is, the nature of how this is passed on from generation to generation) has actually been studied. In the virus, we have certainly reached the borderland between the domains of the living and the non-living, and it is very likely that the first artificial production of a 'living' organism will be that of a virus.

We may now ask the question, whether from the chemical point of view, there is something common in the essential constituents of all living matter, right from the viruses to the largest beings. The answer to this is in the positive, and all living matter consists largely of just two types of materials known as proteins and nucleic acids, both of which consist of special types of molecules known as 'macromolecules'. These molecules have the special property that they contain a very large number of atoms, thousands and sometimes as many as millions of them, and that they consist of a large number of smaller units linked together in the form of long chains. Proteins and nucleic acids may be said to form the twin bases of life. Proteins form the bulk of animal tissue and the main component of the cells of all organisms, the part known as protoplasm. In contrast to this, the so-called nuclei of cells, the part in which reside their hereditary characteristics, consist largely of nucleic acids. The nucleic acids determine not only the nature of the progeny that an organism will produce but also the type of protein that it will synthesize and thus indirectly the way in which its metabolism (or growth) would progress. The exact nature of the protein-nucleic acid relationship is only just being unravelled and it is leading to some fascinating results.

## Structure of Proteins

The molecules of proteins consist mainly of carbon, hydrogen, nitrogen and oxygen and occasionally sulphur. Their molecular chains are built up of units known as amino acid residues, a typical one of which is shown in Fig. 1. The side group R in the residue may be one of twenty different types, according to which we have twenty amino acids

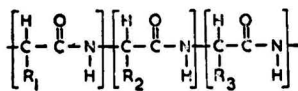


Fig. 1 — A schematic diagram of a protein chain [The atoms within brackets form an amino acid residue, one of the units in the chain of the macromolecule]

\*A dissertation by Dr G. N. Ramachandran, Director, University Grants Commission Centre of Advanced Study in Physics, Madras University, Madras, on the occasion of the presentation of the Shanti Swarup Bhatnagar Memorial Award in Physics for the year 1961 at the National Physical Laboratory, New Delhi, 14 January 1965.

Contribution No. 152 from the Centre of Advanced Study in Physics, University of Madras, Madras 25.

with different names, such as glycine, alanine, serine, arginine, and so on. If we denote the different amino acids by different letters of the alphabet, a protein molecule may be pictured as a long sentence written in this alphabet. Just as every sentence has a specific sense, a protein molecule having a definite amino acid sequence also has a specific function in the tissues. The sequence has been determined in some proteins such as insulin and ribonuclease, and vigorous efforts are going on in laboratories all over the world to determine the sequences in various other important proteins and in some cases, even a partial synthesis of a protein has been achieved from the known sequence.

It should be mentioned, however, that unlike with the simpler molecules, the chemical composition does not make the complete story of a macromolecule. Thus, the molecular structure of a protein does not get completely specified by its amino acid sequence alone, but requires in addition the specification of the configuration (or conformation) of its molecular chain. The situation is best understood by considering a long chain of beads, each bead having a hook and an eye attached to its opposite sides. Then it is possible for different parts of the chains to be cross-linked to one another through these hooks and eyes, forming a complicated but compact agglomeration. This is what happens in most of the so-called globular or crystalline proteins, such as insulin and haemoglobin, and the hook-eye linkage occurs through what are known as 'hydrogen bonds'. Every active protein has a precise conformation in this sense; if the conformation is modified, say by treatment with chemical reagents, the activity of the protein is lost, although its chemical composition is in no way changed. The protein is then said to be denatured; sometimes it is possible to renature the protein and bring back the natural folding of its chain.

The determination of the exact way in which the molecular chain of a protein is folded is, therefore, vital for our understanding of its function. Attempts in this direction have been going on with several crystalline proteins in various laboratories, but success has been achieved so far in only two related blood proteins. The molecular architecture has been practically completely elucidated in myoglobin and the run of the chain has been determined for haemoglobin. These studies won the Nobel prize for the Cambridge scientists J. Kendrew and M. F. Perutz.

Occasionally, however, the linkages may occur in a regular manner in a protein chain and the chain may coil up and form a long helical rod. The best known example of this is the famous alpha helix (Fig. 2) with 3.6 residues per turn, which was discovered in 1951 by Prof. Linus Pauling of California and his collaborators. These rod-like protofibrils may then aggregate together and form strong protein fibres. This is what happens in hair, muscle and related proteins, which have been classified under the term fibrous proteins.

### Structure of Collagen

Although the conformation of a number of fibrous proteins was clarified by the work of Pauling, that

of one class known as collagen, which occurs in tendon and bone (in general in connective tissue) was still an open question. The first pointer towards the correct solution, namely that the ultimate unit consists of three helices, was given by Ramachandran and Kartha<sup>1</sup>. Unlike the alpha helix, in which the different residues in the same chain are linked by hydrogen bonds, the neighbouring helical chains are connected together by hydrogen bonds in collagen and these stabilize the triple-helical structure. A comparison with the X-ray diffraction pattern showed that each of the helices in the triple helix has three and one-third residues per turn and that the three chains are all coiled further about the common central axis. The molecular architecture of the coiled-coil arrangement was first worked out in 1955 by Ramachandran and Kartha<sup>2</sup> and then refined, the best dimensions being reported in 1960-62. The developments and the latest results are summarized in an article by the author<sup>3</sup>.

The triple-helical structure of collagen (Fig. 3) is now universally accepted and has been confirmed by various studies (physical, chemical and biochemical) made in different laboratories. Synthetic analogues of collagen have been prepared, in which the residues are all glycine or proline or hydroxyproline (three of the most commonly occurring

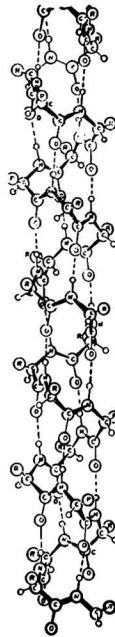


Fig. 2 — The well-known alpha helix of Pauling, in which every amino acid residue is linked to its fourth neighbour by a hydrogen bond

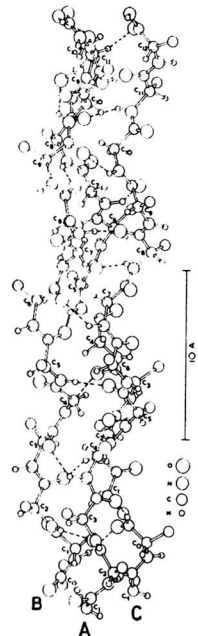


Fig. 3 — The collagen triple helix structure worked out at the Madras University

amino acids in collagen) and in each case the macromolecules have been found to organize themselves as triple chains exactly as collagen does. A minor point of controversy, as to whether the number of hydrogen bonds occurring for every three residues is two, as proposed by the author and his associates or only one as has been suggested by some workers at Cambridge, has been settled in favour of the former by the recent work of three independent workers in the United States in 1964. Two of these studies were on deuterium and tritium exchange and the third on the physical-chemical data of collagen, such as the shrinkage temperature. All these studies show clearly that the number of inter-chain hydrogen bonds is two for every three residues. Thus, not only the basic triple-helical structure but also the details of the molecular conformation, as proposed by the author and his associates, can be said to be fully vindicated.

### General Problems of Protein Conformation

We may now pass on to more general problems of protein conformation. In view of the fact that two types of helical chains (the alpha helix and the collagen helix) and a few other straight chains (also discovered by Pauling and coworkers) do occur in some proteins, the general question may be asked as to what are all the possible types of helices that may occur for a chain consisting of amino acid residues. This question has been tackled in the laboratories of the Madras University during the last few years. In fact, it raises the auxiliary question as to what are the possible relative orientations of two amino acid residues which are linked together. It turns out that the latter is best expressed in terms of two angles denoted by  $(\phi, \phi')$ , which are the angles by which the first and the second residues are rotated about the two single bonds by which they are joined together at the common carbon atom, starting from a standard conformation. The range of allowed values of the pair  $(\phi, \phi')$  worked out purely from theory<sup>4</sup> is shown in Fig. 4, and is seen to be supported by experimental data. Thus, future workers on protein structure need restrict their attention only to the narrow range of conformations (about 20 per cent of all the possible ones) which have been marked out in Fig. 4. So also, it has been possible to show that only certain types of helices can occur for protein chains, which again will turn out to be very useful for scientists working on protein structure.

At the same time as the above investigations on proteins were being conducted, studies have also been going on in the laboratories of the Madras University on the molecular conformation of simpler compounds related to proteins, such as crystals of amino acids and simpler peptides, whose structures have been solved by X-ray diffraction. In this connection, a number of new techniques have been developed in the field of X-ray crystallography, the most important of which is the proposal of two new types of Fourier synthesis, known as the alpha and the beta syntheses<sup>5</sup>. The beta synthesis in particular has turned out to be very fruitful.

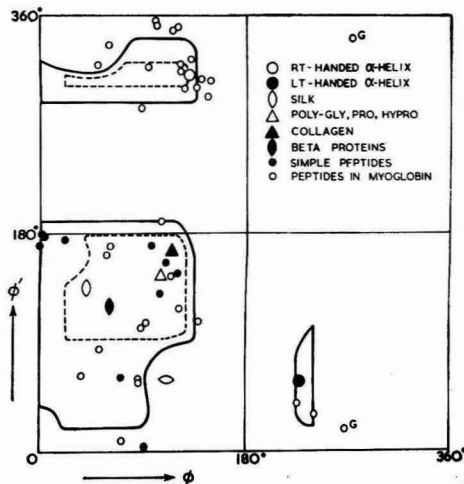


Fig. 4 - Range of allowed values (within the thick lines) for the pair of angles  $(\phi, \phi')$  which specify the conformation of a pair of amino acid residues. The observed data are also marked

### Structure of Nucleic Acids

The other important component essential for the sustenance of life is the nucleic acids. Unlike proteins, they contain, in addition to carbon, hydrogen, nitrogen and oxygen, also the element phosphorus; hence the importance of phosphorus for life. There are two types of nucleic acid, known as ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). Of these, DNA is the one which controls the genetics and ultimately also all the activities in the organism. On the other hand, RNA plays an essential part in protein synthesis and, therefore, in its growth and metabolism. The chains in both DNA and RNA consist of units (as in proteins), known as nucleotides. However, unlike proteins, there are only four types of nucleotides in each.

The conformation of DNA was the first to have been worked out. If we denote the four types of nucleotides by the numbers 1, 2, 3, 4, then they have the peculiar property that, if a double helix is built out of them, then unit 1 is linked to unit 3 and unit 2 to unit 4 by means of hydrogen bonds. Thus, the nucleotide sequence in one chain is complementary to that in the other chain. This brilliant idea of Watson and Crick at Cambridge was remarkably confirmed by the X-ray studies of Wilkins in London. All three of them were awarded the Nobel prize in physiology and medicine in 1962 for this work, which has far-reaching consequences in genetics and reproduction. Because of the unique way in which the units pair together, it is possible to obtain an exact (complementary) replica of each chain of the DNA molecule. Thus, from one double chain of DNA, two other exact copies of it can be obtained. This is what is believed to occur when cells divide.

RNA has the function of directing the synthesis of proteins having a definite amino acid sequence

from the pool of amino acids available in the body, say from the digestion of the food taken. Each protein is synthesized under the action of definite RNA molecules, the latter again being ultimately produced by the DNA in the genes. In fact, there seems to be some sort of coding between the sequence of nucleotides in the RNA and that of the amino acid residues in the protein chain. This idea of a coding, which was in the nature of a hypothesis until about two years ago, has now been completely established. The first evidence for it was obtained by Nirenberg and collaborators in Washington and the data have been greatly extended and the nucleotide code for practically all the amino acids obtained by Prof. Severo Ochoa of New York, who incidentally had been awarded the Nobel prize earlier for the first synthesis of RNA-like material. What has emerged is that each amino acid residue is coded by a sequence of three nucleotide units.

Thus nucleic acids are seen to be essential for the synthesis of proteins. Conversely, the production of nucleic acids themselves requires the presence of protein-like materials like enzymes. The two together, therefore, form a mutually interacting system in which each leads to the synthesis of the other. This is the main feature of all living systems and all the other activities are only subsidiary. As a matter of fact, the smallest living organism, namely the virus, consists of nothing but protein and nucleic acid, that is of nucleo-protein molecules, an intimate mixture of the two at the molecular level.

### Conclusion

Thus, from the chemical point of view, life appears to be just the consequence of one of the types of molecular organization — two types of macromolecules, each synthesizing the other and mutually interacting with each other. Can we hope to produce such a system completely in the laboratory? It is not impossible, for several of the intermediate steps have already been achieved. Scientists have taken a nucleic acid molecule, broken it into bits and put them back together; they have made protein under the influence of nucleic acids; they have made changes in the nucleic acid and shown that the proteins produced after this are also changed; they are very near to finding the law which connects the sequence of units in the nucleic acid and that of the residues in the protein produced by it, and so on. We are living in a most exciting era, and perhaps the researches of the next few decades may lead to some far-reaching revelations about the nature of life.

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## Artificial Transmutation of the Gene\*

IT is 100 years since Gregor Mendel presented his paper on 'Experiments in plant hybridization' in which he propounded the laws of heredity. The science of genetics was, however, born only in this century largely because of the failure of earlier workers to separate continuous from discontinuous variation in their thought and work. Though young in years, genetics has grown with remarkable vigour and occupies today a core position in the conceptual structure of biology. The laws of genetics have helped to solve the centuries-old puzzle of the mechanisms underlying the basic unity as well as the breadths of diversity and depths of differentiation of living organisms. More important, a new biological era has been opened up where man can exert either a purposeful or unfortunately a destructive influence on evolution.

As a science, genetics has demonstrated the value of 'hybrid vigour' not only in thwarting Malthusian predictions on the relationship between population growth and food production but also in fostering the growth of a scientific discipline itself. The 'narrow domestic walls' which Tagore deprecated in a human society are even more harmful in a scientific discipline, since by causing inbreeding depression they promote conclusions based on hallucinations. By integrating the principles and tools of mathematics, chemistry and physics with those of conventional biology, genetics has exploited hybrid vigour in its own growth. Genetic determinants occupy a dominant place today in the scientific work reported at all international congresses dealing with the life sciences — whether it be a congress of biochemistry or biophysics or botany. It is unfortunate that much of the work on genetics in India is still confined only to plant breeding institutes and the immense implications of this science for medicine and animal breeding have remained practically ignored. No university in our country yet has a department or professorship in genetics and the solitary question on Mendel's work which usually finds a place in B.Sc. papers in botany and zoology is the hot favourite for omission under the democratic right of 'choice' vested in the students. This is particularly unfortunate since our country, as in many other fields, had in ancient times developed the most advanced ideas on evolution as evidenced by the concept that God manifested himself through different life-forms — first as fish, and later as mammal.

### Experimental Genetics

It was recognized towards the end of the last century that chromosomes have the faculty of replication; in other words, the capacity for continuous expansion. Early in this century the Dutch scientist,

Hugo de Vries, postulated that the genetic determinants located on chromosomes occasionally undergo mutations, or permanent changes, which are themselves replicable. Thus, an unlimited degree of elaboration of hereditary characteristics can be attained. de Vries saw in this process nature's most potent evolutionary tool. As a broad generalization, evolution can be pictured as a process of the 'muddling through' of microbes into men as a result of recombination and selection acting upon blind mutations. Simple organisms such as bacteria or viruses, with a new generation every 10 or 20 min. and with enormous populations consisting of millions and billions of individuals could well adjust to the vagaries of the environment by mutation alone. Due to the low frequency of spontaneous mutations, evolutionary progress in more complex organisms would result in a blind alley if it were entirely dependent on the occurrence by chance of mutations of the right type. The higher organisms have hence relied heavily on the exchange of genetic information with each other, a process popularly known as sex! No wonder then that de Vries wished very much that man could find a way of artificially altering the gene, thereby gaining control over the most powerful of nature's evolutionary mechanisms. This dream was realized when Prof. H. J. Muller of the United States showed in 1927 that the sluggish natural mutation rate, which forms the chief basis of organic evolution, can be artificially accelerated by exposing living organisms to X-rays. A new hope was thus raised for the practical breeder who had until then been compelled (to quote Muller's words) "to remain content with the mere making of recombinations of the material already at hand, providentially supplemented, on rare and isolated occasions, by an unexpected mutational windfall". The discovery of methods of causing the artificial transmutation of the gene opened up new vistas in genetic research. The possibility of obtaining mutants in which the synthesis of specific metabolites was blocked ushered in the science of biochemical genetics and the elevation of viruses and bacteria to the genetic throne, in the place of the fruit fly, *Drosophila melanogaster*, which had reigned as the 'Queen of Genetics' for over four decades! The knowledge gathered in recent years on the structure, function and mode of organization and replication of the genetic determinants has already been recognized in the form of several Nobel awards. We now know that except in a few viruses, deoxyribonucleic acid (DNA) is the carrier of the hereditary codescript of the cell. The information needed to specify all the species and individual characteristics of every organism is recorded in its DNA in terms of non-overlapping triplet code of bases. During gene replication this information is reproduced by the unidirectional assembly of new DNA strands, each complementary in base sequence to the single strand serving as template, the result being the formation of two daughter molecules of DNA, which are exact replicas of the parent

\*A dissertation by Dr M. S. Swaminathan, Head of the Division of Botany, Indian Agricultural Research Institute, New Delhi, on the occasion of the presentation of the Shanti Swarup Bhatnagar Memorial Award in Biological Sciences for the year 1961 at the National Physical Laboratory, New Delhi, 14 January 1965.

molecule. The translation of genetic information into protein structure is achieved by the transcription within the nucleus of a specific DNA code sequence into the complementary sequence of bases in single stranded RNA molecule. This messenger RNA leaves the nucleus and serves as the template for the assembly of amino acids into a polypeptide chain, the ribosomes in the cytoplasm serving as the sites for this reaction. Each specific DNA base triplet would specify a particular amino acid and the sequence of base triplets determines the sequence of amino acids in the final polypeptide product. Thus, we now know how genes beget proteins and this knowledge has helped in designing experiments for attacking the gene at the molecular level and also for ascertaining the effect of a gene mutation on the protein chain. An early study of this type is that of Ingram of UK, who discovered that in the abnormal haemoglobin causing the disease known as 'sickle-cell anaemia', a glutamic acid residue is replaced by valine in the protein chain.

Prof. Melvin Calvin remarked in a recent symposium that the nature of matter can be conveniently considered at four different levels — axioms, aons (a new term for the leptons and baryons), atoms and aggregates of atoms. In a similar way, the possibilities for experimentally manipulating the gene can be considered at four different levels — a base pair in DNA (the purines, adenine and guanine and the pyrimidines, cytosine and thymine), a nucleotide (nitrogenous base-sugar phosphoric acid combination), a cistron (a section of a chromosome that has a unitary function and may consist of several thousand nucleotides) and a chromosome (the gene strings of one human chromosome have been estimated to contain some  $4 \times 10^9$  nucleotide pairs). Elegant experiments demonstrating alterations, both structural and numerical, at the level of the individual base pairs have been performed in micro-organisms. In higher organisms like the crop plants, experiments lending themselves to a precise interpretation of the causal mechanism involved in an induced mutation cannot be performed. Only two major categories of mutations can be usually recognized — those associated with visible chromosome structural changes and those with no such detectable change. The new knowledge from molecular biology has, however, provided many new classes of mutagens and attempts can be made to relate an observed effect to a change at a molecular level, although these cannot be definitely proved. The successful survival of a higher organism depends upon a high degree of integration and coordination of function at the level of the individual cell and of the organ. Because of their delicately balanced co-adapted genotype, such organisms are more often than not affected unfavourably when a mutation arises. It is hence that geneticists have been very concerned not only about the damage that will be done to later generations by the fallout from nuclear test explosions but also by the increasing use of radiations and radiomimetic chemicals in medical diagnoses and cure. In plants, however, a significant advance in crop production can be made even if one out of 1000 mutants is of a progressive type. Mutation breeding has, therefore, become a powerful

instrument in modern plant breeding and in the following are briefly summarized some results of applied value in a few crop plants and some of wider biological significance from the work carried out during the last few years by Swaminathan and his associates at the Indian Agricultural Research Institute (IARI), New Delhi. Results of considerable economic value could be obtained only because of the effort expended in standardizing methods for raising the frequency of induced mutations to very high levels (every treated seed in barley and wheat can now be made to yield one or more mutations) and for altering the proportion of mutations associated with invisible in contrast to visible chromosome changes.

### Mutations

The mutations induced can be grouped into the following four classes according to the number of genes involved and the phenotype produced.

*Micro-mutations* — These involve changes in quantitative characters and are hence of the greatest value to the breeder. Such mutations affecting several genes can be detected only through the use of suitable biometrical procedures. Work carried out at IARI has shown that there is immense scope for increasing the number of ear-bearing tillers, the number of grains per ear, the weight of grains and the protein content in the grains in wheat. In the oilseed plant, *Brassica campestris* var. *toria*, in which the chromosome number had been doubled two decades ago through the use of another method of chromosome engineering, progress in the development of superior tetraploid lines had come to a standstill, owing to the lack of variability in the population for the number of secondary and tertiary branches. By subjecting the tetraploid line to treatment with gamma rays, this deficiency was overcome and the way paved for attempting a major break-through in the yield of this plant.

*Mutations affecting single characters* — One of the principal attractions of the mutation breeding technique is the possibility of rectifying solitary defects in a variety without disturbing its good qualities and adaptive characteristics. Two good examples of this category of mutation from IARI are: (1) the development of the awned wheat variety N.P. 836 from the awnless strain N.P. 799; and (2) the introduction of dense hairiness and consequently of resistance to jassids in the long-staple cotton variety *Mescilla acala*.

*Macro-mutations* — Such mutations involve changes in a whole constellation of characters and have hence a striking phenotypic effect. The stiff-strawed and non-lodging mutants isolated at IARI in wheat, barley and rice are examples of this type. These mutants have not only a shorter and thicker culm but invariably also a more dense ear and more stiff leaves. Such mutants are of great practical interest since they confer upon the plant a morphological frame vital for it to be grown under conditions of high soil fertility and abundant water supply.

*Systemic mutations* — Mutations which either simulate an already existing taxon or necessitate the creation of a new systematic unit fall under

this category. Such mutations are of great value in tracing phylogenetic trends and demonstrate that the evolutionary scale can sometimes be traversed by jumps of larger quanta. They raise several questions in our current ideas in the field of plant geography. It has been possible to create from one variety of bread wheat (*Triticum aestivum*) all the known sub-species of this species, namely *spelta*, *macha*, *vavilovi*, *compactum* and *sphaerococcum*. Also, from a variety of the tetraploid wheat species, *Triticum turgidum*, mutants having the key characteristics of *T. dicoccum*, *T. durum* and *T. pyramidale* have been isolated. Thus, the artificial transformation of one species into another, which is one of the two major goals set for twentieth century biology by Jacques Loeb in his book *The dynamics of living matter* published in 1906 may be said to have been attained (the other goal is experimental abiogenesis, a field in which also great progress has been made).

While we can now artificially generate in a single variety of wheat or barley almost the entire range of variability found in a world collection of germplasm, it is still rather difficult to obtain mutations giving rise to characteristics seldom observed naturally. This is because of the fact that all non-lethal mutations, which can pass through the somatic and gametic sieves, tend to survive in populations unless they are of negative selection value. One may ask whether mutation research will represent a major advance from the standpoint of plant breeding, if the mutations which can be induced artificially are the same as are found in nature. Work at IARI has shown that for the following reasons the answer to this question is in the affirmative. First, the ability to create in a single well-adapted strain the variability found in a world collection is definitely an advantage, as has been clearly shown by the new varieties developed in a short period of time in wheat, barley, rice and cotton. Secondly, new characters which are not found within the limits of a species are observed in material treated with mutagens. Thus, it has been possible to isolate a mutant in the variety N.P. 797 of *Triticum aestivum* with adventitious branching in the ear, a characteristic recorded in nature only in *T. turgidum* var. *mirabile* (popularly known as 'Miracle' or 'Mummy' wheat). The incorporation of this branching character in commercial wheat varieties could lead to substantial gains in yield. Thirdly, new alleles of already known loci occur in mutation experiments. Fourthly, more subtle variations in phenotype arising from new recombinations of genes can be created. Finally, mutations for polygenically determined characters and the release of hidden genetic variability due to crossing-over in the regions adjacent to the centromere (where normally crossing-over is rare) are of definite value in breeding work. Mutation research should, however, be regarded only as a valuable supplement and not as a substitute to the conventional methods of plant breeding. Mutation breeding is unique in one respect. While with some of the great practical achievements in plant breeding like the exploitation of hybrid vigour in maize, a theoretical understanding of the reasons for the enhanced vigour of the hybrid has not been an

essential prerequisite for economic gains, the reverse is true of mutation breeding. The more one knows about the genetic architecture of the material and the mechanism of action of the mutagen, the greater will be the chances of getting worthwhile results. It is hence that I believe that the theoretical understanding currently being built up at the IARI of the various processes connected with induced mutagenesis would yield rich dividends in the near future.

It was mentioned at the outset that genetics provides the key to the understanding of the basic unity of the living world. It follows, therefore, that the genetical knowledge gained from one test organism may lend itself for extrapolation to totally different organisms. It also emphasizes the importance of avoiding the 'single track' approach to taking decisions of biological significance. One example from the work carried out at IARI illustrates each of these two points.

In 1956 it was observed that in plant species in which multiples of a basic chromosome number exist (technically known as polyploids), fast neutrons produce very many more chromosome breaks in the polyploid than the diploid. Thus, in species of wheat (*Triticum* sp.) fast neutrons produced 10 times as many breaks in the hexaploid species with 42 chromosomes as in the diploid or the tetraploid species with 14 and 28 chromosomes respectively. In contrast, X- and gamma-radiation did not reveal such a property. Such an enhanced ability for chromosome breakage in polyploid cells, together with the relative independence of neutron action of cellular oxygen levels, suggested that neutrons may be of great value in the treatment of advanced malignancies characterized by a high degree of endopolyploidy in the constituent cells.

#### Indirect Radiation Effects on Cells

The action of radiations on cells can be classified into two major groups — direct and indirect. These two groups, however, are not mutually exclusive. In both, one of the main initiating events seems to be the formation of a free radical. In the direct action, this radical is formed in a genetically important molecule and may destroy that molecule by chemical rearrangements, while in the indirect action the radical migrates from an unimportant molecule to an important one. Several studies have been carried out at IARI to assess the radio-mimetic potency of the indirect component of radiation action. The data reveal that: (a) chromosome aberrations occur in the root meristems of barley, onion and broad bean when they are cultured on irradiated substrates; (b) potatoes exposed to 20,000 rads of gamma rays for inhibiting sprouting as well as orange and apple juices pasteurized with 200,000 rads of gamma rays cause a low frequency of chromosome breaks in barley root meristems; and (c) there is a 2- to 4-fold increase in the spontaneous mutation frequency in the fruit fly (*Drosophila melanogaster*), when the flies are reared on a medium pasteurized with 150,000 rads of gamma rays. The extensive research on the wholesomeness of irradiated food carried out in the United States and Europe prior to our work had all been designed to

detect possible somatic effects but were not at all planned for identifying probable genetic harm. The recent tragic experience with  $\alpha$ -(N-phthalimido)-glutarimide (commercially known as phthalidomide and by several other names), which induces chromosome breaks in onion root tips, has stressed the necessity of remembering the generation as yet unborn in all our attempts to make life easy for ourselves. Chemicals with carcinogenic and mutagenic properties are finding ever-increasing applications in various spheres of life and unless serious biological thinking is directed towards such problems, on the lines so convincingly pleaded by Rachael Carson in her book *The silent spring* we may cause the gradual deterioration of the genetic endowment of man.

One of the most significant discoveries of this century is the unravelling of the biochemical constitution and mode of functioning of the gene. Much of this knowledge has come through our ability to cause experimentally the transmutation of the gene and observe its consequences in the proteins produced. Prof. J. Lederberg has drawn attention, under the term 'euphenics' to the enormous further possibilities for rectifying sporadic infirmities in man, that will be opened up by modern genetics in its attack on problems of development and of gene mutation. To a country like ours faced with the urgent task of enhancing food production, the significance of modern genetics for the production of new varieties of plants and new breeds of cattle is even greater.

## Antishielding Factors of Halogen Ions in Crystals\*

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THE antishielding factor  $\gamma_{\infty}$  plays a significant role in the theory of electric field gradients in ionic crystals in view of its surprisingly large magnitude. Theoretical values have been evaluated for a number of ions using the methods of Sternheimer and coworkers<sup>1-3</sup> or of Das and Bersohn<sup>4</sup>. A wide variety of NMR, NQR, ultrasonic and dislocation studies on single and mixed crystals of alkali halides have been carried out in recent years. These investigations have yielded at least a rough estimate of the antishielding factor of halogen ions in crystals. While in the case of positive ions the calculated antishielding factors could be used successfully for explaining the field gradients obtained from NQR or NMR measurements, the situation is far from satisfactory in the case of negative ions, particularly halogens. Hence it is considered that it would be of interest to briefly review the results of all these investigations and to compare the values of  $\gamma_{\infty}$  derived for Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> with the idealized theoretical values calculated using the free ion wave functions. A significant feature which emerges out of this detailed study is that values derived for halogen ions from these diverse investigations show approximate agreement, though they are much smaller than the theoretical values. Calculations of field gradients using the point charge model in a few cases also confirm this conclusion. Possible reasons for the difference between the values of  $\gamma_{\infty}$  theoretically calculated and those deduced from the several experimental data have also been discussed in some cases.

\*Paper presented at the Symposium on Solid State Physics, held at the National Physical Laboratory, New Delhi, in April 1964.

### Theory of Antishielding Factor

It was first pointed out by Rabi that the hyperfine splittings due to the nuclear quadrupole moment include the effect<sup>1</sup> of an electric quadrupole moment induced in the electron shells. Sternheimer<sup>1</sup> estimated values of the induced quadrupole moments in a core of closed shells for boron, aluminium, selenium, gallium, indium, etc., using valence electron functions obtained by means of the Thomas-Fermi type potential. As the accuracy of all nuclear quadrupole moment determinations is dependent on this factor, rigorous theoretical calculations have since been taken up in a large number of cases.

In the theory of electric field gradients in ionic crystals, the individual ions are assumed, to a first approximation, to have spherical symmetry and the quadrupole couplings with their own nuclei vanish. The field gradients at a nucleus would thus originate solely from charges external to the ion, i.e. from neighbouring ions in crystals with lower than cubic symmetry or from imperfections in crystals. These charges, supposed for simplicity to be fixed in space, produce at the nucleus of the ion a field gradient described by the numerical tensor  $V_{jk}^e$  ( $e$  denoting external) and the corresponding quadrupole coupling is given by

$$H^e = \sum_{j,k} Q_{j,k} V_{j,k}^e \quad \dots(1)$$

where  $Q_{jk}$  is a tensor representing the quadrupolar charge distribution of the nucleus. There is, however, an additional contribution to the coupling that is due to the distortion of the spherical electron shells of the ion by the external charges. Let  $V_{jk}^i$

be the operator describing the field gradient produced by the electrons of the ion at the nucleus. The expectation values  $V_{jk}^0 = \langle \Psi_0 | V_{jk} | \Psi_0 \rangle$  vanish because of the spherical symmetry of the unperturbed wave function of the ion  $\Psi_0$ , calculated in the absence of the external charges. If the effect of the external charges on the ion can be treated as a perturbation, the new ionic wave function will be  $\Psi_0 + \Psi_1$  to a first approximation, where  $\Psi_1$  is small and without loss of generality may be assumed orthogonal to  $\Psi_0$ . The new values of the ionic field gradient will be

$$V_{jk} = \langle \Psi_0 + \Psi_1 | V_{jk} | \Psi_0 + \Psi_1 \rangle \approx 2 \langle \Psi_0 | V_{jk} | \Psi_1 \rangle \quad \dots(2)$$

Using first order perturbation theory we obtain a linear relation<sup>2,3</sup> between the external field gradient  $V_{jk}^e$  and the gradient  $V_{jk}$  due to the distorted ion

$$V_{jk} = \gamma_{\infty} V_{jk}^e \quad \dots(3)$$

The total gradient is  $(1 + \gamma_{\infty}) V_{jk}^e$  where  $\gamma_{\infty}$  is called the antishielding factor.

The effect of the external charges can be treated perturbation-wise in three mathematically different ways:

(a) Matrix mechanical perturbation theory can be used as was done by Cohen (Thesis, University of California, unpublished). This method suffers from the requirement that energies and wave functions of excited states of the unperturbed atomic system must be known.

(b) One can find the exact solution of the inhomogeneous wave equation for the first order perturbation of the wave functions as was done by Sternheimer and coworkers<sup>1-3</sup>. This is the most accurate procedure in principle, but in practice is rather difficult to carry out. Numerical solution of the differential equation involves troublesome cumulative errors due to the finite intervals of integration.

(c) One can use a variation of parameters method as was done by Das and Bersohn<sup>4</sup>. A modified function  $\Psi = \alpha(\Psi_0 + \Psi_1)$  is used to describe the ground state of the ion in the presence of external charges, where  $\alpha$  is a normalization coefficient,  $\Psi_1$  is a trial function, the form of which is chosen from considerations of symmetry and simple expediency. The expectation value  $\langle \Psi | H | \Psi \rangle$  where  $H$  now includes the interaction of external charges with the ion is minimized with respect to the parameters contained in  $\Psi_1$ . When  $\Psi_1$  has been determined in this way the expectation value of the interaction of the ion with the nuclear quadrupole moment is then calculated with the corrected function  $\Psi$ . This procedure is in principle less accurate than method (b) but much simpler to carry out and does not involve any cumulative error. Moreover, where analytical wave functions are available, the variational method has the additional advantage that it obviates numerical integration.

The results of methods (b) and (c) above are in reasonable agreement in a majority of cases.

*Physical significance of the antishielding factor* — The simple physical basis for the antishielding effect may be illustrated<sup>5</sup> using the expression

given below for the potential energy ( $V_Q$ ) of an electron in the field of a classical nuclear quadrupole moment  $Q$

$$V_Q = -e^2 Q (3 \cos^2 \theta - 1) / 4r^3 \quad \dots(4)$$

where  $r$ ,  $\theta$  are the polar coordinates of the electron with respect to the nucleus,  $\theta$  being measured from the axis of  $Q$ . For positive values of  $Q$  the potential is attractive along the axis and repulsive along a direction normal to it. The electrons can lower their energy by two distinct modes of charge rearrangement. First, there can be an angular shift of charge at constant radius which conserves the total charge in each spherical shell. The electron density increases along the axis and decreases normal to the axis. Since the electron charge is negative, this angular excitation gives rise to negative electronic quadrupole moment, i.e. to shielding of the nuclear quadrupole moment. The rearrangement is greatest at small values of  $r$  so that quadrupole moment produced by angular excitation may be relatively small. Secondly, there can be a radial shift of charges inward along the axis and outward in a direction normal to the axis. This radial excitation gives rise to a positive electronic quadrupole moment, i.e. effecting an antishielding of  $Q$ . Since the radial shift of charge density should propagate outward to the outer regions of the ion, the antishielding effect should be relatively larger than the shielding effect. One can present a precisely analogous argument for perturbation of the ion by the local field gradient and arrive at the same conclusions.

It has been shown by Burns<sup>6</sup> that the term  $(1 + \gamma_{\infty})$  multiplies not only the effect of an external charge but also the effects of all external moments — dipole, quadrupole, etc.

The antishielding factor has been used with various measures of success in explaining quadrupole couplings of alkali halide gases and ionic solids, nuclear quadrupole spin lattice relaxation times, ultrasonically induced nuclear spin transitions, NMR acoustic absorption, etc. The existence of the antishielding effect has been demonstrated by all these diverse experiments. Most of these investigations indicate that theoretical values of  $\gamma_{\infty}$  are fairly reliable for the positive ions but too large for the negative ions<sup>7</sup>, particularly in the case of halogens. In this review article, the discussion is mainly confined to the antishielding factors of halogen ions in crystals.

### Theoretical Values of $\gamma_{\infty}$

Theoretical values of  $\gamma_{\infty}$  for Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> (free ions) are collected and given below:

Ion	Theoretical value of $\gamma_{\infty}$	Ref.
Cl <sup>-</sup>	-56.6	2, 3
	-49	8
	-27	7
Br <sup>-</sup>	-99	8
I <sup>-</sup>	-179	8

In calculating the values of  $\gamma_{\infty}$  of Cl<sup>-</sup> Hartree-Fock functions were used. For Br<sup>-</sup> and I<sup>-</sup> no such accurate functions were available and hence

an interpolation procedure involving a knowledge of the wave functions of neighbouring ions was used to obtain approximate wave functions. Wave functions for Br<sup>-</sup> were interpolated from tabulated functions of Ge, As, Rb<sup>+</sup> and for I<sup>-</sup> from those of Ag<sup>+</sup> and Cr<sup>+</sup>. So a high degree of accuracy cannot be claimed for the  $\gamma_{\infty}$  values reported<sup>8</sup> for Br<sup>-</sup>, I<sup>-</sup> values. Burns and Wikner<sup>7</sup> used contracted wave functions for Cl<sup>-</sup>. The  $3p$  wave function was contracted by a linear scale factor so that the experimental value of the susceptibility in the solid could be obtained.

**Values of  $\gamma_{\infty}$  Deduced from Experimental Data**

Several experimental investigations, mostly on alkali halide crystals, have been made and these studies give an idea of  $\gamma_{\infty}$  for the halogen ions in crystals. It would be of interest to discuss the methods of evaluating  $\gamma_{\infty}$  from the various experimental data.

*Spin lattice relaxation times* — Although there is conclusive evidence<sup>9</sup> available now establishing the fact that in sufficiently pure ionic crystals the coupling between the lattice vibrations and the nuclear quadrupole moment can be the main relaxation mechanism in cases where the nuclear spin  $I > \frac{1}{2}$ , there exist at present relatively few data on nuclear relaxation times. In the ionic model of Van Kranendonk<sup>10</sup> for cubic crystals and the extension of the model by Das *et al.*<sup>11</sup> for body-centred cubic crystals, the nearest neighbour ions are considered to be effective in causing relaxation. The acoustic modes of Debye spectra are assumed to describe the phonon distribution in which second order Raman processes are the most important. The expression obtained for the transition probability ( $W$ ) from  $m$  to  $(m+\mu)$  is given by

$$W(m, m+\mu) = \gamma^2 |Q_{\mu m}|^2 CT^{*2} E_{\mu}(T^*) \quad \dots(5)$$

where  $C = \frac{27e^2}{32\pi d^3 v^2 \mu^3}$ ;  $e$ , the electronic charge;  $d$ , the density of the crystal;  $v$ , the velocity of sound;  $a$ , the nearest neighbour distance;  $T^*$ , the reduced temperature =  $T/\Theta$ ;  $\Theta$  being the Debye temperature; and  $Q_{\mu m}$  is the quadrupole matrix element connecting the two states  $m+\mu, \mu$ .

$$\left. \begin{aligned} E_{\mu\pm 1}(T^*) &= 1330(1-0.0056/T^{*2}) \\ E_{\mu\pm 2}(T^*) &= 476(1-0.0056/T^{*2}) \end{aligned} \right\} \dots(6)$$

for  $T^* > 0.5$ .  $\gamma$  is a measure of the polarization of atomic orbitals by nuclear quadrupole moment and perhaps includes any covalency effects and is introduced by assuming that actual ionic charge is  $\gamma_e$  instead of the simple electronic charge  $e$ . The introduction of this enhancement factor  $\gamma$  brings the calculated relaxation times closer to the measured values. Alternatively, values of  $\gamma$  could be deduced from the measured relaxation times. More reliable estimates of  $\gamma$  for negative ions could be made (assuming the theoretical value of  $\gamma$  for positive ions), from the measured relaxation times of the two ions in the same crystal. Thus a value of 20 for  $\gamma$  is derived<sup>12</sup> for Cl<sup>-</sup> in sodium chloride crystal assuming the theoretical value for Na<sup>+</sup>.

*Ultrasonic saturation* — The possibility of affecting the nuclear magnetization in solids by means of ultrasonic waves has been indicated by Kastler<sup>13</sup> and Al'tshuler<sup>14,15</sup>. Most of the experiments conducted in this field are based on ultrasonic saturation of the nuclear resonance resulting in a change of the nuclear magnetization which is examined subsequently by transient magnetic resonance methods.

The existence of nuclear quadrupole transitions induced by acoustic vibrations was first demonstrated by Proctor and Tanttala<sup>16</sup> by saturation of zero magnetic field resonance of Cl<sup>35</sup> in NaClO<sub>3</sub> crystal at a frequency of 30.57 Mc/s. In later experiments acoustic transitions were induced between nuclear Zeeman levels in ionic cubic crystals where the static quadrupole interaction vanished except for crystal imperfections. Although electric quadrupole transitions  $|\Delta m| = 1$  and  $|\Delta m| = 2$  have comparable intensities, the acoustic frequency chosen was systematically twice the nuclear Larmor frequency to ensure that the transition induced corresponding to  $|\Delta m| = 2$  was unambiguously of the electric quadrupole type rather than magnetic dipole.

It could be shown<sup>17</sup> that for  $I = 3/2$ , if the nuclear spin levels are equidistant, spin-spin interactions maintain a distribution of their populations which could be described by a spin temperature and that under these conditions externally induced transitions corresponding to  $|\Delta m| = 2$  induced by the ultrasonic waves with a probability per unit time  $W$  reduce the nuclear polarization to a steady state value given by

$$\langle I_z \rangle = \frac{I_0}{1 + \frac{1}{2}WT_1} \quad \dots(7)$$

where  $T_1$  is the spin lattice relaxation time. A measurement of  $\langle I_z \rangle$  immediately after the ultrasonic saturation of the nuclear magnetic resonance yields the value of  $W$ . The transition probability  $W$  can be computed exactly if the amplitudes of the changes  $\delta V_{ij}$  in the electric field gradient at the nucleus caused by the ultrasonic vibration are known in addition to the nuclear quadrupole moment. The difficulty in evaluating  $W$  is that the exact theoretical relationship between  $\delta V_{ij}$  and the stresses  $W_{ik}$  caused by the ultrasonic vibrations may not be the one obtainable by the point charge model. However, ultrasonic experiments may help in the determination of the four index tensor  $S$  relating the changes  $\delta V_{ij}$  to the stresses  $W_{kl}$  as follows:

$$\delta V_{ij} = \sum_{k,l} S_{ij,kl} W_{kl} \quad \dots(8)$$

The introduction of the polarization factor corresponds to the assumption that if  $S'$  is the tensor calculated using the point charge model, the real tensor  $S$  is related to  $S'$  by a single constant  $S = \gamma S'$ . The experimental determination of the tensor  $S$  or  $\gamma$  requires a knowledge of the stresses ( $W$ ), i.e. of the amplitude, the wavelength and the polarization of the ultrasonic vibrations. The amplitude could be deduced from the acoustic energy stored in the sample. In view of the considerable uncertainties involved, the estimated  $\gamma$  values may not be

reliable. On the other hand, more reliable values could be obtained for the ratio of the amplification factors of the positive and negative ions by comparison of relative saturation behaviour of either spin in the same crystal. In a single crystal of NaI the ratio so measured<sup>18</sup> is 10.9. Assuming the theoretical value of  $\gamma$  for Na<sup>23</sup> the value of  $\gamma$  for I<sup>-</sup> comes out to be about 50.

Taylor and Bloembergen<sup>19</sup> attempted to produce a well-defined mode of oscillation in a cylindrical rod cut from a single crystal of NaCl. The amplitude of acoustic vibration was obtained from a careful measurement of the displacements at the end of the rod. Ultrasonic saturation of Na<sup>23</sup> and Cl<sup>35</sup> nuclear resonance was obtained.  $\gamma$  value of Na<sup>23</sup> comes out close to theoretical value. From the measured ratio  $\gamma_{\text{Cl}^{35}}/\gamma_{\text{Na}^{23}} = 1.8$ , a value of  $\gamma_{\text{Cl}^{35}} = 9$  is obtained. Taylor and Bloembergen pointed out that covalent effects may play an important role in the determination of the effects of an oscillating electric field near the nucleus.

*NMR acoustic absorption* — Ultrasonic transitions can in principle be detected by the direct absorption of ultrasonic energy by the sample which results in an increase in the load on the ultrasonic generator when the resonance condition is satisfied. Bolef and Menes<sup>20</sup> observed NMR acoustic absorption in single crystals of KI and KBr. The absorption in this case differs from normal NMR primarily in the method of coupling to the nuclear spin system. In NMR, transitions are induced among the nuclear spin levels by the interaction of the r.f. magnetic field with the nuclear magnetic dipole moment. In NMR acoustic absorption, transitions are induced among the same levels, but by the interaction of the nuclear electric quadrupole moment with the electric field gradient produced by the lattice vibrations. Thus the selection rules and the transition probabilities will differ from those in normal NMR. The effect of the acoustic wave is to create a time varying strain and hence electric field gradient in the locality of the nucleus. Bolef and Menes<sup>20</sup> have worked out the transition frequencies and probabilities for  $I = \frac{5}{2}$  and  $\frac{3}{2}$  with and without static quadrupole interactions. For the case  $I = \frac{5}{2}$ , the acoustic absorption  $\alpha$  due to the nuclear spin system is given as

$$\left. \begin{aligned} \alpha_{m,m+2} &= (21\pi^2/1600)(Ne^4Q^2/\rho c^3kT)\nu^2g(\nu)q_1^2\sin^4\theta \\ \alpha_{m,m+1} &= (21\pi^2/400)(Ne^4Q^2/\rho c^3kT)\nu^2g(\nu)q_1^2\sin^2\theta\cos^2\theta \end{aligned} \right\} (9)$$

In Eq. (9),  $N$  is the number of spins per cc.;  $T$ , the temperature;  $\rho$ , the density of the crystal;  $c$  is the velocity of the wave,  $q_1$  is the first derivative of  $g$  with respect to  $\delta$  ( $\delta$  is the peak value of the time varying strain caused by the sound wave);  $\nu$ , the frequency and  $g(\nu)$  the shape function of the absorption line. The technique of observing the resonance is one in which the absorption of energy by the nuclear spins from the acoustic wave is observed as an additional attenuation of the wave in the sample. This attenuation results in a change in the electric impedance of a piezoelectric transducer which drives the sample. The transducer impedance is made to control a Pound-Watkins type of spectrometer through an inverting and matching network.

From the observed values of  $\alpha$ , Bolef and Menes<sup>20</sup> derived that

$$e^2Qq_1/h = 300 \text{ Mc/s. (for I}^{27} \text{ in KI)}$$

$$e^2Qq_1/h = 82 \text{ Mc/s. (for Br}^{81} \text{ in KBr)}$$

Considering the uncertainties in various measurements they quoted the values to be correct to within a factor 1.5 for observations made in KI and perhaps the factor being slightly larger in the case of KBr.

Assuming a point charge model in which the quadrupolar nucleus interacts with the six nearest neighbour ions Bolef and Menes<sup>20</sup> obtained

$$e^2Qq_1 = 12\gamma e^2Q/a^3 \quad \dots(10)$$

where  $a$  is the lattice constant.

The values of  $\gamma$  derived using Eq. (10) are 26 for Br<sup>-</sup> in KBr and 38 for I<sup>-</sup> in KI.

*Mixed crystal experiments* — Estimates of anti-shielding factors of halogens could also be made from NMR experiments on mixed crystals of alkali halides. Kawamura *et al.*<sup>21</sup> observed striking reduction in intensity of the satellite lines of Na<sup>23</sup> in NaCl crystal when small amounts of NaBr are added to NaCl. Both Cl<sup>-</sup> and Br<sup>-</sup> being monovalent ions, the excess charge effect is ruled out and hence Kawamura *et al.* have assumed that the local strains due to difference of ionic radii of Cl<sup>-</sup> and Br<sup>-</sup> are causing the effects observed.

The energy levels of the nucleus having a spin  $I$  split into  $2I+1$  levels specified by the magnetic quantum number  $m$ . The energy separation between adjacent levels is given to a first order by

$$E_{m,m-1} = h\nu_0 - (2m-1)(1-3\cos^2\theta) \frac{3e^2Qq}{8I(2I-1)} \dots(11)$$

In Eq. (11),  $\nu_0$  is the resonance frequency;  $\theta$ , the angle between the external magnetic field and the axis of the electric field gradient. The transition  $m = \frac{1}{2}$  to  $-\frac{1}{2}$  is unaffected by first order quadrupole effect. The second order shift of the central line is given as

$$h\Delta\nu = A(1-9\cos^2\theta)(1-\cos^2\theta) \quad \dots(12)$$

where

$$A = \frac{9}{64} \frac{2I+3}{4I^2(2I-1)} \frac{e^4Q^2q^2}{h\nu_0}$$

If we write  $a_0$  and  $a_i$  as the radii of solvent and solute ions, the relative displacement ( $\Delta a$ ) of two neighbouring ions at a distance  $r$  from the solute ion is given on the continuum model by

$$\Delta a = (a_i - a_0)a^3/r^3 \quad \dots(13)$$

The change in the electric field gradient corresponding to the compressional displacement will be

$$\Delta eq = 6e(a_i - a_0)/r^3a \quad \dots(14)$$

Hence we have the frequency shift for first order broadening as

$$h\Delta\nu = \frac{18e^2Q(a_i - a_0)}{r^3a} \gamma \frac{(2m-1)(3\cos^2\theta - 1)}{8I(2I-1)} \dots(15)$$

If  $\Delta\nu$  is so widely spread out then the satellites would be utterly unobservable. Considering the

signal to noise ratio in their experiments, this value of  $\Delta\nu$  corresponds to 10 kc/s. The term  $r$  represents the radius of the critical sphere which bounds the region around  $\text{Na}^{23}$  in which the solute can effect the satellites and was obtained from a double logarithmic plot of signal intensity versus concentration of the solute. The value of  $\gamma$  could be determined from measurements of the first order broadening. Of more interest is the asymmetric broadening of the central line by second order perturbation observed when the solute concentration is increased to about 10 per cent, when there is an appreciable probability of finding a solute ion next to the Na nucleus. From such measurements a value of  $\gamma$  close to the theoretical value has been deduced for  $\text{Na}^{23}$ . Otsuka and Kawamura<sup>22</sup> studied this effect in  $\text{Br}^{79}$  and  $\text{Br}^{81}$  resonance in the mixed crystal of  $\text{KBr-NaBr}$ . Only the second order broadening could be studied in this system as the satellites were already smeared by first order broadening even in the pure  $\text{KBr}$  crystal. In Eq. (12) since  $\theta$ , the angle between  $H$  and the axis of the electric field gradient, varies as the minority ion moves on the sphere of radius  $r$  around the nucleus, the frequency shift will take a series of values corresponding to the possible locations of the minority ion on the spherical surface. If there correspond many such possible orientations for a given  $r$ , we shall have a broad frequency spectrum having two peaks whose separation is given by

$$\Delta\nu_0 = \frac{25 A}{9 \hbar} = \frac{225}{16} \frac{2I+3}{4I^2(2I-1)} \frac{e^4 Q^2}{\hbar\nu_0 r^6} \left(\frac{a_i - a_0}{a}\right) \gamma^2 \dots (16)$$

Since  $\Delta\nu_0$  varies as  $1/r^6$ , it can be assumed that if the minority ion comes within a certain critical sphere the line is so much shifted that it contributes nothing to the peak intensity. Thus the peak intensity of the integrated absorption curve will be proportional to the probability that the minority ion does not come within this critical sphere. Assuming  $\Delta\nu_0$  tentatively as the theoretical dipolar line width, values obtained for  $\gamma$  are 35 for  $\text{Br}^{79}$  and 39 for  $\text{Br}^{81}$ . Considering the uncertainties in the method  $\gamma$  may be taken as 40 for both.

**Dislocation studies** — It has been shown (W. A. Robinson, Doctorate thesis, University of Washington, 1956, unpublished) that an averaged field gradient would result by dislocations in a crystal. The density of dislocations was estimated by Otsuka<sup>23</sup> from measurements of anisotropy of NMR. The reduction in intensity of  $I^{27}$  resonance in deformed crystals of  $\text{KI}$  was measured by Otsuka. From a comparison with measurements on  $\text{Br}$  in  $\text{KBr}$ , he has estimated  $\gamma \approx 50$  for  $\text{I}$  in  $\text{KI}$ .

**Double resonance of F centres** — The magnitude and sign of  $e^2 Qq$  were determined by Feuchtwang<sup>24</sup> from electron nuclear double resonance (ENDOR) measurements on  $F$  centres in  $\text{KCl}$  crystals. Calculations have been made of the electric field gradient 'seen' by the  $\text{Cl}$  nucleus in the lattice near a  $F$  centre. This gradient is caused by three factors: (i) the net positive charge associated with a negative ion vacancy, (ii) the  $F$  electron charge density, and (iii) polarization of the lattice induced by the  $F$  centre. Feuchtwang has concluded that

the theoretical value of  $\gamma$  for  $\text{Cl}^-$  is probably too large by a factor of 2 or more.

**Quadrupole resonance** — Barnes *et al.*<sup>25</sup> carried out detailed calculations of the ionic field gradient for a number of compounds representing several types of infinite layer structure such as  $\text{CdI}_2$ ,  $\text{CdCl}_2$ ,  $\text{BiI}_3$ , etc. In no case the coupling due to ion lattice alone was sufficient to explain the observed interactions unless  $\gamma_\infty$  values larger than theoretical ones are used and this assumption of a value higher than the theoretical value appears to be untenable. They suggest that the empirical values of  $\gamma_\infty$  are more reasonable. In the case of  $\text{CdI}_2$  crystal the presence of two non-equivalent  $\text{I}^-$  lattice sites provides an opportunity to compare the ratio of the coupling constants (independent of  $\gamma_\infty$ ) predicted by the ionic model. As the experimentally observed difference between coupling constants is so much smaller than that predicted by the ionic model, they concluded that the ionic field gradient makes a small contribution to the total interaction in these cases. The experimental difference is consistent with the value based on ionic field gradient in conjunction with empirical value of  $\gamma_\infty$  when effects of covalency are also considered.

The values of  $\gamma$  determined from various kinds of experiments are presented in Table 1. The measured  $\gamma_\infty$  values of halogen ions in alkali halide crystals are seen to be much smaller than the theoretical values and seem<sup>7</sup> to be around 10, 35 and 45 for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  respectively.

In the case of alkali halide gases consistent values<sup>6</sup> of  $\gamma_\infty$  quite close to the theoretical values (where Hartree-Fock wave functions are available) were obtained for the metallic ion from the measured quadrupole coupling constants in a series of compounds as, for example,  $\text{Na}^{23}$  in  $\text{NaCl}$ ,  $\text{NaBr}$ , etc. But  $\gamma_\infty$  values obtained for the halogen ions using a similar procedure are widely divergent. Hence it was concluded that perturbation theory is applicable to the alkali ions but not to the easily deformable halogen ions.

TABLE I COMPARISON OF VALUES OF AMPLIFICATION FACTORS  $(\gamma - 1/\gamma_\infty)$  EVALUATED FROM EXPERIMENTAL STUDIES, WITH THEORETICAL VALUES

Method	Value of $\gamma$		
	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
Spin lattice relaxation	20	—	—
( $\text{NaCl}$ )			
Ultrasonic saturation	9	—	50
( $\text{NaCl}$ )			( $\text{NaI}$ )
NMR acoustic absorption	—	26	38
( $\text{KI}$ )		( $\text{KI}$ )	( $\text{KI}$ )
Mixed crystal experiments	—	40	—
( $\text{KBr-NaBr}$ )			
Dislocation studies	—	—	50
( $\text{KI}$ )			( $\text{KI}$ )
Suggested <sup>7,25</sup> empirical values of $\gamma_\infty$	10	35	45
Theoretical values (free ions)	58	100	180

(The molecular formulae within parentheses represent the crystals in which the ions are studied.)



The idealized model of ionic crystals used as a basis in most of these investigations is inadequate<sup>5</sup> in three respects:

(i) Since the ions overlap, the effects of overlap have to be treated by the orthogonalization procedures of Lowdin.

(ii) The excited states of the negative ion are changed by incorporation of this ion in the crystal. As the outer regions of the ion contribute significantly to  $\gamma_{\infty}$ , the low lying excited states must be important when the first order wave function is expanded in terms of wave functions of the excited states. For a negative ion in a crystal even the lowest excited levels correspond to states in which an electron is stripped from the ion, i.e. exciton formation or excitation to the conduction band. Hence  $\gamma_{\infty}$  of negative ions must change when they are incorporated in the crystal.

(iii) There may be a small transfer of charge from negative ion to positive ion, which represents the effects of covalency. When such transfer takes place a hole remains in the  $\beta$  shell of the halogen ion which contributes significantly to the field gradients at the halogen nuclear site. This contribution varies more rapidly with interionic separation than the charge contribution so that the relative importance of charge transfer is increased for field gradients produced by distortion of a cubic crystal.

Kanda<sup>26</sup> has estimated the percentage covalency from measurements of chemical shifts. Yosida and Moriya<sup>27</sup> carried out a detailed study of the consequences of covalency in NMR of ionic crystals.

Das and Dick<sup>28</sup> have shown that the available experimental data on first and second order effects on NMR in solid solutions of NaCl-Br, NaBr-Cl and KBr-Na can be explained adequately using the theoretical antishielding factors for the free ions—Na<sup>+</sup>, Br<sup>-</sup>. They criticized that the simple compression theory used in deriving  $\gamma$  values in most of the experiments<sup>20,21</sup> may lead to erroneous estimates of the displacement of lattice points and also neglects the important contribution from the displacements and electronic polarization of the ions adjacent to the nucleus whose nuclear quadrupole interaction is being considered. Das and Dick have suggested that in general in imperfect crystals the calculated values of  $\gamma_{\infty}$  for both positive and negative free ions are reasonable and may be used to explain observed splittings and shifts in frequency of NMR lines if the field gradients due to charges and dipoles of the ions of the crystal are calculated carefully. Even for the pure crystals in which the nuclei are already at sites of less than cubic symmetry, they suggest that it is reasonable to use free ion values in the calculation of ionic contribution to the field gradients and ascribe the difference between this and observed value to covalent or overlap effects between neighbouring ions rather than ignoring these effects altogether and trying to explain the observed field gradient by an unreasonable alteration of  $\gamma_{\infty}$  from the free ion value.

On the other hand, Watson and Freeman<sup>29</sup> are of the opinion that the theoretical  $\gamma_{\infty}$  values of the free

ions Br<sup>-</sup>, I<sup>-</sup> appreciably over-estimate the antishielding effect appropriate to experiments in crystals though very likely less severely than is the case for Cl<sup>-</sup>. The over-estimate could easily be by a factor of 2 for these ions. It appears that the position regarding the values of antishielding factors of halogen ions appropriate to experiments in crystals is still far from satisfactory. Hence there is need for extensive experiments on first and second order effects on NMR of these ions in predominantly ionic crystals and their solid solutions along with detailed theoretical study of crystal field effects, interionic exchange, etc., using an approach of the unrestricted Hartree-Fock type.

### Summary

The concept of the antishielding factor ( $\gamma_{\infty}$ ) in the theory of electric field gradients in ionic crystals is outlined. The physical significance of  $\gamma_{\infty}$  is explained using the expression for the potential energy of an electron in the field of a classical nuclear quadrupole moment. Approximate methods using quantum mechanical perturbation theory are outlined for calculating  $\gamma_{\infty}$ . Theoretical values of  $\gamma_{\infty}$  for Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> calculated from free ion wave functions have been compared with the values deduced from different types of experimental observations on halogen ions in crystals. The detailed study shows that values of  $\gamma_{\infty}$  derived for halogen ions from these observations on crystals differ considerably from the theoretical values calculated using free ion wave functions, the latter values always being higher. In view of the large disparity between the theoretical values of  $\gamma_{\infty}$  and those deduced from the different types of experimental observations, there is need for further experimental studies on first and second order effects on NMR of these ions in predominantly ionic crystals and their solid solutions. Also detailed theoretical investigation of crystal field effects, interionic exchange, etc., using an approach of the unrestricted Hartree-Fock type, is necessary.

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## Recent Advances in the Chemistry of Rutaceae Alkaloids

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THE family Rutaceae comprises about one hundred and fifty genera with sixteen hundred species<sup>1</sup>. Of the four important sub-families<sup>2</sup>, Rutoideae and Toddalioidae are almost equally versatile in producing alkaloids. With one exception, Flindersioideae is known to produce furanoquinolines exclusively. Aurantioideae is the only known source of simple quinazolines.

Alkaloids of diverse structural types, viz. quinoline, furanoquinoline, acridine, quinazoline, protoberberine, 1,2-benzophenanthridine, aporphine, protopine, canthinone, imidazole, pyrrolidine, oxazole and  $\beta$ -phenylethylamine bases, have been encountered in Rutaceae. Some of those types, viz. furanoquinoline and acridine, are restricted only to and thus diagnostic of this family. Like acridines, with a few exceptions, quinolines and quinazolines have also been found to be associated with furanoquinolines though the reverse is not true<sup>3,4</sup>.

The earlier work in this field has adequately been dealt with in the well-known series of *The alkaloids* of Manske and Holmes. Price<sup>5</sup> summarized especially those considered to be originated from the 'anthranilic acid unit' known before 1956. We, therefore, wish to list here the Rutaceae alkaloids known up till now and to discuss the detailed structural studies\* of those not yet reviewed. We have not included those of doubtful existence or the structures of which are not yet known.

### QUINOLINE BASES

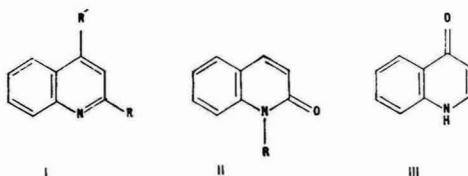
Quinoline bases which include those derived from quinoline itself (I), 2-quinolones (II) and

4-quinolones (III) (Table 1) are next in abundance to the furanoquinolines in the family Rutaceae. Apart from the Angostura alkaloids<sup>5,32</sup> most of them have been isolated comparatively recently. The more recent additions to the quinoline bases of novel structural types came from *Lunasia* and a few other species. 2-Aryl substitution and an isopentane side chain at position 3 of the quinoline moiety are the important structural features of considerable biogenetic significance.

### General Characteristics

With a few exceptions, the naturally occurring quinolines are oxygenated at position 4. The aromatic ring often carries OCH<sub>3</sub> or CH<sub>2</sub>O<sub>2</sub> substituents. On being heated above melting points, the hydrochlorides of 4-methoxy quinolines suffer loss of methyl chloride by thermal decomposition and then resolidify to higher melting quinolones. Again, when their methiodides are treated with alkali, the corresponding *iso*-compounds are formed consequent on the migration of the CH<sub>3</sub> group from O to N, a property in common with furanoquinolines.

The pattern and the nature of shift in the UV absorption maxima at the longer wavelength region in neutral and acid media are quite diagnostic of the quinoline system. A clear distinction between quinoline and 2- and 4-quinolones is also possible as will be evident in the sequel<sup>33,34</sup>.



\*Note added in proof: After submitting the manuscript we came across an excellent review on the ultraviolet spectra of alkaloids in which the individual spectrum as well as the spectral characteristics of the Rutaceae alkaloids have been extensively covered [Sangster, A. W. & Stuart, K. L., *Chem. Rev.*, **65** (1965), 69].

TABLE I — QUINOLINE ALKALOIDS AND THEIR SOURCES

Alkaloid	Mol. formula	m.p./b.p. °C.	Source	Structure
QUINOLINES (I)				
Quinoline <sup>5a,6</sup>	C <sub>9</sub> H <sub>7</sub> N	237/760 mm.	<i>Citrus aurantium</i> , <i>Galipea officinalis</i> Hancock	Ia, R=R'=H
Quinaldine <sup>6</sup>	C <sub>10</sub> H <sub>9</sub> N	246/760 mm.	do	Ib, R=CH <sub>3</sub> ; R'=H
2- <i>n</i> -Amyl-quinoline <sup>6</sup>	C <sub>14</sub> H <sub>17</sub> N	145-60/13 mm.	do	Ic, R=(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> ; R'=H
4-Methoxy-2- <i>n</i> -amyl-quinoline <sup>6</sup>	C <sub>15</sub> H <sub>15</sub> NO	190-200/14 mm.	do	Id, R=(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> ; R'=OCH <sub>3</sub>
Cusparine <sup>7</sup>	C <sub>19</sub> H <sub>17</sub> NO <sub>3</sub>	92; 110-22	do	Ie, R=(CH <sub>2</sub> ) <sub>2</sub> (3',4'-methylenedioxyphenyl); R'=OCH <sub>3</sub>
Galipine <sup>7</sup>	C <sub>20</sub> H <sub>21</sub> NO <sub>3</sub>	115	do	If, R=(CH <sub>2</sub> ) <sub>2</sub> (3,4'-dimethoxyphenyl); R'=OCH <sub>3</sub>
Galipoline <sup>8</sup>	C <sub>19</sub> H <sub>19</sub> NO <sub>2</sub>	193	do	Ig, Ij but R'=OH
Cusparcine <sup>9</sup>	C <sub>19</sub> H <sub>17</sub> NO <sub>3</sub>	56	do	Ih, Ij but R'=H; 3,4-dihydro
Dubamine <sup>10</sup>	C <sub>16</sub> H <sub>11</sub> NO <sub>2</sub>	96-7	<i>Haplophyllum dubium</i>	IV
4-Methoxy-2-phenyl-quinoline <sup>11</sup>	C <sub>16</sub> H <sub>13</sub> NO	66-7	<i>Lunasia amara</i>	V
4-Methoxy-2-(3',4'-methylenedioxyphenyl)-quinoline <sup>11,12</sup>	C <sub>17</sub> H <sub>13</sub> NO <sub>3</sub>	116-7	do	VI
Orixine <sup>13</sup>	C <sub>17</sub> H <sub>21</sub> NO <sub>6</sub>	152	<i>Orixa japonica</i> Thunb.	X
Nororixine <sup>14</sup>	C <sub>16</sub> H <sub>19</sub> NO <sub>6</sub>	199-200	do	XI
2-QUINOLONES (II)				
1-Methyl-2-quinolone <sup>6</sup>	C <sub>9</sub> H <sub>9</sub> NO	74	<i>Galipea officinalis</i>	IIa, R=CH <sub>3</sub>
Casimiroin <sup>15</sup>	C <sub>12</sub> H <sub>11</sub> NO <sub>4</sub>	202-3	<i>Casimiroa edulis</i> Llave et Lex	XVI
Lunacridine <sup>16,17</sup>	C <sub>17</sub> H <sub>23</sub> NO <sub>4</sub>	85-6	<i>Lunasia amara</i>	XX
Hydroxylunacridine <sup>17</sup>	C <sub>17</sub> H <sub>23</sub> NO <sub>5</sub>	100-2	do	XXII
Hydroxylunidine <sup>17</sup>	C <sub>17</sub> H <sub>21</sub> NO <sub>6</sub>	124-5	do	XXIV
Lunidine <sup>18</sup>	C <sub>17</sub> H <sub>21</sub> NO <sub>5</sub>	65-6	do	XXV
Lunilonine <sup>18</sup>	C <sub>17</sub> H <sub>19</sub> NO <sub>5</sub>	118-9	do	XXVI
Balfourolone <sup>19</sup> (artifact)	C <sub>17</sub> H <sub>23</sub> NO <sub>5</sub>	99-100	<i>Balfourodendron riedelianum</i>	XXII
Homobalfourolone <sup>20</sup>	C <sub>18</sub> H <sub>25</sub> NO <sub>5</sub>	137	do	XXIII
4-QUINOLONES (III)				
1,2-Dimethyl-4-quinolone <sup>21</sup>	C <sub>11</sub> H <sub>11</sub> NO	178-9	<i>Platydesma campanulata</i> Mann.	XXVII
Pilokeanine <sup>21</sup>	C <sub>16</sub> H <sub>21</sub> NO <sub>3</sub>	Picrate, m.p. 216 (decomp.)	do	XXVIII
7-Methoxy-1-methyl-2-phenyl-4-quinolone <sup>17,22-24</sup> (Éduline <sup>24</sup> )	C <sub>17</sub> H <sub>15</sub> NO <sub>2</sub>	198-200	<i>Lunasia amara</i> , <i>L. quercifolia</i> <i>Casimiroa edulis</i>	XXIX
Lunamarine <sup>25</sup>	C <sub>18</sub> H <sub>15</sub> NO <sub>4</sub>	245-7	<i>L. amara</i>	XXX
Lunasia 1 <sup>26</sup>	C <sub>18</sub> H <sub>15</sub> NO <sub>4</sub>	228-30	do	XXXI
Gravoline <sup>27</sup>	C <sub>17</sub> H <sub>15</sub> NO <sub>2</sub>	205	<i>Ruta graveolens</i>	XXXII
Éduline <sup>15</sup>	C <sub>17</sub> H <sub>15</sub> NO <sub>3</sub>	186-7	<i>Casimiroa edulis</i>	XXXVII
2- <i>n</i> -Propyl-4-quinolone <sup>45</sup>	C <sub>12</sub> H <sub>13</sub> NO	166-8	<i>Boronia ternata</i>	—
1-Methyl-2-phenyl-4-quinolone <sup>30</sup>	C <sub>16</sub> H <sub>13</sub> NO	144-5	<i>Balfourodendron riedelianum</i>	—
1-Acetoxyethyl-2-propyl-4-quinolone <sup>3a</sup>	C <sub>15</sub> H <sub>17</sub> NO <sub>3</sub>	112	<i>Boronia ternata</i>	—
PYRANOQUINOLINE				
Flindersine <sup>28,29</sup>	C <sub>14</sub> H <sub>13</sub> NO <sub>6</sub>	185-6	<i>Flindersia australis</i>	XXXVIII
Lunacrinol <sup>17,26</sup>	C <sub>16</sub> H <sub>19</sub> NO <sub>4</sub>	201-3	<i>L. amara</i>	XLI
Isobalfourolone <sup>30</sup>	C <sub>16</sub> H <sub>15</sub> NO <sub>4</sub>	204-5	<i>Balfourodendron riedelianum</i>	XLI
Khaplofoline <sup>31</sup>	C <sub>14</sub> H <sub>15</sub> NO <sub>2</sub>	272-4	<i>Haplophyllum foliosum</i>	XLII

A pronounced bathochromic shift of the longer wavelength maxima in passing from neutral to acid medium characterizes the quinolines including their 4-methoxy derivatives. On the other hand, a hypsochromic shift of the typical bifurcated maxima (310-350  $m\mu$ ) in alcohol to a single peak (303-313  $m\mu$ ) in strong acid medium is a distinctive feature of the 4-quinolones and their 2-substituted derivatives; the twin maxima of the 3-substituted ones remain unaffected under similar condition. Identical shift in the basic medium has only been observed with 4-quinolones and not with their 2- and 3-substituted analogues<sup>35</sup>. 2-Quinolones exhibit the same type of spectra in alcohol, dilute acid and dilute alkali. In sufficiently alkaline (10 per cent) medium, however, only the maximum around 275  $m\mu$  is affected — either bathochromic shift or complete disappearance of the peak has been observed.

The infrared spectra of 2- and 4-quinolones show a number of bands in the 1450-1700  $cm^{-1}$  region. In general, it appears<sup>36,37</sup> that the C=O group of the 2-quinolones absorbs at a higher frequency than that of the comparable 4-quinolones. Price and Willis<sup>38</sup>, however, showed that the frequency of the C=O absorption band is hardly a reliable guide in characterizing them. Because, 2- and 4-pyridones also absorb<sup>39</sup> in the frequencies of C=O absorption of 2-quinolones (1635-1665  $cm^{-1}$ ) and 4-quinolones (1620-1645  $cm^{-1}$ ) respectively. Moreover, 2- and/or 4-methoxylated quinolones show a strong band in the region where the normally regarded characteristic C=O band of 4-quinolones absorbs. They, however, considered the frequency of the NH absorption band to be helpful in differentiating between the systems. Thus, the 2-quinolones seldom absorb above 3160  $cm^{-1}$  in the solid state, while 4-quinolones exhibit a broad band in the 2500-3300  $cm^{-1}$  region.

#### Dubamine (IV)

The base has been isolated from *Haplophyllum dubium*. The initially assigned molecular formula,  $C_{14}H_9NO_2$ , has subsequently been revised to  $C_{16}H_{11}NO_2$  and the earlier proposed 3,4-methylene-dioxy acridine structure was also found to be untenable<sup>40</sup>. For,  $KMnO_4$  oxidation of dubamine yields oxalyl-anthranilic acid or quinaldic acid depending on whether the reaction is run in acetone or aqueous  $H_2SO_4$ . A 2-piperonyl quinoline (IV) structure was thus proposed and substantiated by its synthesis<sup>41</sup>.

#### 4-Methoxy-2-phenylquinoline (V)

It occurs in *Lunasia amara*. It has a molecular formula,  $C_{16}H_{13}NO$ . The UV spectrum of the base in ethanol shows maxima at 254 and 294  $m\mu$ , the latter exhibits a bathochromic shift to 316  $m\mu$  in the spectrum of its hydrochloride in the same solvent. Pyrolysis of its hydrochloride, m.p. 256-8°, to 2-phenyl-4-quinolone (identified by its synthesis from ethyl anthranilate and acetophenol diethyl-ketal<sup>42</sup>) and the formation of the *iso*-base from its methiodide with alkali pointed towards structure (V) for the original base. The structure was confirmed by the synthesis of 4-methoxy-2-phenylquinoline from 2-phenyl-4-quinolone<sup>11</sup>.

#### 4-Methoxy-2-(3',4'-methylene-dioxyphenyl)-quinoline (VI)

The base,  $C_{17}H_{13}NO_3$ , was also found in *Lunasia amara*. It has been characterized by the bathochromic shift of the UV maxima in acid medium, behaviour of its hydrochloride at the melting point similar to the hydrochloride of 4-methoxy-2-phenyl-quinoline (V) and finally by its synthesis<sup>12</sup>. 2-(3',4'-Methylene-dioxyphenyl)-4-quinolone (XXXVI) was converted to the 4-methoxy derivative in the usual way<sup>12</sup>.

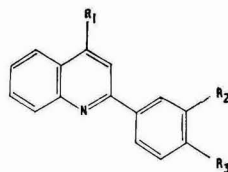
Gravecolinine, later isolated from *Ruta graveolens*, has been shown<sup>12</sup> to be identical with this compound.

#### Orixine (X) and Nororixine (XI)

Orixine,  $C_{17}H_{21}NO_6$ , was isolated from the root bark of *Orixa japonica*<sup>13</sup>. On treatment with dry hydrogen chloride it affords nororixine, which has also been encountered in the same source later on<sup>14</sup>. Both of them contain one  $CH_2O_2$  bridge, a 1,2-glycol system and a terminal  $CH_3$  group. Methylation of nororixine furnishes iso-orixine (VII), m.p. 127°, with one  $OCH_3$  and one  $NCH_3$  groups.

On  $HIO_4$  oxidation, orixine and nororixine afford acetone along respectively with 2,4-dimethoxy-7,8-methylene-dioxy-3-quinoline acetaldehyde (VIII), m.p. 122°, and 4-methoxy-7,8-methylene-dioxy-1,2-dihydro-2-oxo-3-quinoline acetaldehyde (IX), m.p. 230°, having UV spectra similar to their parent compounds. Therefore, oxidation of the side chain without any change of ring structure must have occurred. Again, dithioacetal of compound (VIII) on catalytic reduction and subsequent treatment with dry hydrogen chloride gives a carbostyryl derivative (XII). The product which is identical in all respects with the 2-quinolone prepared by the catalytic reduction of kokusagine (XLIIIc) was also obtained from nororixine<sup>14</sup>.

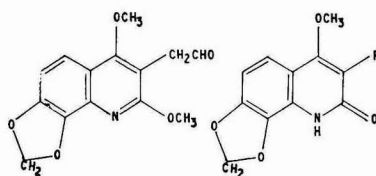
The above reactions suggest structures (X) and (XI) for orixine and nororixine respectively. The



IV,  $R_1=H$ ;  $R_2R_3=O-CH_2-O-$

V,  $R_1=OCH_3$ ;  $R_2=R_3=H$

VI,  $R_1=OCH_3$ ,  $R_2-R_3=O-CH_2-O-$



VIII

IX  $R=CH_2CHO$

XII  $R=C_2H_5$

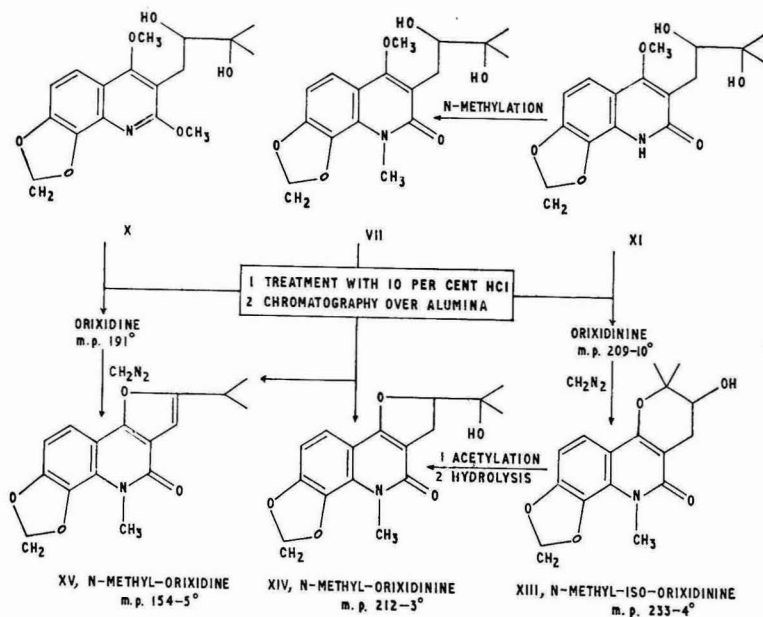


CHART 1

assigned structures received further support from the NMR studies<sup>43</sup> of N-methyl-iso-orixidine (XIII), N-methyl-orixidine (XIV), including their acetates and N-methyl-orixidine<sup>44</sup> (XV) as shown in Chart 1. The interrelationship among orixine (X), nororixine (XI) and iso-orixine (VII) is particularly clear therein.

#### Casimiroin (XVI)

This non-basic substance,  $C_{12}H_{11}NO_4$ , was isolated from the seeds, trunk and root bark of *Casimiroa edulis*<sup>15</sup>. The UV and IR spectra are indicative of a 2-quinolone structure. On boiling with conc. HCl, it gives a phenolic substance, casimiroinol,  $C_{11}H_9NO_4$ , m.p. 323°, which on methylation regenerates the original compound.

Casimiroin contains one  $OCH_3$ , one  $NCH_3$  [contained in a tertiary (-CONCH<sub>3</sub>) rather than a secondary amide as shown by the absence of any active hydrogen atom] and one  $CH_2O_2$  groupings. Although very resistant to acids and alkalis under ordinary conditions, casimiroin yields casimiroinol and its ethyl ether, casimiroitine,  $C_{13}H_{13}NO_4$ , m.p. 171°, when boiled with ethanolic alkali.

On reduction with  $LiAlH_4$ , casimiroin affords a ketone,  $C_{11}H_{11}NO_3$ , m.p. 108-9°, free from OH or  $OCH_3$  function. Assuming a 1-methyl-4-methoxy-2-quinolone structure (XVI) for casimiroin, this ketone (XVII) could arise via the compound (XVIII). The validity of this mechanism has been secured by the actual isolation of the intermediate product (XVIII) without the use of an acid.

On oxidation with  $H_2O_2$ , casimiroin furnishes an amino acid (XIX),  $C_9H_9NO_4$ , m.p. 181°, which on treatment with acetic anhydride followed by

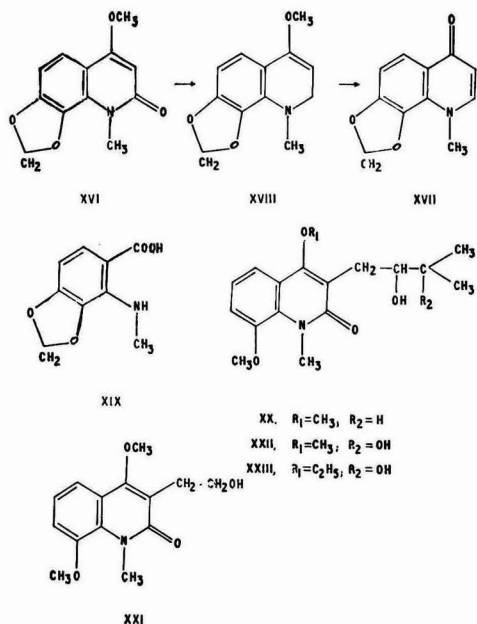
methylation regenerates casimiroin. Therefore, not only the position of the  $CH_2O_2$  group but also the structure (XVI) of casimiroin is proved<sup>46</sup>.

#### Lunacridine (XX)

The isolation of lunacridine,  $C_{17}H_{23}NO_4$ ,  $[\alpha]_D^{20} +28^\circ$ , was first reported by Boersma<sup>16</sup> and subsequently by others<sup>17</sup>. The UV spectrum both in alcohol and in N HCl shows  $\lambda_{max}$ . 239, 257, 285, 294 and 333 m $\mu$ . The IR spectrum exhibits bands at 3370 (OH) and 1634  $cm^{-1}$  (N-acyl C=O). The displacement of the latter peak to 1644  $cm^{-1}$ , when acetylated, is regarded<sup>38</sup> as a criterion for a 2-quinoline derivative with a side chain OH function capable of interacting with the C=O group. Vigorous acid treatment converts lunacridine to (+)-lunacrine,  $C_{16}H_{19}NO_3$ , with the sign of optical rotation opposite to that of the natural one. The structure of lunacridine will be dealt with later along with lunacrine with which it is interconvertible. However, lunacridine is, in all probability, an artifact that might have originated from the alkali sensitive water-soluble *Lunasia* bases during the process of isolation<sup>17,22</sup>.

#### Hydroxylunacridine and Balfourolone (XXII)

Hydroxylunacridine,  $C_{17}H_{23}NO_5$ ,  $[\alpha]_D^{20} +31.5^\circ$ , isolated from *Lunasia amara*<sup>17</sup>, and balfourolone,  $[\alpha]_D^{20} -36^\circ$ , from *Balfourodendron riedelianum*<sup>19</sup>, are optical isomers containing two active hydrogen atoms, two  $OCH_3$  and one  $NCH_3$  groups. Hydroxylunacridine<sup>47</sup> shows UV and NMR (particularly with respect to the signals of the aromatic hydrogen,  $OCH_3$  and  $NCH_3$  protons) spectra identical with those of lunacridine. The physical methods thus



indicated a 3-alkyl-4,8-dimethoxy-1-methyl-2-quinolone structure for hydroxylunacridine. The detailed interpretation of the NMR spectrum for the presence of  $-\text{CH}_2\text{CHOH}-\text{C}(\text{OH})(\text{CH}_3)_2$  side chain at position 3 has been advanced. The chemical evidences for the nature and position of the side chain have also been secured as follows:

Oxidation of hydroxylunacridine with periodic acid furnishes, in addition to acetone, an aldehyde which on  $\text{NaBH}_4$  reduction yields a crystalline alcohol (XXI),  $\text{C}_{14}\text{H}_{17}\text{NO}_4$ , m.p.  $120-1^\circ$ . The same alcohol is also obtained by the action of aqueous alkali on the methiodide of dihydro- $\gamma$ -fagarine<sup>47</sup>. Thus hydroxylunacridine must have the structure (XXII).

Balfourone has independently been shown to have the same structure, and it has definitely been established to be an artifact resulting from the base-catalysed ring opening of 4-O-methyl-balfouronium salt (LXIIIb) during the isolation procedure (cf. formation of lunacridine).

It is interesting to note that the structurally corresponding alkaloids of the two genera, *Balfourdendron riedelianum* and *Lunasia amara*, possess absolute configurations almost invariably opposite to one another. Such occurrence of enantiomorphs in different genus is rather uncommon<sup>19</sup>.

**Homobalfourone\* (XXIII)**

This alkaloid,  $\text{C}_{18}\text{H}_{25}\text{NO}_5$ , has also been isolated from *Balfourdendron riedelianum*<sup>20</sup> as a companion of balfourone.

\*The discoverer of this alkaloid called it 4-O-ethyl analogue of balfourone. For the convenience of discussion, it has been so named by the reviewers on the basis of its relationship with balfourone.

The base on periodic acid oxidation yields acetone and an aldehyde. The latter on  $\text{NaBH}_4$  reduction followed by acetylation and dealkylation affords a product identical with the compound obtained from balfourone in the similar manner. The above degradation and the fact that it has one  $-\text{CH}_2-$  group more than balfourone (XXII) led to the structure (XXIII) for the base, confirmed by its synthesis. Balfouridine (LXIV) on treatment with ethyl iodide furnished 4-O-ethyl-balfouronium iodide that on further alkali treatment afforded a base identical with the natural compound.

**Hydroxylunidine (XXIV)**

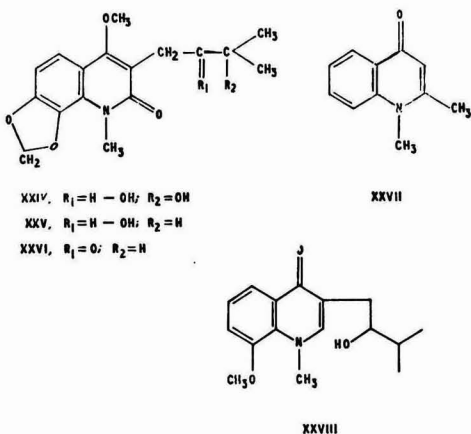
The base,  $\text{C}_{17}\text{H}_{21}\text{NO}_6$ ,  $[\alpha]_D +27.6^\circ$ , has been isolated from *Lunasia amara*. The UV spectrum shows maxima at 228, 267 and 318  $m\mu$  with shoulders at 237, 260 and 330  $m\mu$  both in alcohol and in acid. The IR shows sharp peaks at 1642, 1623, 1595 and 1063  $\text{cm}^{-1}$  and weaker bands at 1048 and 940  $\text{cm}^{-1}$ . Though somewhat different from those of hydroxylunacridine (XXII), these data clearly support the presence of a 2-quinolone system. Labat's test and NMR spectrum show the presence of one  $\text{CH}_2\text{O}_2$  group in the molecule. Structure (XXIV), the methylenedioxy analogue of hydroxylunacridine, has, therefore, been suggested<sup>17</sup> for it.

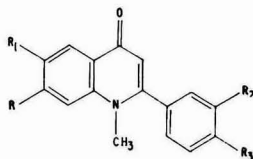
**Lunidine (XXV)**

Lunidine,  $\text{C}_{17}\text{H}_{21}\text{NO}_5$ , obtained from *Lunasia amara* var. *repanda*<sup>18</sup>, contains one acylable OH function. The UV spectrum of the base is identical with that of hydroxylunidine. Structure (XXV) for lunidine suggested on the basis of its mass and NMR spectra has been confirmed by its conversion to (+)-lunine (LXV) analogous to the transformation of lunacridine to (+)-lunacrine<sup>33</sup>.

**Lunidonine (XXVI)**

Recently isolated from *Lunasia amara*<sup>18</sup>, lunidonine,  $\text{C}_{17}\text{H}_{19}\text{NO}_5$ , shows identical UV spectrum with that of hydroxylunidine. The structure (XXVI) for lunidonine follows from its formation from lunidine (XXV) by  $\text{CrO}_3$  oxidation. The IR, NMR and mass spectra of lunidonine are also compatible with the assigned structure.





- XXIX, R = OCH<sub>3</sub>; R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H  
 XXX, R = OCH<sub>3</sub>; R<sub>1</sub> = H; R<sub>2</sub>-R<sub>3</sub> = -O-CH<sub>2</sub>-O-  
 XXXI, R = H; R<sub>1</sub> = OCH<sub>3</sub>; R<sub>2</sub>-R<sub>3</sub> = -O-CH<sub>2</sub>-O-  
 XXXII, R = R<sub>1</sub> = H; R<sub>2</sub>-R<sub>3</sub> = -O-CH<sub>2</sub>-O-  
 XXXVII, R = R<sub>2</sub> = R<sub>3</sub> = H; R<sub>1</sub> = OCH<sub>3</sub>

### 2-n-Propyl-4-quinolone

It has recently been isolated from the leaves and terminal branches of *Boronia ternata*. The structure rests on its alkaline KMnO<sub>4</sub> oxidation to N-butyl-anthranilic acid, m.p. 177-8<sup>o</sup>, and comparison of its salts with the known ones.

### 1,2-Dimethyl-4-quinolone (XXVII)

This compound, C<sub>11</sub>H<sub>11</sub>NO, has also been recently isolated<sup>21</sup> as picrate, m.p. 234-6<sup>o</sup>, from the Hawaiian plant, *Platydesma campanulata*. It is free from OCH<sub>3</sub> group. The UV spectrum of the alkaloid in alcohol exhibits *inter alia* twin peaks at 322 and 336 m $\mu$  which undergo hypsochromic shift to a single peak at 303 m $\mu$  in acid, typical of 4-quinolone system with perhaps a 2-alkyl substituent<sup>35</sup>. The NMR spectrum in CDCl<sub>3</sub> (with tetramethyl silane as internal standard) shows two peaks at  $\delta$  = 2.34 and 3.59 for two sets of CH<sub>3</sub> protons. On the basis of these physical evidences and by analogy with the naturally occurring quinolones, the base has been assigned the structure (XXVII). The final confirmation was secured through its synthesis from 2-methyl-4-quinolone by N-methylation<sup>21</sup>.

### Pilokeanine (XXVIII)

The alkaloid, C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>, an opaque oil, has been separated as picrate, m.p. 216<sup>o</sup> (decomp.), from the leaves of *Platydesma campanulata*<sup>21</sup>. It contains one OCH<sub>3</sub> and one NCH<sub>3</sub> groups. The UV spectrum of the base in ethanol shows maxima at 215, 242, 248, 325 and 336 m $\mu$ . Like 1-methyl-4-quinolone and more specifically 8-methoxy-1-methyl-4-quinolone<sup>33</sup>, the long wavelength maxima of pilokeanine showed hypsochromic shift to an indefinite maximum at 309 m $\mu$  in dil. acid. The IR spectrum in chloroform shows a band at 3676 cm.<sup>-1</sup> assignable to an alcoholic OH function and the other bands at 1629, 1608, 1570, 1473 and 1449 cm.<sup>-1</sup> support a 4-quinolone structure.

The position of the side chain as in the suggested structure (XXVIII) of pilokeanine has been assumed by analogy with other naturally occurring 4-quinolones. The nature and location of the OH group in the side chain has been inferred on the basis of CrO<sub>3</sub> oxidation. The UV spectrum of the product isolated as picrate, m.p. 187-90<sup>o</sup>, remained unaltered with the picrate of the original base.

The structure, however, is essentially speculative and needs further confirmation.

### Lunamarine (XXX)

Lunamarine<sup>25</sup>, another *Lunasia* alkaloid, C<sub>18</sub>H<sub>15</sub>NO<sub>4</sub>, contains a OCH<sub>3</sub>, a NCH<sub>3</sub> and a CH<sub>2</sub>O<sub>2</sub> groups. The physical properties indicate its close structural similarity with 7-methoxy-1-methyl-2-phenyl-4-quinolone<sup>22</sup>. The structure (XXX) proposed for lunamarine has been confirmed by its synthesis<sup>17</sup>.

### Lunasia I (XXXI)

The UV, IR and NMR spectral studies of this *Lunasia* alkaloid, C<sub>18</sub>H<sub>15</sub>NO<sub>4</sub>, revealed the structure (XXXI), further confirmed by its synthesis from piperonyl-*p*-anisidine<sup>18</sup>.

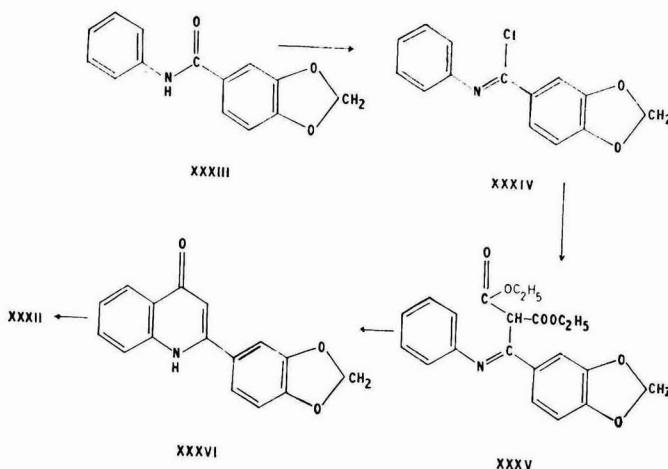


CHART 2

**Graveoline (XXXII)**

This alkaloid from *Ruta graveolens*<sup>27</sup>, C<sub>17</sub>H<sub>13</sub>NO<sub>3</sub>, contains a NCH<sub>3</sub> and a CH<sub>2</sub>O<sub>2</sub> groups. It shows UV maxima at 245, 322 and 335 m $\mu$  and IR bands at 1623, 1603 and 1575 cm<sup>-1</sup>, typical of a 4-quinolone structure. The assigned 1-methyl-2-(3',4'-methylenedioxyphenyl)-4-quinolone structure (XXXII) for graveoline has subsequently been confirmed by its synthesis<sup>49</sup> following essentially the method of Elderfield *et al.*<sup>50</sup> as shown in Chart 2.

N-phenyl-piperonylamine (XXXIII) was converted to chloroimide (XXXIV) which on condensation with malonic ester yielded (XXXV). Subsequent hydrolysis, decarboxylation to 2-(3',4'-methylenedioxyphenyl)-4-quinolone (XXXVI) followed by N-methylation afforded graveoline (XXXII).

**Eduline (XXXVII)**

Eduline, C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>, occurs in *Casimiroa edulis*<sup>15</sup>. The structure has recently been settled by Beyerman and Rooda<sup>51</sup> as 6-methoxy-1-methyl-2-phenyl-4-quinolone (XXXVII). The synthesis of eduline has been achieved as follows:

Condensation of *p*-anisidine with ethylbenzoyl acetate affords 6-methoxy-2-phenyl-4-quinolinol, m.p. 309-12°. Methylation of the latter with dimethyl sulphate and 30 per cent sodium hydroxide furnished a product identical in all respect with eduline.

**PYRANOQUINOLINE BASES**

Of the four alkaloids (Table 1) known with this ring system, flindersine represents the angular type and its structure (XXXVIII) has adequately been dealt with<sup>5,32</sup>. The rest are of linear type.

**Isobalfourodine and Lunacrinol (XLI)**

Isobalfourodine, [ $\alpha$ ]<sub>D</sub> +15°, a *Balfourodendron* alkaloid, shows UV spectrum identical with a synthetic dihydropyranoquinoline derivative (XXXIX). The base when treated with acetic anhydride in pyridine affords balfourodine (LXIV) acetate (XL) which on saponification regenerates (+)-isobalfourodine. The reaction shown in Chart 3 not only settles the structure (XLI) for isobalfourodine but also provides evidence of ring expansion of balfourodine during acetylation under comparatively drastic condition<sup>30</sup>.

Lunacrinol, a *Lunasia* alkaloid, [ $\alpha$ ]<sub>D</sub> -14°, has been shown<sup>26</sup> to have the same structure. As such, it is the optical isomer of isobalfourodine.

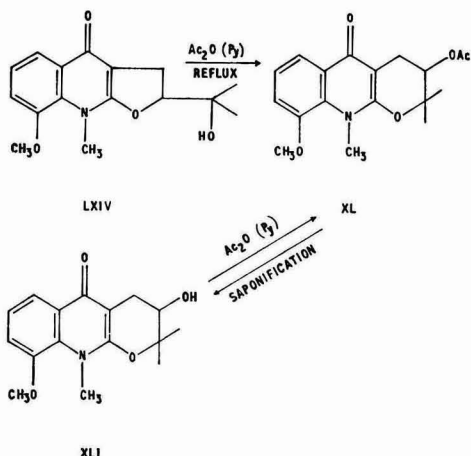
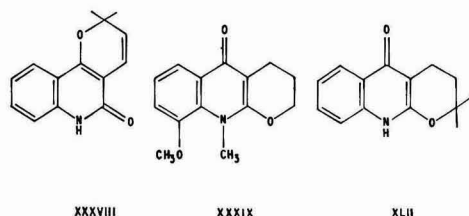


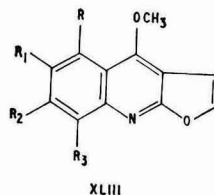
CHART 3

**Khaplofoline (XLII)**

Khaplofoline, C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>, an optically inactive base, has recently been isolated by the Russian workers<sup>51</sup> from the underground parts of *Haplophyllum foliosum*. It exhibits UV maxima at 234, 310 and 322 m $\mu$ . It forms a N-methyl derivative, m.p. 120-1°, with KMnO<sub>4</sub> in acetone, the base affords oxalyl-anthranilic acid, m.p. 189-90°, while CrO<sub>3</sub> oxidation yields acetone and acetic acid. On the basis of the above evidences, structure (XLII) has been proposed for khaplofoline which, however, needs further confirmation.

**FURANOQUINOLINE BASES**

Furanoquinoline alkaloids (Table 2), having the general structure (XLIII), exclusively occur in the family Rutaceae. The subfamily Flindersioideae seems to produce only furanoquinolines, exception being noted in *Fl. australis* from which a pyranoquinoline, flindersine (XXXVIII), has been reported<sup>29</sup> as the sole product. About thirty of them have so far been encountered in nature. Skimmianine<sup>68,80</sup>, the most abundant one, is the earliest known and dictamine<sup>53</sup> is the simplest member of this class of compounds.



**General Characteristics**

All the naturally occurring tricyclic furanoquinolines are linear and oxygenated at position 4. With the exception of maculosine (LX), the oxygen



TABLE 2—FURANOQUINOLINE ALKALOIDS AND THEIR SOURCES

Alkaloid	Source
Dictamnine [XLIIIa, R=R <sub>1</sub> =R <sub>2</sub> =R <sub>3</sub> =H; C <sub>12</sub> H <sub>9</sub> NO <sub>3</sub> ; m.p. 132-3°]	<i>Aegle marmelos</i> Correa <sup>12a</sup> , <i>Boeninghausenia albiflora</i> Meissner <sup>52</sup> , <i>Casimiroa edulis</i> <sup>53</sup> , <i>Dictamnus albus</i> Linn. <sup>53</sup> , <i>Evodia littoralis</i> Endl. <sup>54</sup> , <i>Flindersia acuminata</i> <sup>55</sup> , <i>Fl. pubescens</i> <sup>56</sup> , <i>Fl. dissosperma</i> Domin. <sup>57</sup> , <i>Fl. pimenteliana</i> <sup>58</sup> , <i>Glycosmis arborea</i> (Roxb.) DC. <sup>73</sup> , <i>Hortia arborea</i> Engl. <sup>58</sup> , <i>Phebalium nudum</i> <sup>59</sup> , <i>Skimmia repens</i> Nakai <sup>60</sup> , <i>Zanthoxylum planispium</i> <sup>61</sup> , <i>Z. ailanthoides</i> <sup>62</sup> , <i>Z. alatum</i> <sup>62a</sup>
Skimmianine [XLIIIb, R=R <sub>1</sub> =H; R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>14</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 176°]	<i>Acronychia baueri</i> Schott <sup>63</sup> , <i>Aegle marmelos</i> Correa <sup>64</sup> , <i>Boronia ternata</i> <sup>45</sup> , <i>Casimiroa edulis</i> Llave et Lex <sup>23</sup> , <i>Chloroxylon sweetenia</i> DC. <sup>65</sup> , <i>Choisya ternata</i> <sup>66</sup> , <i>Fagara angolensis</i> <sup>67</sup> , <i>Eriostemon difformis</i> <sup>68</sup> , <i>E. coccineus</i> <sup>68a</sup> , <i>E. thryptomenioides</i> <sup>68a</sup> , <i>E. tomentellus</i> <sup>68a</sup> , <i>Fagara coco</i> (Gill) Engl. <sup>68</sup> , <i>F. manchuria</i> Honda <sup>69</sup> , <i>F. viridis</i> <sup>68a</sup> , <i>F. zanthoxyloides</i> Lam. <sup>70</sup> , <i>Flindersia bennettiana</i> <sup>71</sup> , <i>Fl. bourjotiana</i> F. Muell <sup>72</sup> , <i>Fl. dissosperma</i> Domin. <sup>57</sup> , <i>Fl. laevicarpa</i> <sup>58a</sup> , <i>Fl. maculosa</i> <sup>57</sup> , <i>Fl. pubescens</i> <sup>71</sup> , <i>Gleznovia verrucosa</i> <sup>58a</sup> , <i>Glycosmis arborea</i> (Roxb.) DC. <sup>73</sup> , <i>G. pentaphylla</i> <sup>74</sup> , <i>Haplophyllum bucharicum</i> <sup>75</sup> , <i>H. foliosum</i> <sup>76</sup> , <i>H. pedicellatum</i> <sup>75</sup> , <i>H. perforatum</i> <sup>75</sup> , <i>Hortia arborea</i> <sup>58</sup> , <i>Melicope farena</i> Engl. <sup>77</sup> , <i>Lunasia amara</i> <sup>58a</sup> , <i>Murraya omphalocarpa</i> <sup>58a</sup> , <i>Orixa japonica</i> Thunb. <sup>78</sup> , <i>Phebalium nudum</i> <sup>59</sup> , <i>Poncirus trifoliata</i> <sup>58a</sup> , <i>Ruta graveolens</i> <sup>27,79</sup> , <i>Skimmia japonica</i> Thunb. <sup>80</sup> , <i>S. laureola</i> Hook. <sup>81</sup> , <i>Vepris bilocularis</i> <sup>81a</sup> , <i>Zanthoxylum planispium</i> <sup>61</sup> , <i>Z. ailanthoides</i> <sup>62</sup> , <i>Z. rhetsa</i> <sup>82</sup>
γ-Fagarine [XLIIIc, R=R <sub>1</sub> =R <sub>2</sub> =H; R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>13</sub> H <sub>11</sub> NO <sub>3</sub> ; m.p. 142°]	<i>Aegle marmelos</i> <sup>83</sup> , <i>Casimiroa edulis</i> <sup>53</sup> , <i>Fagara coco</i> <sup>68,84</sup> , <i>Glycosmis arborea</i> <sup>73</sup> , <i>Haplophyllum pedicellatum</i> <sup>85</sup> , <i>Hortia arborea</i> <sup>58</sup> , <i>Phebalium nudum</i> <sup>59a</sup> , <i>Zanthoxylum planispium</i> <sup>61</sup> , <i>Z. alatum</i> <sup>6a</sup>
Evolitrine [XLIIId, R=R <sub>1</sub> =R <sub>2</sub> =H; R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>13</sub> H <sub>11</sub> NO <sub>3</sub> ; m.p. 114-5°]	<i>Cusparia macrocarpa</i> <sup>30a</sup> , <i>Evodia littoralis</i> <sup>54</sup> , <i>Orixa japonica</i> <sup>44</sup> , <i>Phebalium nudum</i> <sup>59a</sup> , <i>Platydesma campanulata</i> <sup>21</sup>
Kokusaginine [XLIIIe, R=R <sub>1</sub> =H; R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>14</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 171°]	<i>Acronychia baueri</i> <sup>77,87</sup> , <i>Evodia alata</i> <sup>88</sup> , <i>E. littoralis</i> <sup>54</sup> , <i>E. xanthoxyloides</i> <sup>94</sup> , <i>Flindersia collina</i> Bail. <sup>89</sup> , <i>Fl. maculosa</i> Lindl. <sup>90</sup> , <i>Fl. pubescens</i> <sup>56</sup> , <i>Fl. schottiana</i> <sup>96</sup> , <i>Glycosmis pentaphylla</i> <sup>74</sup> , <i>Lunasia amara</i> <sup>58a</sup> , <i>Orixa japonica</i> <sup>91</sup> , <i>Phebalium nudum</i> <sup>59a</sup> , <i>Platydesma campanulata</i> <sup>21</sup> , <i>Ruta graveolens</i> <sup>79</sup> , <i>Vepris bilocularis</i> <sup>81a</sup>
Maculosidine [XLIIIf, R=R <sub>2</sub> =H; R <sub>1</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>14</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 184°]	<i>Balfourodendron riedelianum</i> <sup>30</sup> , <i>Eriostemon difformis</i> , <i>E. brucei</i> , <i>E. thryptomenioides</i> , <i>E. tomentellus</i> <sup>68a</sup> , <i>Flindersia maculosa</i> <sup>90</sup> , <i>Fl. pubescens</i> <sup>56</sup>
Acronyridine [XLIIIf, R <sub>1</sub> =H; R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>14</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 136-7°]	<i>Acronychia baueri</i> <sup>77,87</sup> , <i>Melicope farena</i> <sup>92</sup>
6-Methoxydictamnine [XLIIIf; C <sub>13</sub> H <sub>11</sub> NO <sub>3</sub> ; m.p. 134-5°]	<i>Platydesma campanulata</i> <sup>21</sup>
Haplopine [XLII; C <sub>13</sub> H <sub>11</sub> NO <sub>4</sub> ; m.p. 203-4°]	<i>Haplophyllum perforatum</i> <sup>93</sup>
Kokusagine [XLIIIi, R=R <sub>1</sub> =H; R <sub>2</sub> R <sub>3</sub> =CH <sub>2</sub> O <sub>2</sub> ; C <sub>13</sub> H <sub>9</sub> NO <sub>3</sub> ; m.p. 201°]	<i>Evodia xanthoxyloides</i> <sup>94</sup> , <i>Orixa japonica</i> <sup>91</sup>
Maculine [LIII; C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub> ; m.p. 196-7°]	<i>Flindersia acuminata</i> <sup>55</sup> , <i>Fl. bennettiana</i> <sup>71</sup> , <i>Fl. dissosperma</i> <sup>57</sup> , <i>Fl. maculosa</i> <sup>90</sup> , <i>Fl. schottiana</i> <sup>96</sup> , <i>Fl. xanthoxyloides</i> <sup>95</sup>
Flindersiamine [LVIII; C <sub>14</sub> H <sub>11</sub> NO <sub>5</sub> ; m.p. 206-7°]	<i>Balfourodendron riedelianum</i> <sup>30</sup> , <i>Flindersia bennettiana</i> <sup>71</sup> , <i>Fl. bourjotiana</i> <sup>72</sup> , <i>Fl. collina</i> <sup>89</sup> , <i>Fl. dissosperma</i> <sup>57</sup> , <i>Fl. maculosa</i> <sup>90</sup> , <i>Fl. pubescens</i> <sup>56</sup> , <i>Fl. xanthoxyloides</i> <sup>95</sup> , <i>Teclea sudanica</i> <sup>123a</sup> , <i>Vepris bilocularis</i> <sup>81a</sup>
Evolatine [XLIIIj; R=R <sub>2</sub> =H; R <sub>1</sub> =OCH <sub>3</sub> ; R <sub>3</sub> =OCH <sub>2</sub> CH(OH)C(OH)(CH <sub>3</sub> ) <sub>2</sub> ; C <sub>15</sub> H <sub>21</sub> NO <sub>6</sub> ; m.p. 201-2°]	<i>Evodia alata</i> <sup>88</sup>
Evoxine [XLIIIk; XLIIIj except R <sub>1</sub> =H; R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>15</sub> H <sub>21</sub> NO <sub>6</sub> ; m.p. 154-5°]	<i>Choisya ternata</i> <sup>96</sup> , <i>Evodia xanthoxyloides</i> <sup>96</sup>
Evoxoidine (artifact) [XLIIIi, R=R <sub>1</sub> =H; R <sub>2</sub> =OCH <sub>3</sub> ; R <sub>3</sub> =OCH <sub>2</sub> COCH(CH <sub>3</sub> ) <sub>2</sub> ; C <sub>15</sub> H <sub>19</sub> NO <sub>6</sub> ; m.p. 136-7°]	do
Evodine [LIX; C <sub>18</sub> H <sub>19</sub> NO <sub>5</sub> ; m.p. 153-4°]	do
Maculosine [LX; C <sub>17</sub> H <sub>17</sub> NO <sub>6</sub> ; m.p. 229-30°]	<i>Flindersia dissosperma</i> <sup>97</sup> , <i>Fl. maculosa</i> <sup>90</sup>
Lunasin <sup>+</sup> [XIIIa; C <sub>17</sub> H <sub>22</sub> NO <sub>5</sub> ; picrate; m.p. 143-4°]	<i>Lunasia quercifolia</i> <sup>119</sup>
Lunacrine [LXI; C <sub>16</sub> H <sub>19</sub> NO <sub>3</sub> ; m.p. 117-8°]	<i>Lunasia amara</i> <sup>11,16</sup> , <i>L. quercifolia</i> <sup>22</sup>
Hydroxylunacrine [LXIV; C <sub>16</sub> H <sub>19</sub> NO <sub>4</sub> ; m.p. 201-3°]	<i>L. amara</i> <sup>17</sup>
Balfourodine [LXIV; C <sub>16</sub> H <sub>19</sub> NO <sub>4</sub> ; m.p. 188-9°]	<i>Balfourodendron riedelianum</i> <sup>19</sup>
O-Methyl-balfourodinium [LXIIIb; C <sub>17</sub> H <sub>22</sub> NO <sub>4</sub> ; perchlorate; m.p. 124-5°]	<i>B. riedelianum</i> <sup>30</sup>

TABLE 2—FURANOQUINOLINE ALKALOIDS AND THEIR SOURCES—Contd

Alkaloid	Source
Lunine [LXV; C <sub>16</sub> H <sub>17</sub> NO <sub>4</sub> ; m.p. 228-9°]	<i>Lunasia amara</i> <sup>16</sup> , <i>L. quercifolia</i> <sup>23</sup>
Hydroxylunine [LXVI; C <sub>16</sub> H <sub>17</sub> NO <sub>5</sub> ; m.p. 228-30°]	<i>L. amara</i> <sup>17</sup>
Haplophyllidine [LXVII; C <sub>18</sub> H <sub>21</sub> NO <sub>4</sub> ; m.p. 110-1°]	<i>Haplophyllum perforatum</i> <sup>76</sup>
Dubinidine [LXVIII; C <sub>15</sub> H <sub>17</sub> NO <sub>4</sub> ; m.p. 132-3°]	<i>H. dubium</i> <sup>10</sup>
Dubinine [LXVIII; monoacetate; C <sub>17</sub> H <sub>19</sub> NO <sub>5</sub> ; m.p. 186°]	<i>H. dubium</i> <sup>97</sup>
Platydesmine [LXIX; C <sub>16</sub> H <sub>17</sub> NO <sub>3</sub> ; m.p. 137-8°]	<i>Platydesma campanulata</i> <sup>81</sup>
Ifflaiamine [LXX; C <sub>15</sub> H <sub>17</sub> NO <sub>2</sub> ; m.p. 62-63°]	<i>Flindersia iffiaiana</i> <sup>98</sup>
PYRANOFUROQUINOLINE	
Medicosmine [LXXIII; C <sub>17</sub> H <sub>15</sub> NO <sub>3</sub> ; m.p. 138-9°]	<i>Medicosma cunninghamii</i> Hook. f. <sup>99</sup>
Acronyidine [LXXIV; C <sub>18</sub> H <sub>17</sub> NO <sub>4</sub> ; m.p. 151-3°]	<i>Acronychia baueri</i> <sup>83</sup>

atom is mostly included in a OCH<sub>3</sub> and only in a few cases as C=O function (e.g. *Lunasia* alkaloids). The aromatic ring is frequently substituted with OCH<sub>3</sub> at one or more positions and less so with a CH<sub>2</sub>O<sub>2</sub> bridge at 6, 7- or 7, 8-positions. In a very few cases, e.g. evoxine (XLIIfk), usually position 7 is substituted with isopentane ether; maculosine with such substitution at C-4 is again an exception. In limited cases, the 2- or 3-positions of the furan ring (usually dihydro) are variously substituted by alkyl or hydroxyalkyl side chain.

### General Approach to Structure Elucidation

In the early studies on furanoquinoline alkaloids (e.g. dictamnine<sup>60</sup>, skimmianine<sup>100,101</sup>,  $\gamma$ -fagarine<sup>68</sup>), mild KMnO<sub>4</sub> oxidation proved to be of much value. This process affords a mixture of an aldehyde and an acid. The latter on being heated with conc. HCl or HBr undergoes simultaneous demethylation and decarboxylation to 2,4-dihydroxyquinoline derivatives with OCH<sub>3</sub> function(s) in the aromatic ring remaining unaffected, e.g. mono- and dimethoxy-2,4-dihydroxyquinolines from  $\gamma$ -fagarine<sup>102</sup> and skimmianine<sup>103</sup> respectively. The structures of the degradation products were established by synthesis. This sequence of reactions simultaneously secured the number and position of the OCH<sub>3</sub> group(s) as well as the linearity of the furan ring fusion to the quinoline nucleus<sup>100</sup>.

One of the most important proofs of the linear tricyclic system and a very helpful approach to the structure elucidation of furanoquinolines has later been advanced by Ohta and his collaborators<sup>104,105</sup>. Hydrogenolysis of a furanoquinoline in presence of PtO<sub>2</sub> in acetic acid results in the formation of a tetrahydro compound which is either 3-ethyl-4-methoxy-2-quinolone itself (in case of dictamnine) or its derivative with substituent(s) in the aromatic

ring in position(s) corresponding to those in the parent compound.

More recently, the physical methods are being taken advantage of in the structure determinations of this class of compounds. Besides UV and IR spectra, NMR spectroscopy has been successfully applied particularly in case of *Lunasia* alkaloids<sup>106</sup>. The present-day structural studies of the furanoquinolines have thus been comparatively simple.

Grundon and McCorkindale<sup>97,107</sup> have developed a method of synthesis for dictamnine and  $\gamma$ -fagarine. This method has been applied with advantage in the synthesis of evolitrine<sup>108,109</sup>, maculine<sup>110</sup> and flindersiamine<sup>111</sup> with some variations starting from the appropriately substituted aniline.

### Evolitrine (XLIIfd)

Evolitrine, which is 4,7-dimethoxy-furo-(2,3-*b*)-quinoline<sup>112</sup> (XLIIfd), has simultaneously been synthesized by the Australian<sup>113</sup> and Japanese group of workers<sup>108,109</sup>. The method of Cooke and Haynes<sup>113</sup> as shown in Chart 4 is the simpler one. 5-Methoxy-methylanthranilate was condensed with succinic anhydride and the methyl ester (XLIV) cyclized in presence of sodium in toluene to methyl-1,2-dihydro-7-methoxy-4-hydroxy-2-oxo-3-quinoline acetate (XLV). The latter was converted to methyl ether, reduced with LiAlH<sub>4</sub> to (XLVI) and subsequently cyclized with polyphosphoric acid to dihydroevolitrine (XLVII). Bromination with N-bromosuccinimide followed by dehydrobromination completed the synthesis of evolitrine (XLIIfd).

Ohta and his collaborators<sup>108,109</sup> utilized the method of synthesis of dictamnine by Grundon and McCorkindale<sup>107</sup>.

### Maculosidine (XLIIfg)

Maculosidine has already been suggested<sup>97</sup> to have 4, 6, 8-trimethoxy-furo-(2, 3-*b*)-quinoline (XLIIfg)

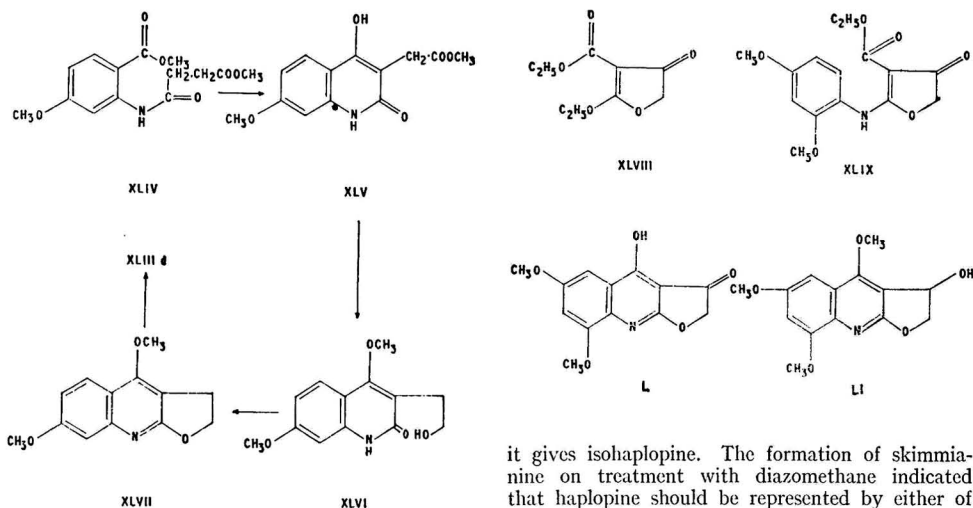


CHART 4

structure. Further degradative evidences in support of the proposed structure have been advanced. Hydrogenolysis of the base with  $\text{PtO}_2$  provides 3-ethyl-4,6,8-trimethoxy-2-quinolone, m.p.  $126-7^\circ$ . This on demethylation furnishes 6,8-dimethoxy-3-ethyl-4-hydroxy-2-quinolone, the structure of which was substantiated by its synthesis from 2,4-dimethoxyaniline and ethyldiethylmalonate<sup>114</sup>.

Finally, maculosidine itself has been synthesized by Govindachari and Prabhakar<sup>115</sup>. Condensation of 2,4-dimethoxyaniline with ethyl-2-ethoxy-4,5-dihydro-4-oxo-furan-3-carboxylate (XLVIII) gave ethyl-4,5-dihydro-2-(2,4-dimethoxyanilino)-4-oxo-furan-3-carboxylate (XLIX). The latter on being heated in diphenyl ether solution at  $245^\circ$  for a short period afforded 2,3-dihydro-4-hydroxy-6,8-dimethoxy-3-oxo-furo-(2,3-b)-quinoline (L). The corresponding O-methyl compound on  $\text{NaBH}_4$  reduction yielded 2,3-dihydro-3-hydroxy-4,6,8-trimethoxy-furo-(2,3-b)-quinoline (LI). Dehydration of the latter with  $\text{KHSO}_4$  furnished the desired product.

#### 6-Methoxydictamnine (XLIIIh)

The base,  $\text{C}_{13}\text{H}_{11}\text{NO}_3$ , was obtained<sup>21</sup> from *Platydesma campanulata* as the major constituent. It contains two  $\text{OCH}_3$  groups. The UV spectrum shows maxima at 249, 261, 295, 307, 333 and 350  $\text{m}\mu$  in ethanol. The nature of the curve is suggestive of a furanoquinoline alkaloid<sup>5</sup> resembling more closely that of 6,8-dimethoxydictamnine<sup>114</sup>. The structure has been proved<sup>21</sup> by isomerization of the compound with methyl iodide and identification of the product with 6-methoxy-isodictamnine<sup>99</sup>.

#### Haplopine (LI)

The alkaloid,  $\text{C}_{13}\text{H}_{11}\text{NO}_4$ , has been isolated from the seeds of *Haplophyllum perforatum* by the Russian workers<sup>93</sup>. It contains two  $\text{OCH}_3$  and one phenolic OH groups. On being heated with methyl iodide

it gives isohaplopine. The formation of skimmianine on treatment with diazomethane indicated that haplopine should be represented by either of the alternative structures, 7-hydroxy-8-methoxy- or 8-hydroxy-methoxydictamnine. The conversion of evoxine (XLIIIk) to haplopine by KOH fusion definitely establishes the structure of haplopine as 7-hydroxy-8-methoxydictamnine (LI).

#### Maculine (LIII)

The assigned<sup>110</sup> structure of maculine, i.e. 4-methoxy-6,7-methylenedioxy-furo-(2,3-b)-quinoline (LIII) has recently been proved by its synthesis<sup>116</sup> as shown in Chart 5. Condensation of 3,4-methylenedioxy aniline (LIVa) with diethyl- $\beta$ -benzyloxyethylmalonate (LVa) furnished 3-( $\beta$ -benzyloxyethyl)-6,7-methylenedioxy-4-hydroxy-carbostyryl (LVI). The methyl ether of the latter on cyclization with polyphosphoric acid yielded dihydromaculine (LVII). Dehydrogenation of the dihydro-furan ring was achieved as in the case of evolitrine.

#### Flindersiamine (LVIII)

It has recently been synthesized by Govindachari and Prabhakar<sup>111</sup> starting from 2-methoxy-3,4-methylenedioxy aniline (LIVb) and 2-ethoxyethylmalonate (LVb) following essentially the method of Grundon and McCorkindale<sup>107</sup> for the synthesis of dictamnine and  $\gamma$ -fagarine (not shown in Chart 5).

#### Evodine (LIX)

Evodine,  $\text{C}_{18}\text{H}_{19}\text{NO}_5$ ,  $[\alpha]_D^{20} -3^\circ$  ( $\text{CHCl}_3$ ),  $\lambda_{\text{max}}$  220, 252, 258, 325 and 340  $\text{m}\mu$ , was encountered in *Evodia xanthoxyloides*<sup>96</sup>. Its structure has been established<sup>117</sup>. The IR spectrum indicated the presence of one OH and a  $=\text{CH}_2$  grouping in the base. Virtually the structure became apparent from the NMR spectrum which is typical of a furanoquinoline showing the presence of four aromatic protons, two  $\text{OCH}_3$ , one OH, a terminal methylene and an allylic methyl  $\beta$ - to a deshielding function.

Evodine forms an acetate, m.p.  $126-7^\circ$ . On catalytic hydrogenation, it affords the same hexahydro derivative, m.p.  $164^\circ$ , obtained from dihydro-evoxidine, m.p.  $137^\circ$ , by the same process. On ozonolysis, evodine furnishes formaldehyde and an

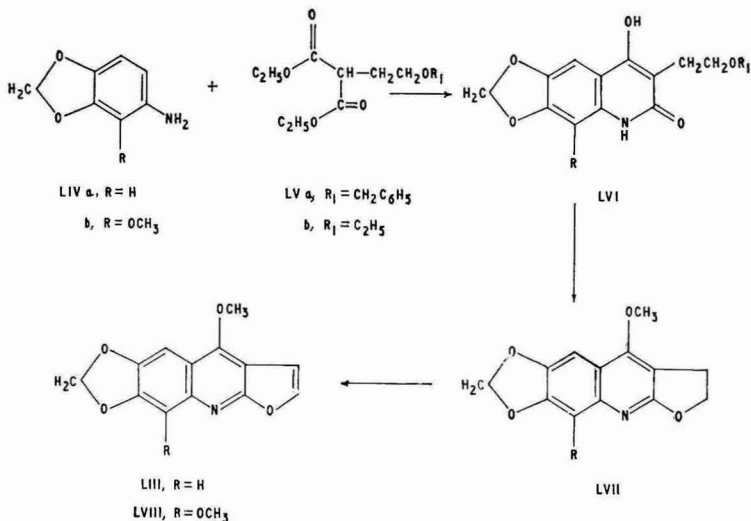
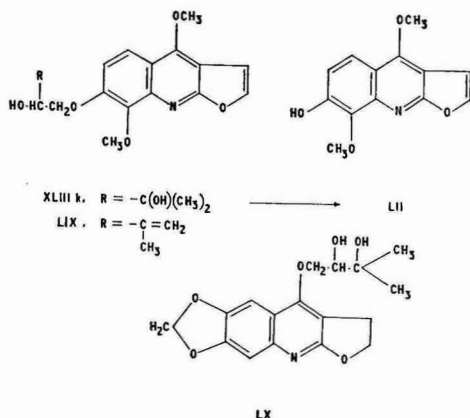


CHART 5



acid. The latter on NaBH<sub>4</sub> reduction and subsequent HIO<sub>4</sub> oxidation furnishes formaldehyde and acetic acid.

On the basis of the above evidences structure (LIX) has been assigned to evodine.

#### Maculosine (LX)

Maculosine, C<sub>17</sub>H<sub>17</sub>NO<sub>6</sub>, [α]<sub>D</sub> -36° (pyridine), isolated from *Flindersia maculosa*<sup>90</sup>, and later from *Fl. dissosperma*<sup>57</sup>, contains a CH<sub>2</sub>O<sub>2</sub> but no OCH<sub>3</sub> group. On oxidation with HIO<sub>4</sub>, it gives acetone, formaldehyde and a product which on hydrogenolysis affords 3-ethyl-4-hydroxy-6,7-methylenedioxy-2-quinolone.

On the basis of the above observations coupled with the other physical data, structure (LX) has been advanced<sup>114</sup> for maculosine.

#### Lunacrine (LXI)

Lunacrine<sup>118</sup>, a *Lunasia* alkaloid, C<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>, [α]<sub>D</sub> -50°, contains one OCH<sub>3</sub> and one NCH<sub>3</sub> groups. Kuhn-Roth determination indicates the presence of one CCH<sub>3</sub> though the value might account for a *gem*-dimethyl group. It is resistant to catalytic hydrogenation. The UV and IR spectra are characteristic of a 4-quinolone system.

When refluxed with 15 per cent alcoholic KOH, lunacrine furnishes a phenol (LXII), C<sub>16</sub>H<sub>21</sub>NO<sub>4</sub>, m.p. 160°, [α]<sub>D</sub> -77.6°. The phenol (LXII) on treatment with diazomethane yields lunacridine (XX) which in turn by the influence of *α*-toluene sulphonyl chloride in pyridine regenerates (+)-lunacrine. Again, lunacridine hydroperchlorate, m.p. 148°, melts on reheating at a higher temperature (194°) to give lunasine (LXIIIa) perchlorate which on being heated in acetonitrile in the presence of a large excess of LiBr produces (+)-lunacrine<sup>33</sup>, lunasine<sup>119</sup> being the methyl lunacrinium ion, the relationship between lunacridine (XX), lunasine (LXIIIa) and lunacrine (LXI) is evident (Chart 6).

The NMR spectrum, for the details of which the original paper<sup>106</sup> should be consulted, confirms the location of the OCH<sub>3</sub> function at 8-position and the presence of an isopropyl side chain in the dihydrofuran ring in addition to all the other features of the structure of lunacrine (LXI).

#### Hydroxylunacrine and Balfouridine (LXIV)

Hydroxylunacrine, C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub>, containing one oxygen atom more than lunacrine differs from the latter only in respect of the side chain. The NMR spectrum showed the absence of the tertiary hydrogen atom of the isopropyl side chain. Structure (LXIV) has thus been assigned to it<sup>17</sup>.

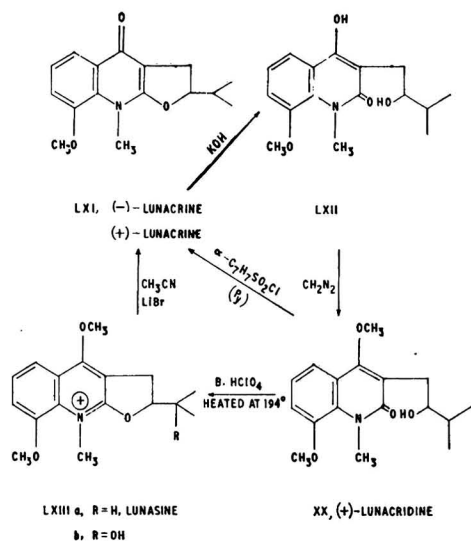


CHART 6

Balfourodine<sup>19</sup>,  $[\alpha]_D +49^\circ$ , isolated from *Balfourodendron riedelianum*, is the dextrorotatory variety of hydroxylunacrine from *Lunasia amara*.

The methiodide of balfourodine (LXIIIb) on treatment with alkali produces balfourolone (XXII), thus supporting the furanoquinoline structure for balfourodine. The possibility of the linear pyranoquinoline structure (XLI) for it (vide Chart 3) was excluded on the basis of the UV spectra of various synthetic models. The spectrum of dihydrofuranquinoline was found to be identical with that of balfourodine<sup>30</sup>.

#### Lunine (LXV)

Lunine,  $C_{16}H_{17}NO_4$ , isolated from *Lunasia* species<sup>16,17,22</sup>, contains one  $NCH_3$ , one  $CH_2O_2$  but no  $OCH_3$  group. The NMR spectrum<sup>106</sup> is compatible with the structure (LXV) assigned to it.

#### Hydroxylunine (LXVI)

Hydroxylunine,  $C_{16}H_{17}NO_5$ , contains one oxygen atom more than lunine. Their UV, IR and NMR spectra are almost the same. However, the NMR reveals that their structural relationship should be the same as that between lunacrine (LXI) and hydroxylunacrine (LXIV) and hence the structure (LXVI) has been proposed<sup>17</sup> for it.

#### Haplophyllidine (LXVII)

Haplophyllidine,  $C_{15}H_{21}NO_4$ ,  $[\alpha]_D -16^\circ$  (acetone), an alkaloid from *Haplophyllum perforatum*<sup>75</sup>, contains two  $OCH_3$  groups, one of which must be in position 4. Formation of a monoacetate, m.p. 147-8°, shows the presence of one alcoholic OH group in the molecule. Catalytic hydrogenation of the base over  $PtO_2$  affords tetrahydrohaplophylli-

dine, m.p. 134-6°, by hydrogenolytic cleavage of the furan ring. The tetrahydro compound forms a diacetyl derivative, m.p. 123-4°.

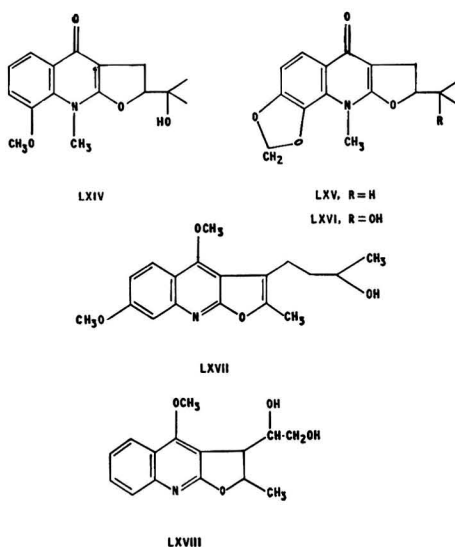
Kuhn-Roth or Perceron's method of oxidation indicates the presence of two  $CCH_3$  groups. The facile formation of acetic acid from haplophyllidine and of propionic acid in oxidative degradations suggest the presence of a  $CH_2CHOHCH_3$  group in the side chain.

The possibility of the site of the second  $OCH_3$  function (other than that at C-4) is least likely since  $KMnO_4$  oxidation does not give either  $\gamma$ -fagarinic aldehyde and/or acid. The position 7 has, therefore, been assumed to be more probable by analogy with the majority of similar alkaloids of this class. Any definite evidence is, however, lacking. The structure (LXVII) has thus been proposed for haplophyllidine<sup>130,121</sup>.

#### Dubinidine (LXVIII)

Dubinidine,  $C_{15}H_{17}NO_4$ ,  $[\alpha]_D -63^\circ$ , another alkaloid of *Haplophyllum dubium*<sup>10</sup>, is a dihydrofuranquinoline base. It affords a monoacetyl derivative, m.p. 186°, later on obtained as naturally occurring dubinine<sup>97</sup> from the same source.

Oxidation with  $HIO_4$  or  $KMnO_4$  in acidic solution gives formaldehyde and another aldehyde, dubininal,  $C_{14}H_{13}NO_3$ , m.p. 82-83°,  $[\alpha]_D +62^\circ$ . The latter contains one  $CCH_3$  but no OH group and is resistant to acid hydrolysis. Oxidation of the base with  $KMnO_4$  in acetone, on the other hand, yields dictamninc acid showing the absence of any substituent in the aromatic ring. Clemmensen reduction of the base furnishes a compound,  $C_{14}H_{17}NO_3$ , containing a OH, a  $OCH_3$ , a  $NHCO$ , two  $CCH_3$  and a hydrolytically cleaved dihydrofuran ring. On the basis of the above observations together with the IR data, the structure (LXVIII) has been proposed for dubinidine<sup>122</sup>.



**Platydesmine (LXIX)**

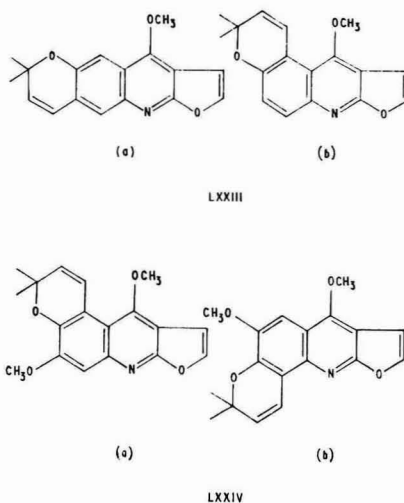
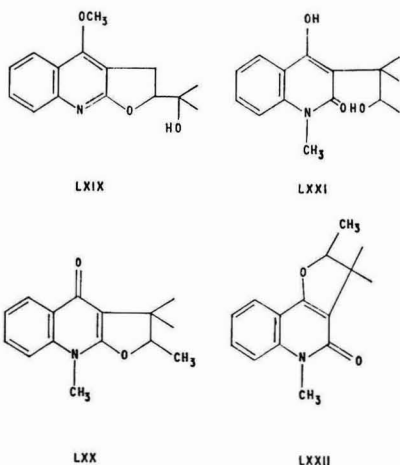
The base,  $C_{15}H_{17}NO_3$ , has been isolated from the bark and root of *Platydesma campanulata*<sup>21</sup> collected from Hawaii. The UV spectra in ethanol and in ethanolic HCl are identical with those of dihydrodictamnine. The IR spectrum shows a band at  $3584\text{ cm}^{-1}$  suggesting the presence of an alcoholic OH possibly tertiary in nature. Besides that of the molecular ion at  $m/e$  259, the mass spectrum of the base shows a peak at  $m/e$  200 indicating the exclusion of a  $C_2H_3O_2$  or a  $C_3H_7O$  fragment from the original compound. In the absence of any evidence of the presence of an acetate or methyl carboxylate or an ether linkage in addition to the dihydrofuran ring, a  $C_3H_7O$  moiety contained in a tertiary alcoholic side chain has been inferred. The position of the side chain at C-2 of the structure (LXIX) advanced for platydesmine has been suggested by analogy with balfourodine and hydroxylunacrine (LXIV). Further confirmation of the structure is necessary.

**Ifflaiamine (LXX)**

This new alkaloid,  $C_{15}H_{17}NO_2 \cdot H_2O$ , picrate, m.p.  $207-9^\circ$ ,  $[\alpha]_D^{20}$ ,  $-0.6^\circ$  (?), has been isolated from the wood of *Flindersia iffliana*. The anhydrous base is a gum. It contains one  $NCH_3$ , a  $CCH_3$  and no  $OCH_3$  group. The UV spectrum in alcohol and alkali shows maxima at 215, 236, 251 (sh), 298 (inflection), 309 and 320  $m\mu$ . In 0.2N acid, the maxima are exhibited at 216, 235, 294 and 315  $m\mu$  (inflection). The IR spectrum in  $CHCl_3$  shows peaks at 1508, 1541, 1585 and 1617  $cm^{-1}$ . Unlike all the other alkaloids from *Flindersia* species, iffliamine exhibits UV and IR spectra similar to 2-alkoxy-4-quinolone.

Iffliamine on saponification yields a phenol (LXXI), m.p.  $220-2^\circ$ . The latter when refluxed with 6N HCl recycles to give the original base along with a compound which has been given the structure (LXXII) on the basis of its spectral properties.

The above facts led to the suggested<sup>98</sup> structure (LXX) for iffliamine. The attempted synthesis of



the base proved to be futile. The structure itself needs further confirmation.

**PYRANOFUROQUINOLINE BASES****General Approach to Structure Elucidation**

Medicosmine<sup>99</sup> and acronyidine<sup>63</sup> (Table 2) are the only two known members of this class. The presence of a dimethylpyran ring in both has been established by the isolation of  $\alpha$ -hydroxy-isobutyric acid by  $KMnO_4$  oxidation and of acetone and acetaldehyde on vigorous alkaline hydrolysis. A phenol produced by the latter process gives the clue to their basic furanoquinoline structure. Hydrogenation affords a tetrahydro derivative and the dihydropyrano-ethylquinolone corresponding to each one confirms the linear furanoquinoline structure. The details of the structure arguments are already reviewed by Price<sup>5</sup>. The alternative structures (LXXIII) for medicosmine and (LXXIV) for acronyidine still need confirmation. However, the angular attachment of the dimethylpyran ring is pretty certain in case of acronyidine.

**ACRIDINE BASES**

Structures of all the acridine alkaloids known up till now (Table 3) and represented by a general structure (LXXV), except arborimine, have exhaustively been dealt with by Price<sup>5,126</sup>. With the exception of acronyidine for which the alternative structure (LXXXVI, a and b) has been proposed,

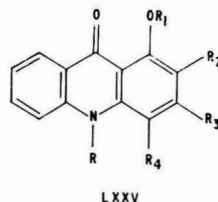


TABLE 3 — ACRIDINE ALKALOIDS AND THEIR SOURCES

Alkaloid	Source
Melicopine [LXXVa, R=R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> =OCH <sub>3</sub> ; R <sub>3</sub> R <sub>4</sub> =CH <sub>2</sub> O <sub>2</sub> ; C <sub>17</sub> H <sub>15</sub> NO <sub>5</sub> ; m.p. 178-9°]	<i>Acronychia acidula</i> F. Muell <sup>122</sup> , <i>A. baueri</i> Schott <sup>63,87</sup> , <i>Melicope jarena</i> F. Muell <sup>92</sup>
Melicopicine [LXXVb, R=R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> =R <sub>3</sub> =R <sub>4</sub> =OCH <sub>3</sub> ; C <sub>15</sub> H <sub>13</sub> NO <sub>5</sub> ; m.p. 133-4°]	<i>Acronychia baueri</i> <sup>63</sup> <i>Melicope jarena</i> <sup>92</sup>
Melicopidine [LXXVc, R=R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> R <sub>3</sub> =CH <sub>2</sub> O <sub>2</sub> ; R <sub>4</sub> =OCH <sub>3</sub> ; C <sub>17</sub> H <sub>15</sub> NO <sub>5</sub> ; m.p. 121-2°]	<i>Acronychia baueri</i> <sup>63,87</sup> , <i>Evodia alata</i> F. Muell <sup>96</sup> , <i>E. xanthoxyloides</i> <sup>94</sup> , <i>Melicope jarena</i> <sup>92</sup>
Evoxanthine [LXXVd, R=R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> R <sub>3</sub> =CH <sub>2</sub> O <sub>2</sub> ; R <sub>4</sub> =H; C <sub>16</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 175-6°]	<i>Balfourodendron riedelianum</i> <sup>90</sup> , <i>E. alata</i> <sup>88</sup> , <i>E. xanthoxyloides</i> <sup>94,96</sup> , <i>Teclea grandiflora</i> <sup>23a</sup>
Evoxanthidine [LXXVe, R=R <sub>4</sub> =H; R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> R <sub>3</sub> =CH <sub>2</sub> O <sub>2</sub> ; C <sub>15</sub> H <sub>11</sub> NO <sub>4</sub> ; m.p. 312-3°]	do
Xanthevodine [LXXVf, R=H; R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> R <sub>3</sub> =CH <sub>2</sub> O <sub>2</sub> ; R <sub>4</sub> =OCH <sub>3</sub> ; C <sub>16</sub> H <sub>13</sub> NO <sub>5</sub> ; m.p. 213-4°]	do
1,3-Dimethoxy-10-methyl-acridone [LXXVg, R=R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> R <sub>3</sub> =H; R <sub>4</sub> =OCH <sub>3</sub> ; C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ; m.p. 163-4°]	<i>Acronychia baueri</i> <sup>63</sup>
1,2,3-Trimethoxy-10-methyl-acridone [LXXVh, R=R <sub>1</sub> =CH <sub>3</sub> ; R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; R <sub>4</sub> =H; C <sub>17</sub> H <sub>17</sub> NO <sub>4</sub> ; m.p. 168-70°]	<i>E. alata</i> <sup>124</sup>
Xanthoxoline (artifact?) [LXXVi, R=R <sub>1</sub> =R <sub>4</sub> =H; R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>15</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 265-7°]	<i>E. xanthoxyloides</i> <sup>96</sup>
1-Hydroxy-2: 3-dimethoxy-10-methylacridone (artifact?) [LXXVj, R=CH <sub>3</sub> ; R <sub>1</sub> =R <sub>4</sub> =H; R <sub>2</sub> =R <sub>3</sub> =OCH <sub>3</sub> ; C <sub>16</sub> H <sub>15</sub> NO <sub>4</sub> ; m.p. 176-7°]	<i>Acronychia hallophylla</i> <sup>5a</sup> , <i>E. alata</i> <sup>88</sup> , <i>E. xanthoxyloides</i> <sup>96</sup>
Arborinine [LXXVII; C <sub>20</sub> H <sub>19</sub> NO <sub>3</sub> ; m.p. 175-6°]	<i>Acronychia baueri</i> <sup>87</sup>
Arborinine [LXXVII; C <sub>16</sub> H <sub>13</sub> NO <sub>4</sub> ; m.p. 176°]	<i>Glycosmis arborea</i> (Roxb.) DC. <sup>125</sup>

the structures of all the other members of this group are well established.

### General Characteristics

Brown and Lahey<sup>127</sup> made a detailed study of the UV spectra of a number of naturally occurring acridones and related compounds. Acridone itself shows maxima at 251, 254, 295, 308, 380 and 399 m $\mu$ , the one at 300 m $\mu$  region serves to distinguish it from anthracene and acridine. The shift of these characteristic maxima depends on the number, position and nature of the substituents. It is thus possible to trace the relationships among the various members of this group. While OCH<sub>3</sub> substitution at position 2 causes bathochromic shift, the same function at positions 1 and 3 induces hypsochromic shift of the longer wavelength band.

Lamberton and Price<sup>63</sup> later observed that contrary to the observation of Brown and Lahey<sup>127</sup>,

the increase in the intensity of the band in the middle region of the spectrum of 10-methylacridone consequent on the introduction of a OCH<sub>3</sub> group in position 4 was not as great as for the 1- and 4-methoxy derivatives. Further, the prediction that a OCH<sub>3</sub> group in position 4 would also be expected to cause greater shift of the longer wavelength in the same direction than when the same function is in any other position of the 10-methylacridone moiety could not be substantiated by actual measurements<sup>63</sup>.

When position 3 is oxygenated, as all the naturally occurring acridones are, 1-hydroxy-10-methylacridone exhibits pronounced bathochromic shift of the longer wavelength maxima of the corresponding methyl ether. This has been termed<sup>127</sup> as 'nor-effect'. Replacement of the OH with acetyl instead of a methoxy group hardly affects the absorption curve. Unlike other alkaloids of this class, the UV maxima of acronycine are shifted to longer wavelengths because of the presence of conjugated double bond in the dimethylpyran ring.

With fully substituted benzenoid ring, e.g. melicopicine (LXXVb), both the shorter and the longer wavelength bands are shifted bathochromically.

### General Approach to Structure Elucidation

Oxidation with nitric acid provides the most important clue to the structures. With the exception of acronycine, this process degrades the molecule partly to 4-quinolone-3-carboxylic acid (N-methylated in the appropriate cases) that can be decarboxylated to the basic quinolone while the other part carries the substituents. This reaction coupled with the molecular formula and functional group analyses, therefore, not only shows that a benzenoid ring is fused to a quinolone nucleus but also locates the position of the substituents.

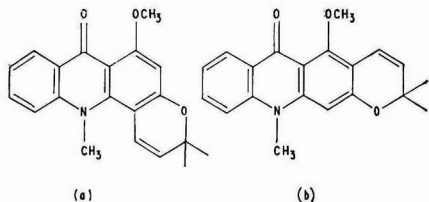
### Arborinine (LXXVII)

This optically inactive yellow crystalline alkaloid, C<sub>16</sub>H<sub>15</sub>NO<sub>4</sub>, isolated<sup>125</sup> from the leaves of *Glycosmis arborea* (Roxb.) DC., is phenolic in nature and contains<sup>128</sup> one NCH<sub>3</sub> and two OCH<sub>3</sub> groups. The UV spectrum in ethanol shows maxima at 217, 274 and 395 m $\mu$  with shoulders at 265 and 319 m $\mu$ . The IR spectrum exhibits a series of sharp and strong bands at 1637, 1587, 1550, 1493, 1460, 1316, 1282, 1143, 1105, 1053, 990 and 855 cm<sup>-1</sup>.

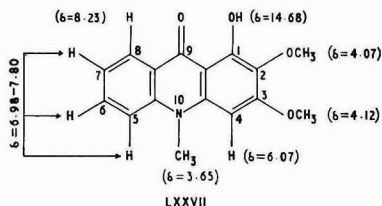
Arborinine is stable to boiling 20 per cent alcoholic potassium hydroxide. It forms a crystalline acetate, m.p. 209-10°, and a methyl ether, m.p. 167-8°.

Virtually the structure of arborinine became apparent through the NMR spectral studies (in CDCl<sub>3</sub> with SiMe<sub>4</sub> as internal standard using a 60 mc Varian spectrometer). The data were compatible with three alternative structures, viz. 2,3-dimethoxy-(LXXVII), 2,4-dimethoxy-(LXXVIII) or 3,4-dimethoxy-(LXXIX) 1-hydroxy-10-methylacridone, the assignments being indicated against (LXXVII).

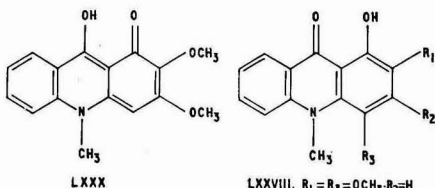
Biogenetically, structure (LXXVIII) appeared unlikely since all the naturally occurring acridine alkaloids known so far are invariably oxygenated<sup>126</sup>



LXXVI



LXXVII



LXXX

LXXXVIII,  $R_1 = R_3 = OCH_3, R_2 = H$

LXXXIX,  $R_1 = H; R_2 = R_3 = OCH_3$

at positions 1 and 3. The identity of arborinine with 1-hydroxy-2,3-dimethoxy-10-methylacridone (LXXVII)<sup>88,96</sup> was finally established by direct comparison with the base and its methyl ether<sup>124</sup> previously reported from *Evodia* species.

While that from *Evodia* species might be an artifact originated from the corresponding trimethoxy compound<sup>129,130</sup> during isolation involving acid treatment, arborinine must be considered as an actual constituent of *G. arborea* since it readily separates out of petroleum ether extract of the plant materials on cooling without the use of any acid<sup>125</sup>.

The suggestion of Banerjee *et al.*<sup>131</sup> that the tautomeric form (LXXX) would better explain the lack of reactivity of arborinine towards aqueous alkali appears to be untenable on NMR evidences which distinctly favour structure (LXXVII) for arborinine. Because the signal from one of the aromatic protons is shifted quite far down field ( $\delta = 8.23$ ), the reason of which must be assigned to its being *peri* to a C=O group, a condition fulfilled by the structure (LXXVII). The tautomeric structure (LXXX) rather than having a C=O adjacent to the benzene ring contains a OH function and, if anything, this shifts the adjacent benzene ring signal towards the lower field. Nevertheless, it is not possible to rigorously eliminate the equilibrium between the structures (LXXVII) and (LXXX), the former undoubtedly predominating.

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(To be continued)

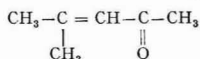
## Mesityl Oxide as an Extracting Agent

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MESITYL oxide finds wide applications as an extractant for actinide elements like thorium, uranium, etc.<sup>1</sup> It has, therefore, acquired considerable importance in the field of atomic energy. The literature on mesityl oxide has gradually accumulated, but it is still scattered at present. An attempt has been made in this article to review the literature up to early 1964.

Mesityl oxide (mol. wt 98.14) is a colourless mobile liquid, b.p. 128.7°C.; density (20°C.) 0.8539 (Ref. 2). Its solubility in water is 0.03 g./ml. and it has dielectric constant 15. It is also known as 3-pentane-2-one-4-methyl and has the following structure:



### Synthesis

Mesityl oxide is usually synthesized by the self-condensation<sup>3</sup> of acetone under vigorous conditions, such as in the presence of quicklime using sodium alkoxides or hydrochloric acid as the condensing agent. The intermediate product formed is the diacetone. Continued condensation produces phorone, isophorone, mesitylene and xylitone. Grinevich and Zaitsev<sup>4</sup> obtained mesityl oxide in about 82.5 per cent yield by the condensation of acetone with ammonia, and subsequent hydrolysis of the intermediate product at 95°C. The use of acetone as an eluant in chromatography<sup>5</sup> on alumina for prolonged duration formed mesityl oxide and diacetone.

### Complexing Characteristics

On passing a mixture of mesityl oxide and steam on calcium phosphate at 250-450°C., it was found that the catalyst catalyses the hydrolytic cleavage of mesityl oxide to form Me<sub>2</sub>CO due to the dealdolization of diacetone alcohol<sup>6</sup>. The donor characteristics of the carbonyl group and its angular

variations were also studied<sup>7</sup>. Ultraviolet spectra of mesityl oxide showed increase in the intensity of carbonyl 280 mμ bond due to the donor-acceptor interactions in solutions of carbonyl compounds<sup>8</sup>. Here the carbonyl oxygen behaves as an electron acceptor analogous to the hydrogen in the hydrogen bonding. Studies on the extracting efficiency of neutral organic oxygen containing solvents also confirmed the results that the oxygen atom acts as the electron donor in the complex between the extracting solvent and the extracted species<sup>9</sup>.

*Complexes with platinum and other metals*—Mesityl oxide readily forms yellow-coloured crystalline complexes<sup>10</sup> with platinum or palladium metals. They are obtained by interaction of mesityl oxide and palladium chloride<sup>11</sup> or hexachloroplatinic acid. The probable composition of such complexes is (C<sub>6</sub>H<sub>9</sub>OPdCl)<sub>2</sub> and C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>OPt respectively. Such complexes were found to be soluble in basic solvents and showed no absorption in the normal ketonic stretching region. The chlorides of ruthenium, rhodium and iridium can also possibly form such complexes. Mesityl oxide is capable of forming complex compounds<sup>12</sup> with osmium tetroxide also.

*Extraction of thorium*—For the first time mesityl oxide was used as an extracting agent for thorium<sup>13</sup>. The solution was saturated with aluminium nitrate (2.5M) and 8.5 per cent by volume of 1.2M nitric acid was shaken with equal volume of mesityl oxide, to extract as much as 99.9 per cent of thorium; sulphate, fluoride, arsenate, borates and phosphates did not interfere as the latter were complexed with aluminium from its nitrate.

Banks and Edwards<sup>14</sup> attempted to replace aluminium nitrate with alkali metal nitrates, but sodium nitrate proved to be ineffective, while lithium nitrate proved fruitful. However, uranium, zirconium, iron in traces, vanadium, yttrium and phosphate interfered in such extractions<sup>15</sup>. Traces of

aluminium, indium, tin (II) and platinum (IV) were also extracted; but metals like beryllium, magnesium, titanium, manganese, cobalt, nickel, zinc, molybdenum and lead were not extracted at all. Clear-cut separation<sup>16</sup> of thorium from lanthanides, especially yttrium, was feasible by fractional extraction. The method suffered from the disadvantage of coextraction of zirconium with thorium; the former should be previously removed by fluoride precipitation.

Spedding and Kant<sup>17</sup> purified thorium by liquid-liquid extraction with mesityl oxide. Various salting-out agents like the nitrates of alkali and alkaline earth metals, ammonium, aluminium and manganese were tried. It was found that mesityl oxide, which is capable of donating an electron pair to coordination bond, was capable of separating as much as 78 per cent thorium from rare earths. Similar extraction procedures were applied to the thorium targets<sup>18</sup>.

*Extraction of uranium* — Mesityl oxide, isophorone, etc., were used for the extraction of uranium and thorium from their nitrates<sup>19</sup>. The extractability of small amounts of ketone or aldehyde condensate of semicarbazide.

The sulphocyanide complex of uranium was easily extracted from phosphoric acid solution with mesityl oxide<sup>20</sup>. The interference of iron (III) was eliminated by maintaining high concentration of phosphoric acid.

Infrared spectrometric examination<sup>21</sup> of uranium-mesityl oxide complex at 1196-1246  $\mu$  showed the complex to contain 2-3 molecules of water per molecule of uranyl nitrate, regardless of the number of solvent molecules attached. The nature of the infrared spectrum was different from that of the uranium complex with either methyl ethyl ketone or TBP.

Liquid-liquid extraction<sup>22</sup> of uranium (VI) with mesityl oxide can also be carried out from solution of 1M nitric acid containing about 15 per cent of a salting-out agent like sodium nitrate, with equal volume of mesityl oxide. Efforts are being made to develop a method for the selective extraction of uranium (VI) in the presence of thorium (IV), and zirconium (IV).

*Extraction of radio elements* — The extraction of traces of thorium ( $10^{-12}$  g./ml.) from 15 per cent nitric acid containing aluminium nitrate was carried out with mesityl oxide<sup>23</sup>.  $U_{X1}$  and radiothorium were used. It was observed that isotopes of thorium

and bismuth were not quantitatively extracted. The isotopes of radium and lead remained behind, while those of uranium and polonium were extracted.

*Other applications* — In addition to the use of mesityl oxide as an extracting agent it finds many other applications. For instance, it is used as paint remover<sup>24</sup>, as a solvent for polymers<sup>25</sup> and nitrocellulose<sup>26</sup> and as fuel<sup>27</sup> for motors.

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# Ion-Exchange Membranes: Synthesis & Applications

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**A**N earlier communication set forth the developments in the preparation and application of ion-exchange membranes during the period 1958-60. Since then there have been rapid strides in this field and the present review attempts to cover the major advances made during the period 1960-63. It deals with the preparation of homogeneous and heterogeneous ion-exchange membranes and with the various applications and related studies. As before, the subject matter has been treated countrywise.

## Homogeneous Membranes

*UK and the Continent* — Polyethylene film has been a favourite material under study besides polyvinyl chloride and polystyrene. Chlorosulphonation of polyethylene followed by treatment with hypochlorite solution to reduce the resistivity has been adopted to produce cation-exchange membranes<sup>1,2</sup>. Conducting strong cation-exchange membranes have been obtained by heating polyethylene granules with styrene and a peroxide catalyst in a closed vessel and later compressing to yield a sheet which is treated with chlorosulphonic acid<sup>3</sup>. High strength uniform ion-exchange membranes have been obtained from copolymers of styrene and polyethylene derivatives, which can undergo ammonolysis or sulphonation<sup>4</sup>. Swelling polyethylene film at elevated temperatures in styrene containing divinylbenzene and peroxide catalyst aims at the formation of a three-dimensional polystyrene network throughout the polyethylene for further preparation of both types of ion-exchange membranes<sup>5</sup>. Monomeric styrene is adsorbed on films of polyethylene or polyvinyl chloride and the materials polymerized prior to sulphonation<sup>6</sup>. Permselective membranes from unplasticized polyvinyl chloride have been obtained by treatment with chlorosulphonic acid<sup>7</sup> and after crosslinking with ethylenediamine hydrate and further treatments<sup>8</sup>. Films of polystyrene with polyethylene or polyvinyl chloride have been first heated together and later extruded into a film and finally converted to the desired membrane<sup>9</sup>. Polyethylene film was crosslinked by high energy radiation and then grafted with styrene and further treated<sup>10</sup>. Aqueous emulsions of a polymer of styrene with suitable combinations have also been used<sup>11</sup>. Membranes for the purification of alkali liquors by dialysis have been prepared from styrene, divinylbenzene and benzoyl peroxide mixed with 4-vinylbenzene sulphonate<sup>12</sup>. By casting thin membranes from styrene-divinylbenzene mixtures with benzoyl peroxide catalyst at suitable temperature, cation-exchange membranes with varying degrees of sulphonation have been prepared and their infrared spectra studied<sup>13</sup>. The preparation of both types of membrane from etherified aromatic hydroxy compounds with ionogenic groups and formaldehyde has been reported<sup>14</sup>; a method has

been developed to improve the storage life of an ion-selective membrane by incorporating in it a high boiling, water-soluble alcohol, such as glycerol or ethylene glycol<sup>15</sup>.

*USA* — Rods from phenolsulphonic acid<sup>16</sup> and membranes, rods and filaments or particles from polyethylene and other polymeric aliphatic materials have been prepared<sup>17</sup>. Conditioned polyethylene as a permselective membrane has been obtained by swelling the film in *p*-xylene and annealing at a high temperature. Permselectivity of the film to *para* with respect to *ortho* and *meta*-xylene is obtained and this depends on the degree of swelling, temperature, polymer crystallinity and treating compound. Such membranes could be useful for preferential separation of mixtures<sup>18</sup>. Based on vinyl chloride, acrylonitrile film forming copolymers, membranes have been prepared and studied<sup>19</sup>. Molecular dispersions of uncrosslinked polyelectrolytes in an uncrosslinked film forming polymer have been utilized for preparing selective membranes<sup>20</sup>.

*Japan* — Heat treatment of a sulphonated polyethylene film in 0.5N sodium chloride solution has been claimed to improve its selectivity for univalent ions<sup>21</sup>. Polyethylene membrane is soaked in chlorosulphonic acid and then in sodium hydroxide to obtain cation-exchange membranes<sup>22</sup>. Preparations of anion-exchange membranes based on styrene, divinylbenzene, chloromethylated polystyrene<sup>23</sup> or from soaking polyethylene in a mixture of styrene and divinylbenzene, heating and treatment with titanium tetrachloride and dichloroethane prior to chloromethylation and amination, have been reported<sup>24</sup>. Graft copolymers of styrene and polyethylene obtained by  $\gamma$ -ray irradiation are suitable starting materials for the preparation of cation- and anion-exchange membranes<sup>25,26</sup>. Crack resistant ion-exchange materials have been prepared using polystyrene, styrene, butadiene, divinylbenzene, ethylbenzene and plasticizers<sup>27</sup>. Anion-exchange membranes having permselectivity for acids have been prepared from copolymers of styrene and butadiene by treatment with trimethylamine<sup>28</sup>. Treating such a styrene-butadiene copolymer with a Friedel-Craft's catalyst to effect cyclization among polymer chains is reported to improve the properties of the cation-exchange membrane obtained by sulphonation<sup>29</sup>. A mixture of styrene-butadiene copolymer and polyethylene has been used for preparing anion-exchange membranes<sup>30</sup>. Homogeneous membranes of the poly(vinyl sulphonic acid) type have also been reported<sup>31</sup>. Collodion membranes of different permselectivities to cations have been prepared by casting three-layered films from a suitable solvent prior to treatment with potassium hydroxide to impart the desired properties<sup>32</sup>.

*USSR* — Homogeneous polymer membranes have been obtained from copolymers of styrene sulphonate

and olefinic compounds where the copolymerization is initiated by ultraviolet light. This is followed by crosslinking and suitable treatment<sup>33</sup>. Membranes with complex-forming properties have been prepared and studied<sup>34</sup>.

*Other countries* — Nitrocellulose-coated cellophane membrane exhibiting cation-exchange properties has been prepared and studied in a three-compartment electro dialysis cell<sup>35</sup>.

### Heterogeneous Membranes

*UK and the Continent* — Sintered metals have been used as membranes for electro dialysis of concentrated solutions in a patented process wherein the pore size is changed by infiltration with compounds such as silver chloride and magnesium silicate<sup>36</sup>. Permeable membranes, especially for water purification, are prepared by polymerizing (under the influence of high voltage electrons, X-rays or  $\gamma$ -rays) monomers or polymers carried on chemically resistant porous substrates, glass film or polythene<sup>37</sup>. By impregnating parchment film with a composition which will yield ionogenic groups after suitable treatments, cation- and anion-exchange membranes have been prepared and studied<sup>38</sup>. By milling together a mixture of polystyrene and polyethylene and sulphonating the resulting sheet, cation-exchange membranes have been obtained<sup>39</sup>. Heterogeneous ion-exchange membranes have been prepared as finely divided suspensions in a polyhydroxy compound and crosslinked with isocyanates in the presence of a suitable support<sup>40</sup>.

*USA* — The preparation of ion-exchange films and fibres from polyacrylonitrile aqua gels has been reported<sup>41</sup>. Selectively permeable diaphragms have been obtained by pouring over a suitable web of acid-resistant material, viscous products of reaction mixtures capable of yielding ion-exchange membranes<sup>42</sup>. Elastomeric selective membranes have been prepared by vulcanizing a dry blended mixture of potentially ion-exchange active polymer and a polymeric diluent and converting them to yield the ionogenic groups by suitable treatments<sup>43</sup>. Dual film combinations for membrane permeation have been reported wherein a thin film of high selectivity, low permeability composition is cast on the surface of a thicker film of low selectivity but high permeability material to combine the properties of strength and selectivity in the resulting membrane<sup>44</sup>.

*Japan* — Membranes based on a fabric of polyvinyl chloride fibre<sup>45</sup>, polyvinyl alcohol fibre<sup>46</sup> and glass cloth<sup>47</sup> have been reported. Acid treatment of polymers and copolymers of acrylonitrile fibre converted the nitrile group to carboxylic and subsequent casting on polyvinyl alcohol film yielded the membranes<sup>48</sup>. Saran net is soaked in a mixture of styrene, butadiene, divinylbenzene copolymer suspended in a suitable medium and later sulphonated<sup>49</sup>. Powdered cation-exchange resin has been mixed with styrene-butadiene in a petroleum fraction and the resultant resin is cast on a saran net<sup>50</sup>. Styrene-butadiene copolymer has been used for the preparation of anion-exchange membranes<sup>51</sup> and membranes having a high mechanical strength have been reported from the same copolymers used

along with polyethylene or chlorinated polyethylene<sup>52</sup>. Irradiating a thin membrane obtained by hot rolling a mixture of styrene-butadiene copolymer and later treatment with sulphuric acid yields a cation-exchange membrane<sup>53</sup>. Thinly resin-coated cation-exchange membrane exhibiting permselectivity between uni- and bivalent cations has been prepared with the aid of glass cloth and polystyrene-butadiene copolymer<sup>54</sup>. A saran net is dipped in a mixture of glycerol epichlorohydrin reaction product with bisphenol and 2-methyl-5-vinyl pyridine<sup>55</sup>.

*USSR* — The properties of various heterogeneous membranes based on styrene-divinylbenzene copolymers dispersed in rubber have been studied<sup>56</sup>. Highly basic anion-exchange membranes have been obtained from a mixture of crosslinked polymer containing a mobile halogen atom in the side chain with a thermoplastic polymer by hot moulding to form a ribbon or sheet and reinforcing with nylon prior to amination<sup>57</sup>.

*Other countries* — The properties of ion-exchange films prepared with PVC and other synthetic fibres have been studied<sup>58</sup>. Sheets of cellulosic materials have been impregnated with aqueous formaldehyde and heated with suitable reagents to yield the necessary ionogenic groups<sup>59</sup>. Membranes based on rubber have been prepared and investigated<sup>60</sup>.

### Fundamental Investigations and Applications

*UK and the Continent* — Measurements of bi-ionic potentials and conductivities of ion-exchange membranes with improved accuracy and precision have been described<sup>61</sup>. An examination of the quasi-thermodynamic representation of the ion fluxes in a bi-ionic system consisting of cation-exchange membranes has been made<sup>62</sup>. The electrochemical behaviour of ion-exchange membranes has been studied in mono-ionic, bi-ionic and tri-ionic systems and transport numbers calculated<sup>63</sup>. Using radioactive tracers of sodium and chlorine, their fluxes across a cation-exchange membrane at various external solution concentrations were determined<sup>64</sup>. Transference studies, water transport, counter-ion transfer number and different donating and receiving electrolytes have been studied<sup>65</sup>. Various theories on membrane potentials have been studied in detail and the e.m.f. of cells containing a cation-exchange membrane made from crosslinked polymethacrylic acid measured. It has been found that there is no justification for the calculation of membrane potentials from first principles<sup>66</sup>. Deviation from the steady state conditions noted in ion transfer through permselective membrane has been reported. The current density affected the maximum spread of oscillation<sup>67</sup>. Electrophoresis of a homogeneous solution across a bed of membranes in ion-exchange cells has been studied and based on earlier theories of 'membrane oscillator' it has been suggested that the electrode membrane system could develop 'neg' conductivity resulting in instability and oscillations<sup>68</sup>. The electrochemical properties of ion-exchange membrane junction have been investigated<sup>69</sup>. The relationship between structure and electrochemical characteristics has

been established in anion-exchange membranes and it has been shown that the water content, passage of water through the membrane and the conductivity rise with the number of basic amine groups<sup>70</sup>. Measurements of the permeability of ion-exchange membranes have revealed that the apparent diffusion coefficient for salt in the membrane is very small compared to that of free solution<sup>71</sup>. The penetration of electrolyte water or solution into a heterogeneous cation-exchange membrane has been reported to depend on the space formed as a result of the differences in the swelling properties of the resin and the binder used. Increased crosslinking helps better selectivity<sup>72</sup>. In concentrated solutions for ion-exchange across a cation-exchange membrane, equations have been derived which relate the diffusion potential and the ion and solvent fluxes with its electrical conductivity and electro-osmotic permeability<sup>73</sup>. Four different membranes have been studied for determining the activity of counter ions in dilute solutions<sup>74</sup>. The correlation between the tortuous path and the membrane thickness has been established in a water-swollen membrane<sup>75</sup>. Studies on adsorption of radio nuclides on sulphonated polystyrene films<sup>76</sup> and complex formation by means of ion-exchange membranes<sup>77</sup> have also been reported. The possible use of ion-exchange membranes as electrolytes for fuel cells has been considered<sup>78</sup>.

Specially designed gaskets for use between the membranes have been claimed to provide a rapid and simple means of producing a stack<sup>79</sup>. In a multicell apparatus claimed to be useful in life-boats for desalting sea water, reversal of electrical polarity and all liquid currents is effected in a single action<sup>80</sup>. Provision of half cells within intermediate cells for the removal and supply of liquids has been reported<sup>81</sup>. Combination of series and parallel flow of solution within the compartments has been adopted for electro dialysis<sup>82</sup>. Salting and desalting chambers joined in parallel have also been investigated<sup>83</sup>. Thin ring spacers compressed between end electrodes allow passage of liquids to the cells by means of slots in them<sup>84</sup>. By regularly disturbing the flow of direct current at short intervals during electro dialysis of sea or brackish water, it is claimed that the deposits on the membranes are lower than when using uninterrupted d.c. flow. Chemical treatment of the water prior to electro dialysis is thus avoided<sup>85</sup>. A portable unit for personal use, consists of interchangeable filtering unit with ion-exchange resins and activated charcoal<sup>86</sup>. By means of equations and nomograms, the general laws of electro dialysis have been considered and costs of desalting analysed<sup>87</sup>. Membrane supports for electro dialysis<sup>88</sup> and preassembled units for electro dialysis<sup>89</sup> which could be dismantled have been reported.

By placing a suitable ion-exchange resin between the cation- and anion-exchange membranes, electrolytic interconversion of metal salt solutions has been achieved<sup>90</sup>. Using membranes selectively permeable to ions of the same sign and allowing the electrolyte to flow through all the compartments it has been possible to interconvert electrolytes<sup>91</sup>. Concentration of dissolved salts by electro dialysis<sup>92</sup>

and a method to separate salts from electrolytes and some non-electrolytes based on electrolytic blocking effects<sup>93</sup> have been reported. A method for purifying water contaminated by radioactive substances by electro dialysis has been patented<sup>94</sup>.

*USA* — The rate of diffusion of strontium in three types of membranes has been studied and shown to depend on the degree of saturation of the membranes<sup>95</sup> and to follow the predictions of the theory of ionic interdiffusion<sup>96</sup>. Diffusion through pores has been suggested for three vinyl membranes<sup>97</sup>. Ion excluding and ion exchanging properties for salt filtering in different membranes have been investigated at 40 atm. applied pressure; salt rejection has been found to depend on a high concentration of the required functional group and restricted interchain distances<sup>98</sup>. A non-homogeneous structure containing ion-permeable areas or pores and ion-impermeable areas (that are responsible for the condenser-like properties of the membrane) has been studied as a model. The rate of penetration of ions of different sizes has been studied in the ion-permeable parts and a pore size of the order of 4 Å. in radius has been suggested<sup>99</sup>. A heat effect observed in electro dialysis system has been regarded as the electrochemical analogue of Peltier effect<sup>100</sup>.

A detailed study of the various factors involved in ion transport across membranes has been reported<sup>101</sup>. Univalent cation transfer rates in different membranes have been studied and it has been shown that the ratios of the single ion diffusion coefficients are independent of the degree of crosslinking and capacities of the membranes<sup>102</sup>. Thermo-osmosis effects have also been reported<sup>103</sup>. A detailed analysis of the diffusion of ions in membranes based on generalized Planck-Teorell equations has been reported<sup>104</sup>. The possible application of ion-exchange membranes as electrolytes for the construction and use of fuel cells has been widely studied<sup>105-13</sup>.

The use of capsules composed of hemispherical elements containing a magnetic element helps in the separation of salts with the aid of cation- and anion-exchange membranes and after a cycle of operation, regeneration by scavenging has been reported<sup>114</sup>. In an apparatus for the electroforetic separation of mixtures showing little or no electrical conductivity, porous ion-exchange resins have been used along with the membranes with other suitable arrangements<sup>115</sup>. For reducing scale formation on membranes in cells the use of membranes with lower selectivity or non-selective membranes has been recommended<sup>116</sup>. The conditions that control the allowable level of supersaturation of calcium sulphate in the waste stream of electro dialysis have been studied and various inhibitors tried<sup>117</sup>. A unit consisting of three parts made up of ion-exchange, electro dialysis and buffer tank has been suggested for water demineralization<sup>118</sup>. By using membranes exposed to X-ray (and thus made heat resistant) in electro dialysis cells it has been shown that at higher temperatures of operation the degree of desalting is increased<sup>119</sup>.

The principles of process design involved in electro dialysis has been discussed in detail by Mintz<sup>120</sup>. Permselective membranes have been

employed for demineralization utilizing the osmotic pressure and without the aid of any electrical energy<sup>121</sup>. For the anodic production of halogens, teflon-based anion-exchange membranes have been used<sup>122</sup>. The decomposition of products of electrolysis of salts of aliphatic acids could be minimized and the contamination with unelectrolysed salt reduced to a great extent by using permselective membranes<sup>123</sup>. The preparation of salt-free sodium hydroxide<sup>124</sup> and a combined ion-exchange and electro dialysis technique in an electrolysis cell<sup>125</sup> have been reported. Some applications of the membranes in the fractionation of fission elements<sup>126</sup> and in coulometric aqueous acid base titration<sup>127</sup> have been reported.

*Japan*—Cation-selective membranes have been used as electrolyte thermocouple and good agreement reported between the measured and calculated value of e.m.f.<sup>128</sup>. Studying the transport behaviour of some inorganic cations across sulphonic acid membranes, the preferential impermeability of barium ions across the membranes has been attributed to the low concentration of free barium ions<sup>129</sup>. Equations have been derived theoretically for various membrane phenomena resulting in transport across polymer membranes<sup>130</sup> and exchange equilibria on ion-exchange membranes studied<sup>131</sup>. The transport behaviour of weak acids and weak bases across ion-exchange membranes has been shown to be  $pH$  dependent<sup>132</sup>. A study of the selective permeability of cations through cation-exchange membranes has revealed that in systems containing mixtures, calcium and magnesium reduce the selectivities and increase the permeability of the remaining ions<sup>133</sup>. Detailed investigations on the self-diffusion coefficients and mobilities of ions in cation-exchange membranes have been reported<sup>134</sup>. Diffusion of mixed electrolytes through membranes has been measured and the ratio for each component in a mixed electrolyte calculated and compared to that in a single electrolyte solution<sup>135</sup>. Permeability of uranyl ions<sup>136</sup> and acidic amino acids<sup>137</sup> through membranes has been studied.

Employing the membrane electrode method, the permeability of ions in permselective colloid and ion-exchange membranes has been investigated<sup>138</sup>. A mechanism has been proposed for anomalous conduction across ion-exchange membranes<sup>139</sup> and the conductivity of membranes at different relative humidities has been measured<sup>140</sup>. A series of investigations on the permselectivities for sulphate ions against chloride ions<sup>141</sup> for sulphate, sulphite and thiosulphate<sup>142,143</sup> and for barium<sup>144</sup> have been reported.

Current efficiency in electro dialysis is reported to improve by placing membranes between electrodes in such a manner that anions pass downward through the anion-exchange resin membranes<sup>145</sup>. A cell containing membranes and an ion-exchange liquid has been designed for desalting or concentration of electrolytes<sup>146</sup>.

Membranes have been used in the preparation of sodium hydroxide<sup>147</sup>. Semitechnical scale investigations on the preparation of sodium sulphite from sea water<sup>148</sup> and the electrolytic concentration of sea water<sup>149</sup> have been reported. Recovery of sub-

stantial quantity of sulphuric acid from waste by using anion-exchange membranes<sup>150</sup> and the production of ammonium or alkali metal salts of high purity from waste acids with the aid of cation-exchange films and suitable cell arrangement<sup>151</sup> are of topical interest. A novel procedure of dyeing one membrane with thionine and another saturated with a solution of ascorbic acid and placing them between platinum gauze electrodes helps in inducing photopotential when the cell is illuminated on the dyed side. Thus, an analogue of semiconductor photovoltaic cell is claimed<sup>152</sup>. Cation-exchange membranes have been used in the preparation of silica sol from sodium silicate<sup>153</sup>.

*USSR*—The mechanism of cation diffusion in membranes has been studied<sup>154</sup> and rectification of an electrical current on the boundary of ion-exchange membranes reported<sup>155</sup>. The electrode properties of different types of membranes have been studied<sup>156,157</sup> and the possible application of ion-exchange membranes to high voltage electro dialysis has been reported<sup>158</sup>. The relation between the electrical conductivity of the membrane to those of the components used in its preparation<sup>159</sup> and diffusion to the transport number<sup>160</sup> have been reported. Electro dialysis of bentonite suspension<sup>161</sup> and potentiometric titrations using ion-exchange membranes<sup>162</sup> have been studied. The desorption of ions from ion exchangers by electro dialysis has been investigated under constant electric current and this has revealed that sodium and potassium exchangers electro dialyse more easily than barium and calcium exchangers. Higher temperature and higher voltage lower the velocity of desorption<sup>163</sup>. The limiting diffusion current for a locally prepared membrane has been investigated<sup>164</sup> and compared with that for other membranes<sup>165</sup>. Processes for mass and heat transfer in membranes under non-isothermal conditions have been studied<sup>166</sup>.

An assembly for the electrochemical desalting of ocean water with special techniques adopted to effect desalting with different types of waters has been reported<sup>167</sup>. Hygienic evaluation of water after removal of salts by electro dialysis has pointed to the use of activated carbon to remove flavour; the resulting water was found to be non-toxic<sup>168</sup>.

Locally prepared membranes have been used for desalting and concentration of sodium chloride solution<sup>169</sup> and their performance compared with that of other membranes in uranium hydrometallurgy<sup>170</sup>. The possible applications of the membranes for the separation of anions of stronger acids from those of organic acids have been indicated on the basis of the experimental data<sup>171</sup>. Electro dialysis of amino acids<sup>172</sup> and applications of membrane electrodes in systems containing hydrogen fluoride and its salts<sup>173</sup> and for the measurement of hydrogen ion concentration in aqueous solution<sup>174</sup> have been reported. Pilot plant investigations on the electrochemical demineralization of water have indicated the need for pretreatment of water and reduction in the distance between membranes to a minimum<sup>175</sup>. A commercial apparatus for the electrochemical desalination of sea water, operating on the batch principle and having a capacity of 0.5 ton/hr, has been reported<sup>176</sup>.

*Other countries* — Concentration in polarization in electro-dialysis has been studied in detail. Results obtained in the electrometric measurements on interfacial concentration have been found to agree with those expected from simple concepts based on Nernst idealization for film-controlled mass transfer operations. In systems having mass transfer with natural convection, the significance of apparent interfacial concentration values has been considered in relation to the current distribution over the membrane<sup>177</sup>. The determination of transport numbers of counter ions in membranes and the relation between true and apparent transport numbers of counter ions in cation-exchange membranes have been reported. It has also been shown that increase in electro-osmotic permeability results from increase in current<sup>178-80</sup>. Measurements of anion activity in electrolytic solutions with anion-exchange membrane electrodes, cation activity with membranes having no binders, potentiometric titrations with anion resin membranes<sup>181</sup> and with clay electrodes for calcium-potassium equilibrium<sup>182</sup> have all been reported. The cell design and layout for the recovery of salts from geothermal water have been provided<sup>183</sup>. Salt reduction using natural brackish water samples and water transport during electro-dialysis have been studied<sup>184</sup>.

## Reviews

During this period various reviews<sup>185-204</sup> and other publications<sup>205</sup> have appeared.

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# REVIEWS

FLUID DYNAMICS TRANSACTIONS: Vol. 1, edited by W. Fiszdon (Pergamon Press Ltd, Oxford), 1964. Pp. 397. Price £5

This volume contains some twenty-six papers presented at a symposium held by the Polish Academy of Sciences in 1961 and spread over the following topics: mathematical methods, hypersonic flow, rarefied gasdynamics, magneto-hydrodynamics and gasdynamics. The majority of the papers are written in English.

M. Bernal considers a class of solutions of a general system and finds the conditions for the existence of a solution of Cauchy's problem. General applications to unsteady and steady three-dimensional compressible flows are given. The method does not require the assumption of the potentiality of the flow.

A. A. Dorodnitsyn gives a method of integral relations to make boundary layer calculations using a computer. The Pohlhausen type of solution, which is also similar, becomes unreliable when we consider modern boundary layer problems, where, apart from friction, one has to consider heat transfer, dissociation, chemical reactions, etc. The applications of the method to the classical boundary layer (compressible and incompressible) and to the case in which chemical reactions are in equilibrium are given. The method proposed permits one to obtain the solution with the accuracy desired.

The disadvantage of this method is that the computer is a must for it. Even in the case of the classical boundary layer, it is noted that to obtain any accuracy of a fourth order solution, the computer time is hundred times that required by the method of integral relations.

M. Kwyzanskii and J. Litwiniszyn discuss functional operations and certain solutions of the Smolouchowski equation in separate contributions.

S. M. Bogdonoff and I. E. Vas have presented a very interesting account of the experiments on hypersonic flows carried out by them. Detailed studies of the separated flows have been made using visual observations, wall pressure distribution and heat transfer in a range of Mach number of 10-20 and Reynolds number of 4-5 million.

The results obtained are compared to comparable phenomena in the supersonic region and the new features of the flow are discussed. Some practical applications of separated laminar flows and comparison with available theories are indicated. It is also expected that the wedge separation results approach the cavity results for large shear layer to separation region ratios, but the effect of wedge separation and reattachment on a basic cavity flow has yet to be determined.

J. R. Buring has considered the effect of surface catalytic efficiency on stagnation point heat transfer. Previous theoretical studies by Scala and Goulard had shown that for a frozen flow, higher the catalytic efficiency of the surface, the more easily do atoms recombine there and liberate their

energy of dissipation. The experiments described by the author were done in a shock tube of 5 cm. diam. in a range of shock numbers of 2-18.

The experimental results show the same trends as the theory, but the reduction in heat transfer rate is not nearly as large as expected. The reasons for the discrepancy may be that the flow in the boundary layer is not frozen, the value of catalytic activity of SiO may not be accurate or the flow outside the boundary layer is not in equilibrium.

Belotserkovskii and Chushkin have considered the case of a steady supersonic flow past a blunt symmetrical profile and a blunt body of revolution at zero incidences in an inviscid fluid. Numerical solutions using a computer have been given. The mixed flow region has been calculated by the method of Dorodnitsyn and the supersonic region by the method of characteristics.

The computed results have been compared with various experimental results and are found to lie very close to them.

Fiszdon has given a method of determining the linearized supersonic flow in a divergent nozzle with oscillating walls. This investigation forms an essential part of the problem of flutter of elastic divergent nozzles. It is presumed that this method is being used in the latter problem.

Yurev has considered the theory of plane gas flows. This is based on Tricomi's equation for transonic flows and an approximation has been obtained, which is supposed to be better for transonic Mach numbers. But it is doubtful whether the approximation is really valid for the transonic range, since a mixed type of flow has to be really considered (cf. reviewer's approximation in the *Proceedings of the seminar on aeronautical sciences*, National Aeronautical Laboratory, Bangalore, 1961, p. 196).

Chomiak has considered the perennial problem of the viscous liquid drop in a turbulent gas and contributed to an understanding of the oscillations of a liquid drop of small viscosity. Recently others (Chandrasekhar, Reid and Hodgkinson) have treated other facets of the problem.

The volume is nicely bound and edited and has something for every one working in the field of fluid dynamics and would be valuable as a reference book in any research institution interested in fluid mechanics.

Y. V. G. ACHARYA

L'EFFET MÖSSBAUER ET SES APPLICATIONS À L'ÉTUDE DES CHAMPS INTERNES by A. Abragam (Gordon & Breach Science Publishers, New York), 1964.

Pp. viii+70. Price \$ 1.95 (paper), \$ 3.95 (cloth) Within three years of the discovery of the Mössbauer effect (1958), Rudolf Mössbauer received the Nobel prize. This reflects not so much perhaps the importance of the effect in itself, as its usefulness as an extremely fine tool in varied branches of physics. These branches, as listed by the author,

are (i) nuclear physics, (ii) solid state physics, (iii) magnetism, (iv) relativity, and (v) theoretical physics (quantum mechanics and the theory of photon emission/absorption).

The book is a systematically presented basic course on the Mössbauer effect and its principal applications. The first half covers the relevant theoretical concepts. Almost the whole of the remainder deals with  $\text{Fe}^{57}$ , by far the most useful Mössbauer isotope. In this part of the book, the concepts developed in the first part are illustrated with appropriate experimental data. The other very suitable Mössbauer isotope is  $\text{Sn}^{119}$ , which is dealt with in a small section at the end of the book. Although only these two isotopes are discussed in the book, the reader at the end is in a position to tackle any other without the author's help.

The first or theoretical part of the book starts with the theory of resonant absorption of gamma rays when the atoms are in the gaseous state. This leads to the necessity of incorporating these atoms in a crystalline lattice for efficient resonance absorption. A general expression for the resonant absorption coefficient as a function of energy is derived in terms of the self-correlation function for the position of the absorbing atom. This is then specialized to the case of a simple lattice in the harmonic approximation, and such a lattice is extensively discussed. A particularly illuminating section contrasts the absorption spectra when the absorbing atoms form part of (i) a classical oscillator (as when mounted on a vibrating diaphragm), and (ii) a quantum mechanical oscillator (as in a crystal lattice). The relationship between these two cases is explained.

Further on, the following effects associated with the Mössbauer velocity spectrum are discussed: (i) isomer (or chemical) shift, (ii) electric quadrupole splitting, and (iii) magnetic dipole splitting. The usefulness of experiments using polarized sources and/or absorbers as well as cases in which (ii) and (iii) coexist are comprehensively discussed. The absence of the second order Doppler shift from this list is probably an oversight. Unfortunately, the book lacks an index.

It seems to be the only book which presents a basically complete course on the Mössbauer effect, giving a lucid exposition in only seventy pages.

R. FATEHALLY

ANALYSIS OF ANCIENT METALS—Instrumental Series of Monographs on Analytical Chemistry; Vol. 19, by Earle R. Caley (Pergamon Press Ltd, Oxford), 1964. Pp. xi+173. Price 70s.

The book, somewhat uncommon of its kind, is a practical guide book to the museum analyst for the identification and analysis of ancient metals and alloys (and their corrosion products), written on the basis of the author's own long experience (25 years) in the analytical examination of materials of this class. No unnecessary attempt has been made to quote elaborate references to the common analytical methods which are readily available in standard treatises, but selected references to the widely scattered literature on the subject have been

listed at the end of each chapter. Emphasis has rightly been laid on methods found most practicable by the author in his efforts to combine reliability with simplicity. Though based primarily on classical chemical procedures, the recommended methods include a judicious use of a few modern techniques such as emission spectrography, X-ray fluorescence, neutron activation and other physical methods of analysis.

Separate chapters have been devoted to gold, silver, copper, iron and their alloys. Lead and tin alloys, platinum, antimony and zinc are discussed in one chapter. The very real sampling problem of ancient objects deservedly forms the first chapter, and preparation of reports the last. The chapters are short and easy reading.

The book is well printed but the price, judged from the fact it has no plates or diagrams, appears high.

J. GUPTA

THE MECHANICS OF AEROSOLS by N. A. Fuchs; translated from the Russian by R. E. Daisley & M. Fuchs; edited by C. N. Davies (Pergamon Press Ltd, Oxford), 1964. Pp. 408. Price 120s.

Aerosols are of great importance in varied branches of pure and applied sciences including numerous human activities. In spite of the widespread concern, the information on the subject has not so far been well integrated and the research results are scattered in reports and journals of widely different branches of science and technology. The publication of the book is, therefore, a significant landmark in the compilation of literature on the subject. It is a translation of the Russian book published in 1955, but now revised, enlarged and brought up to the year 1960.

The title of the book 'The Mechanics of Aerosols' needs further clarification about the areas covered. The clarity is obtained by the titles of the chapters entitled Classification of aerosols, size and shape of aerosol particles, Steady rectilinear motion of aerosol particles, Non-uniform rectilinear motion of aerosol particles, Curvilinear motion of aerosol particles, Brownian motion and diffusion in aerosols, Convective and turbulent diffusion of aerosols, Coagulation of aerosols, and Dispersal of powders as aerosols.

In these the subjects have been developed from a fundamental scientific angle and the basic theories and experimental results on aerosols have been critically discussed, sometimes making suggestions about areas for future research. As the physical properties of aerosols depend strongly on the particle size, after mentioning the various methods of determining particle size, different mathematical formulae have been introduced in the first chapter to represent distribution curves. Next follows a detailed account of the theoretical and experimental investigations on the motion of the aerosol particles under the influence of various external forces, which are covered in the next five chapters. The last two chapters are concerned with processes of deposition, coagulation and the reverse, dispersal and breaking up of aggregates, which are of direct practical value.

Within the confines of a volume of about 400 pages, the author has assembled a wealth of information from a large number of references (about 900 references of research papers, reports and books have been listed). These have ably displayed both progress and contemporary research activity. The book is particularly valuable for the compilation of extensive discussions on the fundamentals such as the equations of motion, precipitation, coagulation and dispersion relating to the behaviour of aerosols that can be found nowhere in such a concise form.

Research workers in the fields of physical chemistry, physics and meteorology will find this book a very useful guide and source of information on the subject.

A. B. BISWAS

MAHESHWARI COMMEMORATION VOLUME edited by T. S. Sadasivan (Indian Botanical Society, Madras), 1963. Pp. xxxiv+330. Price Rs 32 or £ 2 10s. or \$ 7.00

This special volume of the Indian Botanical Society has been published to commemorate Prof. Maheshwari's completing 60 years and is dedicated to him for the yeoman services he has rendered to the science of botany in India and plant morphology in particular. Prof. Sadasivan in his dedication has aptly assessed Prof. Maheshwari's valuable services by stating that "Prof. Maheshwari is to be regarded as father, mother and attending gynaecologist for the subject of plant morphology and embryology in India". The present volume bespeaks in a befitting way the esteem with which he is held by his colleagues in the field and by the Indian botanists in general.

The volume contains 37 articles contributed by botanists all over the world, covering a wide range of botanical subjects — taxonomy, morphology, cytology, genetics, physiology and biochemistry — and dealing with almost all groups of plants, viz. algae, fungi, bryophytes, pteridophytes, gymnosperms and angiosperms. This kaleidoscopic review brought about by the joint endeavours of no less than 50 contributors vividly portrays the advances that are taking place in various phases of botany and is quite befitting the scientist it is intended to honour. One new genus of palaeozoic seeds (*Maheshwariella*) and one species of *Oldenlandia* (*O. maheshwarii*) are dedicated to the honoured scientist. The articles are published in the alphabetical order of the contributor's names and avoids regimentation of the various fields treated.

Besides papers on topics of specialized interest, the volume has an introductory chapter on Prof. Maheshwari's biography and his contributions to botany. It is concluded by a list of publications by Prof. Maheshwari and his associates, covering nearly 35 years of dedicated service to botany.

The volume is well edited and printed, and will be welcomed by all botanists not only as a tribute to the great scientist but also for the variety of topics it has brought under one cover.

K. R. RAMANATHAN

MAGNETIC AND ELECTRIC SUSPENSIONS by P. J. Geary (British Scientific Instrument Research Association, Kent), 1964. Pp. 170. Price 50s.

This monograph, the sixth in the series of SIRA survey of instruments in parts, contains a review of the literature on magnetic and electric suspensions, in which magnetic and electrostatic forces are used for the reduction of mechanical friction and wear of bearings and guides or for wholly contactless suspensions (levitation). The first chapter is introductory, dealing with the theory, techniques and applications of magnetic and electric suspensions. This is followed by chapters on magnetic relief of mechanical bearings, magnetic flotation with lateral guides, electromagnetic levitation with autoregulation of the suspension current, electromagnetic levitation by eddy currents, magnetic levitation using superconductors, and electric levitation with autoregulation of the suspension voltage. In the other half of the book, abstracts of 345 literature references from the year 1839 to 1963 are given. As has been pointed out in the book: "the object of these surveys is to gather together and correlate published information about the design, construction and functioning of the working parts of measuring instruments". This object is fully achieved and for detailed information one can refer to the original literature cited. The book should be of immense use to designers and manufacturers of instruments and precision apparatus.

C.C.P.

HIGH POLYMERS: Vol. XIII, edited by Norman G. Gaylord (Interscience Publishers Inc., New York), 1963. Pp. xiv+491. Price \$ 16.00

Historically, synthesis of polyethers is of great significance since the original researches of Staudinger in this field led to the modern concept of macromolecules. Systematic work on the development of techniques of polymerization of previously considered unpolymerizable ethers has led to their commercial products.

The book under review is Part I of the thirteenth volume of the well-known *High Polymers* series and covers polyalkylenes, oxides and other polyethers; Parts II and III, which have also been published, are devoted to epoxy resins and polyalkylene sulphides and other polythioethers. Besides a brief introduction, Part I has six sections written by specialists. In the 5-page introduction, the editor outlines the importance and future scope of the various polyethers. The chemistry of polymerization of aldehydes and their properties are dealt with extensively in Section I. Polymerization and properties of both ethylene oxide and propylene oxide are discussed in a detailed manner in Section III. The following section is devoted to an elaborate discussion on the condensation of ethylene oxide and propylene oxide with water, alcohol, fatty acids, amines, amides, etc., with particular reference to their use as surfactants. Several practical formulae for household and industrial polishes, such as floor and furniture polishes, based on these products are listed and their applications in cosmetics, pharmaceuticals, leather, metal, paper, rubber are well brought out. There is a brief description

of the rather new and relatively less known 1, 3; 1, 4 and higher epoxides, which are more of an academic interest and have not as yet found a suitable place in the industry. The chemistry and kinetics of the formation of polyurethanes, technology of the preparation of flexible and rigid foams, application of polyurethanes in the field of adhesives, coatings and rubbers are adequately described in Section VI. The last section presents brief summaries of original publications on the synthesis of polyacetals.

One important feature of the publication is the compilation of latest information which, in view of growing interest and competition in these versatile products, does not find way in literature. The long lists of references at the end of each section are undoubtedly a useful asset to the book.

It is a useful reference book and would be a valuable addition to science libraries and particularly those specializing in the synthesis and application of polymeric materials.

S. L. KAPUR

#### GOLD MINING INDUSTRY IN INDIA (Geological Society of India, Bangalore), 1963. Pp. 131

This volume forms the first memoir published by the Geological Society of India and embodies the Proceedings of the Symposium on Gold Mining Industry in India, organized under the auspices of the Society at Bangalore in August 1960. The memoir brings together for the first time a unified and comprehensive account of the gold mining industry in India, its present status and future prospects.

The volume contains eleven papers in all by specialists who deal with the many and varied facets of the gold mining industry, with special emphasis on the geological aspects. M. S. Krishnan, in his paper on 'The gold mining industry in India', presents an admirable summary review of the gold occurrences in the world. The main lode deposits in India occur in Mysore State (Kolar gold fields and Hutti gold fields) and in the adjoining district of Anantpur, where mines were worked in the earlier part of the century. Although several gold-bearing veins have been reported from the Bihar and Orissa region, they have not proved worthwhile prospects. For future supplies, the known deposits of Kolar, Hutti and Anantpur will have to receive greater attention. The author makes a vigorous plea for systematic prospecting work all over the country and the development of the deposits under competent and technical management. The paper by B. Rama Rao deals with the gold occurrences in Mysore and examines the prospects of the deposits for large-scale exploitation. The author reviews the history of eight auriferous blocks and discusses their relative importance for further exploratory work. B. C. Roy summarizes the investigations carried out by the Geological Survey of India, and also outlines the proposed programme of investigation during the Third Five Year Plan. The programme includes investigation in detail of the gold fields in Wynad, Hutti, Gooty and Singhbhum-Manbhum and other places to evaluate the economic potentialities of the

deposits. S. Narayanaswami's paper entitled 'The gold fields of South India' presents a review of the geology of the gold fields, the structure of the auriferous lodes and its control on gold mineralization. The paper traces the past and present activity of the more important gold fields of Southern India, with particular reference to Kolar, Ramagiri, Gadag and Wynad. Exploration and prospecting in the Kolar gold fields are reported in a paper by P. N. V. Raghavan. The paper gives a brief general account of the general geology and of the fault and lode systems in the Kolar gold fields. The organization of the exploration department, the methods of exploration in use, and the results of recent investigations are also described. Ziauddin and Ramchandra present a general summary of the work on the geological mapping and structural study of the gold-bearing lodes in the Kolar gold fields. The development of the western lodes in the Kolar gold fields has been examined in a paper by S. V. Subramanyam. The paper describes the lithological control and structural pattern of the reefs and outlines the future programme of exploration which might extend considerably the life of the mine. An interesting paper on 'Some problems connected with deep mining' has been presented by Issacson. The author reviews the special problems of mining at depth, such as high environmental temperatures, high rock pressure and difficulties in safe and economic hoisting. The manner in which these problems are being contended with in the Kolar gold fields are examined and discussed with special reference to ventilation and air cooling, dust suppression, fires and ground control research. The memoir also includes papers on the 'Geology of Ramagiri gold field, Anantpur district, Andhra Pradesh' by M. Krishna Murthy, 'Geology of Gadag gold field, Dharwar district, Mysore State' by S. Narayanaswami and Mohammed Ahmed and 'Gold occurrences in parts of Chotanagpur' by R. N. P. Arogyaswami. The memoir concludes with a note on the working results, development and expansion of the Hutti Gold Mines Co. Ltd.

The Geological Society of India is to be complimented for the publication of this excellent memoir, which would contribute much to the proper understanding of the problems connected with the gold mining industry in India and its future development.

S. BAGCHI

#### ADVANCES IN MACHINE TOOL DESIGN AND RESEARCH edited by S. A. Tobias & F. Koenigsberger (Pergamon Press Ltd, Oxford), 1964. Pp. vi+500. Price £ 8

The publication contains twenty-seven articles presented at the Fourth International Machine Tool Design and Research Conference held at the Manchester College of Science and Technology during September 1963. Most of the papers relate to the results of recent research conducted in the field of machine tools, cutting tools and metal cutting technology. One of the papers refers to the physical and mechanical properties of cast iron on engineering design. There are three articles, expressing the viewpoints of the users of machine

tools referring to requirements in design and performance of machine tools and some new ideas about the machine tools of the future are also expressed. Economic and technological problems of the replacement of machine tools are discussed in one paper. The papers are not strictly confined to metal cutting machine tools only, as there are three papers referring to sheet metal forming, including the method of explosives. Development of bearings for precision grinders and high speed micro-finishing is discussed by two Japanese authors. Development of new instruments such as a photo-electric microscope and methodology of research referring to control systems containing non-linearities are also included.

The articles have not been grouped according to any discipline and the authors are from many different countries like UK, USA, Czechoslovakia, Japan, Sweden, West Germany, East Germany, France, Italy, Poland and Yugoslavia. Although it is known that considerable progress in research and production technology of machine tools has been made in recent times in the USSR, no author from that country has submitted any paper. The authors are from universities and the machine tool industry and a few articles are from the theses submitted by graduate students for their academic work. Most of the articles have a summary or conclusion or both, thus making it easy for the busy reader to get an idea of the contents and conclusions of the paper. The subjects chosen are so wide in their fields of application that it is unlikely that any single reader would be interested in the details or contents of all the papers. Selected references have been given for most of the articles.

The articles published in this volume can be broadly classified under the following main headings: (1) Machine tool design, research and calculation methods; (2) The cutting process and cutting tools; (3) Machine tool utilization and the machine tools of tomorrow; (4) Control systems of automation; (5) Metal pressing machines; (6) Design and performance of machine tool elements; and (7) General.

Advances in research and development and their utilization in the field of machine tools and cutting tools is not so spectacular as in aeronautics, electronics or even in the field of agricultural implements or machines. Although new and larger sizes of single purpose or general purpose machine tools are being built in countries like USA, UK, West Germany, Japan, Switzerland and Czechoslovakia, application of research and investigation and interest of academic institutions had been slow and meagre in the field of machine tools. It is gratifying to note that twenty-seven papers from most of the machine tool producing countries have been submitted and discussed at the conference. Some interesting points and conclusions from some of the papers presented are given below.

F. Koenigsberger, in his paper on 'Problems of communication between research and industry', states that means are urgently required for conveying important techniques and results of research to men in industry. He also explains, by examples, the use of graphs, charts and nomograms in interpreting results of research in a simple manner.

Monk has described the design features of the numerically controlled jig borer with particular emphasis on the control system to produce precision machining.

Ogden, in his paper on 'Mechanical aspects of electronically controlled machine tools', traces the progress made in the introduction of electronic control in machine tools and discusses some aspects of mechanical design of the machine tool, to keep in line with the developments of the control system. Design of some elements in the machine tool such as screw-drives, hydraulic ram, rack and gears as well as slideways requires improvement when machine tools are controlled electronically.

Two Japanese authors have described the experimental results achieved by using their special bearings for precision lathes and grinders, which are required to produce high surface finish even on soft materials.

An article describing the physical and mechanical properties of different types of cast iron by the British Cast Iron Research Association concludes by stating that some more work on the relief of stress by the method of vibrations in machine tool castings is obviously desirable.

The developing countries of the world are laying high emphasis on setting up capacity in their own countries for producing the latest types of highly sophisticated machine tools, in many cases by copying foreign models. There are three extremely interesting and thought-provoking articles on the users points of view of the future machine tools. The three authors, from highly industrialized countries, in their critical but constructive remarks have appealed to the designers to put themselves in the position of salesmen and evaluate the operational efficiency of their machine tools from cost considerations rather than from technical perfections alone and so realize the importance and necessity of incorporating in their future designs means for the ease and convenience of manipulation, setting up and maintenance, so as to limit the non-productive timings to the barest minimum. These three papers should be more widely read in the developing countries as India, to avoid copying machine tools which may not be suitable for the economic and technological needs.

As the title of the edition indicates, it is a collection of papers referring to latest researches and advances in the field of machine tools and cutting tools. As such seminars and publication of papers have now become an annual feature, grouping into fields of technical activity of the articles subjectwise in later publications is suggested. The papers are of interest to research workers and technologists in the field of machine tools.

R. V. RAMIAH

BIOCHEMICAL ENGINEERING by F. C. Webb (D. Van Nostrand Co. Ltd, London), 1963. Pp. viii+743. Price £ 6

Biochemical engineering as a distinct subject has now come to be established and is now taught at both graduate and postgraduate level. It is as well that this development occurred after the distinct emergence of chemical engineering, for this new science

combines and extends the principles of chemical engineering, biochemistry and biology in a manner most useful for the development of industries using biological raw materials and processes. A major portion of world's farm products is used for food and feed and a small part as industrial raw material for production of such diverse materials as solvents, pharmaceuticals and industrial enzymes. To write a balanced book on a subject covering such wide fields is a difficult task, but Dr Webb has achieved singular success. This has been possible due to the careful planning of a postgraduate course in biochemical engineering and due to the author's wide industrial experience. The few earlier books on this subject have been restricted to specific industries or a few aspects. Dr Webb's book gives a broader treatment and combines in a balanced way fundamental principles and unit operations of significance to biological industries with examples of practical and large-scale applications. With a pleasant freedom from a rigidity of approach, problems of food processing are discussed under unit operations while other fermentation products are discussed as unit processes.

Rightly, a good chemical engineering background is assumed and hence the emphasis in the earlier chapters on fundamental data is on aspects of living processes, control of microorganisms, proteins and enzymes. Then follow chapters on colloids and electrophoresis, emulsion, reaction kinetics, energy in biological systems and redox systems. The examples chosen to discuss the principles are of biological significance. The mathematical treatment and discussion of principles of analytical techniques are adequate as an introduction and to follow their implications.

The following chapters discuss aspects of mass transfer particularly applied to aeration in industrial fermentation; heat transfer with examples of canning; reduced temperature preservation with examples of meat preservation and dehydration including freeze-drying. The chapter on isolation of products covers conventional filters, solvent extraction, adsorption and chromatography and includes a discussion on ion-exchange resins. New unit operations of significance to biochemical engineering, air sterilization and radiation sterilization and disinfection by chemicals have also been discussed adequately.

The chapter on equipment design restricts discussion only to the peculiar requirements of biochemical engineering processes such as prevention of contamination by undesirable microbes and trace metals, ease of cleaning and sterilization. The design of individual equipment is discussed earlier under unit operations.

The remaining chapters discuss commercial enzymes, yeasts, antibiotics, other fermentation products such as vitamins, organic acids, vaccine manufacture and are treated more to cover the biochemical aspects of these products. The last chapter on the important aspect of effluent disposal is adequately treated both from the biological and process points of view.

Each chapter has a bibliography of important textbooks, reviews and recent papers. The printing and production of the text, tables and illustrations is pleasing.

The reviewer thoroughly enjoyed reading the book and recommends it to postgraduate students and all those concerned with the operation and control of industries using biological processes or raw materials.

V. S. GOVINDARAJAN

AGRICULTURE — SCIENCE AND TECHNOLOGY FOR DEVELOPMENT: Vol. III (United Nations, New York), 1963. Pp. viii + 309. Price \$ 8.00 (cloth) The final report of the United Nations Conference on the Application of Science and Technology for the Benefit of the Developing Countries, held in Geneva in 1963, appeared in 8 volumes of which the present one on agriculture is the third. This is a well summed up volume covering over 500 papers, many of them contributed from developing countries dealing with every aspect of agriculture. In the three hundred and odd pages of the book the subject has been divided into five major heads dealing with the background, developing plant resources, developing animal resources, developing framework and the industrialization of agriculture.

Planning and development of land and water resources in tropical and underdeveloped areas is rightly shown to depend upon the determination of climate and soil conditions, the essential requirements for the crop production. In tropical regions where rainfall is irregular, careful consideration of the water budget based on water balance sheets was indicated as a guide to expanding agriculture.

It has been rightly pointed out that field experiments particularly for demonstration to farmers should be conducted as frequently as possible to infuse confidence in farmers to take up better scientific practices. A larger amount of useful information on microelements, use of fertilizers, irrigation water and its use coupled with social and economic problems has been discussed.

The importance of plant breeding for evolving varieties with higher yield potentials, greater cultural reliabilities, greater resistance to diseases and pests, improvement of quality, both nutritional and industrial, has been indicated. A few examples of success with new varieties in increasing the average yield of rice in the United Arab Republic by 60 per cent over the last 5 or 6 years and increasing wheat yield by 23 per cent in New Zealand within three years as a result of plant breeding are worth noting. As one-third of the world's land is covered by forests, almost the same amount as is covered by agriculturally productive lands, the need for properly planned rational forest development integrated into the economic planning of the country as a whole is, therefore, very significant.

Life-stock breeding, feeding, disease control, dairy technology and fisheries have been discussed. The evils of over-grazing, the necessity of improving the feed and forage crops, correction of mineral deficiencies in soils and the value of legumes have been discussed. Maintenance of animal health is considered as one of the important activities among the many that make up farming.

An efficient dairy industry can be the agent for providing people with regular source of animal proteins and with an increased intake of certain minerals, vitamins and energy. Technological



development in this branch suitable for the local conditions should be given a high priority. Importance of fish production is stressed in view of the high quantity of protein, reaching as much as 25 per cent by weight in some species, and the high content of certain amino acids that are lacking in the cereals that form the staple diet in many developing countries.

It was suggested that basic research in agriculture could be left to the developed and the more advanced among the developing countries. Agrarian reforms, education through schools and extension service, cooperation between extension and research, proper training of agricultural scientists and technicians, form the starting point for agricultural development as a whole. Importance of cooperatives, proper marketing, credit facilities and mechanization of agricultural operation have been discussed.

The last part deals with the handling, storing and processing of agricultural products, nutrition policy, agricultural mechanization and planning agriculture as an industry and way of life. In spite of the industrialization, most of the world's food is still produced with muscle power. The importance of machinery is, therefore, stressed in assisting farmers for increasing the production.

Although the subjects discussed are technical and need scientific knowledge to follow, the presentation in this volume is lucid enough for a layman to follow with ease. The book is a very useful addition to the literature in agriculture both for the researcher and the student.

C. DAKSHINAMURTHI

**BOOK NOTES**

**BASIC TECHNICAL MATHEMATICS WITH CALCULUS** by Allyn J. Washington (Addison-Wesley Publishing Co. Inc., Massachusetts), 1964. Pp. xii+595. Price \$ 8.75

Thorough understanding of basic concepts in mathematics and the techniques of translating them in practical problems are essential requisites for students pursuing technical courses. The book under review meets this need for those students of technical courses with little basic knowledge of mathematics and science and presents a judicious combination of the fundamental concepts of algebra, trigonometry and calculus spread over 27 chapters. The first twenty chapters comprise algebra and trigonometry and serve as a prelude to better understanding of the latter chapters devoted to calculus and its applications. The book concludes with a chapter

dealing briefly with differential equations of first and second order.

The subject matter of each chapter is supplemented by a good number of solved examples and many more are set as exercises for the student. In keeping with the main aim that the book is meant for technical courses, the topics and the examples presented — mainly those of calculus and differential equations — are designed to lay stress on their practical applications.

The inclusion of elementary ideas of statistics, complex numbers and Fourier series helps the student to acquaint himself with these topics for further study and enhances the value of the book. The appendices dealing with scientific notations, significant figures, the use of slide rule, etc., and the trigonometric tables assist the user of the book in computational work.

The get-up and printing of the book are excellent although the price appears to be rather high considering the type of user for whom it is meant.

D. S. R. MURTY

**PUBLICATIONS RECEIVED**

**TACHEOMETRIC TABLES** by F. A. Redmond (Asia Publishing House, Bombay), 1961. Pp. xx+256. Price Rs 15.00

**ELEMENTARY VECTORS** by E. O. Wolstenholme (Pergamon Press Ltd, Oxford), 1964. Pp. vi+95. Price 12s. 6d.

**INTERPRETED INFRARED SPECTRA: Vol. 1**, by Herman A. Szymanski (Plenum Press Inc., New York), 1964. Pp. vii+293. Price \$ 10.75

**ULTRASONIC CUTTING** by L. D. Rozenberg, V. F. Kazantsev, L. O. Makarov & D. F. Yakhimovich (Consultants Bureau Enterprises Inc., New York), 1964. Pp. xi+142. Price \$ 17.50

**BIOLOGICAL EFFECTS OF MAGNETIC FIELDS** edited by Madeleine F. Barnothy (Plenum Press Inc., New York), 1964. Pp. ix+324. Price \$ 16.00

**ULTRASOUND: PHYSICAL, CHEMICAL AND BIOLOGICAL EFFECTS** by Isaak Efimovich E'piner, translated from the Russian by F. L. Sinclair (Consultants Bureau Enterprises Inc., New York), 1964. Pp. viii+371. Price \$ 22.50

**GUIDE TO GAS CHROMATOGRAPHY LITERATURE** by Austin V. Signeur (Plenum Press Inc., New York), 1964. Pp. 351. Price \$ 12.50

**CLASSICS OF SCIENCE: Vol. II — THE DISCOVERY OF RADIOACTIVITY AND TRANSMUTATION** edited by Alfred Romer & Gerald Holton (Dover Publication, New York), 1964. Pp. xi+233. Price \$ 1.65

# NOTES & NEWS

## Nearly perfect reflecting mirrors

A major advance in mirror technology has been achieved at the Bell Telephone Laboratories, New York, in the development of mirrors that reflect nearly 100 per cent of the incident light. This is effected by coating a mirror blank with many layers of optically transparent dielectric material in a way that virtually eliminates light scattering from the reflective surface. As mirrors made by this technique are so highly reflective, a laser using these mirrors will emit several times more light than one using conventional mirrors. These mirrors could be used as efficient light-focusing elements in a laser communication system and will also be useful in interferometry and Raman spectroscopy.

By carefully controlling the thickness and composition of the mirror coatings, it has been possible to produce 'broadband' mirrors that can reflect more than 99.5 per cent of the light over the visible spectrum range from 4200 to 7600 Å. In conventional methods increase in mirror reflectivity is achieved by increasing the number of dielectric layers made of materials having alternately high and low indices of refraction on a mirror blank; however, when more than fifteen dielectric layers are deposited, reflectivity is not improved, due to scattering or absorption of light by these layers. In the new technique light loss due to scattering from each layer has been reduced sufficiently so that many more layers could be deposited advantageously by using dielectric material in chunks instead of the usual powder form, evaporating them at a precise temperature just below the melting point and preparing them properly. This way the number of large particles deposited on the blank which scatter more light is reduced.

During the deposition process when the precise thickness, i.e.  $\lambda/4$ , is reached for the dielectric

material with a high index of refraction (such as zinc sulphide), the deposition is changed to that of a low index material (such as thorium oxyfluoride or cryolite), thus forming a full layer. In this way 35 layers are applied; the addition of each layer increases reflectivity very close to 100 per cent.

Since the common practice of cleaning the substrates before deposition by exposing them to a glow discharge can often result in large particles being sputtered on to the clean surface, the substrate surface was cleaned carefully and kept uncontaminated before being placed in the bell jar so that the glow discharge cleaning could be eliminated.

A highly accurate method of monitoring the thickness of each layer as it is being deposited has also been devised. In this method layer thickness is monitored by using a very stable light source — a gas laser operating at 6328 Å. Part of the laser beam is directed at a solar cell whose output enters a radiometer. The other part of the beam strikes a monitoring slide in the bell jar and the reflected light of wavelength  $\lambda$  from the slide is directed to another solar cell whose output also goes into the radiometer. The original and reflected outputs are compared and the recordings of maximum and minimum reflectivity indicate respectively when the high and low index material is having a thickness of  $\lambda/4$ . The accuracy of this technique stems from the high signal-to-noise ratio of the laser monitoring system. The use of a 6328 Å. light source does not limit one to obtaining reflective coatings at only that particular wavelength [News from Bell Telephone Laboratories, New York].

## Wavefront shearing interferometer

A wavefront shearing interferometer which is smaller and simpler than previous designs, particularly suitable for detecting the aberrations of the lenses of astronomical

telescopes, has been developed at the NBS Institute for Basic Standards of the US Department of Commerce. The interferometer works on the principle that when the light coming from a lens is split by a semi-reflecting surface into two components and then recombined with a slight shear between the two beams, the shape of the resulting interference fringes is a function of the shape of the wavefront. Hence, in operation, the shearing interferometer shows the wavefront of a beam of light that passes through a lens to be spherical if the lens is free from aberrations. The amount of deviation from the spherical wavefront gives a measure of the imperfection of the lens. By observing the interference pattern by splitting, shearing and recombining the light that passes through a lens, the aberration of a lens is readily detected. This instrument is handy and needs no further attention after the initial adjustments at the manufacturer's end [J. Franklin Inst., 278 (1964), 158].

## Mounting thin sections for electron microscopy

In electron microscopy, media with three-dimensional polymer structure, like methacrylate, epoxy, polyester and styrene resins have the advantage that they are immune to electron bombardment and preserve the fine structure of the tissue, but their resistance to degradation reduces the contrast between tissue and background.

Contrast between tissue and background is maintained by mounting the thin sections directly on grids. The contrast is enhanced by electron staining. To avoid movement of the sections under the electron bombardment, the thin sections are strongly adhered to the supporting grids by using an adhesive. The grids are treated with a 0.3-0.5 per cent (M/V) solution of chloroprene rubber in toluene, removing the excess fluid and drying.

Thin sections are transferred by holding the edge of the grid with a pair of fine forceps and pressing it gently over floated sections, so that the liquid surface is depressed. The grid is then removed from the water surface and adhering liquid removed with filter paper or a

Boiden gas spray. The sections are stained as usual; the coating on the grid protects it against the action of acidic or basic reagents.

Sections with holes or splits should be exposed for a short time to weak bombardment to stabilize them. As the sections are attached to the grid around each of its holes, movement caused by the rupture of the section under the beam does not extend beyond the hole where it occurs. This method, therefore, is suitable for observations especially under high magnification [*J. Electronmicrosc.*, **13** (1964), 27].

### New vacuum gauge

Recent studies made on the field emission of electrons from fine metal points at the Royal College of Science and Technology, Glasgow, have led to the design of a vacuum gauge which could actually count the number of molecules in the evacuated space. The emission current from tungsten points, a few thousand Angstroms in diameter and highly contaminated with absorbed gas, was used to measure the pressure down to  $10^{-5}$  torr. When a voltage is applied to the tungsten point so that it becomes a cathode, a stream of electrons can be drawn away from it, by a high electric field in the neighbourhood. The electrons collide with the absorbed gas molecules and consequently ionize some of them. The molecules become slightly positively charged as a result of these collisions and, therefore, are attracted back to the cathode. When each ion makes an impact with the cathode it disturbs the layer of absorbed gas and sets up a sharp fluctuation in the value of the emission current. In the application of this effect, the fluctuations have to be recorded electronically since they last for a few thousandths of a second. At a pressure of  $10^{-10}$  torr the fluctuations would occur about one in 3 min.

Apart from being able to count single molecules, the gauge is free from the X-ray background and voltage breakdown effects found in conventional ionization gauges. The gauge is extremely robust, has only two components and is cheap. Unlike the hot filament

ionization gauge which can record pressure only down to  $10^{-17}$  torr, the tungsten point gauge has no lower limit of pressure that can be measured [*Discovery*, **25** (No. 10) (1964), 15].

### Anemometer using sonic waves

A new method of measuring the velocity and direction of wind at ordinary anemometer heights about 70 ft uses a directed beam of sonic waves as the probe for observing the Doppler frequency shift in the scattered sonic waves. This technique dispenses with the use of any local sensor, artificial target or any structure above the ground.

In this method a sonic beam at a given frequency is directed towards a point in space which consists of volume elements carried by the wind. The Doppler frequency shift by these elements is scattered and a new Doppler frequency shift is received at the receivers. From the measurement of the Doppler shift experienced between the frequency emitted by the source and that observed at the receiver, the velocity of the wind is calculated.

The source used is a powerful Levavasseur whistle (frequency, 10 c/s.) mounted at the focus of a 4 ft diam. parabolic reflector (1.5 ft focus) which produced a peak sound intensity of 110 db. (10 mW./sq. ft) at a distance of 70 ft. The two receivers placed in orthogonal directions with respect to the source consisted of highly sensitive and stable piezoelectric type ceramic microphones mounted at the focus of 4 ft parabolic reflectors.

A series of 300 experiments conducted on winds from 3 to 25 m.p.h. revealed that there is a good agreement between the results thus obtained and the anemometer measurements, within 1 m.p.h. for speed and  $5^\circ$  for direction. The method may prove useful in studies of air turbulence [*Bull. Amer. Met. Soc.*, **45** (1964), 571].

### Electronic null indicator for glass electrode measurements

An inexpensive electronic null indicator which is likely to find application in the measurement of

potentials of electrochemical systems using glass 'sensors' has been developed at the Central Electrochemical Research Institute, Karaikudi. The instrument, in conjunction with the usual student potentiometer and galvanometer, can be used to measure pH of solutions to the required accuracy using glass electrodes in spite of the high impedance of glass electrodes.

The instrument consists of a cathode follower circuit employing Philips 4067 electrometer tube which acts as an impedance transformer from a high input impedance level to a low output impedance level so as to drive a centre zero microammeter or galvanometer. Inverse current feedback is inherent in the cathode follower circuit and stabilizes the circuit against drift and provides good linear response. Asymmetric potential and temperature compensation circuits have also been provided and one of the meter leads is in the ground potential [*Curr. Sci.*, **33** (1964), 612].

### Staining method for cells

The common biological test to distinguish damaged cells from unaffected cells is to stain them with cosin or trypan blue. The cells taking the stain are assumed to be damaged and the others undamaged. But the work of L. Black and M. C. Berenbaum of St Mary's Hospital, London, using the above technique to study the damage to rabbit white blood corpuscles, caused by immune sera, showed erroneous results.

The proportion of cells taking the stain range from 0 to 90 per cent depends on the concentration of stain and serum and the staining time. They conclude that the dye exclusion test only distinguishes between damaged and undamaged cells within certain limits, and principally by the nature of cells. The limits seem to be large with some types of tumour cells and with others as in the above study are narrow enough for the test to prove reliable.

A new method 'Intravital fluorescence microscopy' has been proposed by M. Sherif, University of Alexandria, Egypt, for cancer cells in organisms. It involves staining the tissue with a dye

that fluoresces when irradiated with ultraviolet light. The dye acridine orange combines with human nucleic acids to form chemical complexes depending upon the nucleic acid whether present in normal or cancerous cells. Each complex has its own characteristic fluorescence spectrum.

The acridine-nucleic acid complexes are examined under a microscope, with a magnification of X17, fitted with a side arm containing a mercury vapour lamp or ultraviolet source. Light from the lamp is reflected into the target area by a 45° plate having both good reflecting properties for ultraviolet light and good transmission properties for the visible wavelengths of the returning fluorescent light. Filters remove unwanted wavelengths leaving only the green, yellow and red which characterize the acridine nucleic acid complexes [*New Scientist*, 24 (1964), 312].

#### A new electron microscope preparation technique

The traditional sectioning technique adopted for the electron microscopic preparations has the disadvantage of uncertainties, resulting from the formation of artifacts during fixing and imbedding of the specimen, and the deformation or the destruction of tissues, cells and their fine structures. In a new freeze-etching technique developed by Dr H. Moor of the Institute for General Botany at the ETH, Zürich, living parts of tissues are frozen in a fraction of a second down to a minimum of -100°C., so that the cells are not damaged in any way, their structure and capacity of survival being maintained. The solidified preparation is cut, and chipped under vacuum so that a flat surface through ice and the object can be obtained. By low vacuum sublimation of ice, the surfaces of the enclosed object are made visible, i.e. the etching of the cutting surface creates a relief of the object. By means of a combined platinum-carbon evaporation, a very exact replica of this relief can be made. Afterwards the preparation needs only be thawed off. The replica can be loosened from the object and transferred to an object holder.

Contrary to the thin layer method, the freeze-etching technique not only supplies cuttings of preparations but also surface views of the cells and their membrane systems, like views of the plasma skin with partly broken away cell walls, surface views of cell nucleus, vacuoles, mitochondria, etc., and fracture surfaces of these cell organelles. The freeze-etching method thus offers completely new possibilities, particularly for research on biological and medical living objects, like microorganisms, plant cells and animal tissues.

#### Enzymatic dissection of the mammalian ovary

A new method of enzymatic dispersal of both embryonic and adult tissues using the proteolytic enzyme, Pronase, has been developed by Howard S. Grob, presently of the Department of Physiology and Pharmacology, College of Dentistry, New York University, New York.

To obtain isolated follicle cells the ovaries of rats and mice were removed, dissected free of fat and oviducts, chilled, washed and exposed for varying intervals to 0.5 per cent Pronase, a partially purified protease from the actinomycete, *Streptomyces griseus*, made up in a Ca<sup>++</sup> and Mg<sup>++</sup> free balanced salt solution at pH 6.8-7.0. The ovaries were placed in enzyme solution at 37.5°C. and were agitated every 10 min. The dispersed cellular material thus obtained was periodically examined under a microscope and the viability of the cells was assessed with nigrosin [*Exp. Cell Res.*, 15 (1958), 112]. The first subunits to be liberated were the outermost follicle or corpora lutea or both. The cellular elements were collected either by mild centrifugation or filtration on Millipore filters, washed with saline and resuspended in a balanced salt solution containing 0.5 per cent nigrosin.

Attempts for the enzymatic degradation of the ovary with other proteolytic enzymes (trypsin, chymotrypsin, pancreatin, collagenase and elastase) could not yield the step by step degradation of cell material obtained with Pronase.

The advantages of this method are: (1) ovaries from animals in

the follicular phase of the estrus cycle yield follicles in all stages of maturation, (2) the embryonic cells so obtained can be grown in cultures and they retain their function [*Science*, 146 (1964), 73].

#### Inheritance without genes

Ever since Gregor Mendel pounded the laws of heredity, the geneticists have assumed that the genes play the main role in heredity, and the cytoplasm surrounding the nucleus is relatively unimportant. Though many instances of inheritance through cytoplasm have been suggested, unfortunately studies on the precise nature of this cytoplasmic inheritance have not yielded conclusive results.

Cytoplasmic inheritance in *Paramecium aurelia* has been thoroughly investigated. Some paramecia are described as 'killers' since they discharge lethal particles which kill other (sensitive) paramecia if the latter take up the toxic material from the surrounding water. There are other paramecia called 'mate killers' which kill sensitive paramecia only when they conjugate (a sexual process characteristic of paramecia). The killer paramecia were once thought to demonstrate cytoplasmic inheritance in the clearest possible way. The ability to kill was inherited and was determined specifically by a factor located in cytoplasm. All these killer paramecia have characteristic particles which were first described by T. M. Sonneborn (1943) as kappa particles. They are known to exist in two forms, the 'B' particles, non-reproducing and liberating the toxic agent into the water and the 'N' particle, producing more 'N' particles which transform into 'B' particles. In mate killer paramecia another type of particles, practically filling the cytoplasm known as mu, have been observed. The kappa and the mu particles are maintained in the cytoplasm only when some other much smaller particles known as 'metagons' are also present. To maintain mu particles, certain genes must be present in the nucleus, and when these are removed the mu particles eventually disappear but only after 8-15 cell divisions. It is suggested that the

genes possibly maintain metagons in the cytoplasm and the loss of the genes results in the loss of metagons leading ultimately to the disappearance of mu particles. The presence of even one metagon is sufficient to maintain a large number of mu particles. Thus metagons act as an intermediary link in the gene, culminating in the formation of what is necessary to maintain the mu particles. Originally, metagons were thought to be incapable of replication without these initiating genes. But Gibbson and Sonneborn, at Indiana University in the United States, have shown that under certain conditions they can reproduce for an indefinite period and if this is true metagons could well be the basis for certain types of cytoplasmic inheritance.

Careful experiments with *Didinium*, a unicellular animal which engulfs paramecia with remarkable ease, show that kappa and mu particles can actually be maintained in *Didinium*. An initial meal of paramecia with mu particles followed by paramecia without mu particles still results in the perpetuation of mu particles in *Didinium*. This study has shown that the mu particles can be kept in *Didinium*, if they have also eaten some metagons and that one initial feeding is sufficient to supply them to the repeatedly dividing *Didinium*. This ability of metagons to multiply in the completely different habitat of the *Didinium* was the most surprising result of the experiments. The metagons in some respects resemble messenger RNA of the cell, but unlike messenger RNA, the metagons are both stable and capable of replication.

The discovery of the metagon as a stable gene product existing in the cytoplasm and capable of acting as an intermediary or messenger of the gene is an important development. The conversion of the metagon into a replicating form when transferred into the cytoplasm of another organism is even more remarkable. The replicating metagon can be compared with an RNA virus. This comparison leads to a speculative idea that some viruses may arise in this way [*Discovery*, 25 (1961), 23].

## Progress Reports

### Warren Spring Laboratory, UK

The annual report of the laboratory for the year 1963 shows that even though the research activities have been spread over a wide field extending from air pollution studies and chemical engineering to some aspects of human sciences, emphasis has been laid on such work having immediate applications in industry. However, some long-range basic investigations which may be ultimately useful to industry have also been planned.

The work of the laboratory in air pollution studies is concerned mainly with gathering information on the distribution and with methods of abatement of the two principal pollutants, namely smoke and sulphur dioxide. Studies on smoke concentration and distribution of sulphur dioxide in London have been made during 1961-62 and especially during the London fog of 3-7 December 1962 and general guidance rules for permissible heights of chimneys have been framed based on the data collected. A pilot plant capable of removing sulphur dioxide from flue gas has been designed and erected. The pilot plant is capable of treating 16,000 cu. ft of gas per hour and is very economical since the sulphur dioxide is removed from the flue gas by adsorption on semi-coke produced from peat in the plant and is recovered in a concentrated form during a desorption stage, thus leaving the absorbant ready for re-use.

The research programme in chemical engineering and process development covered four main subjects, viz. mass and heat transfer, automatic and computer control of chemical plant and process, the mechanics of particles and slurries and catalysis and related studies in surface and solid state chemistry. The analytical solution of the partial differential equations describing the transient response of a continuous counter-current transfer process to a disturbance is being evaluated using a computer. Although the theory is only applicable to continuous processes, such as those observed in packed distillation columns, it is expected that it should give a

good approximation for plate columns also. The theoretical analysis has been found to agree quite closely with some preliminary experimental results obtained from a 6-plate distillation column. Further progress has been made in applying Schlieren techniques to the study of gas-liquid systems. The break-up of the large bubbles to the smaller ones which characterize the froth above a sieve tray has been shown to be accompanied by the formation of many tiny bubbles which are estimated to be 5-50  $\mu$  in diameter. Experience gained from this work is finding practical application in the study of methods of contacting gases and liquids during chemical reactions. In studies in particle mechanics, two principal lines of research have been followed: an investigation of the factors affecting the cohesive behaviour of powders, and a general but significant investigation into the blending of powders and particles; besides some attention has also been given to methods of particle size analysis. During the year a new apparatus useful for carrying out tensile tests on powder masses under conditions of shear and tensile stresses has been developed.

In the field of electrical properties of solids, studies have been made on the rectifying properties of *n-p* junctions in ferric oxide, and the resistivity and seebeck voltage of *p*-type ferric oxide; these studies have led to the development of *p-n* rectifying junctions of these materials. In the course of a sponsored investigation in the laboratory, it has been found possible to modify the normal shape of a crystal by performing the crystallization in the presence of a stirred suspension of an inert solid. Applications of this discovery are being investigated in cases where conventional milling is difficult or dangerous. The research programme in catalysis and related subjects included both basic and applied projects under three general headings: (i) the structure of supported metal catalysis, (ii) surface catalysed oxidation, and (iii) catalytic reactions of halogens over metal surfaces. A pebble-bed separator developed by the laboratory primarily to deal with the problem of the discharge of oily water from a ship has found

applications in industry for separation of some industrial effluents. In the field of mineral processing, the research activities have covered several aspects such as studies of grindability, gravity concentration, flotation, high tension separation, etc., and a number of new methods and techniques which will find immediate industrial applications have been developed.

In the field of human sciences, in a project sponsored by the Royal Mint, an ergonomically designed coin inspection unit has been constructed and a prototype of the distribution mechanism required to arrange the coins in a regular pattern on a moving belt has also been built. Other studies in progress are the elucidation of ergonomic considerations which should determine the design of hand and foot controls and improvements to the dental chair and associated equipment to reduce the disabilities resulting from an unfavourable working posture of dentists.

#### ***The British Nonferrous Metals Research Association***

The annual report of the British Nonferrous Metals Research Association for 1963 presents an account of its research activities spread over an extremely wide field of inspection control and rapid analytical methods pertaining to the non-ferrous metals. The study of the mode of solidification and dispersion of shrinkage in production of castings of aluminium bronze has provided useful information on the causes of scatter in tensile properties and the effect of composition and variations in casting conditions on the tensile properties. In the search for the optimum combination of ductility and corrosion resistance in high strength aluminium castings, a new research project on the study of the properties of high purity aluminium silicon alloys hardened with the addition of other metals has been started. Preliminary results from this project show that a small amount of cobalt improves ductility by reducing the particle size of the intermetallics. In the field of casting emphasis has been laid on the methods of production of either large billets and slabs or

thinner slabs involving less subsequent working and consequently less heavy fabricating equipment, to the research activities have been oriented to conform to this emphasis. One such newly oriented research projects is the extension of the use of the Hazlett process for the production of copper and copper alloy strips.

In the field of working and fabrication, a research project on copper wire production was taken up with two objectives, viz. (i) the reduction of die and lubricant costs and (ii) the avoidance of sticking by strand annealing. The role of individual impurities in raising the softening temperature of the finished copper has also been studied. It is generally known that high softening temperatures can result in 'springiness' when a standard annealing treatment is given. The purpose of this investigation is to prepare common ground for 'springiness' testing, so as to make sure that the method of testing not only reflects the quality of copper but also the performance of copper wire in the normal manufacture of electrical machinery. Some factors affecting the extrudability of lead and lead alloys in the continuous extruding machine and the structural changes occurring in the hot working of aluminium alloys have been studied. The knowledge of these structural changes would not only help in selecting the appropriate hot working process to achieve a particular result but would also ensure the control of the preferred orientations which is important in high strength extrusions. In the study of corrosion resistance an attempt has been made to produce, synthetically, a normal carbonate film on zinc which would provide a high degree of protection against white rusting. A ten-year programme of soil corrosion tests on cast and wrought aluminium alloys was completed during the year. The studies made have shown the wide range of the corroding power of the various soils studied and also demonstrated that the protection afforded by bitumen coatings in all these cases is considerable. Immediately applicable methods of improving the corrosion resistance of nickel-chromium plating on zinc-

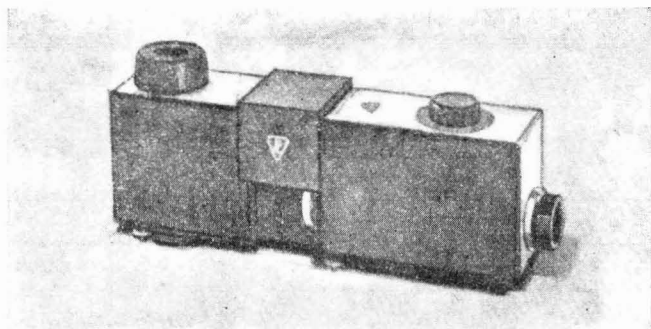
base die castings have been studied. The results obtained so far indicate that a coating to be adequate under the most severe outdoor conditions necessitates the deposition of a more uniform crack-free chromium coating. A study of alternative plating solutions is accordingly being pursued in the search for not only a solution capable of depositing a thicker coating but also for one having a greater throwing power.

#### **Announcements**

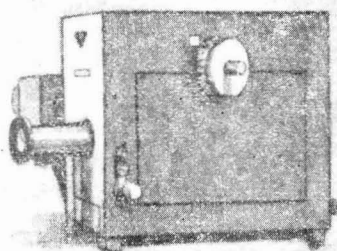
■ *The Indian Hot Dip Galvanizers Association* is a new organization which has recently been formed with a membership of about 50 leading galvanizing firms drawn from all parts of India. The association is a non-commercial, non-profit making body and will provide technical advice and information on the process of galvanizing and the use of galvanized coatings, to both users and manufacturers. They will also hold seminars, conferences and refresher courses primarily for the purpose of improving the techniques and promoting the economical utilization of zinc. The association will be affiliated to the Indian Lead/Zinc Information Centre and will work in close collaboration with similar organizations in the UK, Europe and America. The secretariat is located at 5A Lord Sinha Road, Calcutta 16, to which enquiries may be addressed.

■ *World Calendar of Forthcoming Meetings: Metallurgical and Related Fields* — This new publication will contain basic information about meetings concerned with ferrous and non-ferrous metallurgy, production, working properties of metals, their related engineering and other technologies and services. Every issue, of which there will be six a year, will cover a period of about two years and will be cumulative within that period. Subscription rates are £5 5s. (including surface postage) for the year ending December. Orders should be sent to the Iron & Steel Institute (World Calendar of Forthcoming Meetings), 4 Grosvenor Gardens, London SW 1.

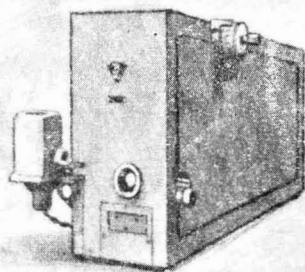
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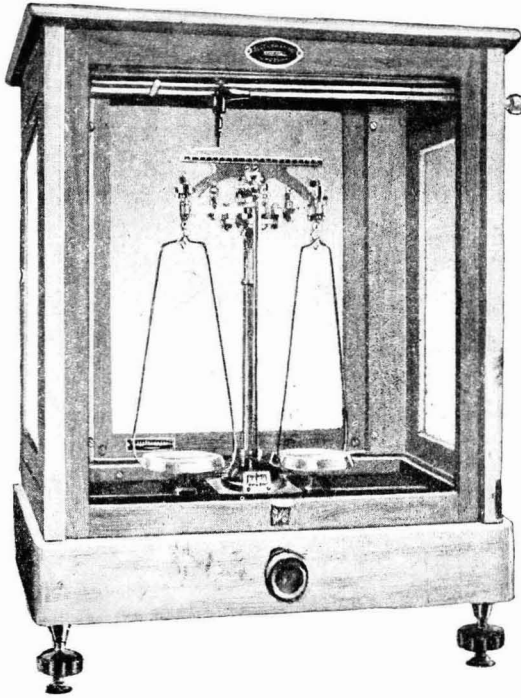
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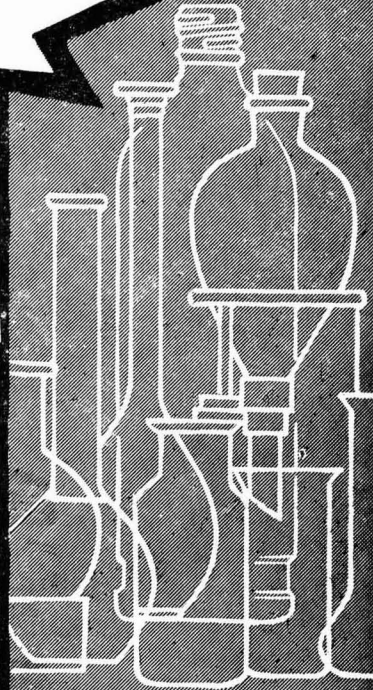
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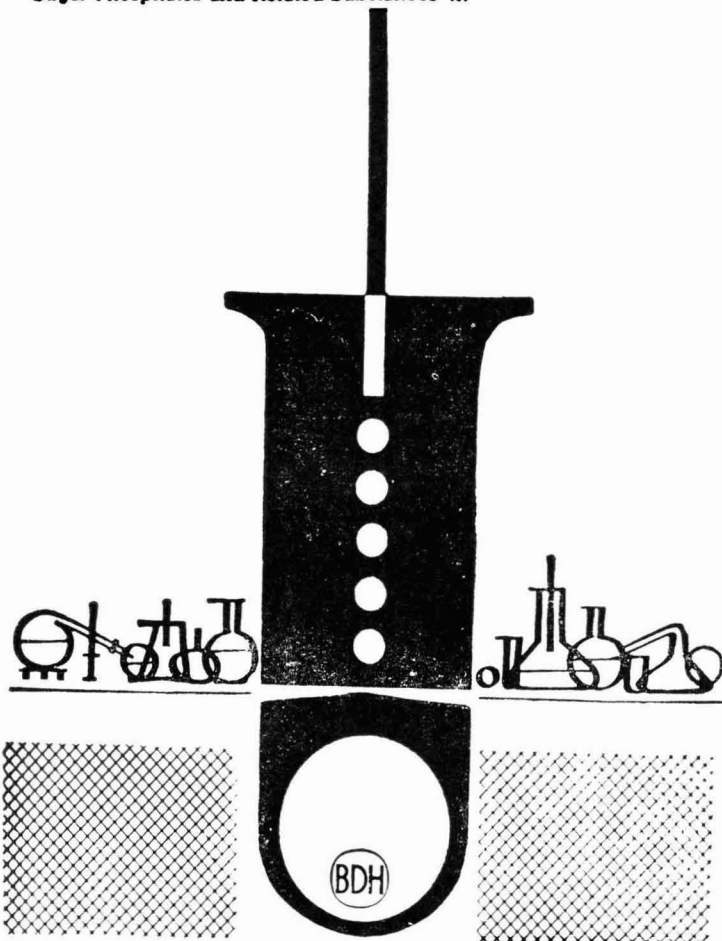
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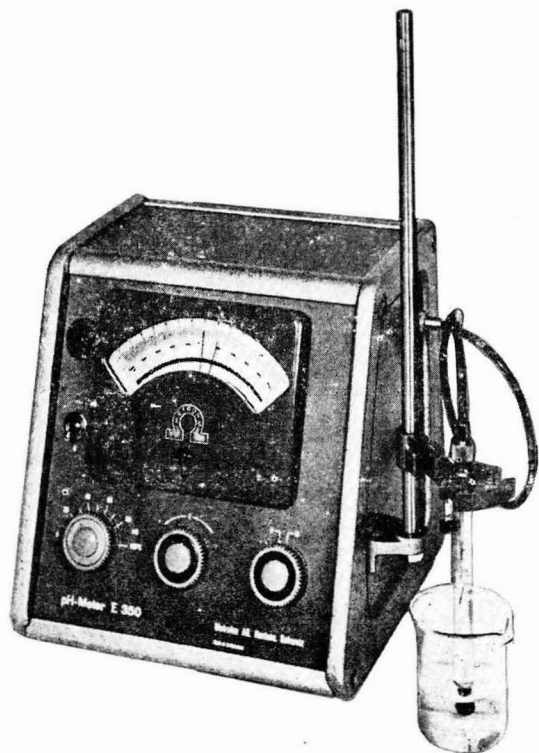
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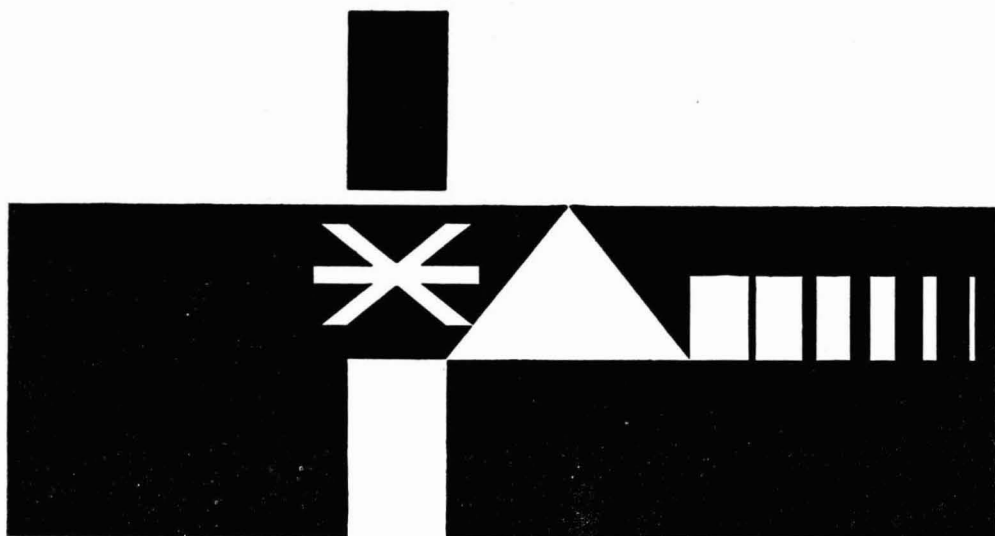
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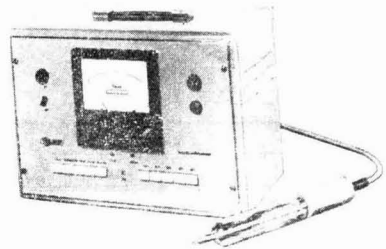
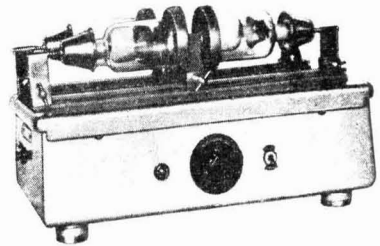
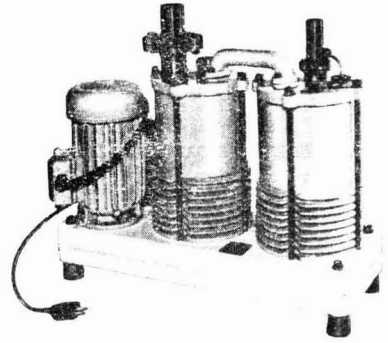


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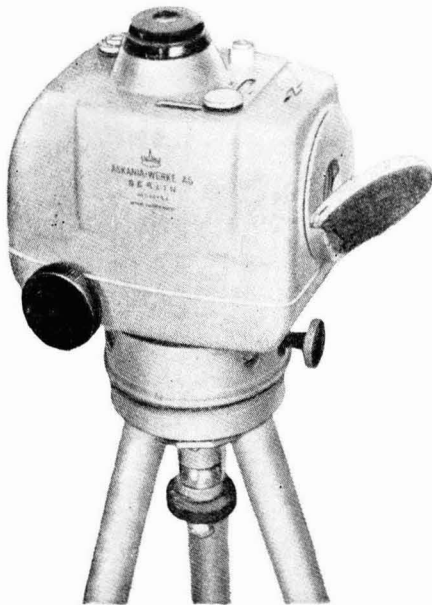
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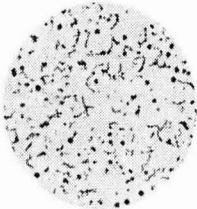
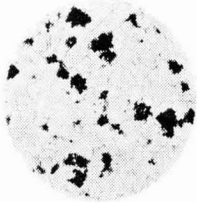




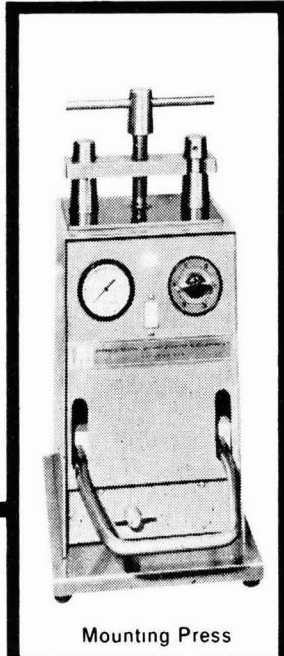
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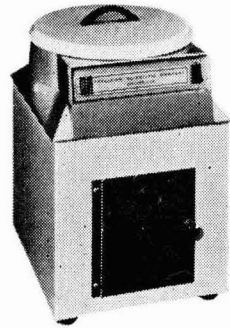
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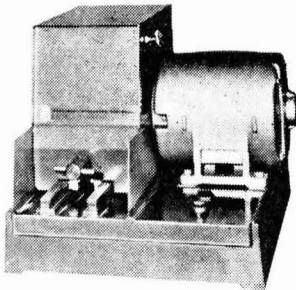
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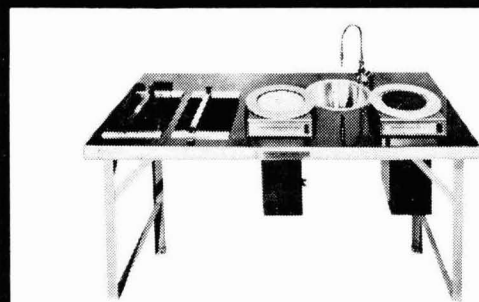
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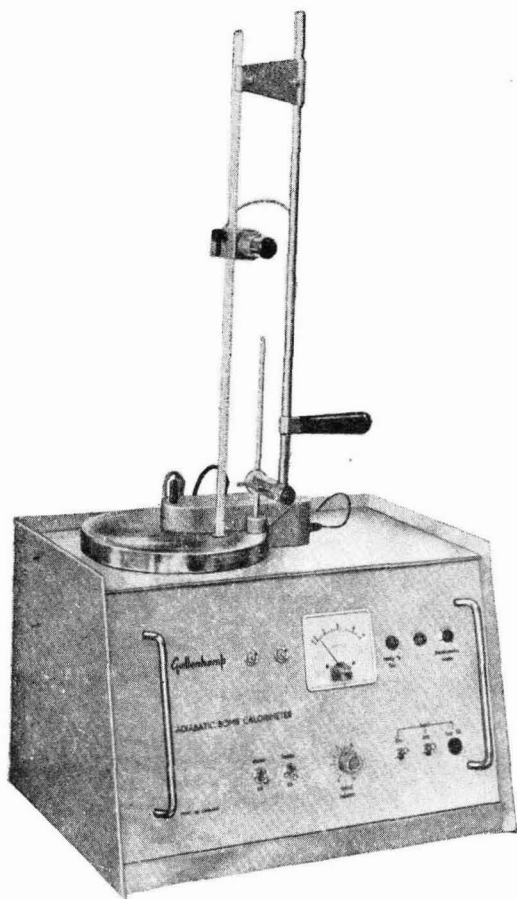
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