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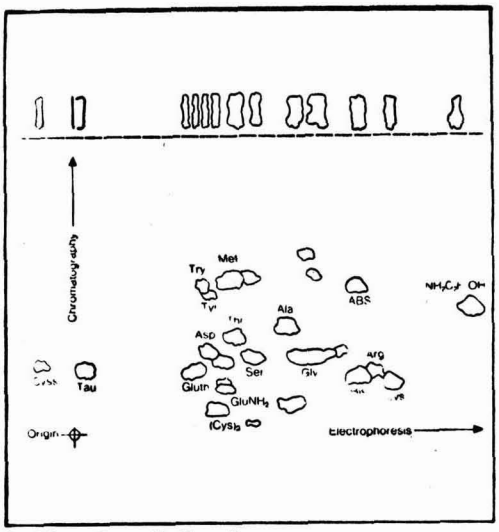

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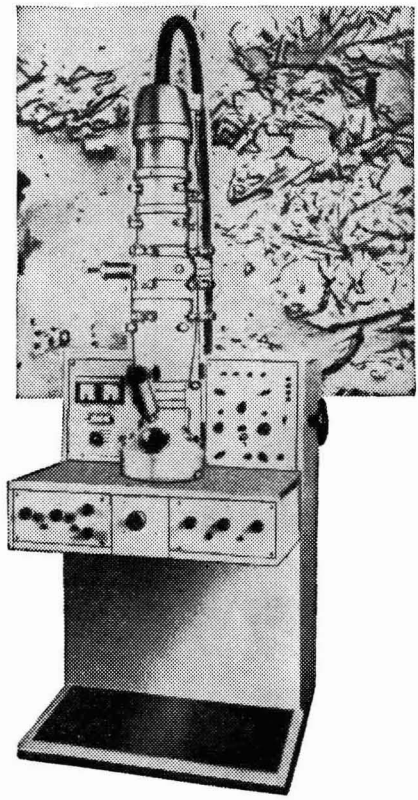

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Current Topics

R & D in Developing Countries

IN the first Nehru Memorial Lecture entitled "Science and Technology in an Unequal World" delivered in New Delhi on 13 November 1967, Prof. P. M. S. Blackett put forth an illuminating analysis of the factors governing the effectiveness of research and development (R & D) effort in developing countries in hastening the rate of economic growth. Basing his arguments on an intimate knowledge of the practices obtaining in UK, Prof. Blackett made out a convincing case for a radical reorientation of the R & D policies in the developing countries so as to derive maximum benefit in the shortest possible time.

The major factors influencing the rate of economic growth through R & D, according to Prof. Blackett, are the deployment pattern of the qualified scientists and engineers (QSEs) and the mode of investment of financial resources. Both QSEs and financial resources being scarce in developing countries, the growth of economy depends largely on the wisdom in choosing the areas for investment as well as in employing the QSEs. That there is no close relationship between R & D expenditure as such and economic growth was illustrated by the example of Japan which while spending a little over half of that spent by UK on R & D has achieved almost three times faster rate of growth of economy compared to UK.

Elaborating the importance of judicious deployment of QSEs, Prof. Blackett observed, "it is extremely important to consider the innovation chain comprising research, development, design, production, marketing and sales and post-sales services as a single whole. The first stages of R & D consume wealth and only the later stages of production and sales produce it. The later stages of the chain cost 4-10 times the initial research; and it is vital to deploy more QSEs, especially engineers and managers, at these stages than in the early stages."

Another important consideration having a vital bearing on the effectiveness of R & D effort is the proper choice of technological projects to invest in. Though special circumstances for each country do come into play in this respect, decisions on projects are again primarily conditioned by the availability of QSEs and capital. A vast body of knowledge in different branches of modern technology is available, and the wide dissemination of this knowledge has narrowed down the so-called 'technology gap' between nations at different stages of development. Thus, it is no longer necessary for each nation to start each project from scratch and carry it through to the stage of industrial production. The ideal policy advocated by Prof. Blackett for developing countries is to "avoid waste of effort on re-invention, re-discovery, re-development, and to decide what to manufacture under licence, what to copy, what to get manufactured by a foreign or jointly owned firm, and finally what to develop from scratch". Otherwise, the limited resources in men and money available would be inadequately distributed over a large number of projects, with the result that many of them will ultimately become unproductive.

Prof. Blackett made another noteworthy point with regard to the attitude of the QSEs themselves towards R & D programmes. Pleading for a greater psychological participation on their part in the process of creating wealth, Prof. Blackett observed, "The wise choice of R & D programmes must often originate in the laboratories... Then individuals will have to make the decision whether to stay in research or to move along the innovation chain towards managerial and industrial end. Probably in India today and also in UK, better managers and entrepreneurs are often more important than better technologists. I would like to see many more trained scientists and engineers setting up their own firms to manufacture specialized goods with a high technological control." When a strong force of QSEs successfully achieves the production and sale of a wide range of products using imported know-how, they can turn to improving imported products and eventually develop a few completely new designs. Prof. Blackett is emphatic in his view that the chance of successfully developing a completely new product for the world market without the practical apprenticeship of actually manufacturing and selling an existent product is not large.

The Koyna Earthquake

D. N. WADIA, F.R.S.*

THIS earthquake has been a puzzle to geologists, as during recorded history the Deccan Peninsula south of the Satpura range has been an area of great stability free from any major seismic disturbances. This region has been wholly immune from any folding or compression by orogenic or tectonic disturbances during a long course of geological ages and has not experienced any earthquake except sympathetic tremors from quakes originating from surrounding regions — land or sea. During the last two centuries, 75 major earthquakes, many of them disastrous, have been recorded in India; all of these were confined to the known seismic belt of the earth crossing India. This belt connecting with the Iranian arc runs through the Makran region, the Sind-Baluchistan border to the Pamir plateau to the north. The southern edge of the belt from Waziristan through Punjab runs along the Himalayan foot to Assam, thence along the Arakan range and connects through the Andaman Islands to Sumatra. The epicentres of the 75 historic earthquakes are all located within or close around this region. Not one of these caused, except sympathetic tremors, any major disturbances, much less any damage, in the Deccan area south of the Satpuras. It is only when the area shaken by the Koyna quake is fully investigated, mapped and the isoseismal lines carefully delineated that any worthwhile deduction can be drawn regarding the origin or the cause of this earthquake.

From the seismograph data so far collected and the area affected by the quake to varying degrees of intensity, as casually reported in the press, some tentative deductions can be made regarding the nature of the Koyna quake. The views presented here may be regarded as provisional till the area is fully and carefully mapped and the seismic data from the 3 or 4 observatories within the area are published and correlated. These views are:

(1) There is no doubt that the Koyna quake is of tectonic origin and not caused by any local subsidence, such as the collapse of an underground cavern; such caverns or chambers are known to exist in the lava-flows underlying Koyna up to a depth of over 4000 ft. Also the assumption that it was due to pressure of water of a large overlying reservoir, or its seepage underground, triggering off any weak structures under strain, cannot hold because of the magnitude of the affected area of Deccan.

(2) It is apparent that this is a deep-focus quake, from the wide area shaken, encompassing the country from Surat in the north to Goa and Bellari in the south and from Ratnagiri to as far as Hyderabad from east to west, an ellipse covering nearly 75,000 sq. miles. The depth of focus of an earthquake has close relationship with the extent of ground disturbed. The focus lies most probably on the basement crystalline complex, belonging to Dharwar system of rocks, underlying the 5000 ft of horizontally bedded lava-flows covering this part of the Deccan. Unlike the undisturbed lava-flows, the Dharwar rocks are closely compressed, plicated and faulted.

(3) From the evidence so far traceable from the few existing data available, it appears probable that the cause of this earthquake lies in the fault system of the Malabar Coast, a well-established tectonic feature of Indian geology. The straight outline of the Malabar Coast from Cutch to Cape Comorin is caused by a major fault — the Malabar fault — which took place in comparatively recent geological times — Pliocene period. A large slice of India subsided underneath the Arabian Sea and the Western Ghats arose to their present height as a consequence. It is probable, as in all major faults, the Malabar fault is accompanied by a system of parallel fractures and the Koyna quake may be due to a slippage along one of these satellite faults. The existence of a chain of hot springs along the Bombay-Ratnagiri line and a considerable rise of the isogeotherms noticed in the borings put down at Cambay by the Oil & Natural Gas Commission and the sharp flexure of rocks noticed at Panvel, near Bombay, are evidences of this fracturing of the crust. What forces have reactivated this long quiescent fault-zone is at present quite obscure.

(4) A correct evaluation of the direction and nature of forces which led to the Koyna earthquake can only be made after the whole ground encompassing the affected ellipse with its axes from Surat to Goa and Ratnagiri to Sholapur is carefully mapped and the isoseismal lines delineated on the map. These lines may throw light on the underground structural pattern of the area shaken. It is possible the isoseismal lines may reveal more than one focus of this earthquake. A careful investigation of the ground during mapping of this region should include any minor uplift or subsidence of the ground and whether any reactivation — increase, or decrease, or total stoppage of water — of the Bombay-Ratnagiri line of springs has taken place. Also borings under drilling within this region may reveal whether there has been any further erratic rise of isogeotherms along the fault-zone.

(5) The magnitude of the seismic phenomena along a large area and the intensity of destruction at the Koyna epicentral tract have, in my mind, greatly exaggerated the real intensity of the Koyna quake. The very local severe damage at Koyna, where over 80 per cent of the houses were destroyed and the large number of shocks, both preceding and following the earthquake, does not imply an earthquake of high intensity. The damage to property and houses is very probably due to defective construction of structures which were temporarily put

*Geological Adviser to the Department of Atomic Energy, Government of India, New Delhi.

up at Koyna. I do not agree with the assessment of the intensity of the Koyna quake at so high a figure as 7·5 on the Richter scale of intensity. If it is established that there have been more foci than one along the fault-zone mentioned above, the present earthquake is of insignificant intensity compared to the great Assam earthquake of 1950, or the still greater one of 1897, when the isoseismal V encompassed nearly 2 million square miles of country and mountainous slides scarred the Assam Himalayan ranges.

There is nothing unusual about the 'premonitary' shocks felt at Koyna since 1963 and the large number of after-shocks following the 11 December occurrence. These are usual accompaniments of tectonic quakes. The after-shocks will continue for some months, but with decreasing frequency and amplitude of vibratory motion.

International Symposium on Macromolecular Chemistry (1967)

SANTI R. PALIT

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32

THIS year the IUPAC Symposium was held in Brussels during 12-17 June, June 14 session being held in the university town of Louvain. The Prague symposium (1965) and the Japan symposium (1966) being rather unwieldy in attendance, size and subject diversification, the Belgian organizers planned to make it restricted in size by limiting the scope of the symposium to only the chemical and structural aspects of high polymers, and to a small number of referred and accepted papers. The total registration was 590, which included 90 from USA and 53 from USSR; the author and Dr Sardesai of Mobil Chemicals, USA, were the only participants from India though another five from India were in the preliminary list.

The official opening in an over-packed hall of 1300-seating capacity was enlivened by a plenary lecture by Dr H. Mark, the pioneering and undoubtedly the most popular polymer scientist. Dr Mark has been utilizing these occasions in all the symposia held in recent years to ably review in his inimitable style the latest development with regard to the physics and chemistry of high polymers, but this time he chose a somewhat different subject, viz. synthetic polymers and their relation to biochemistry, which is "the other end of the spectrum" with respect to the previous two lectures. Prefacing his lecture with a rapid survey of the factors responsible for the helix-coil transition in polypeptides, Dr Mark gave a brief account of the activating effect of neighbouring groups, for example, the oxidizability of SH groups on a polymer chain as affected by the presence of other groups, as also by their spacing in the polymer. He stressed on the easy oxidizability of SH groups in a polymer as compared to that in a monomer and attributed it to cooperative phenomenon in a polymer chain. The bearing of these facts to the behaviour of biopolymers is evident. He dwelt on the latest research on grafting polymers on enzymes, and synthetic polymers as enzyme analogues. He also gave a brief idea of some of the latest researches on biostable polymeric implants within the body which slowly release a drug *in situ*.

Dr Mark further mentioned the recent successful setting of fractured bones inside the body by rapid-setting epoxy polymers. He also discussed the latest work on dental polymers, viz. how polymer science is providing better materials and methods in the field of dentistry. He wound up his talk with a lecture demonstration of how a monomer (α-cyanohexylacrylate), which almost instantaneously sets to a tough film in contact with moisture, has been developed for use by surgeons to stop bleeding during surgical operation. The liquid is continuously sprayed on as the operation proceeds; it so effectively stops bleeding that the conventional tweezers can be dispensed with even with heparinized patients. This technique appears to be a major breakthrough in the field of surgical operation.

The four other plenary lectures were: (i) Transport and exchange phenomenon by Dr A. Katchalsky (Rehovoth, Israel); (ii) Some fundamental aspects of polymer reactions by Dr I. Sakurada (Kyoto, Japan); (iii) New methods of polymerization by Prof. C. E. H. Bawn (Liverpool, UK); and (iv) Supermolecular structures in polymers in relation with their synthesis and chemical structure by Prof. V. A. Kargin (Moscow, USSR).

Dr Katchalsky gave a scintillating exposition of coupled phenomena and steady state thermodynamics as related to flow through membranes, its bearing on reverse osmosis and on the most perplexing biophenomenon, viz. how living cells accumulate material against a concentration gradient, e.g. the so-called sodium pump. That salts have a tremendous effect on biopolymers was successfully demonstrated by him by fibres lifting huge weights on coming in contact with salt solutions. The highlight of the lecture was the demonstration of a machine where a few wheels went on spinning for hours, the whole energy being derived from the interaction of synthetic biopolymers and salt solution — an isothermal engine, so to say, with common salt and water as the fuel.

Dr Sakurada's lecture mainly covered the question of whether a functional group in a high polymer has the same activity or not as when present in a small molecule. Dr Sakurada dwelt over a whole range of reactions bearing on the topic and illustrated his viewpoint with results mainly obtained by his school. Forthright might it be said that a simple answer to Dr Sakurada's basic question is not possible and the result varies widely from system to system and is often highly sensitive to the physical environment. He illustrated his theme with data on hydrolytic and esterification reactions, and also on the effect of degree of polymerization on reaction rate. He also presented his results on equilibrium and kinetic studies with polymers of different kinds of tacticity, the isotactic variety often showing the fastest reactivity. He also illustrated with data the much stronger hydrolytic power of polymeric sulphonic acid, e.g. polystyrene sulphonic acid, as compared to monomeric sulphonic acid and HCl. He attributed it to hydrophobic interaction and presented evidence in its favour. It became evident from his lecture that reactions on polymers and by polymers (catalytic) may differ in degree and sometimes even in kind so much from their low molecular counterparts, that it constitutes a new field of study worthy of close attention.

Prof. Bawn's lecture was learned and informative. Lately, many novel methods of polymerization have been discovered and many have been reported in previous symposia. Prof. Bawn dwelt on a few of them and some new ones. He emphasized the striking development made during recent years in anionic polymerization, particularly in the following two aspects: (i) initiation through electron transfer process, and (ii) the feasibility of producing living polymers by avoiding termination. The electron transfer between an acceptor and donor [Eq. (1)] where the donor is a monomer and the acceptor is either a neutral molecule [Eq. (2)] or an ion [Eq. (3)] to produce initiating species was reviewed, isobutene being cited as a cationically susceptible monomer.

$$A+D \rightleftharpoons [DA \longleftrightarrow D^+A^-] \rightleftharpoons \dot{D}^+ + \dot{A}^- \quad \text{(ground state)} \quad ...(1)$$

$$CH_2=CHR+A \rightarrow \dot{A}^- + \dot{C}H_2\overset{+}{C}HR \quad ...(2)$$

$$CH_2=CHR+X^+ \rightarrow \dot{X} + \dot{C}H_2\overset{+}{C}HR \quad ...(3)$$

Three other general methods of anionic polymerization as illustrated below were discussed.

Ion-pair initiation ...(4)

$$PhC(Me)_2^-K^+ + CH_2=\underset{\displaystyle Ph}{\underset{|}{CH}} \rightarrow PhC(Me)_2CH_2.\underset{\displaystyle Ph}{\underset{|}{CH}}.Ph^-K^+$$

Initiation by NH_2^- in liquid ammonia ...(5)

$$K^+ + NH_2^- + CH_2=\underset{\displaystyle Ph}{\underset{|}{CH}} \rightarrow NH_2CH_2\underset{\displaystyle Ph}{\underset{|}{CH}}Ph^-K^+$$

Free ion initiation and propagation ...(6)

(i) $CH_3O^- + CH_2-CH_2 \rightarrow CH_3O.CH_2.CH_2O^-$ (O)

(ii) Dimethyl sulphoxide having high solvating power for cation and poor solvating power for anion, the $CH_3SOCH_2^-$, obtained by dissolving K in DMSO, initiates.

Prof. Bawn then discussed some recent work on cationic polymerization under the headings of initiation by (a) protonic acids and acid surfaces, (b) Friedel-Craft halides, and (c) carbonium ion salts. With respect to (a), he drew attention to the possibility of intermediate formation of esters; and with regard to (b), the role of cocatalysts was briefly discussed. With regard to (c), Prof. Bawn discussed the recent researches on initiation by triphenylmethyl cation (Ph_3C^+) and tropylium cation ($C_7H_7^+$), both of which polymerize tetrahydrofuran, vinyl allyl ether, vinyl carbazole, acenaphthylene, styrene and many other vinyl monomers. Three types of initiation are possible, viz. (i) addition, (ii) hydride extraction, and (iii) cation radical production by electron transfer. The tropylium salts on addition to olefin produce intense colour due to charge transfer complex formation and the course of reaction can be vividly followed. The initiating power is specific. *p*-Chlorophenyldiazonium phosphonate is an effective initiator for tetrahydrofuran to produce living polymers which can grow to very high molecular weight.

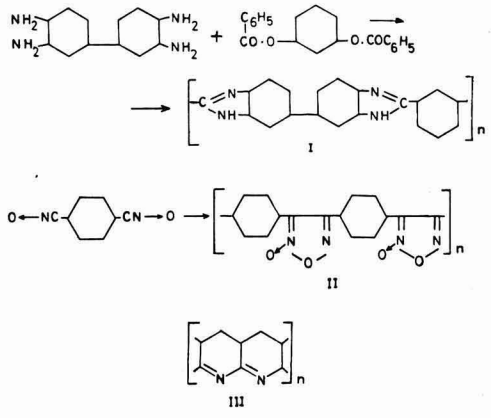
Prof. Bawn concluded his lecture by referring to the recent work on cation radicals as initiators of polymerization produced by chemical oxidation. Typical examples of oxidants for olefins are: $SbCl_5/CH_2=CCl_2$, $SbCl_5/SbCl_3$, $SbCl_3/O_2$, $AlCl_3/CH_3NO_2$ and $BF_3/Pb(OAc)_4$. Photo-induced formation of ion radicals is also possible, a typical example being tetrahydrofuran/maleic anhydride system under photo-excitation.

Prof. Kargin illustrated his lecture with a wealth of data and photograph on the physical structure of polymers. His basic thesis was that the macromolecules organize themselves into what he calls supermolecular structure depending on various internal and external factors and this structure plays an important role in determining the useful property of the polymer. The soundness of his basic thesis was very much evident from his lecture.

Besides the foregoing five plenary lectures, there were a number of main lectures as follows: (1) Synthesis and novel structure of polymers by Dr P. Rempp (France); (2) Infrared spectroscopy and polymer structure by Dr S. Krimm (USA); (3) Nuclear magnetic resonance and optical studies of polypeptide chain conformation by Dr F. A. Bovey (USA); (4) Selective membranes by Dr H. P. Gregor (USA); (5) On new chemical reactions of polymers by Dr R. C. Schulz (West Germany); (6) Advances and trends in the chemistry of polymers with a conjugated system by Dr A. A. Berlin (USSR); (7) Polymer degradation by Prof. N. Grassie (UK); (8) Cation polymerization of α,β-disubstituted olefins by Dr S. Okamura (Japan); (9) Thermostable polymers by Dr C. S. Marvel (USA); and (10) Optical activity and rotatory dispersion in synthetic polymers by Dr P. Pino (Italy).

The multipronged progress of high polymer science on a world-wide front is apparent from the

above list. Out of the ten lectures, four (Nos. 4, 5, 7 and 8) are deeply concerned with chemical synthesis. Dr Okamura's is a novel subject as his monomers are well known to have outstanding inertness towards radical polymerization, a property which has hardly ever received a satisfactory explanation. However, cationic and stereo-regulated polymerization is possible and Dr Okamura presented a detailed picture of the relative activity of *cis*- and *trans*-isomers as also the various kinds of tacticity (isotactic, diisotactic, erythreo-diisotactic, etc.) of the resulting polymers. Dr Marvel's lecture covered the same field as was done by Dr Mark in his opening lectures in Prague and Tokyo with some additional materials. Wearing a polybenz-imidazole jacket of golden brown colour, Marvel lectured on polymers which are stable up to at least 300°C. in air and to 500°C. in an inert atmosphere. Most of these are highly aromatic in structure often with heterocyclic units and are very difficult to fabricate. Typical examples are polyimides (trade name, Vespel and Kapton) obtained by polycondensation from pyromellitic anhydride and p,p'-diaminodiphenyl ether. Such polymers lose less than 10 per cent at 400°C. in 100 hr and char at 800°C. All such polymers in consideration of ease of processability have to be cured after processing for final cyclization. Polyphenyls and polyaromatic heterocyclics, e.g. polybenz-imidazole (golden brown to black, soluble in H_2SO_4, HCOOH, CF_3COOH), have been studied since 1961. Most evaluated has been (I) and its oxaimidazole analogue. Terepthalonitrile oxide polymerizes in solution to a thermostable polymer (II). The remarkable thermal stability of 'black orlon' (half-charred polyacrylonitrile) is well known and is generally attributed to a ladder structure (III).



Many similar ladder structures have been synthesized and they are often dissolved in dimethyl acetamide in the partially laddered state and after being cast into films are finally laddered as much as possible. A complete ladder structure seems not to have been obtained so far. The high thermostability of these partially laddered structures indicate that 600-650°C. may not be the final limit which can be obtained from such structure.

Dr Schulz made an intensive study of the intricate organic chemistry of macromolecules particularly on the following aspects: (i) new reactions on polyacroleins; (ii) new reactions on polymers with anhydride, carbonate or lactone groups; (iii) isomerization on macromolecules; (iv) asymmetric synthesis on polymers; and (v) preparation of polyradicals. It is evident that organic chemists have started in right earnest to use the macromolecules as the reactive units and a new domain in chemistry is in course of being discovered and consolidated. Dr Schulz derived a kind of aesthetic satisfaction in pointing out that with the discovery of stable polyradicals, for example, of the triphenylmethyl type and the DPPH type, all the three possible types of macromolecules, viz. neutral macromolecules, ionic macromolecules (polyelectrolytes) and polyradicals, have now well-characterized representative examples.

Besides the lectures, 92 papers were presented personally by one of the authors. The organizing committee took particular pains to include only those papers in the final programme where it was assured of personal presentation by one of the authors.

The main theme being structure and chemical transformation, there were a few papers on structural (including crystallinity) and conformational studies with the help of physical methods, viz. IR, NMR, ESR and X-ray. There were also isolated papers on physical studies on diffusion in polymers, adsorption by polymers, ion-exchange, membranes, semipermeable polymeric membrane and the like. A new trend, however, was noticeable. There were much more than the normal quota of papers on chemical reactions with the preformed macromolecules as one of the reactive units. Some typical examples are: initiation by lithium derivatives of polymers (similar to initiation by lithium alkyl); catalysis by poly-4-vinyl pyridine; reaction between carboxy carbene and unsaturated polymers; intramolecular rearrangement in polymers; transformation of polyheterocyclics; reaction of polyimides and hydrazine; Hofmann reaction on polyacrylonitrile (presented by the writer); chelate formation between Cu^{2+} and isotactic polyacrylic acid; photolysis and photo-oxidative degradation of polymers; thermal degradation of polyvinyl acetate and of cyclolinear polyphenyl siloxanes; varied kinds of grafting on 'dead' and 'living' polymers through a number of different experimental approach.

All kinds and types of polymerization were presented, anionic appearing to be more under attention. Cyclocopolymerization preceded by charge transfer complex formation was a novel observation. There were just a few papers on polycondensation involving polyesters, terylene and polyarylsulphonyl chloride. There was a couple of papers utilizing the recent idea of polymerization on a polymer matrix.

Initiators are varied and sometimes novel, to name a few: alkali through H-transfer mechanism, alkali at 420°C. (ethylene), trialkyl aluminium/dialkyl zinc, $ZnCl_2/AlBr_3$ (isobutylene), Ziegler-Natta catalysts (N_2- and O_2-containing monomers),

soluble complex (acetylene), boron compounds (diazoalkanes), Ni-carboxyl, lithium derivative of polymers, carbon black (styrene), photo-sensitive complex and photo-polymerization.

Besides the polymers derived from the common monomers, many other polymers were reported, a study of which shows the present preoccupation in this area of research. Semiconducting polymers, viz. highly conjugated polyenes, polyaniline compounds (its leucobase and oligomers), polyporphyrazin, etc., appear to have been receiving a good deal of attention. Some other interesting synthetic polymers are as follows: polychromic polymers, photo-sensitive polymers, polymers containing higher valent iodine, polyisonitriles, polyimides and some other thermostable polymers, polyampholytes, redox polymers based on pyrazolo quinones, optically active polymers (polyamides, poly-alkyl vinyl ketone), trifunctional star polydimethyl siloxane, polyindigo, etc. Evidently a new organic chemistry is in making.

Hospitality was in abundance, there being a reception almost every evening, the hosts being the city, the university and the Society of Chemical Industry. The symposium was concluded by an official banquet after the customary thanksgivings.

International Symposium on Protein Foods & Concentrates: Processing, Consumer Acceptance & Marketing in Countries of South & South-East Asia

AN International Symposium on Protein Foods and Concentrates, sponsored by the Council of Scientific & Industrial Research and the National Institutes of Health (USA), was held at the Central Food Technological Research Institute, Mysore, from 27 June to 4 July 1967. Over 150 participants including representatives of research and technological institutes and industry, both from India and abroad, attended the symposium. Invited papers on various aspects of protein programmes were presented and discussed.

The topics discussed in the 10 technical sessions of the symposium were devoted to: (1) General aspects of protein foods; (2) Economic aspects (resources); (3) Public health and clinical aspects; (4) Toxicology; (5)-(7) Technology and economics of production — concentrates and isolates; (8) Blends and protein-rich formulations; (9) Amino acid production and supplementation; and (10) Consumer acceptance and marketing.

General Problems

The general themes of the symposium were concerned with the nutritional, clinical and public health aspects of protein foods and the production and distribution of such products. Attention was focused on the fact that greatest damage due to protein malnutrition occurs during the first two years of the child when most of the nervous system is formed, thus affecting the whole future learning and behavioural pattern of the child. In India, most of the pregnant and lactating women are undernourished and likewise there is a high incidence of under- and malnourishment among children. In addition to adequate protein in diet, the need for proper balance of different nutrients was emphasized.

Psychological and nutritional factors in clinical investigations are of significance and for such investigations growth studies are considered to be a most reliable method. However, there is need for caution in interpreting the results because of the difficulty in providing suitable controls and also because of the possible incidence of various infections of the subjects in field trials. The effectiveness of public health and applied nutrition programmes is intimately related to population density, particularly in countries like India, and a plea was made for the production and supply of low-priced protein foods to the needy sections of the society. It was pointed out that despite extensive studies on protein foods, no solution has been found to the problem. Discussion centred round the following basic approach: Considering nutrition as a social need, whether the programmes should aim at providing protein foods for the less privileged masses or not. Although the social need was conceded, it was argued that it might not be possible to make an impact with a large group of people and that a beginning made even with a small section of the society would release more food for the masses.

Raw Materials and Technology

Oilseeds — The availability of oilseeds for producing protein concentrates is conditioned by a number of factors. Oilseeds are grown primarily for oil, and the producer has no incentive to produce protein from oilseeds. Thus there is need for socio-economic reorientation of various programmes in agriculture and technology, with particular emphasis on the protein problem. It was suggested that export of cake be banned and effective programmes be instituted for obtaining fertilizers and cattle feeds from non-food sources.

The progress in the technology of production of protein concentrates and isolates from different oilseeds was reviewed. The main points emerging from the discussions thereon were as follows.

In the light of extensive work on different types of soybean protein concentrates and isolates in USA and elsewhere, it was suggested that the production and use of soybean protein concentrate in various protein foods be encouraged and supported in countries where soybean could be grown economically.

Most of the technological problems involved in the production of edible groundnut flour in India have been solved and the value of such flour, suitably supplemented, has been demonstrated. The general view was that high priority should be given to large-scale processing of groundnuts to get edible quality protein-rich flour. Also, the work on the production of groundnut protein isolate has reached an advanced stage and has been handed over to industry for exploitation. Despite its high cost, the isolate has potentially wider uses than the flour. The disposal of large amount of deproteinized fluid (whey) is a serious problem and needs attention.

Giving statistics on the availability of cottonseed in India, a process for the production of edible cottonseed flour was also described which involves no need for foreign exchange and technology. Effective measures for large-scale production of such flour were recommended so that the total protein availability is increased and the import of edible oil is stopped.

The details of a process for the production of coconut protein isolate, developed in Philippines, were presented. In the light of experience gained on protein isolates, it was felt that emphasis should be on the use of whole coconut and the meal from it rather than on the isolate. The availability of this material in abundance in certain regions demands that high priority be given to the work on edible coconut meal.

An industrial process, developed in Mexico, for the production of high quality sesame meal was described. In this process, oxalate toxicity of the meal is removed by removing the seed coat, and the bitterness of the meal is removed by cooking. Sesame meal due to its high methionine content is a good supplement to vegetarian diets.

Fish

Attention was drawn to the abundant fishery resources of the world and to the tremendous scope for exploiting them; the main emphasis was on increasing fish consumption. The most obvious problems are the use of modern techniques and equipment, and the provision of facilities for the formation of cooperatives and limiting of landing areas was suggested. To overcome the high cost of canning and transport difficulties, bulk packing of fish was recommended.

A process for the preparation of fish protein concentrate developed in USA, based on solvent extraction of fish, was reported to have great promise. However, the problems of odour, flavour and cost still need to be overcome for making large-scale production of fish protein concentrate a viable proposition.

Studies on the development of various fish flour-based foods in India were reported and a suggestion was made for setting up small production units. It was felt that national and international agencies should give serious thought to the marketing and promotional aspects of fish foods. Future lines of work to improve the quality and other characteristics of such foods were indicated during the discussions.

New Sources of Protein

The work on the scope of leaf protein for edible purposes carried out during the last three decades was reviewed. A report on the work done in India was also presented. Attention was particularly drawn to the general nutritional efficiency of leaf protein and to the potentialities of increasing protein supplies from land through this approach. The need for systematic work in the protein deficient regions and drawing experts from different disciplines into the programme was stressed. With the abundant scope for utilizing the byproduct vegetation of green vegetable and other commercial crops, it was generally felt that more intensive investigations were called for so as to develop an integrated programme for industrial production of edible leaf protein.

The scientific and technological problems involved in the production of protein from petroleum hydrocarbons were discussed. In India, work on the feasibility of bacterial production of protein from methane, free from carcinogenic contaminants — a problem encountered in the production of yeast protein from petroleum — is hampered due to the non-availability of natural gas. However, it was felt that research on the production of single cell protein from petroleum and other sources should be encouraged.

Improvement of Cereals for Protein Content and Quality

Reviewing the progress of breeding programmes aimed at improving the protein quality of cereals and their yields, it was reported that large areas of land are being brought under high yielding strains of wheat, rice and sorghum in India. The work on forage crops was restricted to increasing yields, with no attention at present to their protein content and quality. Practically all work on quality improvement is concerned with increasing the lysine content of cereals, and no attempt is made to increase the methionine level in lysine-rich pulses, commonly used in India.

Problems of Toxicity

The occurrence of toxic amino acids and proteins and other toxic factors in legumes, including a wide group of glycosides and those causing favism and/or having antivitamin activity was discussed. The main points brought out were that although toxicity is likely to be present in most foods, its level becomes physiologically harmful only in a few extreme cases, and that adequate heating and soaking of legumes usually remove the toxic factors present in them. The chemical nature of most of these factors and their role in human nutrition are still to be investigated.

Studies on the reduction of gossypol content of cottonseed flour, a serious obstacle in its effective

use as food, have shown that exposure to oxygen lowers both bound and free gossypol without damaging the protein quality of the product. The newly developed glandless variety of cottonseed is almost free from gossypol.

The work at the Massachusetts Institute of Technology, Boston, has indicated the possible occurrence of aflatoxin in a wide variety of feeds. Subsequent studies have been concerned mainly with the practical significance of the incidence of aflatoxin, development of sensitive assay methods, measures for the prevention of development of aflatoxin and its removal during processing of food materials. In a review of the detoxification studies on groundnut in India, it was claimed that treatment with hydrogen peroxide not only removes aflatoxin but also bleaches the product without damage to protein or fat. The main problems in the detoxification techniques are their practicability and economics. It was not felt practicable to make detoxification a part of the final processing operation; it was suggested that control measures should be taken of all stages.

In the general discussion on toxicity in food materials, stress was on the importance of biological testing of all new or modified products, particularly those from processes involving drastic treatments. In such cases, the need for a sequence of tests was emphasized, viz. acute toxicity tests, subacute tests, tests using large animals, tests through several generations of animals, and tests with materials stored for short and long intervals. It was stressed that the problems of insecticidal residues and other physiologically deleterious factors needed more intensive studies.

Improvement of Protein Foods by Amino Acid and Mutual Supplementation

Methods for improving protein quality by amino acid supplementation of cereals and protein concentrates along with cost estimates for such fortification were reviewed. The results of studies conducted in Guatemala on amino acid supplementation of different vegetable protein mixtures have emphasized the need for proper balancing of the added amino acids with those already present in the original material.

Studies conducted in India have brought out that protein blends of high nutritive value could be obtained by mutual supplementation of deficient amino acids through a judicious mixing of two or more food materials of vegetable origin. Any residual deficiency could be overcome by further fortification.

Introduction of large-scale fortification of food materials with amino acids should be preceded by extensive testing with two or more animal species and complete information on the clinical performance of the fortified foods and their optimum dosage. The technological aspects of fortification of whole grain and/or flour are still to be solved; the effects of processing and cooking on the amino acids as well as the economics of fortification need detailed study.

On the production of amino acids by microorganisms, particularly lysine, considerable headway has been made in Japan. The microbial process was considered to be the most economical in regions with abundant availability of carbohydrates, like molasses and other materials; a multifermentation approach helps in further economizing the process. During discussions, information on the production of lysine by a continuous synthetic process based on caprolactam, developed in the Netherlands, was provided. The process is reported to have the special advantage of easy control with no danger of contamination, etc.

Processing of Protein Blends and Foods

An infant food and a weaning food, both ready-to-serve, based on groundnut proteins and toned milk, with half the protein derived from vegetable sources, and a variety of processed foods developed at the Central Food Technological Research Institute, Mysore, were reported. The foods possess satisfactory nutritive efficiency and acceptability in trials with children. Investigations are being undertaken to remove the groundnut flavour completely from the products.

Information was presented on the programme under way in Philippines on the production of protein foods for infants and children from the available vegetable sources. The project represents a cooperative effort of several laboratories with a national committee to coordinate the work. A food product based on rice, with added soya and fish, to provide high protein and other nutrients was reported to induce significant improvements in children in trials in South Vietnam. It was pointed out during the discussions that, because of an overall calorie deficiency, both in control and in test diets, it was not easy to assess the efficiency of protein supplementation correctly.

Details of the method of preparing *tofu* and other soybean based fermented foods in Japan were presented. No other oilseed has so far been tried for this purpose.

Processing techniques, involving precooking, incorporation of proteolytic enzymes and subsequent dehydration, to get commonly used pulses in a form fit for quick cooking at high altitudes were described. The problems of cooking other food materials at high altitudes were also discussed.

The advantages of the Wenger process, based on short time/high temperature cooking, in developing various formulations from full fat soya flour were presented and the possible application of this process to a wide variety of food products indicated. One of the significant advantages of this method is the total destruction of microbes during processing. It was generally felt that this principle has great potentialities for exploitation.

Consumer Acceptance and Marketing

As a corollary to the topics discussed earlier, the problems and experience of consumer acceptance and marketing were discussed in a special section. Indian experience, concerned with acceptance trials on a number of products, focused attention on ready acceptability of new foods either among groups which had developed no great discriminating capacity or where sophisticated foods were in use. The

experience of private concerns in production and marketing of nutritious beverages, with particular reference to Saridele in Indonesia and VITASOY in Hong Kong, has shown that their success was greatly conditioned by the availability of foreign assistance in terms of know-how, equipment and even raw materials, when necessary, and that the promotion compaigns helped a great deal in a wide acceptability of their products.

Successful marketing is subject to social changes and appeals. The need for intercommunication among industry, government and technology sectors was stressed and also for a market-oriented policy to motivate participation by private industry.

An interesting analysis of the current pattern of production and distribution of oilseed-based protein foods was presented in a survey report covering a score of developing countries. The production of the foods is done mostly by local private firms, but as subsidiaries of foreign establishments. With most of the basic research restricted to the parent establishments, the applied and developmental studies are done in local centres. The distribution is mostly through the governmental and other institutions, only a small fraction going to retail trade.

Summation

The symposium was useful in bringing together experts on different aspects of protein problems and programmes. It became obvious from the deliberations that the production of protein concentrates and that of processed foods and blends is greatly conditioned by the availability of raw materials. However, the discussion on legumes as a major protein-rich and lysine-adequate raw material was inadequate.

The recommendations made at the closing session included among others the need for emphasis on the production and distribution of protein foods, the practical impact of which would be known only from the results to follow. The seriousness of the problem was recognized more than two decades ago and several conferences have been held since then. Time and again emphasis is laid on the existing channels of production and distribution with not much success. A serious rethinking on these measures is called for to achieve positive results.

Council of Scientific & Industrial Research : Meetings of the Board & the Governing Body

At their meetings held in New Delhi on 24 and 25 November 1967, the Board of Scientific & Industrial Research and the Governing Body of the CSIR sanctioned 93 new research schemes. Approval was accorded in principle to a proposal to give financial assistance to the Automotive Research Association of India, Bombay.

The following are some of the other important decisions taken: (i) The recommendations made in the Reports of the Fourth Plan Committee of the CSIR and the Nihar Ranjan Ray Committee as commented upon by the Group of Scientists were approved. (ii) The Directors will decide about the recruitment to vacant posts, within the framework of the budget allotment and certain basic guidelines, with the approval of the Executive Councils. (iii) A committee should be appointed to identify a few major projects of importance which the laboratories could undertake during the next few years. The consensus of opinion was that where 'know-how' was easily and readily available, this should be purchased and research and development work should be directed towards adaptation of such technologies and further improvements thereon. (iv) Publication of the collected works of Prof. Meghnad Saha under a scheme sponsored for the compilation and publication of important scientific papers of distinguished Indian scientists in the form of collected works was approved. (v) It was decided that assistance should be given to the national laboratories in regard to evaluation, design, and engineering work on the processes developed, by creating facilities for this purpose either for individual laboratories or a group of laboratories engaged in researches in allied disciplines. Engineering consultant firms should be engaged for the preparation of project reports. At the Centre, there should be a small cell to assist the Director-General in the task of examining proposals concerning the setting up of pilot plants, etc.

Ultrasonic Stroboscopes for Dispersion Measurements*

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THREE types of ultrasonic stroboscopes are described in literature. The first type is based on the birefringence produced in certain photoelastic materials strained by ultrasonic waves[1], the second on the modulation of light in the diffraction orders produced by an ultrasonic grating[2], while the third makes use of the modulation of light by an ultrasonic beam as a stroboscopic source to illuminate a second wavefield, the final result being a combination of the total action of both the soundfields.

The first and second types of stroboscopes generally serve as light valves in television, etc. The third type is particularly suited for the study of the velocity of propagation of progressive sound waves and the ultrasonic and phase fields before a transducer.

Bär[3] was the first to develop a theory for these types of ultrasonic stroboscopes and was able to confirm his theoretical predictions experimentally, but he disclosed very few details about his experiments. Later, Fox and Rock[4] followed the methods mentioned by Bär. But a systematic study of Bär's stroboscopes has been recently made by Gessert and Hiedemann[5].

Experimental Procedure

A general optical arrangement used in ultrasonic stroboscopes is shown in Fig. 1. A source of light S illuminates the slit D which forms a bright secondary source at D′. The light from D′ is collimated by a lens L_3. This collimated beam of light passes through the glass tank T_2 containing the test liquid. The lens L_4 forms the image of D′ at D″ and, if the distances are suitably adjusted, an image of the wavefield in T_2 is formed on the screen S′. A second tank T_1 may be placed by the side of T_2 (between L_3 and L_4 or between D′ and L_3). When T_1 is placed exactly at D′, it turns out to be an interesting case where the slit is replaced by a point source and the optical arrangement is specially suited for the study of amplitude and phase variations in an ultrasonic field before a transducer.

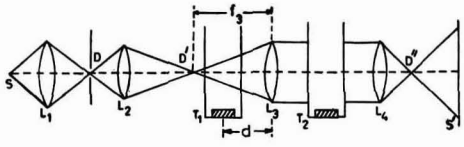

Fig. 1 — General optical arrangement for ultrasonic stroboscopes [S, source of light; D, slit; L_1, L_2, L_3 and L_4, lenses; D′, secondary source; T_1 and T_2, tanks; D″, image of D′; d and f_3, distances of T_1 and D′ respectively from L_3; and S′, screen]

Discussion

When both the tanks are kept side by side between L_3 and L_4 and the two quartzs are adjusted to produce anti-parallel sound beams perpendicular to the incident parallel light, the intensity distribution $I(x)$ of the emergent light at a distance x from the transducer is given by

$$I(x) = \tau\left[1-\tfrac{1}{2}\cos\frac{2\pi x}{\lambda/2}\right] \qquad ...(1)$$

This intensity distribution was experimentally verified by Giacomini[6] and is, in fact, similar to the intensity distribution characteristic of a standing wave, where the distance between two consecutive maxima is equal to half a wavelength of sound.

However, for parallel positioning of the sound beams, no line appears when both tanks contain the same liquid, i.e. when the wavelengths of sound in each tank are exactly equal. But, when the tanks contain liquids of different velocities, there exist two different wavelengths λ and λ' for the same period τ and the observed intensity becomes

$$I(x) = \tau[1-\tfrac{1}{2}\cos\{2\pi x(1-\lambda/\lambda')/\lambda\}] \qquad ...(2)$$

The separation Λ between intensity maxima becomes larger than that for anti-parallel waves in the same liquid and is given by

$$\Lambda = \frac{\lambda}{1-\frac{\lambda}{\lambda'}} \qquad ...(3)$$

Bär pointed out that this arrangement may be specially suited for comparison of two velocities of sound. The velocities may be for different liquids or for the same liquid at different temperatures. A change in velocity may also be brought about by diffusion of one liquid into the other so that the diffusion rates of liquids can be studied by this method.

Eq. (3) can be written in terms of the sound velocities (v and v') in the two liquids as

$$\Lambda = \frac{1}{\nu}\cdot\frac{vv'}{v'-v} = \frac{vv'}{\nu.\Delta v} \qquad ...(4)$$

where $v = \nu\lambda$ and $v' = \nu\lambda'$.

This relationship is illustrated in Fig. 2, taking $v' = 1500$ m./sec. for water as standard liquid. The graph is between Λ and Δv $(= v'-v)$. The fringe width Λ becomes extremely large and this arrangement is very sensitive for small velocity differences of about 20 m./sec.

Hiedemann claimed an accuracy of 99·5-99·7 per cent in velocity determination by this method.

*Paper presented at the convention organized by the Physical Research Committee of the Council of Scientific & Industrial Research at the Banaras Hindu University, Varanasi, in March 1967.

By using extended and homogeneous wavefields at higher frequencies of about 20 Mc/sec. the accuracy of this method can be enhanced to a value of $1{\cdot}1\times10^{-5}$, i.e. 1 in 1000 m. of velocity. As such, this method is suited for precise velocity measurements only at high frequencies.

When the tank T is in divergent light between D′ and L_3, an apparent enlargement of the fringe width takes place. If the magnification is $m = \lambda'/\lambda$, then Λ, the fringe width, can be written as

$$\Lambda = \frac{\lambda}{1-\frac{1}{m}} = \frac{\lambda}{1-\frac{\lambda}{\lambda'}} \qquad ...(5)$$

The relationship between d (the distance between the tank and the lens) and m (Fig. 3) is given by

$$m = \frac{1}{1-\frac{d}{d_{max.}}} = \frac{1}{1-\frac{d}{f_3}} \qquad ...(6)$$

Substitution of Eq. (6) in Eq. (5) gives

$$\Lambda = \frac{f_3.\lambda}{d} \qquad ...(7)$$

Therefore, depending upon the position of the tank T_1 (Fig. 3), the desired enhancement of fringe width can be obtained. A graphical representation of Eq. (7) is given in Fig. 4 for $f_3 = 75$ cm. The graph is a hyperbola as expected from Eq. (7) and verified by experiment.

When the tank T_1 is exactly at D′, i.e. at the focal point of L_3, the soundfield in the tank can be viewed directly. Hiedemann produced clear photographs of the amplitude and phase variations of the soundfield before a vibrating transducer with this set-up. He used it for a direct measurement of the Raleigh phase shift at a liquid-liquid interface.

The third type of stroboscope, described earlier, has been used by Giacomini[6] for precise velocity measurements in liquids even at ordinary frequencies in the range 1-10 Mc/sec. He designed an ultrasonic light modulator to serve as a stroboscopic source for a second ultrasonic beam. The optical arrangement and the details of the light modulator are shown in Fig. 5. Q_1 and Q_2 are a pair of quartz crystals vibrating at the same frequency and producing anti-parallel waves. This was equivalent to the setting up of a conventional standing wave, which generally needs a reflector with a critical requirement for its parallelism. This device operates continuously over a wide frequency range without any need for mechanical adjustment of the crystals. The light beam passing through this cell gets modulated at twice the frequency of the quartz Q_1 and serves as stroboscopic source to illuminate the soundfield generated by the quartz Q_3. Q_3 oscillates at twice the frequency of Q_1. When the frequencies are exact, the sound wavefield gives a system of sharp bright fringes F spaced a wavelength apart. A system of nearly 100 fringes can be easily measured with the help of micrometer screw capable of reading up to $0{\cdot}5\times10^{-4}$ cm.

This arrangement gave an accuracy of 1 in 1500 m. of acoustic velocity and was found suitable for the study of velocity variations in liquids with

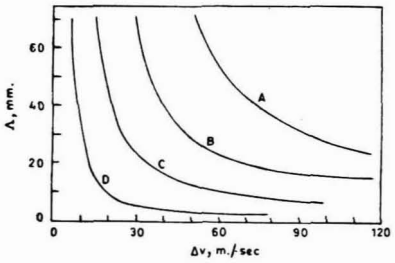

Fig. 2 — Theoretical plot of Eq. (4) for different ultrasonic frequencies (ν) [Values of ν: A, 1 Mc/sec.; B, 3 Mc/sec.; C, 5 Mc/sec.; and D, 10 Mc/sec.]

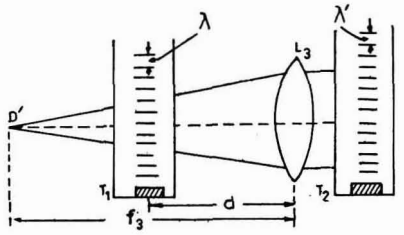

Fig. 3 — Optical arrangement for apparent enlargement of fringe width [D′, secondary source; T_1 and T_2, tanks; L_3, lens; d and f_3, distances of T_1 and D′ respectively from L_3; and λ and λ′, wavelengths]

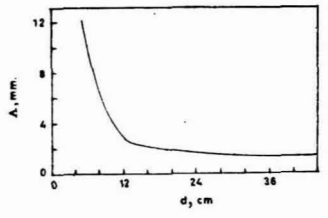

Fig. 4 — Theoretical plot of Eq. (7) for $f_3 = 75$ cm.

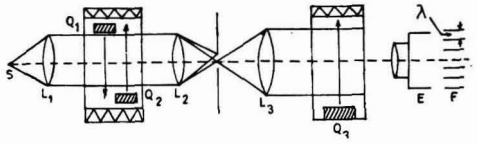

Fig. 5 — Optical arrangement for stroboscope with light modulator [S, source of light; L_1 and L_3, lenses; Q_1, Q_2 and Q_3, quartz crystals; E, eyepiece; F, fringes; and λ, wavelength]

frequency or amplitude of sound. Preliminary measurements were made in acetic acid and water. While a dispersion of 1 per cent could be detected in acetic acid, no evidence of dispersion was found in water. Observations made in palmitic[7] and lauric acids[8] showed no positive evidence of dispersion.

Summary

Three different types of ultrasonic stroboscopes are reviewed and critically examined from the point of view of precise velocity measurements. The first type is based on the birefringence produced in certain photoelastic materials subjected to ultrasonic waves, the second on the modulation of light in the diffraction orders produced by ultrasonic waves, while the third type makes use of the modulated light by ultrasonic waves as a stroboscopic source to study a second ultrasonic wavefield. Since the resultant effect is a combination of the total action of both the soundfields in the third type, it is found to be exceptionally good for precise sound velocity measurements. This set-up is capable of measuring directly the sound wavelength to an accuracy of $0{\cdot}5 \times 10^{-4}$ cm. Observations made in certain liquids with this stroboscope gave an accuracy of 1 in 1500 m./sec. of acoustic velocity.

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Surface Free Energy or Residual Force at the Solid-Liquid Interface

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IN tackling solid-liquid interface problems, rheologists consider adhesion to be more closely allied to mechanical properties than to interfacial forces. Fluid dynamicists analyse the boundary layer of fluid near the solid surface; based on the analysis, far-reaching developments in momentum, heat and mass transfer have taken place. The approaches adopted by the rheologist and the fluid dynamicist do not take into account the effect of solid surface with respect to liquid phase in solid-liquid systems. On the other hand, colloid and surface chemists seek relations involving surface free energies, contact angles and other parameters of thermodynamic significance. At present, the two schools are apparently at opposite ends. It is necessary to evolve a compromise between the colloid chemist's interfacial approach wherein emphasis is predominantly on specific problems involving the adherence of particular adhesive substrate combination and that of the rheologist and the fluid dynamicist in which the general aspect of adhesion or boundary layer is given greater prominence without regard to atomistic picture. Both approaches separately lead to certain results, but in the final analysis the two approaches have to be considered as complementary to each other so as to properly understand the phenomena of adhesion and boundary layer.

Interface Considerations in Momentum Transfer Studies of Various Flow Systems

The surface effect, which is of prime importance in the study of the solid-liquid interfacial phenomenon, is the wetting or non-wetting of solid surface by a liquid. In the flotation system, where the third phase (gas) is introduced, finely divided solids are separated from one another by the interaction of gas-solid-liquid interfaces; separation is facilitated through elaborate control of wetting or non-wetting of the surface of the solid (minerals). That the adhesion of mineral particles to air bubbles in aqueous solutions is related to the state of their surfaces has been established by many investigators. Attachment in aqueous solution is regarded to result from thinning of the boundary layers to such an extent that the molecular attraction forces acquire a sizeable magnitude[1].

The relationship between adsorption energy and the wettability of solid surfaces in aqueous solutions of surface active substances has been examined by Wada[2]. He attempted to derive isotherms for wetting and non-wetting of solid surfaces in aqueous solutions of surface active substances from a fundamental consideration of the adsorbability on solid surfaces.

In the present communication, the effect of solid-liquid interface on momentum transfer in a number of interrelated fluid flow systems — single-, two- and three-phase systems — has been considered.

Simple Static Experiments

Surface tension measurement and ring surface — To study the effect of ring surface on the surface tension values of a liquid, Du Noüy tensiometer was employed, once with the platinum ring and the second time with a thin paraffin wax coat on it. Data presented in Table 1 indicate that for the same liquid, the surface tension values vary considerably in the two cases[3,4]. Data of Young and Coons[5] who made a similar observation employing a ring-balance method are also presented in Table 1 for comparison.

TABLE 1 — EFFECT OF NATURE OF RING SURFACE ON SURFACE TENSION VALUES

Liquid	Ring surface	Surface tension dynes/cm.
DATA OF YOUNG AND COONS[5] (temp. 20°C.)		
$NiSO_4.7H_2O$ soln (28·1 oz./gal.)	Pt-Ir	74·8
do	Nichrome	71·3
do	Cu	75·6
Water	Pt-Ir	74·7
do	Nichrome	81·9
do	Cu	75·6
EXPERIMENTAL DATA (temp. 25°C.)		
Distilled water	Pt ring	71·4
Alcohol (6%)-water soln	do	57·4
do	Paraffin-coated ring	48·2
Distilled water	do	63·1

Measurement of adhesive force by static methods — Some simple experiments were performed to measure the pull weight required to tear apart the bottom circular face of a solid against the solid-liquid adhesional resistances[3,4]. Values of the force required to pull different solid surfaces (metallic, paraffin wax-coated, lampblack-coated) perpendicularly from the liquid surfaces (σ_L, 32-71·4 dynes/cm.) are presented in Table 2. It is evident that for each surface, the magnitude of the adhesive force decreases with decrease in surface tension of the liquid. With water, the force of adhesion is maximum with metallic surface and minimum with lampblack coat; the latter incidentally was found to strongly repel the water film.

Simple Flow of Fluids

Flow through a tube — To study the effect of surface wetting by a liquid on single-phase flow patterns, water was made to flow through the straight section (length 4·25 ft) of a glass tube and the usual pressure drop versus flow rate data were obtained. Later, the glass tube was given a thin uniform coat of hard paraffin wax on the flow surface and the experiment repeated. Data presented in Fig. 1 (A and B) indicate that the resistance to flow decreases on changing the surface from wetting to non-wetting, the effect being more pronounced in the laminar flow range. The effect gradually minimizes with increasing turbulent flow and hardly any effect is observed beyond $Re > 10{,}000$. Severity of disturbances in the flow brought about by the incipience of turbulence gradually makes the small effect due to surfaces insignificant.

Flow down inclined plane[6] — In previous theoretical studies on the flow of a liquid layer with one free boundary generally steady state conditions have been assumed, in which the amount of material per unit volume on the plate was constant. The changing condition at the liquid front in transient flow down an inclined plane distinguishes the present study from earlier work to provide the basis for a new relationship governing the flow

TABLE 2 — NET ADHESIVE FORCE (SOLID-LIQUID) FOR COATED AND UNCOATED BRASS PIECE

(Chemical balance method used for measuring adhesive force; truncated cone-shaped brass piece used; solid bottom, diam., 0·9 cm.; temp., 85·5°F.)

Liquid	Surface tension dynes/cm.	Wt of solid and adhering liquid g.	Net pull wt (uncorrected) g.	Net adhesive force g.
UNCOATED PIECE (wt*, 5·2286 g.)				
Distilled water	71·4	5·2370	5·7100	0·4730
Tap water	70·83	5·2372	5·7064	0·4692
Alcohol (6%)-water	57·4	5·2384	5·6450	0·4066
Aerosol-OT (0·01%)-water soln	38·2	5·2386	5·5200	0·2814
Benzene (commercial)	32·0	5·2297	5·4250	0·1953
PARAFFIN-COATED PIECE (wt*, 5·2456 g.)				
Distilled water	71·4	5·2466	5·650	0·4034
Alcohol (6%)-water	57·4	5·2468	5·575	0·3282
Aerosol-OT (0·01%)-water soln	38·2	5·2504	5·500	0·2496
LAMPBLACK-COATED PIECE (wt*, 5·2288 g.)				
Distilled water	71·4	5·2288	5·330	0·1012

*Including weight of thread.

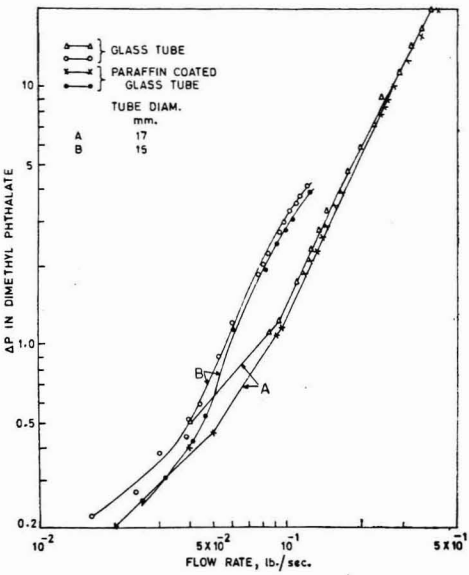

Fig. 1 — Effect of nature of surface on pressure drop with variation in flow rate

properties of Newtonian liquid and sheer-sensitive materials. As an outcome of the work the 'sheer-thinning index' is derived for certain types of dispersions.

The liquid stream changes its effective width under the influence of two variables: (1) wetting of the surface by the liquid, and (2) the shape of the flow stream as it emerges from the reservoir. The more readily the surface wets, the more quickly can the liquid spread in a direction transverse to the direction of flow, and as a result of the lowering of h, the average film thickness, by a process not taken into account in the general theory, and a slight change occurs in the slope of the flow decay curves.

It may be concluded that the slopes of the flow decay curves are identical for all Newtonian systems studied, provided the same reservoir of material is used in all comparisons. A slight dependence of slope on wettability of the surface is recorded.

Flow of annular jets of water[7] — In a recent study on flow mechanics for annular jets of water, it was observed that the wettability of the jet orifice has some influence on the annular jet lengths for varying liquid flow rates. The measurements were made at constant internal gas pressures of 0, 180 and 220 dynes/cm.[2] and varying liquid flow rates and velocities. The results for two different cleaning treatments, light coating with vaseline and rinsing with soap solution, of the jet orifice indicate that the variations in jet lengths in the two cases increase with increasing internal gas pressures. Reproducible results are obtainable only with a clean (non-wettable) orifice.

Flow of Fluid through Solid Particles

Flow through spherical packings — To study the influence of solid-liquid interfaces on the incipient fluidization point, sharp cuts of glass spheres with or without a thin coat of paraffin wax, were fluidized in a conventional batch fluidizer using water as the fluidizing liquid. Variations of the onset of fluidization point with the surface wetting or non-wetting by water are presented in Fig. 2. It is seen that for the same size, the onset of fluidization occurs earlier with glass spheres which have a higher wettability factor with respect to water than a paraffin-coated surface[3]. In an earlier communication[4], the force coefficient of the system for a fluidized bed was correlated with Reynolds and Froude numbers of the particles and a modified Weber number incorporating the wettability factor. The modified friction factor data for the fixed bed where the interface phenomenon is found to be more pronounced in the absence of particle dynamics were related to the wettability of surfaces[3,4].

Effect of wetting agents on viscosity, settling rate and flow property of chalk slurries — For studying the effect of wetting agents on transport of slurries, Alkatrage-C, Duponol LS, Gemex OG, Empilan and Duponol G were used as the wetting agents (Raut, D. V. & Rao, M. N., personal communication). The surface tension of water as well as of chalk slurries is lowered with the addition of wetting agents. This is also reflected in the foam stability values. It was observed that viscosities

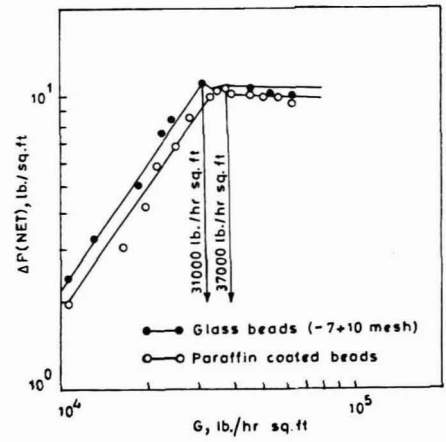

Fig. 2 — Effect of wettability of solid surface on the onset of fluidization

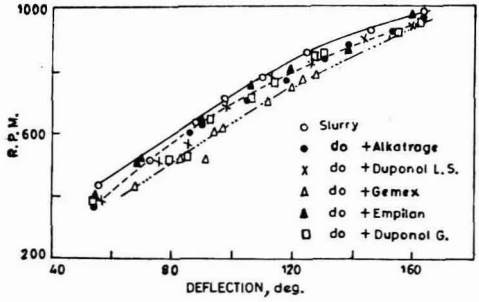

Fig. 3 — Effect of adding different wetting agents on viscosity of chalk slurry

of chalk slurries (23 per cent) vary on adding traces of the wetting agents (Fig. 3), although the viscosity is practically unaltered when the same wetting agents are added to water alone. The viscosity measurements were made using a spring calibrated rotational viscometer.

The settling curves for the 23 per cent chalk slurry with the addition of each of the above-mentioned wetting agents presented in Fig. 4 show that the settling rate of the same slurry changes with the addition of different wetting agents. These variations are consistent with the variations in slurry viscosities observed in the rotational viscometer.

Pressure drop versus flow rate data for chalk slurry (23 per cent), with or without the addition of the wetting agent (Gemex OG), were obtained in a copper tube of diam. 0·1285 in. and 119·5 in. long (Table 3). It is seen that for the same pressure drop, the flow rate decreases substantially on the addition of a little wetting agent in the slurry (10 ml. in 26 lb. of slurry).

The wetting agents increase the wettability of the powders with respect to water and consequently

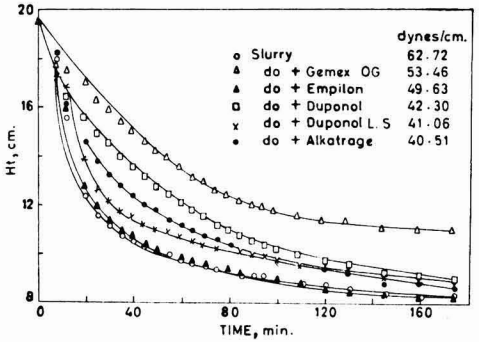

Fig. 4 — Settling curves for chalk slurry alone and with different wetting agents added

TABLE 3 — PRESSURE DROP DATA FOR CHALK SLURRY WITH AND WITHOUT WETTING AGENT

(Consistency of slurry, 23 per cent; sp. gravity, 1·155; pressure drop values determined using a copper tube of diam., 0·1285 in.; length, 119·5 in.)

Pressure drop (ΔP) in. Hg	Vol. collected ml.	Time sec.	Loss of head (ΔH) ft H_2O	Velocity (V) ft/sec.
		WITHOUT WETTING AGENT		
3·70	410	63·2	3·88	2·54
4·35	955	120·2	4·57	3·06
5·20	525	65·0	5·46	3·16
7·60	560	60·2	7·98	3·64
12·50	805	66·4	13·11	4·74
		WITH GEMEX OG ADDED (10 ml./26 lb. slurry)		
4·0	80	30·0	4·20	1·042
4·5	120	50·0	4·73	0·940
5·5	100	22·8	5·78	1·715
7·1	101	14·6	7·46	2·705
7·8	79	11·0	8·20	2·805
9·0	93	10·2	9·45	3·500

the net drag forces between the solid and the liquid act more effectively so as to increase the shear stresses. This is reflected in the increased values of viscosities of slurries in the rotational viscometer, higher settling rates and higher pressure drop for the same flow rate.

Flow through textile filter media — The resistance to fluid flow of a variety of fabrics and filter media investigated by Cunningham *et al.*[8] was expressed by a modified Darcy's law as

$$-\Delta P = K\mu V \qquad ...(1)$$

where ΔP is the pressure drop across filter media; μ, viscosity of the fluid; V, superficial linear fluid velocity; and K, proportionality or resistance constant.

Much of the data for water exhibit markedly increased values of K compared to the data for air and the data for oil exhibit somewhat increased values of K. Thus, although the data for air could be correlated for all types of fabrics, attempts to correlate the flow data for water and oil in a modified friction factor versus Reynolds number plot failed. This may be primarily due to the wetting characteristics of the fluid towards the given filter medium. Tests with a surface active wetting agent added to water indicate a several-fold increase in resistance to flow for both Vinyon cloth and Terry cloth. The results of the above tests lead to the conclusion that wetting effects have a marked influence on the flow resistance of the liquid and cannot be neglected.

Three-phase (Solid-Liquid-Gas) Flow Conditions

The adhesion of spherical particles to a liquid-air interface was studied by Nutt[9] in connection with froth flotation. An equation was derived for the force and work required to detach the particles with or without coating on them from the interface as functions of solid and liquid densities, the surface tension and the angle of contact. The importance of solid surface properties in determining the adhesive force at the interface has been recognized in this work.

The adhesion tension, $\sigma_L \cos\theta$, is sometimes taken as a measure of the wetting power. Many methods are available for determining the surface tension of a liquid, but there are very few methods for measuring solid-liquid contact angles, particularly in the case of powders, methods involving direct observations at the solid-liquid interface being restricted to large particles. In the indirect method due to Bartell and Osterhof[10], the pressure exerted by a liquid entering a mass of the powder in the form of a compressed plug is measured. The displacement pressure and the mean capillary pore radius are related to the adhesion tension; from which the contact angle can be calculated, knowing the surface tension of the liquid.

If the plug were a system of uniform, straight capillary tubes of radius r, the pressure would be

$$P = \frac{2\sigma_L \cos\theta}{R} \qquad ...(2)$$

The difficulty lies in the fact that the pores between the particles are neither straight, nor of uniform bore, nor even of known cross-section. Bartell and Osterhof[10,11] circumvented these difficulties fairly satisfactorily, obtaining a value for R, the radius of the equivalent cylindrical capillary tube, by measuring the pressure set up by a liquid known to wet the powder completely, so that θ is zero, and also by measuring the rate of flow of liquids, under pressure, through the plugs, and applying Poiseuille's law for the flow through capillary tubes. The formula for flow through the plug becomes, when the unknown number of tubes is eliminated from the ordinary formula and the volume v of the liquid in the powder is introduced

$$Q = \frac{R^2 P v t}{8\mu l_0^2} \qquad ...(3)$$

where Q is the volume of liquid passing in time t under pressure P; l_0, the length of the tubes; and μ, viscosity of the liquid. The length of the tubes (l_0) taken as $\frac{1}{2}\pi l$, where l, the length of the plug, is introduced to account for the bending of the tubes around each particle of the powder, and some other complications.

Determination of critical solids holdup by bubble agitation — The critical solids holdup, i.e. the maximum quantity of solids that can be held in suspension in a liquid medium by bubble agitation, is an important prerequisite for the physical design of a batch catalysed bubble-bed reactor. Some aspects of the investigation[3] to obtain a generalized correlation for the critical solids holdup (H_s) were aimed at studying the solid surface properties affecting such holdup. For this, holdup data for the three-phase batch fluidized system, using air as the gas phase, water as the liquid phase, and quartz and coal powders as the solid phase, are presented in Fig. 5. For comparison, the H_s data for coal corrected for the Stokes' velocity group with respect to quartz are shown as the dotted line in Fig. 5. It is observed that the values of the critical solids holdup for coal are considerably higher than those for quartz under identical conditions, even after the Stokes' velocity group correction has been applied and the holdup is a function of the solid-liquid wettability parameter Υ' as

$$H_s \propto (\Upsilon')^{-3.0} \qquad ...(4)$$

where

$$\Upsilon' = \frac{\Upsilon_{\text{less wettable solid}}}{\Upsilon_{\text{maximum wettable solid}}}$$

and

$$\Upsilon = \frac{\text{net adhesive force for the solid-liquid interface}}{\text{surface tension force due to pure liquid}} = (1+\cos\theta) \qquad ...(5)$$

The critical solids holdup is thus a function of the solid surface properties and for solids of different degrees of wettability in a liquid, the solids holdup is much greater with a less wettable solid under identical operating conditions[12].

Entrainment of water drops by air bubbles — In an investigation on the entrainment of water drops by air bubbles released from a single submerged nozzle, the effect of the presence of solid suspension on the entrainment has been studied, employing three solids — coal, quartz and chalcopyrites — with different surface properties with respect to water (Banerji, T. S. & Rao, M. N., unpublished data). A slurry of 8 per cent consistency was prepared with each solid of −200+250 mesh (BSS) size and the average entrained drop sizes corresponding to various air flow rates were determined. Analysis of drop size data showed that at low range of flow rates, i.e. below the critical drop size, the size of entrained drops from the quartz slurry is minimum, with coal slurry coming next; drops entrained from chalcopyrites slurry are maximum in size (Fig. 6).

Factors affecting the performance of packed columns — From experiments on the distillation of deuterium oxide-water and hydrocarbon mixtures using wire mesh packings Norman and Hu[13] observed that the efficiency is determined to a large extent by the wettability of the packing surface. The HETP of a stainless steel mesh Stedman packing for the aqueous system ranged from about 2·5 in. at low boil-up rates to 7 in. near the flood point, whereas the HETP for the hydrocarbon systems varied from 1·5 to 3·5 in. The low efficiency with the aqueous

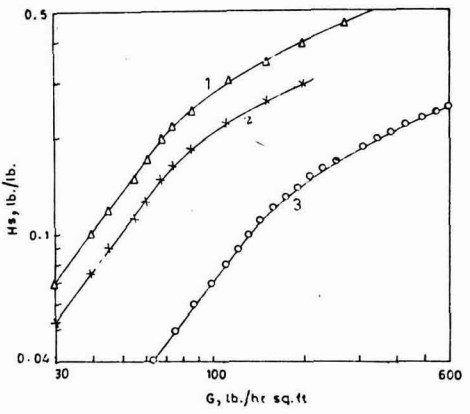

Fig. 5 — Critical solids holdup data as a function of solid surface characteristic [(1) coal (−25+35 BSS mesh); (2) coal corrected for U_t with respect to quartz; and (3) quartz (−25+35 BSS mesh)]

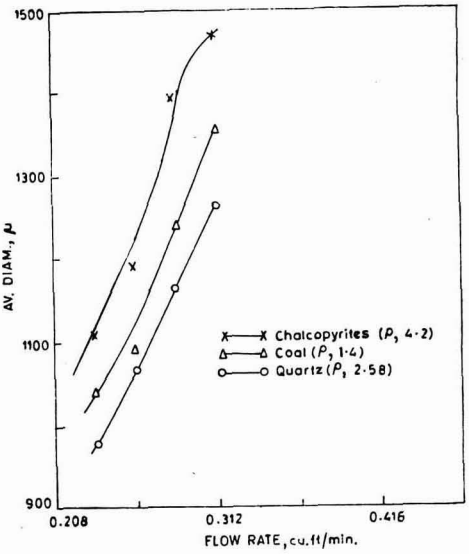

Fig. 6 — Effect of contact angle on entrainment of water drops [Nozzle diam., 3·75 mm.; col. diam., 5·5 in.; and submergence, 2·0 cm.]

system was due to the poor wetting characteristics of stainless steel, which caused the liquid to flow in streaks or rivulets over the packing surface. Treatment of the packing with boiling nitric acid had no effect, but treatment with potassium permanganate solution improved the efficiency of wetting and reduced the HETP to approximately the same range as that of the hydrocarbon systems. This improvement was caused by the deposition of an adherent film of manganese oxide on the metal. Similar results were obtained with ring packings made of

wire mesh. Phosphor-bronze packings were equally effective for the hydrocarbon and water systems.

It was further reported by Norman[14], from studies on the performance of sieve plates, that the contact angle between the liquid and the metal has a significant effect on the weep rate, and on pressure drop and bubble formation.

Thus, although the equations of motion used in the conventional fluid dynamic studies are devoid of the surface free energy terms, the residual force at the solid-liquid interface has to be taken cognizance of when attempting to make a fundamental approach to it.

Summary

The recent investigations on the influence of solid surface wettability on the flow properties of liquids have been reviewed. The treatment has been attempted under two broad heads: (1) studies on the measurement of solid-liquid adhesional forces by static methods, and (2) momentum transfer studies in dynamic flow systems. The dynamic systems considered include single-, two- and three-phase flow systems. It is concluded that for a rigorous analysis of the momentum transport in a dynamic set-up, wettability of the solid surface is an important criterion and cannot be neglected. Data obtained from experiments involving static methods indicate that the magnitude of the solid-liquid adhesional force depends primarily on the wettability of the solid surface.

Nomenclature

D = tube diam., ft
G = mass velocity, lb. (m)/ft^2, hr
ΔH = head loss, ft lb. (f)/lb. (m)
H_s = critical solids holdup, lb. (m)/lb. (m)
K = proportionality or resistance constant in Eq. (1)
l_0 = length of tubes, ft
l = length of plug, ft
L = tube length, ft
P = pressure, lb. (force)/ft^2
ΔP = pressure drop, lb. (f)/ft^2
Q = vol. flow rate, ft^3/sec.
r = radius of the equivalent cylindrical tube, ft
Re = Reynolds number, dimensionless
t = time, sec.
U_t = free settling velocity, ft/sec.
v = vol., ft^3
V = Superficial linear velocity, ft/sec.
γ = wettability factor = $\dfrac{\text{net adhesive force}}{\text{surface tension force}}$
γ' = solid-liquid wettability parameter
= $\dfrac{\gamma_{\text{less wettable solid}}}{\gamma_{\text{max. wettable solid}}}$
μ = viscosity, lb. (m)/ft sec.
π = physical constant (= 3·14159)
σ = surface tension, lb. (m)/sec.^{2}
θ = contact angle, deg.

Subscripts

s = solid
l = liquid

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Naturally Occurring Cyclopropanoids

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THE chemistry of natural products has gained momentum in the last fifteen years mainly due to the successful application of modern physical methods, a better understanding of the organic mechanistic theory and a clearer insight into the complex pathways of biogenesis.

Organic compounds containing small rings, especially cyclopropane derivatives, have posed many difficult problems in the past and, therefore, it is but natural that increasing attention is being paid to this class of compounds during recent years. This has been accentuated, more specially because of the discovery of a large number of naturally occurring compounds containing cyclopropane moiety. There has not been any recent review[1,2] on the chemistry of naturally occurring cyclopropane containing compounds and, therefore, an attempt is made here to present the recent developments in this field.

Naturally occurring cyclopropanoids can be divided into two classes, viz. isoprenoids and non-isoprenoids.

NON-ISOPRENOIDS

Only very few cyclopropane containing compounds are known which are not isoprenoids. They are listed in Table 1 and their structures are given in Chart 1. Except for an amino acid (V) and an alkaloid (VI), all of them are fatty acids.

The structure determination of these fatty acids mainly involves cleavage of the 3-carbon ring and identification of the cleaved olefinic acids[3-5]. Cyclopropenoid fatty acids in oils are determined quantitatively by the modified Halphen test and by their IR absorption at 1008 cm.$^{-1}$ (cyclopropene ring). Cyclopropanoid acids are sometimes estimated by their absorption at 1020 cm.$^{-1}$ (cyclopropane ring)[8,9].

Dihydrosterculic acid (III) is synthesized[10] from oleic acid by the addition of carbene to the double bond by the Simmons and Smith procedure[11].

Biosynthetic studies on cyclopropanoid fatty acids have shown that *Lactobacillus arabinosus* converts oleic acid to dihydrosterculic acid without passing through any intermediate involving the loss of vinylic protons of oleic acid. The additional $-CH_2-$ group originates from methionine methyl[10].

The structure of hypoglycin A (V), an amino acid with hypoglycaemic activity and the only one containing a cyclopropane ring, was determined by three different groups of workers[6,12,13]. Its synthesis[14] involves the production of a methylene cyclopropane system by the condensation of 2-bromopropene with ethyl diazoacetate in the presence of a copper-bronze catalyst followed by the dehydrobromination of the resulting ethyl 2-bromo-2-methylcyclopropanecarboxylate.

Cycloclavine[7] (VI) is, probably, the only non-steroidal alkaloid containing a 3-carbon ring system.

TABLE 1 — CYCLOPROPANE CONTAINING NON-ISOPRENOIDS

Name	m.p. °C.	Source	Ref.
Lactobacillic acid (I)	—	*Lactobacillus arabinosus*	3
Sterculic acid (II)	19·5	*Sterculia foetida*	4
Dihydrosterculic acid (III)	39-40	*Hibuscus syriacus* oil	5
Malvalic acid (IV)	10·5	*Malva verticillata*	5
Hypoglycin* (V)	200-6	*Blighia sapida*	6
Cycloclavine† (VI)	166	*Ipomoca hildebrandti*	7

*$[\alpha]_D$ +10·5°. †$[\alpha]_D$ +38°.

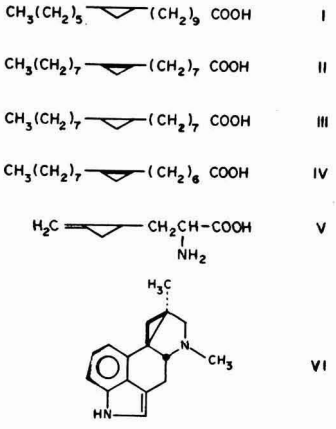

Chart 1 — Naturally occurring cyclopropane containing non-isoprenoids

ISOPRENOIDS

Almost all the remaining naturally occurring cyclopropanoid compounds belong to this class. The rather more frequent presence of cyclopropane ring in isoprenoids can be attributed to the fact that the incipient carbonium ion (or its equivalent) generated during its biogenesis has the distinct possibility of collapsing, by 1,3-elimination into the cyclopropane derivative in a vast number of carbon skeletons.

Monoterpenes

These are discussed under two heads: (i) normal monoterpenes arising via the usual biogenetic route,

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TABLE 2 — CYCLOPROPANE CONTAINING NORMAL MONOTERPENOIDS

Name	b.p., °C./mm.	n_D	$[\alpha]_D$	Source	Ref.
α-Thujene (VI)	152/699	1·4511	−49·3	*Boswellia serrata* Roxb.	15, 18
β-Thujene (VII)	147/739	1·4470	+110·7	*Artmesia vulgaris*	15, 18
d-Sabinene (VIII)	163/760	1·4672	+107·2	*Juniperus sabina* L.	15, 18
α-Thujyl alcohol (IX)	66-67*	—	−22·5	*Artmesia absinthium*	15
Isothujyl alcohol (X)	103/16	1·4630	+108·8	*Artmesia vulgaris*	15, 18
d-Sabinol (XI)	208/760	1·4850	+8·3	*Juniperus sabina* L.	15
d-Sabinyl acetate (XII)	—	1·4707	+79·3	*Juniperus scopulorum*	15, 19
α-Thujone (XIII)	74-75/9	1·4490	−19·9	*Thuja occidentalis*	15
Isothujone (XIV)	231/760	1·4508	+73·4	*Juniperus scopulorum*	15
Umbellulone (XV)	93/10	1·4832	−36·3	*Umbellularia californica* Nuttel	15
3-Carene (XVI)	168/705	1·4735	+15·97	*Pinus longifolia*	15, 20
4-Carene (XVII)	165/707	1·4759	+97·7	*Pinus sylvestris* L.	15, 20
Car-3-ene-5,6-epoxide (XVIII)	83/14	1·4792	−88	*Zieria smithi*	15
Chaminic acid (XX)	105-6*	—	−6	*Chamaecyparis noot katensis*	21-23
Chamic acid (XIX)	142/8	1·4998	+257	do	19, 21
Tricyclene (XXI)	66·5*	—	0	*Tsuja canadensis*	24, 25
Teresantalol (XXII)	122-4*	—	+11·6	*Santalum album*	26
Teresantalic acid (XXIII)	157*	—	−77	do	27, 28
Cyclofenchene (XXIV)	143/748	1·4537	−1·7	American turpentine oil	29

*Melting points, °C.

i.e. by the head-to-tail linkage of two isoprene units, e.g. thujane, carane, etc.; and (ii) abnormal monoterpenes whose formation cannot be explained as above, e.g. chrysanthemic acids.

Normal Monoterpenes

Saturated hydrocarbons of the two well-known classes of monoterpenes containing cyclopropane ring, viz. thujane and carane, are not known to occur in nature. All naturally occurring bicyclic and tricyclic monoterpenes containing a 3-carbon ring are listed in Table 2 and their structures given in Chart 2. Several reviews[15-17,30] have appeared on these monoterpenes and, therefore, a discussion on their structures or syntheses is not attempted here.

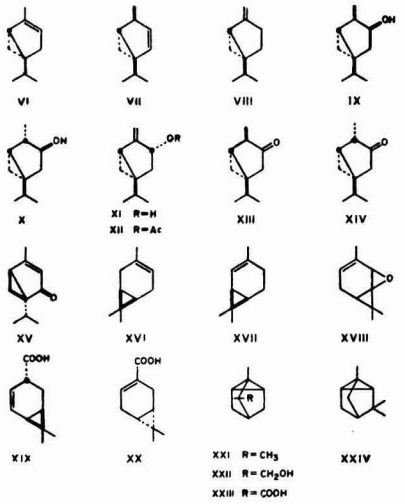


Chart 2 — Normal monoterpenes

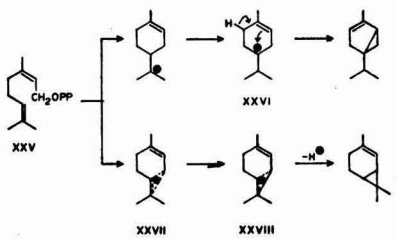


Chart 3 — Biogenesis of cyclopropanoid monoterpenes

The absolute configuration of thujane[18,31] and its oxygenated derivatives and the stereochemistry and reactivity of caranes[32-35] have been the subject of intensive study recently.

Biogenesis — The mode of formation of all these compounds in plants is now fairly well established. Studies with [2-^{14}C]-mevalonic acid have supported the postulate that geranyl pyrophosphate (XXV) is the precursor of all these monoterpenes. The biogeneses of α-thujene and 4-carene are described in Chart 3. Cyclization resulting by the double bond participation with the carbonium ion in (XXVI) leads to α-thujene and if the same intermediate ion is considered in a non-classical sense as in (XXVII), a 1,3-shift will produce (XXVIII) from which 4-carene is easily derived[36,37].

Abnormal Monoterpenes

Chrysanthemic acids — Among the simplest and the earliest known naturally occurring cyclopropane derivatives are the two acids (+)-*trans*-chrysanthemic acid (XXIX) and (+)-*trans*-pyrethric acid (XXX) (monomethyl ester of chrysanthemum dicarboxylic acid[38]). These, however, do not occur as free acids; instead they occur as esters with

TABLE 3 — CHRYSANTHEMIC ACIDS

Name	b.p., °C./mm.	n_D	$[\alpha]_D$	$\lambda_{max.}$ mμ	$\epsilon_{max.}$	Ref.
Chrysanthemic acid (XXIX)	117/5 (m.p. 17-21°)	—	+14·6	—	—	38, 39
Pyrethric acid (XXX)	135/0·1 (m.p. 84°)	1·4909	+88·7	239	—	40
Pyrethrin-I (XXXI)	146/0·0005	1·5252	−14·0	222	38800	38
Cinerin-I (XXXII)	136/0·008	1·5064	−22·0	221	21100	38
Jasmolin-I (XXXIII)	—	—	—	219	21500	41
Pyrethrin-II (XXXIV)	192/0·007	1·5355	+14·7	228	47500	38
Cinerin-II (XXXV)	182/0·008	1·5183	+16·0	229	27900	38
Jasmolin-II (XXXVI)	—	—	—	229	22900	41

certain cyclopentenyl ketols known as pyrethrolones, cinerelones and jasmolones. These are highly active insecticides and are isolated from commercial 'pyrethrum', an extract of *Chrysanthemum cinerariaefolium*. In Table 3 are given the physical properties of all the six known 'pyrethrins' and their structures are given in Chart 4. Their structure and stereochemistry are well established on the basis of sound chemical degradative and synthetic evidence.

Synthesis — The syntheses of chrysanthemic and pyrethric acids are best accomplished by the reaction of ethyl diazoacetate (XXXVII) with the appropriate olefinic compounds (XXXVIII)[42] (Chart 5). Other recent syntheses are the base catalysed intramolecular condensation of 3,3,6-trimethyl-4-hydroxy-5-heptenonitrile (XXXIX) followed by hydrolysis of the cyanide group and conversion of pyrocin (α,α-dimethyl-β-isopentenylbutyrolactone) (XL) through the chloro ester (XLI) to ethyl *trans*-chrysanthemate (XLII)[43] (Chart 5).

Biogenesis — The biogenesis of chrysanthemic acids is very interesting, since they cannot be formed by the usual 'head-to-tail' linkage of two isoprene units. Biosynthetic experiments have shown that both chrysanthemic and pyrethric acids are formed from two isoprene units (2 moles of mevalonic acid) and hence definitely should be isoprenoids[44]. It is, however, possible to visualize two isoprene units fused in an unusual manner ('middle-to-tail')[45] and arising from a carbene type of addition[44] to the olefinic bond of another unit of isopentenyl pyrophosphate (Chart 6). This suggestion finds support in that, monoterpenes, like artmesia ketone, isoartmesic ketone, etc., are postulated[46] to arise by the cleavage of such a vinyl cyclopropyl pyrophosphate. There is less likelihood for the possibility of formation of chrysanthemic acids through the cleavage of 4-carene, as suggested by Ruzicka[47].

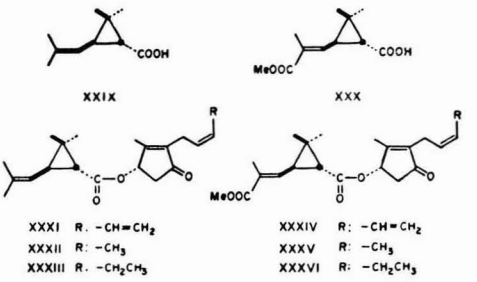


Chart 4 — Chrysanthemic acids

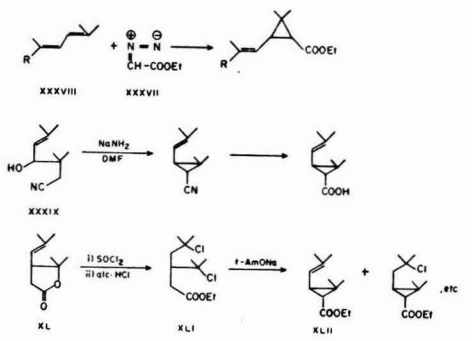


Chart 5 — Synthesis of chrysanthemic acids

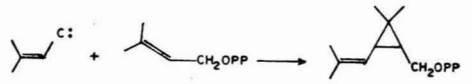


Chart 6 — Biogenesis of chrysanthemic acids

Sesquiterpenes

Most interesting naturally occurring isoprenoids containing the strained 3-carbon ring system are found among sesquiterpenes. These are listed in Table 4 and their structures are given in Chart 7.

Structure

The presence and exact location of cyclopropane ring in these compounds are discerned by (i) physical methods, (ii) degradation to a known derivative of cyclopropane, and (iii) cleavage of cyclopropane ring, and identification of the cleaved products.

Physical methods — Cyclopropane ring, when conjugated with an ethylenic linkage (vinyl cyclopropanes), exhibits UV absorption maxima in the region 204-10 mμ ($\epsilon \sim$ 5000-10,000)[62,67,72] (compare conjugated dienes, $\lambda_{max.}$ 214 mμ). Similarly, cyclopropyl ketones absorb at 210-15 mμ ($\epsilon \sim$ 3000-7000)[62,67,80,81] (however, see Kosover[82]) and when the conjugation of an α,β-unsaturated carbonyl group is extended by a cyclopropane ring, γ- to the carbonyl carbon, the new chromophore absorbs in

TABLE 4 — CYCLOPROPANE CONTAINING SESQUITERPENOIDS

Name	b.p., °C./mm.	n_D	$[\alpha]_D$	Source	Ref.
Calarene (β-gurjunene) (XLIII)	45/0·1	1·5051	+81·8	*Acorus calamus*, *Gurjun balsum*	48-50
Aristolene (XLIV)	—	1·5047	−98·7	*Nardostachys jatamansi* Roxb.	49
Aristolone (XLV)	100-1*	—	−339·4	*Aristolachia debilis*	48, 51
α-Ferulene (XLVI)	110/8	1·5041	+68	*Ferula communis*	52
β-Maaliene (XLVII)	82/1	—	−137	*N. jatamansi* Roxb.	48
(+)-β-Maaliene (XLVIII)	—	—	—	*Mentha piperita* Huds.	53
Maaliol (XLIX)	103-4*	—	+28	*Canarium samonense*	54, 55
(−)-Bicycloelemene (L)	—	—	—	*Mentha piperita* Huds.	53
— (LI)	—	—	—	*Chamaecyparis obtus*	56, 57
α-Cubebene (LII)	—	—	—	Schisandra fruits	58
β-Cubebene (LIII)	—	—	—	do	—
Cyclohimachalene (LIV)	—	—	—	—	—
Aromadendrene (LV)	122/10	1·4978	+24·5	*Metrosideros scandens*	59-61, 115
Alloaromadendrene (LVI)	130/4	1·4994	−21·6	*Perovskia scrophullariaefolia*	59-61
α-Gurjunene (LVII)	76/3	1·5010	−214	*Dipterocarpus turbinatus* Gaertn.	62, 63
Cyclocolerenone (LVIII)	136/5	1·5270	−400	*Pseudowintera colarata*	64
Viridiflorol (LIX)	75*	—	+4·0	*Melaleucioviridiflora*	60
Ledol (LX)	104·5*	—	+40	*Phebalium squamens* Labill	60
Globulol (LXI)	87-88	—	−42·3	*Eucalyptus globulus*	60
Spathulenol (LXII)	—	—	+56	*E. spathulata*	65
Palustrol (LXIII)	118/2	1·4888	−17·8	*Ledum palustra*	66
Thujopsene (LXIV)	120/10	1·5031	−110	*Thujopsis dolabrata*	67, 68
Hinokiic acid (LXV)	169-70*	—	−86	—	—
Mayurone (LXVI)	69-70	—	+253	—	69, 70
α-Santalene (LXVII)	116/6	1·4855	+6·6	*Santalum album*	71
α-Santalol (LXVIII)	166/14	—	+9·0	—	71
Nortricycloekasantalol (LXIX)	86/6	1·4839	−38·5	—	71
Linderene (LXX)	143-5*	—	—	*Lindera strychnifolia*	72
Linderene acetate (LXXI)	79-82	—	+25·7	—	72
Illudin-M (LXXII)	130-31*	—	−126	*Lampteromyces japonicus*	73-75
Illudin-S (lampterol) (LXXIII)	124-5*	—	−165	—	—
Laurinterol (LXXIV)	54-55*	—	+13·3	*Laurencia intermedia*	76
Debromolaurinterol (LXXV)	—	—	−12·2	—	76
Marasmic acid (LXXVI)	173-4*	—	+182	*Marasmus conigenus*	77
Longicycleme (LXXVII)	82/2	1·4888	+33·6	*Pinus longifolia* Roxb.	78
Carabrone (LXXVIII)	90-91*	—	+116·9	*Carpesium abrotanoides*	79

*Melting points.

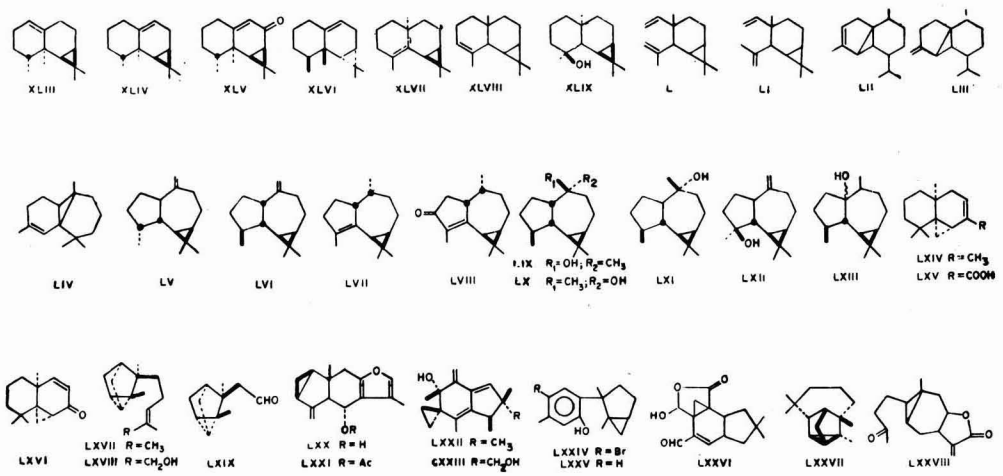


Chart 7 — Cyclopropanoid sesquiterpenes

the region 266-72 mμ (ε 10,000)[55,62,64,83]. However, there seems to be no bathochromic shift[52,87-90] in the absorption maxima of an α,β-unsaturated ketone when cross-conjugated with a cyclopropane ring (cf. umbellulone[84], lumisantonin[85], mayurone[69], etc.).

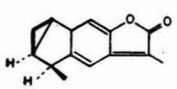
A hypsochromic shift in the UV maximum of epicyclocolerenone[63] ($\lambda_{max.}$ 253 mμ; ε 9300) compared to cyclocolerenone[64] ($\lambda_{max.}$ 264 mμ; ε 13260) and similar other observations[86] support the contention that interaction between cyclopropyl and carbonyl or ethylenic groups is most effective when the plane of the ring and the *p*-orbitals of the carbonyl group or the ethylenic bond, as the case may be, are parallel. This may be the reason for the absorption by certain vinyl cyclopropanes at abnormally high wavelength[89,91,92] ($\lambda_{max.}$ 220-5 mμ). However, it seems that no steric relationship between cyclopropane ring and phenyl group influences the UV spectra of phenyl cyclopropanes[93].

Cyclopropanoid compounds having at least one $-CH_2-$ group show two weak bands in the near IR region at 1·62-1·64 (ε 0·30-1·10) and at 2·21-2·23 μ (ε 1·0-3·0). However, terminal olefins also behave similarly[94].

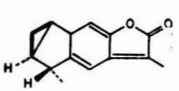
In the IR region a weak band at 3050 cm.$^{-1}$ (C-H stretching), a medium band near 1020 cm.$^{-1}$ (ring deformation) and another medium band at 886 cm.$^{-1}$ (C-H wagging) are used to characterize cyclopropyl group[95]. Tricyclene derivatives absorb[96] near 3050 and 854 cm.$^{-1}$. Compounds containing a *gem*-dimethyl group on a 3-membered ring exhibit only a single band in the symmetrical C-H bending region[97].

The protons on a cyclopropane ring are highly shielded and appear at about τ 9·78 in the PMR spectrum and this is attributed mainly as due to ring current effects[98]. The long-range shielding effect due to the anisotropy of the cyclopropane ring has been studied by various workers recently[99,100].

The configuration of the cyclopropane ring in linderene[72] is assigned by comparing the observed PMR signal pattern of the two protons at C-3 and C-4 of the two triene lactones (LXXIX) and



LXXIX



LXXX

(LXXX) derived from dihydrolinderene and isodihydrolinderene with those anticipated on the basis of Karplus equation, the findings being confirmed by proton decoupling experiments at 100 Mc/s. field.

Degradation to a known derivative of cyclopropane— The isolation of DL-*trans*-caronic acid from the complex mixture of decomposition products obtained by the alkaline permanganate oxidation of chamic acid was of great help in establishing the presence of a cyclopropane ring having a *gem*-dimethyl group in this monoterpenic acid[21].

Oxidation of illudin-S with permanganate yielded cyclopropane-1,1-dicarboxylic acid, and hence the conclusion that it contains a spiro cyclopropyl group[73].

Cleavage of cyclopropane ring — The cyclopropane group present in isoprenoids usually undergoes acid-

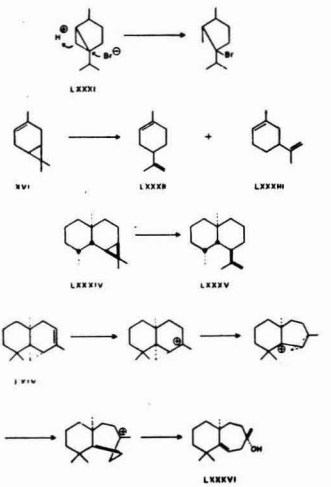


Chart 8 — Cleavage of cyclopropane ring in sesquiterpenes

catalysed cleavage according to Markownikoff's rule. This implies that the proton attacks at the most negative, i.e. the least substituted, centre with the incipient formation of the most stable carbonium ion[101-103].

For example, the 3-membered ring in thujane (LXXXI) opens under the influence of acid to give chiefly cyclopentane derivatives, while carene (XVI) gives, as is to be expected, both dipentene (LXXXII) and sylvestrene (LXXXIII) (see Chart 8).

However, in some cases, conformational aspects assume importance in determining the nature of the cleaved product. Maaliane (LXXXIV), for example, gives mainly one product (LXXXV) with equatorial isopropenyl group, resulting by the cleavage of the axial C_7-C_{11} bond although Markownikoff's rule predicts two products. Maaliol (XLIX)[54], aromadendrene (LV), cyclocolerenone (LVIII), etc., are other examples.

Vinyl cyclopropanes, which are easily susceptible to electrophilic attack, preferentially undergo preliminary protonation of the double bond and then cleavage of the cyclopropane ring. This is the case with thujopsene (LXIV) which gives widdrol (LXXXVI)[104].

Cyclopropyl ketones, in some cases, are susceptible to both nucleophilic as well as electrophilic attack.

Acid promoted opening of the 3-membered ring in certain bridged systems has been studied recently[105]. Lead tetraacetate[106], thallium triacetate[107], mercuric acetate[108], diborane[109], N-bromosuccinimide[110], etc., are some other reagents used to cleave cyclopropane ring.

Synthesis

So far only very few cyclopropane containing sesquiterpenes have been synthesized. The major difficulty encountered in the synthesis of these sesquiterpenes is in the creation of the sterically strained 3-membered ring system, which would easily revert to thermodynamically more stable

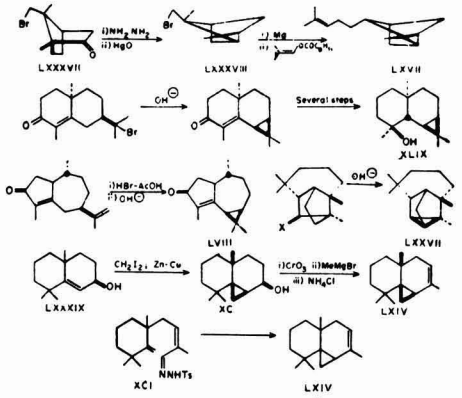


Chart 9 — Synthesis of cyclopropanoid sesquiterpenes

skeletons under equilibrating conditions. The cyclopropane ring, therefore, should be incorporated in the molecule at such a stage in the synthetic scheme when no further acid treatment, which facilitates carbonium ion rearrangements, would be necessary[111].

In the case of α-santalol, the conventional method of tricyclene formation from camphorhydrazone has been used for the creation of the 3-membered ring[112] (LXXXVII → LXVII) (Chart 9).

Successful use of dehydrohalogenative cyclization has led to the synthesis of maaliol[55] (XLIX), epicyclocolerenone[83] (LVIII), longicyclene[113,114] (LXXVII) and (−)-aromadendrene[115].

The synthesis of thujopsene[116] (LXIV) was based on the principle that the addition of carbene with the Simmon's reagent on an allylic alcohol will yield a cyclopropane compound in which the 3-membered ring and hydroxyl group will have a *cis*-arrangement (LXXXIX → LXIV).

Thujopsene has also been obtained in very poor yields by the photochemical irradiation of the tosyl hydrazone (XCI) involving an intramolecular addition process[117].

The base-catalysed condensation at room temperature of α-halogenoketones with methyl vinyl ketones or methyl acrylate leading to the formation of polyfunctional cyclopropanoid compounds[118] should find useful applications in the syntheses of naturally occurring cyclopropane containing isoprenoids. Besides, the modified procedures[119,120] for addition of carbene to ethylenic bonds may also become useful.

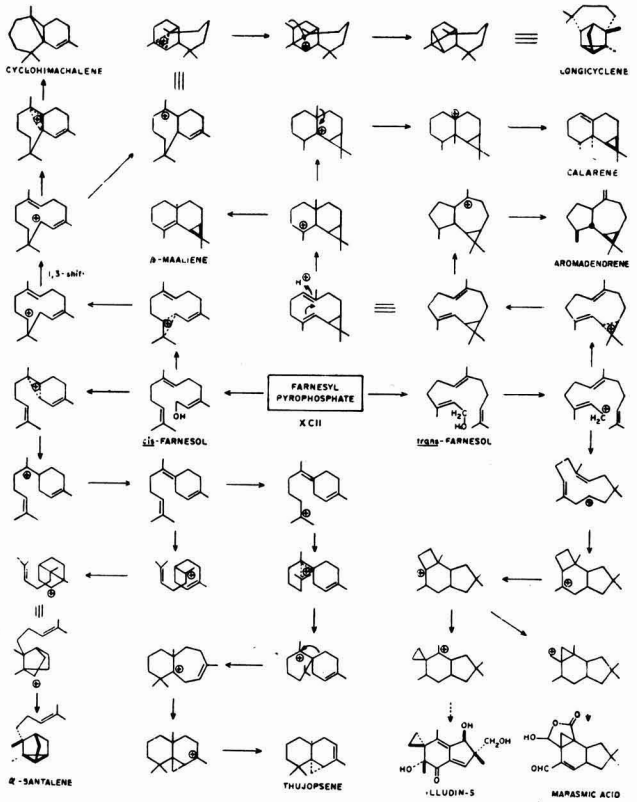


Chart 10 — Biogenesis of sesquiterpenes

TABLE 5 — CYCLOPROPANE CONTAINING DITERPENOIDS

Name	m.p., °C.	$[\alpha]_D$	Source	Ref.
Devadarene (XCIII)	140-8*/2 mm.	+19·83	*Erythroxylon monogynum*	123
Devadarool (XCIV)	125-6	+11·9	—	124-127
Hydroxydevadarool (XCV)	180-1	−3·7	—	131, 132
Trachylobanol (XCVI)	130	−42	*Trachylobium verrucosum*	128
Trachylobanic acid (CXVII)	161	−41 (Me ester)	—	—
Hydroxy trachylobanic acid (XCVIII)	268	−72	—	—
Acetoxy trachylobanic acid (XCIX)	196	−58	—	—
Phorbol (C)	222-5	+54	*Croton tiglium*	129, 130

*Boiling point (bath).

Biogenesis

It is now fairly well established that in the vegetable kingdom sesquiterpenes originate from farnesyl pyrophosphate (XCII). The products resulting by the cyclization of farnesol chain may be divided into those starting from *trans*-farnesol and those originating from *cis*-farnesol. Calarane, maaliane and aromadendrane skeletons are derived from the former, while thujopsene, α-santalene, longicyclene, etc., are derived from the latter. An attempt is made through the schematic correlations (Chart 10) to bring out how a single cationic species gives rise to the formation of such a large variety of sesquiterpene structures which incorporate in them the strained 3-carbon ring system[121,122].

Diterpenes

During the last three years, two novel types of diterpenes, namely devadarane and trachylobane, and a new cocarcinogenic principle, phorbol, all conspicuous because of the presence of a cyclopropane ring in their molecule, have been isolated. They are listed in Table 5 and their structures are detailed in Chart 11.

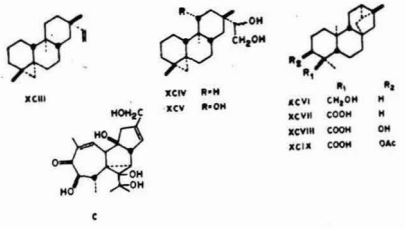


Chart 11 — Cyclopropane containing diterpenoids

The absolute stereostructures of devadarool and related compounds were established simultaneously by two groups of workers, one group correlating it to dolabradiene[124,125] and the second group to rosenonolactone[126,127]. Very convincing physical and chemical evidence has been advanced in support of the proposed structures of trachylobanol[128] and related compounds and of phorbol[129,130]. However, none of the cyclopropane containing diterpenes has been synthesized.

Biogenesis

The precursor of both devadarene and trachylobane types of diterpenes should be geranyl geraniol or geranyl linalool and the presently accepted mode of their biogenesis[123,133] is as shown in Chart 12. The biogenetic pathway to phorbol is not very clear, but it may well be arising through the preliminary formation of a sesquiterpenic unit, similar to picrotaxane skeleton to which may be later condensed an isoprene unit.

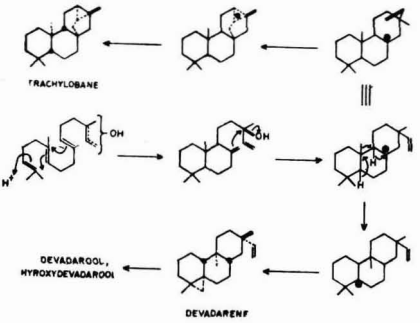


Chart 12 — Biogenesis of diterpenoids

Triterpenes

All the tetracyclic triterpenes known to contain a cyclopropane ring have the latter at the 9-10 position, whereas the pentacyclic triterpene, phyllanthol, has it at the 13-14 position. The structures of the major parent compounds among cyclopropane containing triterpenes, namely cycloartenol, cycloeucalenol and phyllanthol, were established during the last decade and the structures of most others were proved by correlating them with the parent compounds in one way or other. The known cyclopropane containing triterpenes are listed in Table 6 and their structures are given in Chart 13.

Structure

The physical evidences for the presence of cyclopropyl ring in these compounds are: (i) characteristic IR absorption band at 3045 $cm.^{-1}$ (C-H stretching of cyclopropyl methylene group); (ii) UV absorption maxima[134,142] of α,β-unsaturated-γ-cyclopropyl ketones at 269 mμ ($\epsilon \sim 10{,}000$); and (iii) the presence of two symmetrical doublets in the high field region of NMR spectrum[135,151] with the characteristic J value of 4 cps.

Quantitative comparison of intensities of the band in the IR region at 1380 $cm.^{-1}$ (characteristic

TABLE 6 — CYCLOPROPANE CONTAINING TRITERPENOIDS

Name	m.p., °C.	$[\alpha]_D$	Source	Ref.
Cycloartenol (CI)	85-92	+48	*Artocarpus integrifolia*	136, 142
Mangiferolic acid (CII)	181-3	+49	*Mangifera indica*	146
24-Methylene cycloartenol (CIII)	122	+43	*Populus tremuloides*	147-49
Cycloart-23-ene-3β,25-diol (CIV)	200-4	+38	*Tillendsia usneoides*	147
Cyclolaudenol (CV)	125	+46	*Polypodium vulgare*	150, 151
Cycloartenone (CVI)	109	+24	*Artocarpus integrifolia*	141
24-Methylene cycloartenone (CVII)	111-12	+20	Rice bran oil	147
Mangiferonic acid (CVIII)	187-9	+23·5	*Mangifera indica*	152
Hydroxy margiferonic acid (CIX)	190-2	+18·2	—	153
Ambonic acid (CX)	149-55	+9·4	—	152
Norcyclolaudenol (CXI)	139-40	+44	*Polypodium vulgare*	151
Cycloeucalenol (CXII)	138-9	+45	*Eucalyptus microcorys*	154
Phyllanthol (CXIII)	225-6	+43	*Phyllanthus engleri*	136, 155
Acetyl acteol (CXIV)	247-9	−80	*Actea racemosa*	156, 157
Isomangiferolic acid (CXV)	168-70	+29	*Mangifera indica*	152
Ambolic acid (CXVI)	167-9	+31	—	152
Cimigenol (CXVII)	227-8	+38	*Cimicifuga racemosa*	158, 159

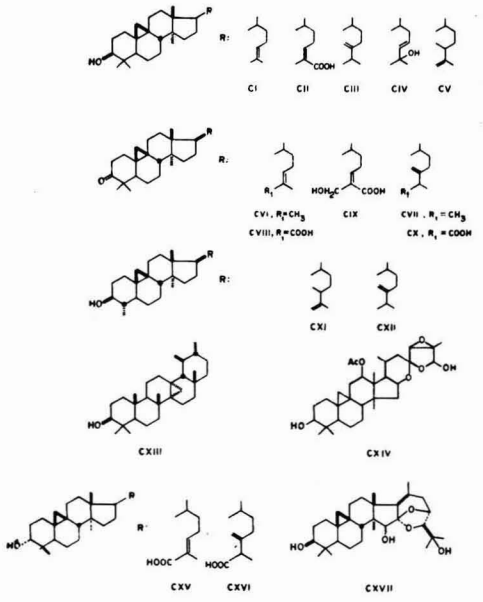


Chart 13 — Cyclopropanoid triterpenes

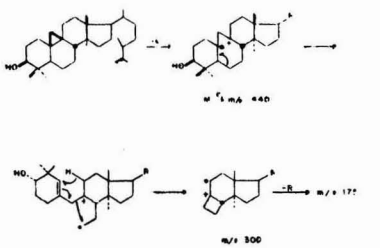


Chart 14 — Mass spectral fragmentation of cyclolaudenol

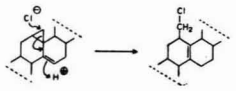


Chart 15 — Cyclopropane ring cleavage in cyclosenegenin

for nongeminal methyl groups) of the deuterated compounds obtained by the cleavage of the cyclopropyl compounds with DCl and of the corresponding non-deuterated compounds (one $-CH_3$ of the latter is replaced by $-CH_2D$ in the former) has been utilized to prove the presence of cyclopropyl group[136].

Although mass spectra of cyclopropane and some of its simple derivatives have been a subject of study recently[137], the mass spectra of naturally occurring cyclopropanoids have not been studied in detail.

Tetracyclic triterpenes containing the 9,19-cyclo function undergo a diagnostically significant fission[138,139] reaction on electron impact involving the cleavage of the 9-10, 9-19 and 5-6 linkages followed by transfer of one of the activated C-11 hydrogens via a 'McLafferty type' rearrangement[140] and with charge retention with rings C and D (Chart 14).

The presence of cyclopropane ring at the 9-10 position in tetracyclic triterpenes invariably leads to the *cis*-fusion of B/C ring junction. Although, according to Markownikoff's rule, acid-catalysed cleavage of the cyclopropyl group in these compounds should result in two products, in practice they cleave only in one direction to give an axial substituent. This is because the alternative cleavage would give the conformationally undesirable B/C *cis*-fusion. Thus, acid-catalysed cleavage[136,141,142] of cycloartenyl acetate results in the almost exclusive formation of lanost-9(11)-enyl acetate, which, incidentally, not only proves the carbon skeleton of the former, but also indicates the position of the cyclopropane ring in the molecule. Phyllanthol, whose C/D ring junction is *cis*, similarly yields α-amyrin[143].

The non-Markownikoff cleavage of the cyclopropane ring in cyclosenegenin[144] is attributed to the conjugation of the 3-membered ring with a double bond which gets protonated first (Chart 15).

Synthesis

Cyclosenegenin (CXVIII) was synthesized[144] from senegenin by the solvolytic removal of the chlorine atom of the latter resulting in the concomitant

formation of cyclopropane ring and abstraction of a hydrogen atom at C-5.

Phyllanthol (CXIII) has earlier been synthesized[145] in a similar manner starting from quinovic acid (Chart 16).

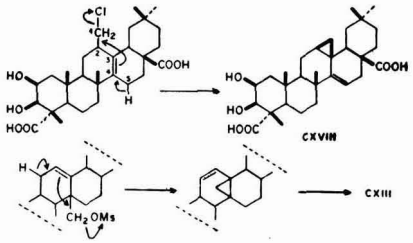


Chart 16 — Synthesis of cyclopropanoid triterpenes

Steroids

Pollinastanol (CXIX) (Chart 17), m.p. 95°, $[\alpha]_D$ +35°, seems to be the only naturally occurring steroid containing a cyclopropane ring. This was isolated[160] in 1964 from the pollen of *Pyrus malus* or *Cirtus ladaniferus*.

Acid-catalysed cleavage of pollinastanyl acetate yielded 14-methyl-9-cholestene-3β-acetate; pollinastanone on bromination and dehydrobromination yielded the unsaturated ketone (CXX) having a UV absorption maximum at 271 mμ (ε 8200) and hence, the structure (CXIX) for pollinastanol[160].

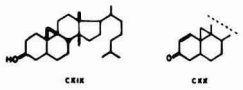


Chart 17 — Cyclopropane containing steroids

Steroidal Alkaloids

During the last five years or so, a large number of steroidal alkaloids containing cyclopropane ring belonging to the ' Buxus alkaloids ' group have been isolated from a few species of Buxaceae. These are listed in Table 7 and their structures are given in Chart 18. The suffixes A, B, C, etc., attached to the names of these alkaloids indicate the various stages of methylation of the two nitrogen atoms attached to C-3 and C-20 of the steroid skeleton and this is explained in Table 8.

All these steroidal alkaloids are characterized by the presence of a cyclopropane ring at the 9-10 position and consequent *cis*-fusion of B/C rings and the presence of one or two methyl groups attached to C-4 (cycloeucalanane or cycloartane type

TABLE 7 — BUXUS ALKALOIDS

Name	m.p., °C.	$[\alpha]_D$	Source	Ref.
Cyclobuxine-D (CXXIII)	245-7	+98	*Buxus sempervirens*	163, 165
Cyclobuxamine-D (CXXIV)	209-11	+30	—	166
Cyclobuxamine-H	—	—	—	163
Cycloprotobuxine-A (CXXV)	207	+75	*B. balarica*	167
Cycloprotobuxine-C (alkaloid L)	200-2	+80	—	168-170
Cycloprotobuxine-D	140-2	+112	*B. sempervirens*	162
Cyclovirobuxine-D (CXXVI)	221-2	+63	—	163, 171
Cyclovirobuxeine-A (CXXVII)	220	−87	—	171
Cyclovirobuxeine-B (alkaloid M)	198-200	−62	—	170-172
Cyclomicrophylline-A (CXXVIII)	232-3	−93	*B. microphylla*	161
Cyclomicrophylline-B (cyclobaleaubuxine)	251-2	−65	—	161, 167
Cyclomicrophylline-C	283-4	−40	—	161
Dihydrocyclomicrophylline-A (CXXIX)	271-2	+37	—	161
Dihydrocyclomicrophylline-F	260	+4·6	—	161
Cyclomicrophyllidine-A (CXXX)	—	−160	—	161
Dihydrocyclomicrophyllidine-A (CXXXI)	—	−33	—	161
Beleanbuxine (N-isobutyryl beleanbuxine-F) (CXXXII)	258	+115	*B. balarica*	173
N-isobutyryl beleanbuxidine-F (CXXXIII)	257	+71	—	174
N-benzoyl beleanbuxidine-F (CXXXIV)	277	+52	—	174
Cyclomalayanine-B (O-coumaryl cyclovirobuxeine-B) (CXXXV)	170	−61	*B. malayana*	171
Buxtauine (cyclomicrobuxinine, cyclobuxoxine) (CXXXVI)	178-81 181-3	+172 +169	*B. sempervirens*	161, 175, 176
Buxpiine (cyclomicrobuxine) (CXXXVII)	173 178-80	+158 +172	—	161, 169
Cyclobuxoxazine (CXXXVIII)	245-6	+29	*B. microphylla*	177
Baleaubuxoxazine-C (CXXXIX)	292	+116	*B. balerica*	174
Cyclokoreanine-B (CXL)	235-6	+109	*B. koreana*	178
Cyclomicrosine (CXLI)	282-4	−33	*B. microphylla*	179
Cyclobuxomicreine (CXLII)	195-7	+37	—	—
Cyclomicrobuxeine (CXLIII)	141-2	+126	—	—
Cyclosuffrobuxinine (CXLIV)	144-9	−67	—	—
Cyclosuffrobuxine (CXLV)	196-8 (167-72)	−92	—	—
Cyclobuxosuffrine (CXLVI)	201-4	−62	—	—
Cyclobuxophyllinine (CXLVII)	181-2	−51	—	—
Cyclobuxophylline (CXLVIII)	194-6	−72	—	—
Cyclobuxoviridine (CXLIX)	182-3	+16	—	—
Cyclomikuranine (CL)	209-11	−3	—	179

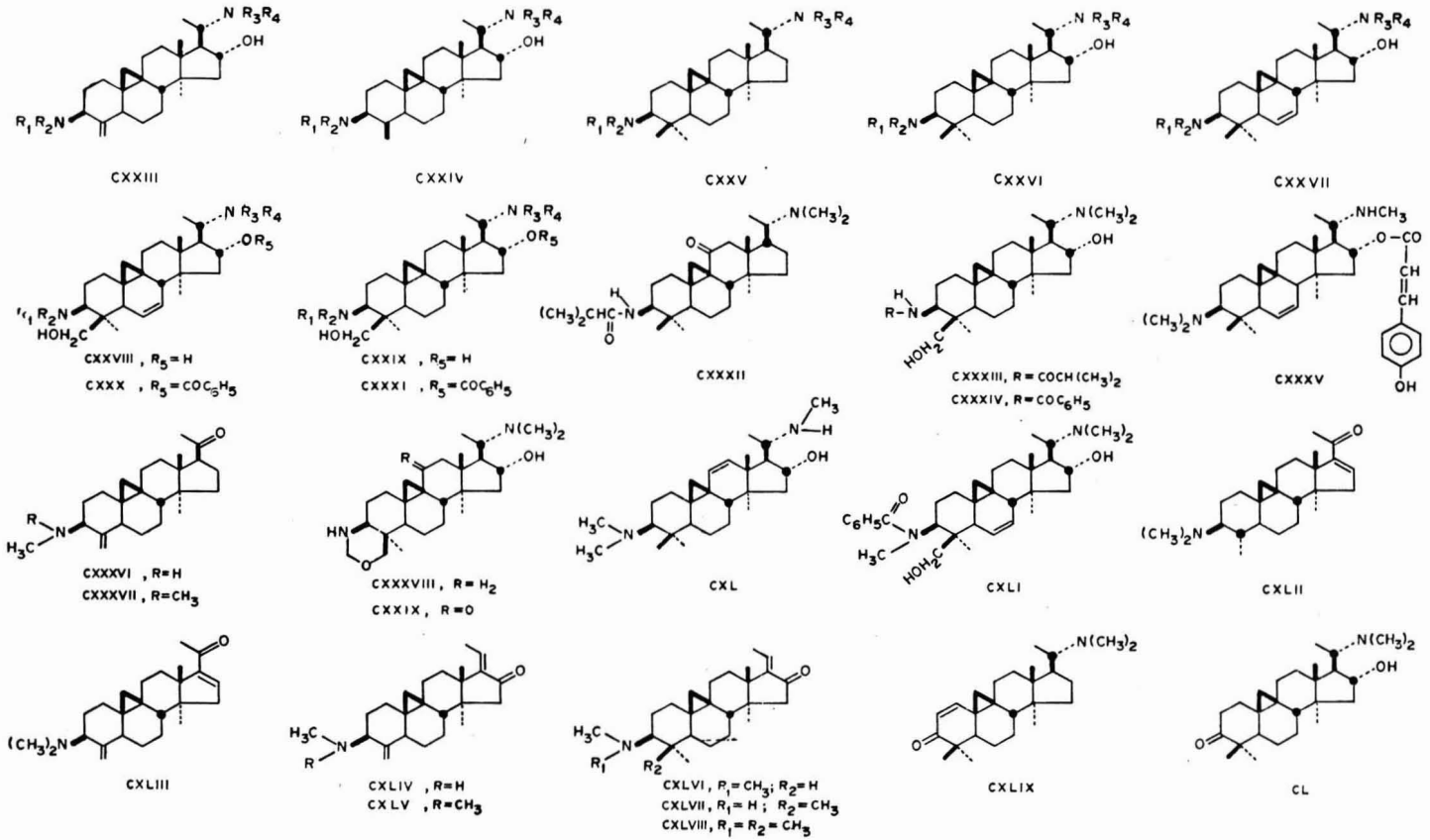


Chart 18 — Buxus alkaloids

TABLE 8 — EXPLANATION OF SUFFIXES A-I IN THE NOMENCLATURE OF BUXUS ALKALOIDS GIVEN IN TABLE 7

Suffix*	C_3-N		C_{20}-N	
	R_1	R_2	R_3	R_4
A	CH_3	CH_3	CH_3	CH_3
B	CH_3	CH_3	H	CH_3
C	H	CH_3	CH_3	CH_3
D	H	CH_3	H	CH_3
E	CH_3	CH_3	H	H
F	H	H	CH_3	CH_3
G	H	CH_3	H	H
H	H	H	H	CH_3
I	H	H	H	H

*It indicates various stages of methylation of two nitrogen atoms attached to C-3 and C-20 of the steroid skeleton.

respectively). Acid-catalysed cleavage of the cyclopropane ring proceeds similar to that of triterpenes[161]. Their structures are determined by degrading them (Ruschig's oxidative desamination) to nitrogen-free compounds and correlating these with derivatives of cyclopropane containing triterpenes. For example, cycloprotobuxine-D (CXXV)[162] and cyclovirobuxine-D (CXXVI)[163] are degraded to the diketone (CXXI) and cyclobuxine-D (CXXIII)[164] to (CXXII) (Chart 19) identical with these compounds derivable from cycloartenol and cycloeucalenol respectively.

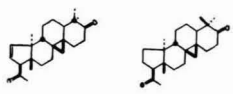


Chart 19 — Common degradation products cyclopropanoid triterpenes and Buxus alkaloids

In 'Buxus alkaloids', the position of the cyclopropyl methylene proton signals in NMR spectra is not appreciably affected by the substituents at C-3, whereas the replacement of the 4α-methyl by a 4β-methyl group (or introduction of a 4,4-dimethyl group) causes a great downfield shift [in 4α-methyl compounds AB quartet at τ 9·82-9·91 and 9·50-9·67 ($J = 4$ cps); in 4β-methyl or 4,4-dimethyl compounds: AB quartet τ 9·62-9·72 and 9·37-9·41][179].

Biogenesis of Triterpenes and Steroids

The triterpenes, phytosterol and the steroidal alkaloids presented here apparently seem to be the intermediate stages postulated in the presently accepted theories of the biosynthesis of steroids from squalene. It is now fairly well established that lanosterol formed by the cyclization of squalene (condensation product of two molecules of farnesyl pyrophosphate) is the precursor to both tetra- and pentacyclic triterpenes and steroids[35,122]. Bloch and his collaborators have clearly shown that in the conversion of lanosterol (CLI) into cholesterol, the C-14 methyl group is removed first and then the two methyl groups at C-4 (Chart 20). However, in all the cyclopropanoid compounds mentioned here, the C-14 methyl group remains intact, whereas C-4 is variously methylated. This can, however,

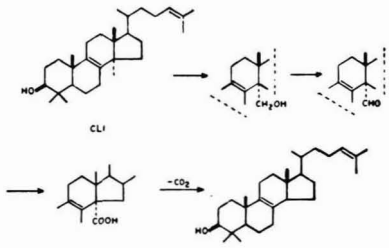


Chart 20 — Removal of C-14 methyl from lanosterol

be suggested as lending support to Bloch's mechanism of the preliminaryr emoval of C-14 methyl, since in the polyprenoids reported here, the C_8-C_9 double bond is replaced by a cyclopropane ring at 9-10 position, the latter probably rendering the oxidation and decarboxylation process of C-14 methyl group more difficult. Also, the existence of these compounds has shown that the two methyl groups at C-4 in lanosterol are removed stepwise, starting with the oxidation of the 3β-hydroxyl group to carbonyl, followed by oxidation of one of the methyl group at C-4 to carboxylic acid and decarboxylation, leading to a carbonium ion at C-4 which stabilizes by hydride transfer or proton removal. The second methyl group is removed by a repetition of the above process[35,122].

Summary

The chemistry of naturally occurring cyclopropane containing compounds is discussed. The structures and syntheses of cyclopropanoid fatty acids, amino acid, alkaloid, mono-, sesqui-, di- and triterpenes, steroid and steroidal alkaloids are briefly described. The importance of these compounds as biogenetic intermediates is pointed out.

Acknowledgement

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Recent Trends in Wheat Research

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THE original home of the bread wheat, *Triticum aestivum* L., is considered to be somewhere near the north-western corner of the Indian subcontinent and so the urge to improve the wheat plant for cultivation has remained with us since the origin of agriculture itself. Notwithstanding the antiquity of this crop in this region, the improvement of the wheats of our country, based on the use of more scientific methods, may be said to date from the first decade of the present century when the Agricultural Research Institute (now Indian Agricultural Research Institute, New Delhi) was founded at Pusa in north Bihar. Until recent years, by far the greatest attention was given to intervarietal and interspecific cross-breeding in order to obtain the best combinations of grain yield, disease resistance, stiff straw, early ripening, drought resistance, grain appearance and *chapati*-making quality[1]. The achievements during this period have been outstanding and noteworthy[2]. More recently, wheat breeding research under the All-India Wheat Improvement Project has been oriented towards the evolution of strains more conducive to the efficient utilization of high fertility and irrigation facilities. As lodging does not permit full expression of genetic potential of our varieties for high yields and so presents a barrier to higher grain production, major efforts are now directed towards exploiting recently discovered 'norin' genes in evolving dwarf strains capable of more than twice the yield obtained with current improved varieties[3]. However, demand for wheat has grown steadily over the past years mainly because of our fast growing population and also due to increasing popularity of wheat grain even in traditionally rice-eating areas. Current wheat breeding programme is amply justifying itself in meeting this growing challenge by developing high yielding varieties and by designing better methods of cultivation. Nevertheless, much remains to be done.

Recent trends in wheat research show that a wide range of techniques including induced mutations, distant hybridization, aneuploidy, alien chromosome addition and substitution, synthesis of new amphidiploids, chromosome structural rearrangements, gene transposition across generic boundaries, regulation of character recombination and exploitation of heterosis are being employed in the development of new and improved strains. These new tools have been briefly reviewed with particular reference to wheat.

Mutation Breeding

Following the important discovery made by Muller[4] in 1927 that the rate of mutations could be greatly accelerated by means of X-rays, mutation breeding is an accepted plant breeding tool by providing an original method of obtaining variation and 'engineering' gene transfer between non-homologous chromosomes through induced translocations. In addition to the ionizing radiations, a large number of chemical mutagens of marked efficiency have been discovered in recent times[5]. Efforts are now directed towards developing this technique to provide the breeder with new and valuable means of obtaining genetic variability and for directing or controlling the incidence and kind of mutation.

An outstanding merit of mutation breeding lies in improving a highly desirable and adaptive genotype with respect to a specific defect without disrupting its delicate system of genic balance. Such artificial rectification of undesirable genes of an organism is termed 'algeny' by Lederberg[6]. If the genetic mechanism determining the expression of a character is known, that character can be incorporated into or eliminated from a desirable variety with ease and confidence. For example, in varieties where expression of a desirable character like that of awning is inhibited by a single dominant allele, incorporation of such desirable trait through irradiation by knocking out the inhibitor is relatively quicker and inexpensive without risking a reshuffle of the adapted genetic architecture of the parent variety[7]. Recently, two improved wheat varieties, evolved by this technique, have been released for commercial cultivation by the Indian Agricultural Research Institute[8,9]. As demonstrated by Konzak[10] in oats, irradiation can also be employed for splitting tight linkages and resolving complex loci[11] in order to obtain rare recombinations, which would not otherwise be possible by conventional hybridization. As a result of painstaking and persistent efforts in Sweden, Germany, USA, Canada and India, quite a large number of superior varieties, developed by mutation breeding, have been released for commercial production[12].

It may be emphasized, however, that mutagenic techniques do not induce new varieties immediately and that the recovery of a desired mutation and the conversion of a raw mutant into a commercial variety are two independent events. Hence, it is essential that the breeder should subject the irradiated or treated population to proper testing and selection procedures, and also to hybridization if required, in order to evolve a really superior strain. Induced branched-ear mutant[13] of bread wheat provides a good illustration of this point. Expressivity of this character is highly variable, conditioned primarily by the genetic background of the carrier plant. Hence, a large number of intervarietal crosses will have to be carefully studied in order to stabilize this promising character prior to developing a 'sorghum-like' strain of wheat capable of producing almost double the number of grains per spike-head in comparison to the controls.

Amphidiploids

Cytogenetic studies on the mechanism of species differentiation have provided basic information on the causes of sterility and difficulties of combining desirable characteristics in interspecific and intergeneric crosses[14,15]. For example, hybrid sterility caused by non-homology among parental chromosomes or by imbalance of chromosome numbers may be overcome by doubling the chromosome number of the sterile hybrid by colchicine treatment. The artificial production of hybrid polyploids, often referred to as amphidiploids or amphiploids, by doubling the chromosome number of a sterile hybrid of desirable parentage is now a recognized breeding technique. The use of the amphidiploid method in breeding has been either to synthesize directly a new plant which could be of direct practical use in commercial production or else to produce an amphiploid which could be used in further breeding work by hybridization with commercial varieties. One of the most interesting and perhaps immediate uses of induced allopolyploids is in the development of ' bridge species ' which may serve as intermediaries in the transfer of disease resistance and other useful characteristics from related species and genera to crop plants[16,17]. Thus, sterility barriers between the hexaploid wheats and diploid or tetraploid relatives possessing disease resistance can be circumvented by using an auto- or allopolyploid combination.

Thanks to the early comprehensive cytogenetic research in polyploid wheat species, led notably by H. Kihara and E. R. Sears, it has been established that these species are derived from related species with lower chromosome numbers[18-22]. Studies on chromosome numbers, karyotype and homology have proved useful in establishing the natural relationships of cultivated wheats and their relatives[23-25]. Such studies help the wheat breeder in the choice of parents and formulating programmes for recombination breeding[26,27]. For example, the use of *Aegilops* as a source of variation in wheat improvement should be strongly urged since there are already two doses of this genus in the common wheat of our fields. On the basis of phylogenetic relationships, a dual system is proposed to be operative in the common wheat[28,29]: a conservative gene complex in the form of a ' pivotal ' genome (A genome of *T. monococcum* which is common to all the wheats) side by side with a pool of recombinable material in the ' modified ' or ' differential ' genomes (B and D genomes, both contributed by *Aegilops* species). This interpretation also stresses the need for relying more heavily on *Aegilops* species for incorporation of useful alien genes in our common wheat varieties, particularly for disease resistance.

The resynthesis of polyploid cultivated plants like the common wheat, although primarily of theoretical interest, can be utilized in practical plant breeding by reconstitution of component genomes[30]. The possibility of synthesizing new species by combining diverse genomes has undoubtedly a fascinating proposition for the plant breeder[31]. In studies of this problem, attention has so far been concentrated on attempts to exploit genetic variation in relatives of common wheat in the genera *Triticum*, *Aegilops*, *Secale*, *Agropyron* and *Haynaldia*. In the wide range of material which has been surveyed so far, no amphiploid has yet been found suitable for immediate utilization in agriculture[32]. Considerable effort is being devoted to the development of *Triticale* forms, combining wheat and rye genomes[33-35]. The underlying idea in the development of *Triticale* is to obtain a new cereal with the milling and baking qualities of wheat combined with the drought resistance and the ability of rye to grow on poor soils. Such a cereal, when finally developed, would be of great value to the regions where rye or a rye-wheat mixture are the main crops. Similarly, frost and drought resistance, saline soil adaptability and perennial habit of *Agropyron* species is being sought to be incorporated in wheat by developing ' perennial wheats '[36].

Developing promising allopolyploids to a commercial level as new crops either by recombining characteristics of separate species which have agricultural value or by synthesizing new species may often require more time and effort on the breeder's part than seems warranted from a short-term point of view. Spectacular progress may not be possible in such projects because the new forms usually will have to compete with those which have long proved successful in nature. There is much to be said, however, in support of a concerted effort to synthesize new species which will suit our needs more adequately than those found in nature.

Alien Gene Transfer

For many years, plant breeders have intended to incorporate favourable characters such as resistance to diseases, drought, etc., from wild species into cultivated wheats. In order to combine in an individual the favourable characters from different species, interspecific and even intergeneric hybrids have been obtained. However, even after a hybrid has been obtained, there is no assurance that the desired character will be transferable unless the chromosome carrying the desired gene pairs with a chromosome of the wheat plant. A cytogenetic approach to the introduction of alien genetic variation becomes primarily necessary in such a situation where there is no meiotic pairing and recombination between the parental chromosomes of a hybrid. Sears[37] opened a new era of wheat breeding when he developed aneuploid stocks in the variety ' Chinese Spring '. Possible uses of these aneuploid stocks (monosomics, nullisomics, telosomics, etc.) were discussed by Sears[38] in 1953. It was initially considered that the difficulties of low fertility, genome interaction, etc., would be overcome by using backcross procedures to add single pairs of alien chromosomes, rather than adding a whole alien genome, to the full chromosome complement of a wheat variety. This type of plants constitute the disomic chromosome addition lines. Although some useful characters of rye were transferred in this way, other disadvantages such as low fertility, cytological instability or disturbances with respect to quality, prevented the direct use of these addition lines in agriculture[39].

With a view to introducing alien variation in a more stable and advantageous way, it was then suggested that many disadvantages associated with the addition lines might be avoided by substituting the alien chromosome pair for a pair of the recipient variety rather than adding an extra pair of chromosomes. The substitution of single pairs of alien chromosomes seems to be the logical climax to the development of systems of handling intergeneric crosses in wheat improvement. However, despite the fact that substitution lines of rye chromosomes in wheat are vegetatively vigorous and the disease resistance brought by the addition of rye chromosomes persists in the substitution state, none of these lines also has been used in agriculture as cultivated form because of their reduced fertility[40,41].

Chromosome Engineering

It is perhaps too much to expect that when a complete chromosome is transferred to another species, the new genotype would function in a fully integrated manner. Sears[42] demonstrated in 1956 that this genic imbalance could be avoided by the use of radiation-induced translocations to introduce into wheat complement small chromosome segments from foreign species removing the need for the transfer of whole chromosomes which used to bring some undesirable characteristics along with the desired trait. The essential features of Sears' brilliant feat of transferring leaf rust resistance from *Aegilops umbellulata* to bread wheat were that the *umbellulata* genome had very restricted pairing affinity with the D genome of wheat and, consequently, backcrossing to wheat eliminated all the *umbellulata* chromosomes except the one carrying resistance which was maintained by selection and cytological counts as an extra chromosome. An ingenious combination of pre-meiotic irradiation of the resistant plants carrying an extra chromosome in the form of an isochromosome (i.e. having the arm conferring resistance in duplicate condition) followed by its transmission through the pollen enhanced the chances of the recovery of male gametes in which a small *umbellulata* segment carrying the resistance had been inserted into the wheat genome. In other words, the combination of a relatively crude tool like radiation with an elaborate cytogenetic technique has led to the development of a precise mechanism for the transfer of specific chromosome segments. Thus, by a logical sequence of steps, procedures have been evolved which enable alien genes to be incorporated into crop plants despite the absence of appropriate meiotic recombination.

It is noteworthy that what has been demonstrated by Sears is the kind of manipulation that might never occur in nature but which has been made possible by an elegant cytogenetic technique. The number of outstanding traits of major economic importance available in world collections of germplasms is undoubtedly very large but they will be of relatively little value in the absence of availability of a precise mechanism for their 'clean' transfer into cultivated varieties. Because of the control which it provides in the synthesis of rare or hitherto improbable genotypes, the 'engineering' approach of cytogenetics is unexcelled. Despite the apparent simplicity of such a programme, however, the intricate chromosome manipulations involved together with the problems of synchronization of the various steps present challenges which require the utmost in ingenuity if they are to be met and overcome.

Intervarietal Chromosome Substitution

There are two main purposes of intervarietal chromosome substitutions: first, to determine the effects of individual chromosomes of a variety when transferred to a common background and to study gene expression, and, second, after determining that disease resistance or some other desirable characteristics is conditioned by a certain chromosome, to substitute this chromosome into an otherwise acceptable variety. To carry out the first objective, the effects of individual chromosomes from other varieties must be assessed in the background of variety Chinese Spring in which the monosomic series was originally produced by Sears. To carry out the second, a set of monosomic lines of that acceptable variety, into which the desired chromosome is sought to be substituted, must be on hand.

The possibility of transferring single intact chromosome pairs from one variety of wheat to another was made possible by the production of a complete monosomic series in the variety Chinese Spring by Sears and by the derivation, by backcrossing, of equivalent series in a number of commercial varieties. This kind of programme demands the development of monosomic series in a large number of commercial varieties in order to obtain the required aneuploid material. In addition, telocentrics of practically all the chromosomes are available now and, hence, we do not have to content ourselves by working with the whole chromosomes, but we may actually determine which arm of a particular chromosome carries the desirable trait and so manipulate its substitution.

This technique promises to be one of the most effective cytogenetic methods in wheat breeding since it permits the transfer, by backcrossing, of linked beneficial genes which do not give clear-cut phenotypic effects. This is done by using the monosomic chromosome as a marker for those genes. Thus, the study of substitution lines offers unique opportunities for handling traits showing quantitative inheritance. For example, Welsh and Hehn[43] pointed out the importance of chromosome 1D (XVII) concerning the milling quality of bread wheats. Obviously, the substitution of this chromosome of a high yielding variety having bad milling quality by the same chromosome of another variety possessing good milling quality will be very profitable. Thus, the technique offers a method of systematically synthesizing improved varieties. The technique depends for its success, however, on basing the work on the best available varieties and being able to identify, or associate, chromosomes with the individual agronomically desirable characteristics. Monosomic series in the varieties Pb. C. 591 and Sonora 64 are in the process of being developed at the Indian Agricultural Research Institute for cytogenetic studies.

Gene Recombination

In the absence of recombination mechanism, the interspecific or intergeneric hybrids tend to revert towards the parental types. An important prerequisite for obtaining gene recombination is homology and consequent effective meiotic pairing between corresponding chromosomes of the parents. However, pairing affinity may not entirely be determined by homology alone. It is well known that the three component genomes of the hexaploid wheats are genetically and cytologically closely related, but this species, instead of forming multivalents, behaves meiotically as if it were a diploid. It is a matter of great significance and interest that cytological research has demonstrated that the regular, diploid-like behaviour of the hexaploid *T. aestivum* is controlled by a gene, or genes, located on the long arm of chromosome 5B (V). Riley and Chapman[44], and Sears and Okamoto[45] showed that in plants of common wheat deficient for chromosome 5B, non-homologous pairing occurred giving rise to multivalent formation. Subsequently, Riley and Kempanna[46] demonstrated that this non-homologous pairing resulted in recombination between homoeologous chromosomes, i.e. between genetically equivalent chromosomes of the three component genomes of the common wheat. Evidence was thus obtained for the genetic control of meiotic pairing of chromosomes in polyploid wheats[47].

One of the significant possibilities in wheat improvement suggested by this discovery is that of expediting gene transfer, through recombination, between corresponding chromosomes of different genomes through the use of stocks nullisomic for chromosome 5B. In this way, wheat breeders will be able to utilize genetic variation from sources thus far inaccessible to them. Amphidiploids deficient for chromosome 5B are multivalent-forming and have allosyndetic pairing and recombination. Such multivalent-forming amphiploids can be backcrossed to wheat, so restoring chromosome 5B and introducing allosyndetic recombinant chromosomes. Alternatively, chromosome 5B-deficient interspecific hybrids, which are of low fertility, can be backcrossed to wheat again to introduce allosyndetic recombinant chromosomes. Another promising possibility in this direction, which can be profitably exploited, is the use of the effects of ionizing radiations, chemicals and environmental conditions on chiasma frequency and, hence, recombination potential.

Duplications

A possible use of induced translocations is to achieve 'directed' duplications of beneficial alleles or of defined chromosome segments showing dose effects[48]. Segmental duplications, which enable us to study the dose effect of agronomically desirable genes, can be produced systematically by crossing two translocation stocks involving the same chromosome pairs but having different exchange points. There is a possibility, theoretically at least, of achieving a complete rearrangement of the genetic architecture of a species according to the will of the breeder by building up a large number of translocation stocks with identified break points and a gene map as complete as possible. Duplications for selected loci can also be obtained in another way in case of the hexaploid common wheat. For example, Sr^6 gene for stem rust resistance carried on the chromosome 2D (XX) of *vulgare* wheat (AA BB DD) was transferred to *durum* (AA BB) by Knott[49] through an induced translocation. This *durum* line carrying the Sr^6 gene can be crossed to *vulgare* and so the Sr^6 gene, backcrossed into the hexaploid common wheat in its new position, can be obtained in four doses. The homoeologous recombination, mentioned earlier, that occurs in lines deficient for chromosome 5B may also permit the accumulation of duplications either directly or through the assembly of lines with different translocations between the same pairs[46,50]. In this work, since *T. aestivum* nullisomic-5B plants are sterile, it is convenient to use plants that are nullisomic-5B and tetrasomic-5D (XVIII) as the extra dosage of 5D compensates for the missing 5B chromosomes, i.e. removes sterility without preventing homoeologous pairing[46]. After the accumulation of homoeologous recombinants, a convenient method of returning to the euploid condition is by crossing to the reciprocal genotype, i.e. nulli-5B tetra-5D $\times$ tetra-5B nulli-5D. The immediate value of duplications, however, must depend upon the usefulness of dose effects, absence of undesirable position effects and on the production of duplications small enough not to interfere with normal bivalent formation. Duplications would also provide surplus genetic material so allowing scope for mutational changes without risking the loss of existing functions.

Haploids

There are several ways in which haploid crop plants can be useful in breeding programmes. An obvious practical use of haploids is the exploitation of the totally homozygous forms that can be produced by doubling the chromosome complements of haploids by colchicine treatment. For example, the Marglobe tomato, which is a doubled haploid, has been grown commercially[51]. Chase[52], who employed genetic markers in the parents to recognize maize haploids, treated them with colchicine to produce homozygous diploids for use as parents in hybrid maize programmes. Haploids (polyhaploids) were also used by Sears[53] in the production of the famous monosomic series in the variety Chinese Spring which has been valuable in intervarietal chromosome substitution work as well as in genetic investigations. More recently, polyhaploids of the variety Holdfast, deficient for a particular chromosome, were the starting point of a series of investigations that have led to the elucidation of the genetic mechanism controlling the diploid-like chromosome behaviour of the hexaploid wheats[50]. Finally, Goodsell[54] and Chase[55] have pointed out yet another practical use of monoploids in maize. Androgenetic haploids, recognized by appropriate genetic markers, have been employed by them in transferring the genotypes of inbred lines into cytoplasm that cause male sterility. This technique has the

advantage, compared with nuclear substitution by backcrossing, that the chromosomal system remains intact.

The utilization of haploids in breeding programmes obviously demands techniques for their ready production, and the most likely way of increasing their frequency is probably by the use of selected pollinators[56]. Kihara and Tsunewaki[57] described the production of haploids in two wheat lines where a nucleus had been substituted into alien cytoplasm. One of these lines (developed from the cross *Aegilops caudata*×*T. aestivum* var. *erythrospermum*) had a frequency of 53 per cent haploids. Recently, a particular stock of the variety Holdfast, monosomic for chromosome 1B (I), has been reported by Riley[58] to produce as many as 35 per cent haploids in successive generations. Haploid production in this stock is not associated with the monosomic condition, but it seems quite possible that pollen of this material permits the development of haploid embryos whereas the endosperm formed is quite normal. If this were so, and this stock were used to pollinate heterozygotes, desirable haploids can be obtained at will by the breeders.

Hybrid Wheat

Heterosis or hybrid vigour has great importance in modern plant breeding programmes and continuous efforts are being made to exploit it to the commercial level in an increasing number of crop plants. The development of hybrid maize, sorghum and *bajra* varieties, which effectively utilize heterosis, has revolutionized the yield potential of these crops. The discovery and elucidation of genetic mechanism governing male sterility and fertility restoration in several crop plants have resulted in major commercial application of this system in crop production[59-61]. Recent discoveries of cytoplasmic male sterility[62-64] and genetic restoration of fertility[65-68] have prompted speculation concerning the possibility of hybrid wheat being grown on a commercial scale. However, an important prerequisite for development of hybrid wheat is sufficient heterosis displayed through specific parental combinations so that yields of hybrids would be significantly increased over the level of current commercial varieties. Hybrid wheat is a relatively new concept in wheat breeding for which production techniques and the economics have not yet been fully worked out[69-71]. It remains to be seen how economically the heterotic effects can be superimposed upon the yield base of the present highest yielding varieties maintaining at the same time high quality standards.

Conclusion

There is immense scope still for the accumulation in our improved wheat varieties of better combinations of all the important agricultural and economic characters, particularly yield, grain quality, disease resistance and adaptation to adverse edaphic and ecological conditions. Recent development of elegant cytogenetic techniques regarding manipulation and exploitation of the genetic variability has given new tools to the wheat breeder and has also provided greater insight into the limitations and possibilities of the conventional, well tried and proven methods that have so far been the means of continued improvement of the wheat crop. It may be concluded that the wheat breeder of today is better equipped for his job because he recognizes the importance of wide genetic variation on which all improvements must ultimately depend, appreciates the scope and limitations of various forms of selection within different kinds of genetic populations, has a greater comprehension of the methods of inducing new genetic variation and obtaining desired character recombinations, and his technical methods of character measurement and evaluation are considerably more efficient. However, it should be more widely appreciated that wheat breeding must not only be acutely aware of the present formidable challenge, but it must also look far ahead and show intelligent anticipation of the future situations so that work on long-term projects may be started well in time. Wheat is outstandingly interesting in its taxonomic botany and phylogenetic relationships, both of which give it, from many points of view, unique features as a cultivated cereal and a subject for improvement by breeding[72]. In view of the tremendous genetic variability available in the wheat species groups and their close relatives, and the ease with which genes can be transferred in this tribe across specific and generic barriers, there is a likelihood that efforts already under way at various wheat breeding centres of the world might result in the synthesis of what will virtually be a new cereal crop.

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REVIEWS

ENGINEERING KINEMATICS by Alvin Slone (Dover Publications Inc., New York), 1966. Pp. x+310. Price $ 2.25

This book, first published in 1941 by Macmillan Company, is republished, unabridged and unaltered, in 1966 by Dover Publications Inc., New York. A large number of books have been published on the subject of mechanisms, as a text for mechanical engineering students. A variety of mechanisms are usually described in various chapters of such books. This book by Alvin Slone was widely hailed for its novel approach when first published. The emphasis has been on fundamental aspects, to enable the students to acquire a thorough understanding of motion, displacement, velocity and acceleration, which are basic to all mechanisms. Mechanisms appear in the text only as illustrations of displacement, velocity and accelerations.

In the chapters on motion, displacement, velocity and accelerations, topics such as cams, screw threads, drives, gears, gear trains, linkages, couplings, etc., are illustrated. A large number of problems are included, which will be useful for the teacher and the taught. This book still remains a classic and deserves to be widely used as a text for a course on mechanisms in engineering colleges.

A. RAMACHANDRAN

STRUCTURAL CONCRETE by K. F. Antia (New Book Company Pvt. Ltd, Bombay), 1967. Pp. 572. Price Rs 35.00

The book under review aims to cover the fundamentals of design, technology and construction of plain, reinforced and prestressed concrete in a single volume and is very timely because presently a designer has to refer to several books, codes and research publications. The book provides all the essential features of structural concrete at one place. Furthermore, the author has recognized and emphasized the importance of design by the load factor method and has taken the Indian codes and standards into consideration. In view of this the author's choice of subject and approach deserves appreciation.

The book is divided into 7 sections and 21 chapters. The author gives, in the introductory chapter, an overall perspective of the subject sketching the recent trends, future developments and economics of concrete construction. The properties of constituting materials of concrete and methods of proportioning them have been dealt with adequately in the second chapter except for the omission of references to the relevant standards. The discussion on variation in strength of concrete in this chapter is highly relevant. Properties of concrete have been discussed from the point of view of design and performance of reinforced and prestressed concrete at great length in the third chapter.

After describing the fundamentals of design, the author has dealt with the design of members in flexure, diagonal tension, shear and bond, etc., by the working stress method in Chapters 5 and 6 in a very systematic and concise manner. Chapters 7 and 8 deal with the design of various types of beams and slabs. The design of columns has been discussed at greater length in Chapters 9 and 10. Inclusion of design aids in the form of charts and tables would have enhanced the value of these chapters.

The design of components of structures by the load factor method has been presented in an excellent manner in Chapters 11-13 of Section 3 and will be of immense help to the designer, as the IS code now permits design of sections by this method. The design aspects of foundation, buildings, industrial structures and other civil engineering structures have been explained fully in Chapters 14-18. The theory of design of shell roofs has also been touched upon briefly.

Section 5 of the book deals with indeterminate structures. The author recommends Kani's method for the analysis of indeterminate structures. Designing of frames and arches has also been discussed.

Several books are available on the subject of prestressed concrete, but in the context of the objective of this book, the treatment had to be brief. Nevertheless, the author has succeeded in bringing out the salient aspects of prestressed concrete in Section 6 in an expert manner. Inclusion of some explanatory sketches and photographs of the popular prestressing system, however, would have made the reading more interesting. Section 7, which deals with the topics of concrete structure and repair, should be of great help to the practising engineers, as it provides many useful hints.

The subject of structural concrete has been very well presented in this book and the treatment of the individual topics is highly satisfactory. This book should, therefore, be of great value to all those who are concerned with the design of concrete structure. Inclusion of suitable references, however, would have made this book more useful for teachers and postgraduate students.

S. M. K. CHETTY & S. K. CHOPRA

CARBOCYCLIC NON-BENZENOID AROMATIC COMPOUNDS by Douglas M. G. Lloyd (Elsevier Publishing Co., Amsterdam-London-New York), 1966. Pp. x+220. Price $ 13.00

The past one and a half decades have seen intense and fruitful activity in the field of non-benzenoid aromatic systems. Since the appearance of the first systematic work (*Non-benzenoid aromatic compounds*, edited by D. Ginsbury) on the subject in 1959, new areas (e.g. cyclopropene derivatives) have been conquered and the theoretical ideas refined and consolidated. Consequently, the appearance of a new book on the subject is both timely and welcome.

The book consists of the following eight chapters: (1) Aromaticity and aromatic character, (2) Derivatives of cyclopropene, (3) Derivatives of

cyclobutadiene, (4) Derivatives of cyclopentadiene, (5) Tropylium salts, (6) Tropones, tropolones and related compounds, (7) Medium and large ring compounds, and (8) Polycyclic compounds.

The general impression which this reviewer gathered is that the book conveys a rather uncritical and, unfortunately, a non-comprehensive treatment of the subject matter and hence falls short of the expectation of research workers in this area. However, the book is recommended as a basis for a series of lectures on non-benzenoid aromatic compounds to M.Sc. students majoring in organic chemistry. The book has been well produced, though from our point of view (at least !) it has been priced on the higher side.

SUKH DEV

GERMANIUM by V. I. Davydov; translated from the Russian by Adam Peiperl (Gordon & Breach Science Publishers Inc., New York), 1967. Pp. 417. Price $ 18.00

Mendeleev's ' Ecasilicon ', known today as germanium, has become one of the most indispensable metals. This rare metal is being widely used in the manufacture of semiconductor devices, power rectifiers, dosimeters for nuclear particles, as an important alloying agent, a catalyst, and in medicine, to cite a few examples. As a result of this, the world's annual production of germanium has sharply increased within a decade or two by about a thousand-fold.

The book contains four chapters and has an appendix on radioisotopes of germanium written by N. P. Rudenko and L. V. Kovtan. In Chapter I, some of the important uses of the metal have been emphasized. Chapter II describes the various minerals and ores of germanium and their deposits in different countries. Chapter III gives a brief description of the recovery of germanium compounds from various sources, the preparation of the metal and its purification. In Chapter IV, a detailed account of the physico-chemical properties of germanium and its compounds, such as oxides, sulphides, halides, hydrides, organo-germanium compounds and germanates, is given. It includes a good compilation of useful and interesting data on the thermodynamics of these compounds. In this chapter there is also a short description of the electrochemical properties and analytical chemistry of germanium. Finally, in the appendix, a description of the isotopes of germanium, their preparation and separation applications and safety measures in handling radio-germanium, is given.

In the book, the stress on various subject matters is unbalanced. For example, the physico-chemical properties of germanium and its compounds cover about three quarters of the volume and, out of the total 282 references, 205 belong to this chapter alone. References given in the book have been collected up to 1963.

However, in view of the scanty compiled information on the chemistry and metallurgy of germanium, this volume should be a welcome addition to the library for reference especially for those working on the compounds of germanium.

P. K. JENA

INVESTIGATIONS IN THE FIELD OF ORGANOLEAD CHEMISTRY by L. C. Willemsens & G. J. M. Van der kerk (International Lead Zinc Research Organization Inc., New York), 1965. Pp. 133

This latest book containing six chapters is an excellent presentation of the results of investigations in the field of organolead chemistry. It gives a summary of the known preparative methods available for various types of basic organolead compounds, and useful suggestions are made for obtaining these derivatives in enhanced yield. The mechanism involved in some of the hitherto unknown reactions is discussed. New methods for the syntheses of functionally substituted derivatives are described; special mention may be made of the use of triphenylplumbyllithium for this purpose. Attention has been drawn to the numerous applications of organolead compounds in the field of modern technology and research. A discussion on the organometallic chemistry of the IV main group elements, included in Chapter I, is a short but excellent review of the trends exhibited by organometallic compounds of this group. The last chapter gives complete experimental details of the processes involved in the preparation of organolead compounds and will be found extremely helpful by all research workers engaged in this field of investigation. Many tables with useful data, index of compounds and about 200 references of the existing literature make it a comprehensive and up-to-date treatise on the subject.

Mention may be made of a few notable omissions in this otherwise excellent publication. The voluminous literature on spectroscopic studies of organolead compounds, particularly the identification of a number of infrared absorption frequencies associated with the lead atom in these compounds finds, no place in the book. The book also does not refer to a large number of coordination compounds formed by the organolead compounds with various donor molecules. The stereochemistry of such compounds, the expansion of covalency of lead atom, and the utilization of vacant *d*-orbitals for this purpose have, unfortunately, not been dealt with.

On the whole, the book gives a vivid account of the general preparative methods and properties of organolead compounds and the authors are to be commended for the wealth of latest information they have presented in this volume. For those working in this field the book is worth possessing.

T. N. SRIVASTAVA

COLORIMETRIC METHODS OF ANALYSIS INCLUDING PHOTOMETRIC METHODS: Vol. 4A, by Foster Dee Snell & Cornelia T. Snell (D. Van Nostrand Co. Inc., Princeton, New Jersey), 1967. Pp. ix+645. Price $ 16.00

This book covers all the important groups of nitrogen containing organic compounds like amines, nitro compounds, amides, anilides, amino acids, proteins and vitamins. Besides, detailed procedures for analysis are given for specific industrial or biologically important compounds like parathion or niacin, etc., not only in its pure form but also under environmental conditions like tissues, blood,

urine, etc., in which they are to be analysed. This is an important addition as, under the above conditions, there are always substances which interfere with the colorimetric estimation; these substances have to be removed and conditions like *p*H, dilution, solvent, etc., have to be readjusted before a proper analysis is made. Wherever necessary, methods of calculation of the result are also given. From these points of view, this book is a valuable aid to the analytical chemist.

The principles of colour development, or the reactions which are responsible for it are discussed very briefly and in general terms. This could have been expanded a little more. One is asked to follow the procedures blindly and thus a critical evaluation of different methods is not possible.

The book will be a good addition for any library as a reference volume.

V. T. ATHAVALE

STARCH: CHEMISTRY AND TECHNOLOGY — Vol. II, edited by Roy L. Whistler & Engene F. Paschall (Academic Press Inc., New York), 1967. Pp. xviii +734. Price $ 30.00

The publication under review is devoted to starch technology and deals extensively with the manufacture and industrial uses of starch and its modified products. Vol. I discussed various fundamental aspects, such as biosynthesis, chemical constitution and physical structure of starch. The two volumes thus cover comprehensively relevant fields of information necessary for the research worker interested in starch chemistry as well as the industrial user of starches.

The material in Vol. II covers broadly four fields. In Chapters 1-5 are discussed manufacturing processes for commercially important starches (maize, milo, wheat, rice, potato, tapioca, arrowroot and sago), whereas Chapters 6-8 cover the use of starch respectively in the paper, textile and food industries, the major industrial users of starch. The preparation, properties and uses of various important modified products and derivatives of starch are discussed in Chapters 9-24. Acid-modified starch, oxidized starch, cross-linked starch, dialdehyde starch, cationic starch, starch esters such as phosphates and acetates, and starch ethers particularly hydroxyethyl starch, are discussed in individual chapters. Also included are other important products, such as amylose, pregelatinized starch, adhesives and dextrose. Chapters 25-27 deal with characterization, analysis and microscopy of starches.

Each chapter, written by an eminent authority in the field, is up to date in information and covers extensively pertinent facts and data related to the subject matter. In a book such as this, covering so wide a subject, one cannot expect a depth of treatment adequate for the specialist in any of the fields discussed. In spite of this, this book presents an excellent combination of extensive coverage and reasonable depth for the student, the research worker, and for the technologist who wishes to extend his breadth of knowledge on the subject. Together with the carefully selected bibliography at the end of each chapter, it could form a good starting point even for the specialist.

Though a combined effort of so many authors, there is little duplication or repetition, and a fair uniformity is maintained in the method of treatment and presentation. Credit and compliments for this should go to the editors.

Written lucidly in simple language and remarkably free from printing errors, the book offers enjoyable reading to anyone interested in starches.

P. C. MEHTA

INSTRUMENTS OF COMMUNICATION by Prof. P. Meredith (Pergamon Press Ltd, London), 1966. Pp. xx+645. Price £ 7 net

Sir Edward Appleton is reported to have observed, in the course of his address to the graduates of Edinburgh University in 1962, that scientists and technologists are "not only inarticulate but also illiterate and irresponsible". There are many things in science, he pointed out, which remain unintelligible because of failure or inadequacy in communication and there are many tracts of common knowledge and understanding which can be substantially increased if adequate attention is paid to communication. Scientists everywhere must take serious note of Sir Edward's words. There is much discussion in recent years on the education of the scientist with emphasis on general education and training in scientific communication, and attempts are not wanting to investigate the causes of 'illiteracy' among scientists and to improve the training of science students in linguistic expression.

The dimensions of the problem of scientific communication have been discussed in a masterly way in this remarkable book under review. The author points out in the preface that his involvement in the problem of scientific communication can be traced back to 1954, when the Department of Scientific & Industrial Research, UK, backed by a research grant, requested him to investigate "the comprehensibility of scientific and technical reports". It was hoped that the author's investigations would lead to the compilation of a 'manual' for science writers. It was clear to the author from the very beginning that there were already many manuals in the field and that the addition of one more to their number would not provide an answer to the complex problem of scientific communication. The author felt that there was clear need for probing deeply into language, "where discovery and understanding, communication and education thought and expression have their common foundation", in order to ascertain how language can be made an instrument of effective scientific communication.

The author has attempted to develop a new approach to the communication of scientific ideas. Words, according to him, are instruments capable of being used for effective communication only if they are scientifically understood, and the words used by scientists have far-reaching properties. The author points out: "The common categories of grammar have become established through generations of social intercourse through conversation and writing in which the insistent demands of everyday life must, by reason of sheer frequency,

have exerted the major influence in shaping the categories of language. A thin, but swelling, stream in this flood of intercourse has, for the last three centuries, been making special demands of its own. This is the stream of communication of scientific discoveries. In this stream, the features of perception and action have assumed dominance over the features of emotion and convention which loom so large in ordinary social intercourse. There has been a resultant strain on language." To relieve the strain and overcome the difficulties of communication, the subtilities and complexities of scientific communication must be clearly analysed and understood. One major difficulty is the problem of translating the immense condensation of meaning in mathematical symbols into verbal forms. A radical strategy of 'coding' must be devised and the coding must be based on "the logic of mathematics, the syntax of language, the facts of science and the needs of man".

The book is the outcome of years of study by an eminent professor well known for his researches in education and scientific communication. It merits close study. The stakes involved in inadequate attention to scientific communication in this age of science are very high indeed, and it behoves scientists and all those engaged in science writing and spreading an understanding of science to interest themselves in the challenging problem of scientific communication. The book serves as an invaluable reference book to science writers and information scientists.

B. N. SASTRI

PUBLICATIONS RECEIVED

THEORY OF LINEAR ACTIVE NETWORKS by E. S. Kuh & R. A. Rohrer (Holden-Day Inc., San Francisco), 1967. Pp. xii+650. Price $ 19.25

HETEROATOM RING SYSTEMS AND POLYMERS by H. R. Allcock (Academic Press Inc., New York), 1967. Pp. xi+401. Price $ 16.50

MEASUREMENT OF THE FLOW OF RESOURCES TO DEVELOPING COUNTRIES (United Nations Publications, New York), 1967. Pp. xv+131. Price $ 1.50 or Rs 9.00

STUDIES ON SELECTED DEVELOPMENT PROBLEMS IN VARIOUS COUNTRIES IN THE MIDDLE EAST (United Nations Publications, New York), 1967. Pp. vi+87

UNCTAD COMMODITY SURVEY, 1966 (United Nations Publications, New York), 1967. Pp. xi+224. Price $ 3.50 or Rs 21.00

FERTILIZATION: Vol. 1, edited by C. B. Metz & Alberto Monroy (Academic Press Inc., New York), 1967. Pp. xiii+489. Price $ 22.00

PROBLEMS IN GEOPHYSICS RELATING TO THE CRUST OF THE EARTH (National Geophysical Research Institute, CSIR, Hyderabad), 1967. Pp. ii+223. Price Rs 2.00

PHOTOCHEMISTRY AND REACTION KINETICS edited by P. G. Ashmore, F. S. Dainton & T. M. Sugden (Cambridge University Press, London), 1967. Pp. xvi+378. Price 75s.

INFRARED SPECTROMETRY OF INDUSTRIAL POLYMERS by C. J. Henniker (Academic Press Inc., New York), 1967. Pp. ix+229. Price $ 10.00

INSTRUMENTATION IN BIOCHEMISTRY: No. 26 (Academic Press Inc., London), 1967. Pp. ix+113. Price 30s. or $ 5.00

INTRODUCTION TO THE THEORY OF PARTIAL DIFFERENTIAL EQUATIONS (D. Van Nostrand Co., London), 1967. Pp. x+214. Price 25s.

TEXT BOOK OF FLUID DYNAMICS (D. Van Nostrand Co., London), 1967. Pp. xiv+399. Price 35s.

PROGRESS IN REACTION KINETICS: Vol. 4 (Pergamon Press Ltd, London), 1967. Pp. vii+523. Price 100s.

NOTES & NEWS

Radio pulses from cosmic ray air showers

Measurements of shower size, arrival direction and core location of cosmic ray air showers and radio pulses from these showers, detected with the help of the Bolivian Air-shower Joint Experiment (BASJE) air-shower array, have helped in establishing correlations between the shower arrival direction and the antenna pattern and between the shower size and the frequency of radio pulses. Correlations have also been found to exist between the radio pulse height and the shower size and between the shower core location and the antenna position.

The investigation was carried out at an altitude of 5200 m. and at a latitude of 16°S. The diameter of the BASJE array was 300 m. and it was triggered on 'large showers' (more than 15 particles in any 2 of the 5 scintillators in the outermost ring of the array and more than 30 particles in the scintillator at the centre of the array) and on 'low-mu showers' (more than 25 particles in any one of the 5 central scintillators, at least one particle in each of the 5 scintillators in the innermost ring and less than 4 particles in the 60 m.² shielded scintillator array).

The correlations established are: (i) 60 ± 18 per cent of the radio showers arrive within 25° of the antenna axis; (ii) the radio shower cores strike at distances up to 300 m. from the antenna, but 75 ± 20 per cent are within 150 m. of the antenna; (iii) of all the showers above the size of 10^8 particles and within 25° of the antenna axis, 46 ± 20 per cent are radio showers, but only $2{\cdot}5 \pm 1{\cdot}5$ per cent in the 10^7-10^8 size range. There were also indications regarding the existence of some correlation between the shower size and the pulse height for showers arriving within 25° of the antenna axis [*Phys. Rev. Lett.*, **18** (1967), 51].

Electron spectroscopy for chemical analysis

A new tool has been added to structural studies in organic chemistry. It uses the Auger and photoelectrons produced by X-rays and correlates the electron spectra from carbon with the molecular structure. In the first study 1,2,4,5-benzenetetracarboxylic acid and sodium benzoate were irradiated with aluminium X-radiation, and the electron lines from the constituent elements, carbon, oxygen and sodium, were obtained in the spectra. Carbon gave two well-defined lines with an energy difference of about 3·8 eV. The relative intensities of the two lines in the compounds were 4:6 and 1:6 respectively, showing that the low energy line corresponds to the carboxyl carbon atom and the high energy line to the ring carbon atom. The observation that the carboxyl line has lower energy is consistent with the fact that the electronegativity of oxygen is more than that of carbon or sodium. Owing to the greater electronegativity of oxygen, there will be less negative charge within a certain atomic distance around a carboxyl carbon nucleus than within the same distance of a benzene carbon nucleus.

The intensity ratios between carbon and oxygen in both cases are also in strict agreement with the ratios calculated from the empirical formulae of the compounds [*Nature, Lond.*, **213** (1967), 70].

Staining procedure for demonstrating multiple forms of aldolase

A simple staining procedure for the detection and identification of the multiple forms of aldolase has been reported from the Department of Chemical Pathology, the Royal Free Hospital, London. The new method which, unlike the conventional methods involving elution and subsequent spectrophotometric assay after electrophoresis, utilizes the ready reducibility of alkaline silver nitrate byproducts of aldolase catalysis is applicable for the rapid location of aldolase on starch gel and other media.

Tissue (human or rat) homogenates in equal amounts (wt/vol.) of 0·24*M* sucrose containing $2{\cdot}10^{-5}M$ EDTA at 20°C. are ultracentrifuged at 80,000 *g* for 30 min. and the crude supernatant fraction (0·05 ml.) is subjected to electrophoresis on vertical starch gel using either citrate-phosphate buffer (*p*H 7·0) and a constant current of 2 ma./cm. for 18-24 hr or Aronsson-Gronwall buffer (*p*H 8·9) and a current of 1·24 ma./cm. After completion of the run, the gel is sliced and the strips corresponding to the application spots are separated. Each strip is overlaid with a Whatman No. 1 paper strip freshly soaked in 2 per cent (wt/vol.) solution of fructose-1,6-diphosphate in 0·1*M* acetate-Tris buffer (*p*H 7·6) containing $2{\cdot}10^{-3}M$ iodoacetate and incubated at 37°C. for 15-60 min. depending on the enzyme activity. The paper strips are then removed and soaked in silver nitrate-acetone solution for 20 sec., dried in air, and transferred to a vessel containing 0·5*M* ethanolic NaOH for about 30 sec. Products of aldolase activity appear as black bands of silver [*Biochim. biophys. Acta*, **132** (1967), 203].

Organic Mass Spectrometry

This new periodical to be published by Heyden & Son Ltd, London, will start appearing from early 1968. To be issued bi-monthly, the periodical will carry papers dealing exclusively with the application of mass spectrometry to problems in organic chemistry. Besides original research papers, review papers and book reviews will also be published. The rate of subscription for institutions is £ 14 ($ 40.00) per annum and for individual subscribers £ 4 ($ 12.00) per annum.

Central Drug Research Institute, Lucknow

The annual report of the Institute for 1964-65 presents its main research activities during the year, highlighting, in particular, the progress made in respect of

13 projects with defined objectives in hand.

Two forms of microfilariae, 'long' and 'short', have been observed in naturally infected jungle crows. A simple method for screening potential nematocidal agent *in vitro* and *in vivo* has been developed. Good cesticidal activity with low therapeutic index has been found in four compounds (BIQ 20, BIQ 22, BQ 20 and Laurodin). Studies on rodents and rhesus monkeys have shown that intrauterine contraceptive devices (IUCD) do not evoke any adverse change in the uterus or in the endocrine mechanism concerned with the ovulation and there is no evidence of abortefacient effect. The action of IUCD has been found to be fully reversible, since pregnancy can ensue without difficulty on removal of the device. Benzfuron and a progesterone derivative have shown interesting antifertility activity. Injections of cadmium chloride into one testis of animals has been found to produce complete sterility. Intraovarian injection causes severe damage to the ovary. 5,7 - Dichloro - 8 - hydroxyquinoline (250 mg./kg.) has been found to be as effective as enterovioform (300 mg./kg.) in experimental amoebiasis of the rat.

A simple and sensitive assay procedure for screening antiviral agents has been developed; the method is based on the use of phage CV X-5 as test virus and *Esch. coli* as the host. It has been found that unlike the T even phage, phage CV X-5 does not induce formation of thymidine kinase in *Esch. coli* B. A simple method for the differentiation and separation of small quantities (5-10 μg.) of native DNA from an excess of denatured DNA has been standardized.

Alcoholic extract of stem bark of *Cassia fistula* and 4-β-N-piperidino - ethylamino - 3,5 - dinitropyridine have been found to inhibit multiplication of RDV in CAM culture when given simultaneously with the virus. A method has been developed for acylating thymidine in the 5-position without prior protection of the 3'-position. Promising respiratory stimulant activity has been observed in two derivatives of 3 - β - phenylethyl - imidazo(4,5 - *b*)-pyridine-6-carboxamide; the activity persists for more than 60 min. in cats. Monoamine oxidase from rat liver has been purified 350-fold by a simple technique based on chromatography over DEAE cellulose. Promising vasodilator and hypotensive activities have been exhibited by *o*-β-di-*n*-propylaminoethoxyanisol. The synthesis of oxytocin has been standardized by a new method which would enable its indigenous production. Experimental hypertension, resembling clinical hypertension, has been produced in rabbits by injection of high molecular weight substances and adrenaline. Hyperlipaemia and rise in blood cholesterol associated with hypercoagulability of blood have been produced in rabbits by injecting cobalt chloride. Marked haemorrhage and ulceration could be produced in rats by a restraint technique involving severe stress of short duration.

Animal sera have been found to inhibit growth of the fungus *Candida albicans* and also to enhance the antifungal activity of some antibiotics. Extract of *Madhuca butyracea* has shown nematocidal and cesticidal activity *in vitro*. It has been found that by storing at a low temperature (−10°C.), virulent strains of *Mycobacteria* can be preserved unchanged for a long period without lyophilization or subculturing. Processes have been developed for the commercial production of diaminodiphenylsulphone and 5,7 - dichloro - 8 - hydroxyquinoline. A laboratory scale method for the preparation of the antibacterial agent, furacin, has been standardized. Gamma-globulin has been prepared from human serum for immunization against viral hepatitis and measles.

Indian Association for the Cultivation of Science, Calcutta

The annual report of the Association for the year 1964-65, besides surveying the research projects completed or on hand in the 9 divisions, lists the research papers published during the year (86). A directory of research in chemistry (1960-64) in India, portraying the national trend in research in various branches of chemistry *vis-à-vis* the international trend, was compiled.

Extensive studies were conducted on crystal structure, crystal imperfection and thermal diffuse scattering. Structure analysis of 3,5-dibromo-*p*-aminobenzoic acid has led to the interesting observation that the halves of 2 molecules form one asymmetric unit. The study has also shown that *p*-aminobenzoic acid crystals belong to the orthorhombic system instead of the monoclinic as reported by earlier workers. Expressions connecting the diffusely scattered intensities from monocyclic crystals with elastic constants have been derived for various reflecting planes and for a few suitable directions of propagation of the thermal waves. Experiments are on hand for the determination of 13 elastic constants of 'anthraquinone' using these expressions.

Data obtained on the thermal conductivity of ammonia over a wide temperature range show the effect of resonance exchange in polar gases which is in fairly good agreement with the theory. A new theory which may possibly be used for determining experimentally the actual composition of a reacting gas mixture at the hot and the cold surfaces of a thermal conductivity cell when there is a departure from the condition of local chemical equilibrium, has been developed. The necessary apparatus is being set up. An all-metal oscillating disc apparatus capable of measuring the viscosity of polar and dissociating gases over a wide range of temperature within 1 per cent accuracy has been set up. Analysis of the potential energy curve obtained for several inert gases on the hybrid potential has shown that the hybrid potential is very close to the elaborate six-parameter potential suggested by Guggenheim and Meglashan. With a view to obtaining for the first time reliable force constants recent data on the viscosity of the dissociating system $N_2O_4 \rightleftharpoons 2NO_2$ have been analysed. The results show that the chemical reaction has no significant contribution to the viscosity of dissociating gas. Helium was liquefied for the first time, thereby opening a vast field of research at helium temperatures.

Data on the paramagnetic susceptibility of copper cesium chloride have been obtained; magnetic measurements, which are in conformity with the results of ESR studies, appear to contradict the existing X-ray data. Work on the construction of a 50 c.p.s. B-H meter has been completed and it has been used for the study of B-H characteristics of various ferromagnetic samples. The cryostat-cum-oven set up earlier for the measurement of magnetic anisotropy in the range 90° to 400°K. has been so modified as to enable measurements below liquid oxygen temperatures.

Studies of the effect of benzoic acid and its related acids on the carbinol base of crystal violet have shown the reaction to be an exothermic one. Construction of a long duration microcalorimeter and a static type of equilibrium still which may be employed for the study of excess thermodynamic properties of polymer solutions is in progress. Dye partition technique using disulphine blue as the dye reagent has been extended for the microdetermination of amines and amino end groups in polymers. Studies are in progress for preparing higher molecular weight polymers out of lower ones by interaction of polymers with appropriate end groups. Synthesis of a few model compounds has been achieved towards a projected synthesis of the diterpenoid alkaloid, atisine. An important bicyclic keto-ester and a tricyclic lactone, towards a projected synthesis of biogenetically significant diterpene, rosenonolactone, have been synthesized. A bridge-head compound having the des N-morphan skeleton has been synthesized. Physico-chemical studies are in progress to establish the structure and stereochemistry of this type of compounds. In order to follow up the uranium(IV)-mercury(II) reaction, a suitable procedure for the separation of uranium(IV) from the reaction mixture by ion exchange has been developed, followed by its estimation at low concentrations by the amperometric technique. The data obtained so far from the systematic investigation of the kinetics and mechanism of nucleophilic substitution in cobalt(III) and chromium(III) complexes have confirmed the occurrence of an SN_2 mechanism in some of these systems.

A pure pectic substance has been isolated from onion and methylated completely. The isolation of a neutral polysaccharide from the whole polysaccharide using the enzyme pectinase, a pure gum-acid from green Bacl-fruit (*Aegle marmelos*), has been achieved. With a view to elucidating the structure of vulcanisate and mechanism of vulcanization of rubber, a quantitative characterization of the vulcanized samples containing different proportions of sulphur ranging from soft to hard rubber stage has been carried out using ozonolysis and chromatographic techniques. The study has shown that the total amount of carbon skeleton escaping sulphuration decreases and the amount of sulphur compound increases as the proportion of sulphur in the stock increases. Investigations on the solution properties of polyuronides have indicated polyuronide to be contractile polymers and polyelectrolytic in nature.

Nutrition Research Laboratory, Hyderabad

The annual report of the Laboratory for the period October 1965 to September 1966 presents the results of studies on some of the major nutritional problems of the country, such as protein-calorie malnutrition, vitamin A deficiency, pellagra and lathyrism. Nutritional disorder and nutrition in pregnancy and lactation are among the other problems investigated.

Systematic studies on varietal differences in the nutritive value, particularly the amino acid composition of different newly developed strains of cereals and millets have been initiated. The results show that the increased yield of these varieties is not associated with impairment of the nutritional quality of the grain.

A strain of groundnut (US 26), resistant to aflatoxin, has been isolated and identified. Study on the role of zinc in the metabolism of *Aflatoxin flavus* has shown that zinc at the level of 5 μg./50 ml. the medium is required for the production of aflatoxin. The production of kojic acid, a possible precursor of aflatoxin, increases with increase in the concentration of zinc in the medium, and in the toxigenic strain it is nearly two times that of the non-toxic strain.

Long-term effects of low and high dietary protein on aflatoxin-induced carcinogenesis have been studied. Low levels of dietary protein tend to inhibit hepatic carcinogenicity due to aflatoxin. A simple method for removing toxin from the seeds of *Lathyrus sativus* by steeping the dehusked seeds in hot water has been recommended; the method can be employed where lathyrism is endemic. A paper chromatographic method has been developed for the detection of adulteration of common pulses and their flour with lathyrus. Field trials to control vitamin A deficiency in children (ageing 6 months to 5 years) have been undertaken by giving a single annual massive oral dose of vitamin A. The cause of the growth failure in guinea-pigs maintained on vitamin C deficient diet has been determined. It has been found that the incorporation of amino acid into tissue protein, in vitamin C deficiency, is altered. Excess of lucine in the diet, in the face of marginal intakes of niacin and tryptophan, leads to the development of nicotinic acid deficiency which results in the production of black-tongue in dogs.

Nicotinic acid in *jowar* has been found to be in an available form. By improved methods, it is now possible to obtain edible cottonseed flour of adequate nutritional quality and fit for human consumption. Cottonseed flour has been tried in the treatment of children suffering from kwashiorkor. Low levels of hydroxyproline in urine in kwashiorkor have been found to be due to protein-calorie deficiency. Among biochemical parameters, determination of inorganic phosphorus has been found to be a more sensitive index for the detection of early rickets in children instead of the alkaline phosphatase level in serum.

Lower iodine value of the fatty acid compared to normal has been found in subjects suffering from phrynoderma. A raised ratio of

trienoic to tetraenoic fatty acid in plasma is now generally accepted as a reliable index of the essential fatty acids; this ratio is significantly higher in the subjects with phrynoderma than in normal children. The results of these studies indicate that phrynoderma is a manifestation of essential fatty acid deficiency in which vitamins of the B-complex group play a significant role.

Milk proteins in the milk samples obtained from mothers lactating for over 6 months have been separated into six bands instead of the usual five. Band 6 has been found to be a basic protein. Results of preliminary studies have indicated it to be a nucleoprotein; its occurrence only in the later stages of lactation suggests that it may be derived from the broken cells of the mammary glands. Further studies on the nature of this protein are in progress.

Shri A. Krishnamurthi

Shri A. Krishnamurthi, Scientist, Publications & Information Directorate, New Delhi, took charge as Chief Editor of the Directorate on 2 December 1967.

Shri Krishnamurthi (*b.* 10 October 1912) had his early education at the Mysore University. After passing his M.Sc. in Organic Chemistry from the Banaras Hindu University in 1935, he joined the Department of Biochemistry, Indian Institute of Science, Bangalore, as a Research Scholar and continued there till 1942, with a two-year break in between (1937-40), when he was the Works Chemist, Mysore Paper Mills, Bhadravati. He later worked as Chemist at the Travancore Plywood & Rubber Industries, Trivandrum (1942-44), and in 1944 joined the Chemical Laboratories, CSIR, New Delhi. In 1946, he joined the staff of the *Journal of Scientific & Industrial Research*, where he had his initiation into the field of scientific editorial work at the able hands of Shri B. N. Sastri. For over two decades, Shri Krishnamurthi has been shouldering the responsibility of running the periodicals brought out by the Publications & Information Directorate. During this period he has been closely associated with the various expansion programmes of the Periodicals Section. He had a large hand in the major reorganization of the *Journal of Scientific & Industrial Research* in 1963, under which its various sections gave place to independent subject periodicals — *Indian Journal of Chemistry*, *Indian Journal of Technology*, *Indian Journal of Pure & Applied Physics*, *Indian Journal of Experimental Biology* and *Indian Journal of Biochemistry*.

In 1957, Shri Krishnamurthi visited about 100 institutions in USA, UK, France, Italy and Switzerland and studied different aspects of the work connected with the collection, preparation, presentation and dissemination of scientific information.

Shri Krishnamurthi is a member of the ISI Documentation Sectional Committee; member, Executive Council, Society of Biological Chemists, India; and member, Editorial Board, *Indian Science Abstracts*.

Shanti Swarup Bhatnagar Memorial Awards

The Council of Scientific & Industrial Research has awarded the Shanti Swarup Bhatnagar Award in Chemical Sciences for 1965 jointly to Prof. R. C. Mehrotra (Dean of Faculty of Chemistry, Rajasthan University) and Prof. Sadhan Basu (Palit Professor of Chemistry, University College of Science, Calcutta). The Award in Medical Sciences has been given to Dr N. K. Dutta (Haffkine Institute, Bombay) and Dr V. Ramalingaswami (All India Institute of Medical Sciences, New Delhi).

Announcements

▪ *Silver Jubilee Research Award*, 1969 — To commemorate its Silver Jubilee in 1969 the Medical Council of India had created a Silver Jubilee Research Award Fund. The Management Committee of the fund has decided to make the next award during November 1969. The award will be open to all citizens of India and foreign nationals who have spent considerable time for research in India, and who had distinguished themselves by outstanding original research in the fields of medical and allied sciences. The value of the award will be Rs 25,000 and a gold medal of the value of Rs 1000. The award, for the present, will be presented once in 5 years at a ceremonial function at which the successful candidates would be required to make an oration.

The award will be made on the basis of nomination of candidates to be submitted along with copies of monographs and reprints of nominees' special study and research.

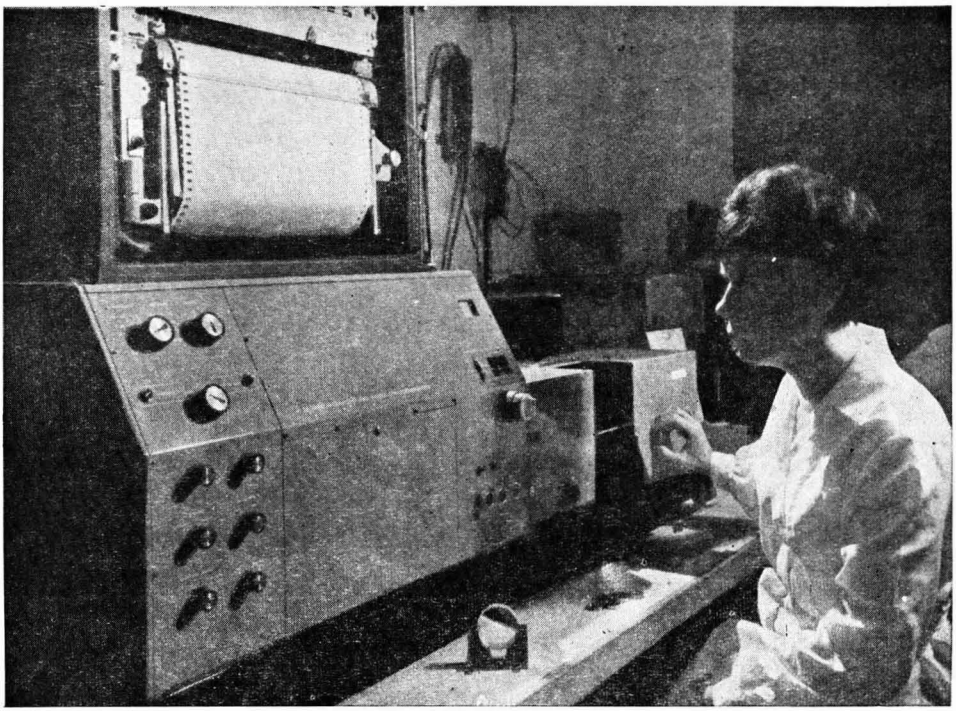
Nomination forms can be had from the Secretary, Silver Jubilee Research Award Fund, Medical Council of India, Temple Lane, Kotla Road, New Delhi 1; completed nomination forms should reach him not later than 31 March 1969.

▪ *Dr B. C. Roy National Award*, 1969 — The Medical Council of India has created an award fund known as 'Dr B. C. Roy National Award Fund' from which the following awards may be given during Oct.-Nov. 1969: (1) to recognize the merit of a good and capable teacher in medicine (civil or military, in various branches) by rotation; (2) to recognize talents in encouraging the development of specialities of different branches of medicine; and (3) to recognize the best services in the field of socio-medical relief and in the establishment of medical organizations and institutions (both civil and military).

The award will be of the value of Rs 2000 each for the above three categories — one award to be given in each category once in 5 years from 1969 onwards. The award will be made on the basis of nominations of candidates to be submitted along with evidence of work done including copies of monographs and reprints of special study. Citizens of India and other nationals who have spent considerable time in India, male or female, are eligible for the award.

Nomination forms are available from the Secretary, Dr B. C. Roy National Award Fund, Medical Council of India, Temple Lane, Kotla Road, New Delhi 1; completed nomination forms should reach him not later than 31 March 1969.

A question of accuracy?



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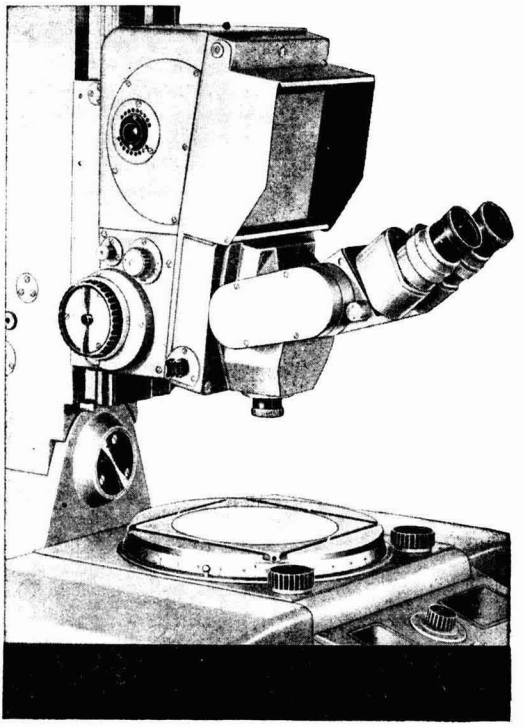

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