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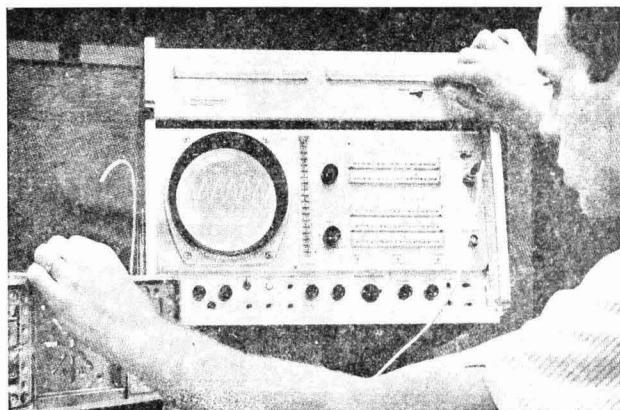
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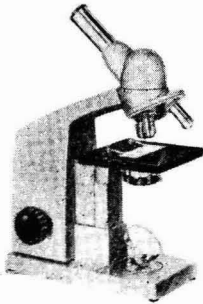
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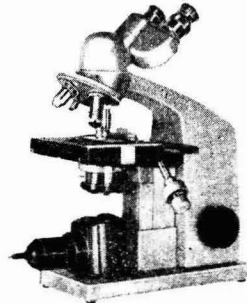
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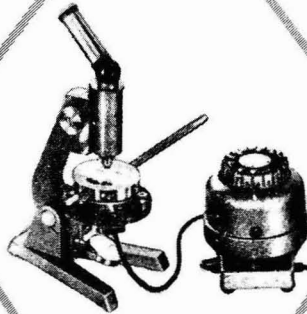
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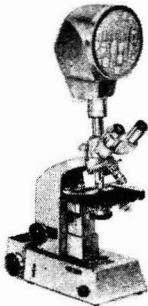
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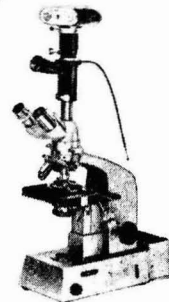
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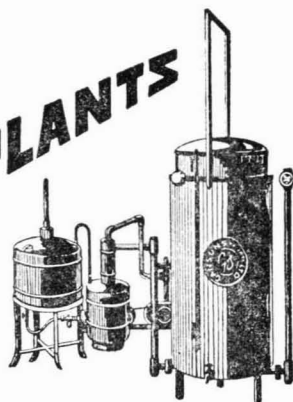
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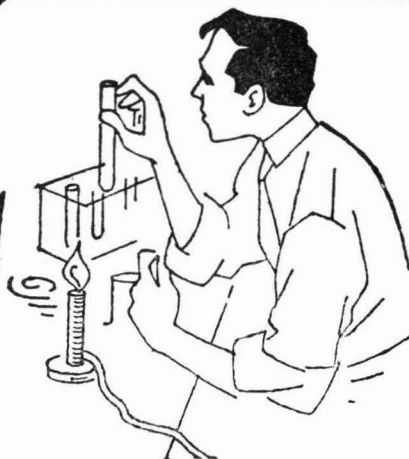
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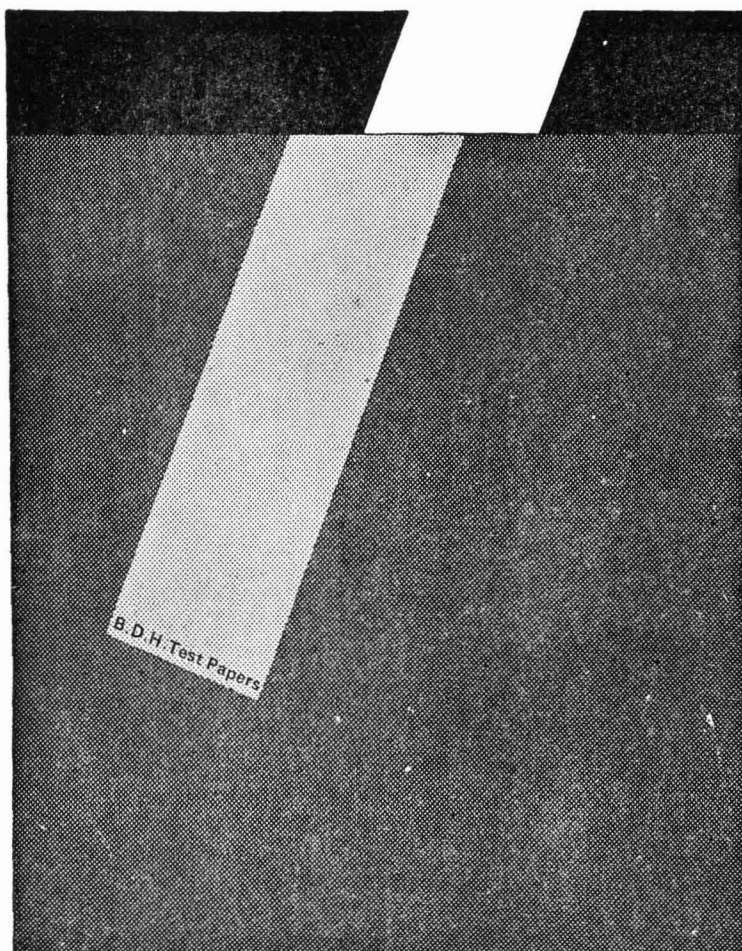
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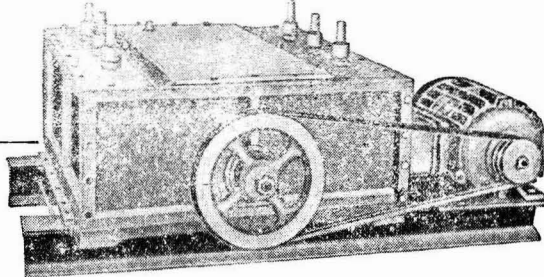
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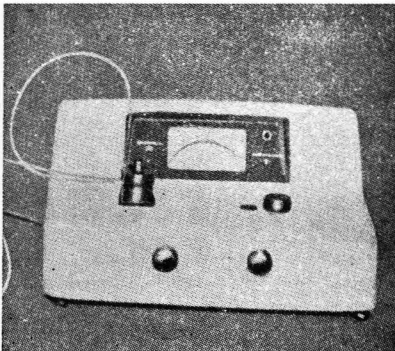
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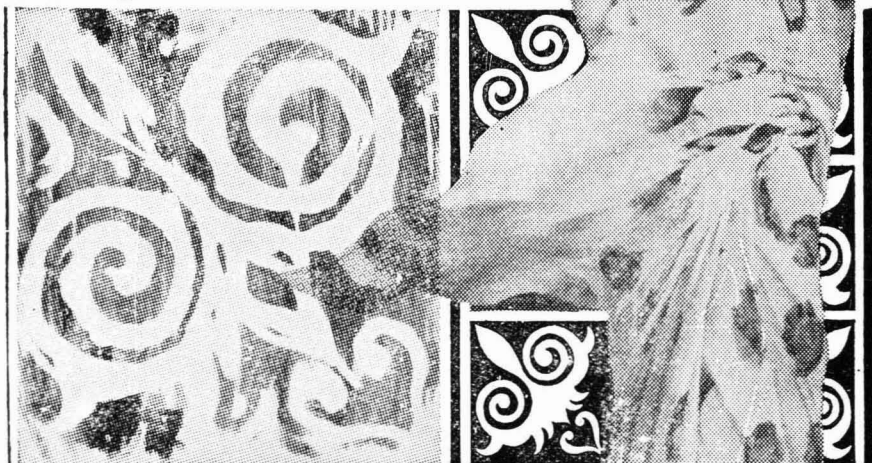
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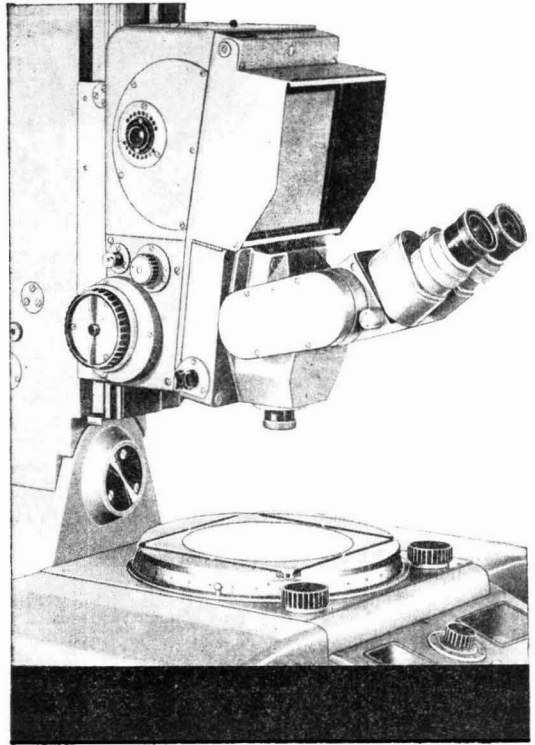
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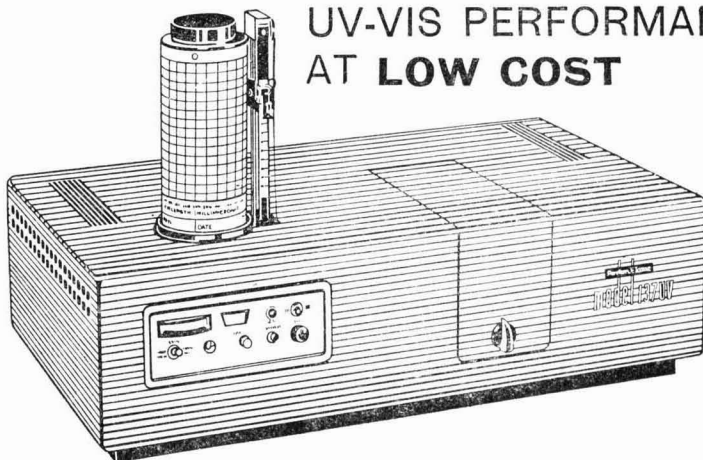
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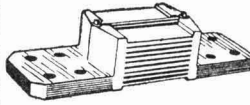
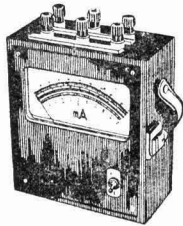
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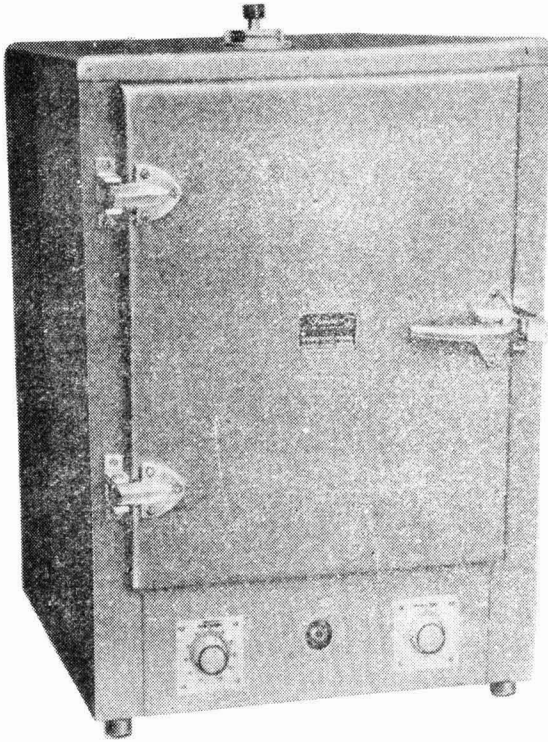
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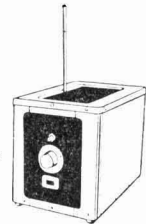
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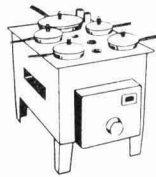


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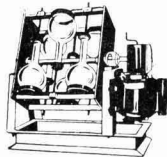


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Current Topics

Symposium on Indian Ocean

THE three-day symposium on Indian Ocean, organized jointly by the Indian National Committee on Oceanic Research (INCOR) and the National Institute of Sciences of India, from 2 to 4 March 1967, was meant to bring together all workers in different disciplines of oceanography from various institutions in the country, and discuss the results of investigations carried out as part of the programme of the International Indian Ocean Expedition (IIOE). Though several symposia and seminars on different aspects of the programme were organized earlier, the present symposium represents the first attempt to take stock of the results of investigations in all the areas during the IIOE and of earlier work. The symposium was well attended, the participants being drawn from several research establishments and universities, and included several foreign delegates. One hundred and fifteen papers covering diverse aspects of oceanography were presented and discussed (see p. 190 for detailed report on the symposium). These are indeed welcome signs of the general awareness of an interest in oceanographic study and research in the country.

Much new knowledge has been gleaned about the Indian Ocean, primarily as a result of the IIOE programme. Apart from this, the establishment of the International Meteorological Centre at Bombay and the Indian Ocean Biological Centre at Cochin, as part of the IIOE programme, has provided valuable training grounds for future oceanographers in two important areas of oceanography.

The papers presented at the symposium reveal that the contributions of Indian workers to different fields of oceanography, with particular reference to seas around India, are substantial. Academic studies of interest are concerned with such topics as origin of the Indian Ocean, evolution of the Indian coastline, theories regarding the origin of the monsoons, etc. Upwelling studies along the coastal regions have yielded basic data on organic production. Circulation patterns in the upper layers of water masses in the Bay of Bengal and the Arabian Sea are better understood now. Chemical oceanographic studies have revealed the distribution characteristics of various chemical factors and nutrients in different

parts of the Indian Ocean. Geochemical studies have provided information on the concentration and dispersal of radionuclides from atomic reactor wastes, the circulatory mixing processes in the sea, and the heavy water content of sea water concentrates and salt bitterns. Results of practical interest have also emerged from investigations relating to marine sediments of the coastal regions, exploration for minerals such as phosphatic deposits, ilmenite, monazite, calcareous deposits, etc. Work in the important field of marine biology, including productivity and Indian Ocean plankton, has formed the groundwork on the proposed atlas on the chemical biology of the Indian Ocean.

Fisheries is a subject of primary importance and immediate concern to India, and the investigations carried out have provided valuable information on fish resources as well as the methodology and techniques involved in locating fisheries and in fishing. Work on mark-recovery studies on commercially important marine fishes of India deserves particular mention as it is the first large-scale attempt at tagging marine fishes in the country.

Thanks to the IIOE programme, oceanographic research in the country got a tremendous fillip, but oceanography is largely in its beginning stages in India and it is still a virgin field full of vast potentialities. Oceanographic research is expensive, and research effort should be wisely directed towards areas which would aid the economy of the country, and investigations which would help in the development of coastal and deep sea fisheries should receive priority. The scientific study of the Indian Ocean and the problems of its practical utilization must be closely connected and always kept in the forefront. The National Institute of Oceanography, which started functioning from January 1966, has chalked out a balanced and phased programme of research, and the knowledge gained from the research programme should be applied to improving the utilization of our marine resources as well as solving problems relating to coastal erosion, pollution, navigation, defence, etc. It would be worth while for the INCOR to organize symposia at suitable intervals to explore ways and means of applying the results of laboratory investigations to large-scale practical situations.

Department of Geology, Andhra University, Waltair : Twenty-five Year Progress Report

U. ASWATHANARAYANA*

Department of Geology, Andhra University, Waltair

ON the completion of a quarter century of its existence as a leading centre of teaching and research in earth sciences in India, the Department of Geology, Andhra University, celebrated its Silver Jubilee recently. Both Nature and Man had a hand in shaping the research interests of the Department. The location of the University in the Precambrian terrain, facing the blue waters of the Bay of Bengal, accounts for the interest of the Department in Precambrian geology, beach studies and marine geology. Under the stewardship of the late Prof. C. Mahadevan, the Department has grown from its humble beginnings into its present status, and he left a profound impression on every facet of the departmental activity, including, of course, the research programmes. Thanks to the generous financial assistance from the University Grants Commission, the Council of Scientific & Industrial Research and the Department of Atomic Energy, the Department is reasonably well equipped and well staffed and should be able to give an even better account of itself in terms of quality and quantity of research output under the able guidance of Prof. A. Sriramadas, the present Head of the Department.

The present review is concerned with some of the areas of earth science to which members of the Department made notable contributions.

Petrology-Mineralogy, Structure and Tectonics of the Precambrian of Parts of South India

The geology and petrology of the chromite-bearing ultramafic rocks of Kondapalle Hill Range, Krishna district, and the petrography, petrogenesis and structure of the Kondavidu Hill Range, Guntur district, constitute some of the earlier investigations to be taken up by the Department. Systematic attempts were made to map geologically the contiguous areas of Andhra Pradesh, quadrangle by quadrangle, and this programme has been fairly successful. The petrology-mineralogy, structure and tectonics of the rocks of the Eastern Ghats (khondalites, charnockites, leptynites, calc-granulites, granites and the so-called 'kodurites') have been the concern of several members of the staff. The mineralogical studies include detailed X-ray and chemical investigation of pyroxenes, feldspars and garnets in charnockites and hybrid rocks. The nature and sequence of the multiple-fold movements to which the Eastern Ghats appear to have been subjected have been examined. Another fruitful area of investigation which is in progress concerns the Cuddapahs (the geological and structural study of the Cuddapah-Archaeon boundary, the geological and structural history and palaeo-

environments of the Cuddapah basin, the nature of the relationship of Cuddapahs with stratigraphic units like Palnads and Pakhals).

More recently the geological and structural studies have been extended to Dharwars and some members of the Department have taken interest in this study. A detailed geological, geochemical and radiometric examination of the Closepet granite complex is in progress under the Indian National Programme of the International Upper Mantle Project.

Economic Mineral Deposits

The Department has been having a strong interest in the manganese deposits occurring in Visakhapatnam, Srikakulam and Koraput districts and notable contributions have been made to our understanding of the geological setting, structure, controls of mineralization, trace elements, ore microscopy, ore beneficiation and industrial utilization of manganese ores. The mineralogy, temperature of formation, controls of mineralization, etc., of the copper minerals of the Mosabani Mine, Bihar, have been investigated. The members of the Department played a major role in prospecting for and proving of the following economic mineral deposits: float iron ores of Gandrai, Krishna district; graphite, magnetite, clay and apatite deposits of East Godavari, Visakhapatnam and Srikakulam districts; copper ores of Yenambail, Khammam district and Garimanipenta, Nellore district; lead-zinc minerals of Karempudi, Guntur district; steatite in the Mutchukota area, Ananthapur district; and radioactive minerals and the micas in the pegmatites of Nellore district. Geology students participated in some of the mineral prospecting programmes which were aided by the Government of Andhra Pradesh.

Geochemistry

The trace element distribution in the Kolar Gold Field Mines, Mysore, and in the manganese ores of Srikakulam and Visakhapatnam districts has been studied. The pattern of movement of trace elements across the contact of Vempalle limestones and dykes has been employed to throw light on the mode of genesis of steatite in the Mutchukota area. The geochemical environment, in which the siliceous black shales of Nagarjunasagar dam site were deposited, has been investigated by using the degree of concentration of and interrelationships between uranium, organic carbon, iron, sulphur, etc. A comprehensive geochemical study of the uranium prospect in the Umrā area, Rajasthan, has been made. The primary and secondary dispersion patterns of uranium, copper, cobalt, nickel, vanadium, magnesium, potassium, sodium and calcium in the rocks, soils and waters have been shown to be conditioned by the geology of the area, climatic and hydrological

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conditions, geochemical factors such as pH and Eh and the geochemical behaviour of the elements concerned. The uranium, thorium and potassium-40 contents of a suite of ultramafic rocks are being determined by neutron activation analysis in an attempt to investigate as to which of them, if any, approximate to Upper Mantle material.

Marine Geology, Beach Studies and Sedimentology

The Department has been a pioneer in marine geological research. The bathymetry of the Bay of Bengal, particularly the shelf region along the east coast of India, has been delineated. The study revealed, among other things, the existence of several submarine canyons along the east coast, some of which were located off the river mouths. The sea floor sediments off the east coast have been extensively sampled and the snapper and core samples thus collected have been analysed for mineralogical composition, grain size distribution, coarse fraction studies, identification of clays by differential thermal analysis and X-rays, radioactivity, distribution of calcium carbonate, organic matter and manganese contents. The data have been employed to work out the physico-chemical nature of the depositional environments of the Bay of Bengal.

The lagoonal environment of the Pulicat lake, Kakinada Bay and the Chilka lake and the deltaic environment of the Godavari delta were examined in considerable detail. The studies include the genesis and physiographic evolution of the lagoon/delta, the geochemistry of the sediments and waters and the nature of the base exchange processes operating, the nature and abundance of the different clay components of the sediments and their trace element content, mineralogy, size and shape of the grains and the carbon-14 age of the shells in the core.

The rotary currents of the Bay of Bengal and the vertical temperature structure of the upper layers of the sea off the east coast of India have been investigated.

Considerable attention was devoted to the nature and magnitude of sand movement along the Visakhapatnam-Waltair beach which is subject to three distinct influences: rhythmic short period tide cycles, random 'cataclysmic' events like rain storms, and beach erosion induced by the construction of the break-water at the entrance of the Visakhapatnam Harbour Channel. Under the auspices of the Department of Atomic Energy, Government of India, a reconnaissance survey was made of the monazite-bearing heavy mineral sand deposits on the beaches of the coast of Andhra Pradesh. The extents of the deposits were delimited and the tonnages of heavy minerals in different patches were estimated. The same agency sponsored a fundamental study of the origin of heavy mineral sand deposits of the south-west and east coasts of India, which involved a detailed sedimentological, mineralogical and radiometric study of river, lake and beach sands of parts of south-west and east coasts. The pattern of distribution of heavy mineral deposits has been shown

to be the consequence of operation of the following factors cumulatively: lithology, structure, weathering and erosion of the geological formations constituting the primary provenance, the geomorphic history and physiography, the gradient of rivers and the quantum of river discharge, the nature of the long-shore currents and sea level oscillations, events leading to the emergence of land, and flooding of river valleys. Local high concentrations of heavy mineral sands may be brought about by coastal erosion (examples: Visakhapatnam and Uppada on the east coasts) and high waves.

The nature, environment, depositional history and fabric of the sedimentary rocks of the east coast of India have been investigated. Heavy mineral suites have been employed as a criterion for the correlation of the sedimentaries in parts of East Godavari and Visakhapatnam districts.

Radioactivity and Geochronology

Radioactivity has been determined for several hundred rocks (khondalites, charnockites, leptynites, granites, schists), sands (beach, lake and river sands) and sea floor sediments off the east coast of India. Radioactivity of rocks has been shown to be conditioned by the chemical composition, mineralogical constitution and petrogenetic history of the rocks concerned. Mineralogical composition, environment of deposition and geochemical factors control the radioactivity of sand and sea floor sediment samples.

Employing the radioactivity decay techniques, the Department did pioneering work on the dating of major orogenic cycles that shaped the Precambrian shield of India. The 'chemical' and isotopic (Pb-U-Th) ages of pegmatitic radioactive minerals and galenas, Rb-Sr and K-Ar ages of whole rocks and mineral separates from different Precambrian belts of India (particularly, the Eastern Ghats and the Cuddapahs) have been determined. The radiometric age data have been interpreted in the light of the geological and structural history of each belt and the post-formation history of the rock/mineral concerned. Some of the orogenic cycles recognizable in India (2600-2700, 1600-1700, 900-1000 million years) are found to be world wide, but a few (450-550 million years, for instance) apparently have counterparts in the Indian Ocean area only.

Geomorphology and Terrain Evaluation Studies

In an attempt to reconstruct the palaeogeography of the Cuddapah basin, the drainage pattern on either side of the Archaean-Cuddapah boundary and the effect of uplift and structure in the southern part of the Cuddapah basin have been studied. The geomorphological and palaeoclimatological significance of coastal laterites has been examined. Under the terrain evaluation programme of the Ministry of Defence, Government of India, the lithology, structure (major and minor), soils (nature, strength), vegetation, water table, etc., of a small area in Visakhapatnam district are being comprehensively investigated.

Research in Indian Medicine

M. SIRSI

Pharmacology Laboratory, Indian Institute of Science, Bangalore 12

THE resurgence of interest in ancient Indian systems of medicine has resulted in the establishment of various institutions devoted to the study of *Ayurveda* all over the country and much interesting and useful work is being done in many of them. However, the results of investigations carried out in these institutions are not easily and promptly available. It is essential that the results of researches from these institutions are published under the auspices of a competent central organization. This would facilitate quick communication among the research workers engaged in this field of study. It is in this context that the starting of the *Journal of Research in Indian Medicine (JRIM)** should be welcomed.

The concepts of Indian medicine, explored and tested under scientific conditions, have the potentialities of making notable contributions to the solution of some of the health problems facing mankind. Close collaboration between teams of workers belonging to *Ayurvedic* and modern systems of medicine to subject the hypotheses and practices of *Ayurveda* to a strict scientific screening as envisaged at the Institute of Indian Medicine, Varanasi, and other institutions in the country is the only way to bring out the hidden treasures of our ancient medical wisdom and apply them for the benefit of mankind.

This type of centralized publication by an authoritative body is all the more necessary since the research communications in this field have so far been published in journals not entirely devoted to Indian medicine and thus could easily escape the attention of fellow workers in the field. Research in Indian medicine is now being conducted not only by institutions and hospitals entirely devoted to Indian medicine but also at various laboratories of research institutes, pharmaceutical firms and medical colleges all over the country. The results of such studies are to be found in hospital bulletins, college magazines and souvenirs, in journals of pharmacy, pharmacology and other publications dealing with medical research in general.

At present, there is no abstracting service to bring the entire research publications of Indian medicine which are widely dispersed in various journals. It is almost impossible to know quickly what has been recently done and what work is currently in progress in this field at various research centres. This has many a time led to duplication of study and has considerably hindered the progress of research.

The *JRIM* should serve as an important medium for the publication of all research communications in Indian medicine. The Central Council of Ayurvedic Research being the sponsors of this journal and the reputed Post-Graduate Institute of Indian Medicine

at Varanasi having been entrusted with the task of editing and publishing the journal, the journal could not have had a more auspicious start and a more congenial environment.

The articles in the inaugural issue present mostly the research activities of the Post-Graduate Institute of Indian Medicine, Banaras Hindu University, Varanasi. Utilizing modern laboratory methods and biochemical techniques an attempt has been made to evaluate the pharmacological properties of some Indian medicinal plants and to place their clinical application on a rational and scientific basis.

The treatment of jaundice due to infectious hepatitis by *Picrorhiza kurroa* Royle ex Benth., the role of *Dalbergia lanceolaria* L.f. in the management of rheumatoid arthritis, the efficacy of *Embelia ribes* Burm. f. in ascariasis, and comparative evaluation of *Ipomoea petaloidea* Choisy as a cathartic are the clinical studies presented in the issue under review. After a brief discussion of hepatitis in general and infectious hepatitis in particular, the results obtained in the treatment of jaundice in infectious hepatitis with *P. kurroa*, singly and with combined therapy in the form of '*Arogyavardhini*' tablets (a herbomineral combination of the drug with copper, mercury, sulphur, iron, etc., and other herbs) and '*Phaltrikadi*' decoction [a herbal combination of *Terminalia chebula* Retz. (Sanskrit: *Haritaki*), *Terminalia belerica* Roxb. (Sanskrit: *Bibhitaka*), *Embelia officinalis* Gaertn. (Sanskrit: *Amalaki*), *Tinospora crispa* Miers ex Hook. f. & Thoms. (Sanskrit: *Amrita*), *P. kurroa* Royle ex Benth. (Sanskrit: *Kutaki*), *Melia azedarach* L. (Sanskrit: *Nimba*), (Sanskrit: *Vasa*) and (Sanskrit: *Chirayata*)] have been detailed, and the beneficial effects have been claimed for the treatment.

The crude drug and petroleum ether extract of *Dalbergia lanceolaria* (Sanskrit: *Gaurakha*) have been found effective in experimental arthritis and good response has been observed in clinical cases of rheumatoid arthritis. The controversy about the identity of *I. petaloidea* Choisy (Sanskrit: *Vidhara*) and its pharmacognostic characteristics, qualitative analysis of Soxhlet solvent extracts and a clinical trial of the resinous and non-resinous portions have been presented. Purgative activity for the resinous portion, almost equal to that of scammony resin, has been claimed.

Crude extracts of some plants have been subjected to pharmacological investigations. Hypotensive effects of extracts of a few indigenous drugs, with special reference to *C. pluricaulis*, have been reported employing anaesthetized dogs and on frog's perfused heart. Fresh juices of *Aristolochia indica* L., *Plumbago zeylanica* L., *Gossypium herbaceum* L. and *Bambusa arundinacea* have been tested for their *in vitro* action on isolated rat and human uteri. The general pharmacological properties of the water-soluble part of the alcoholic extract of the barks of

*The *Journal of Research in Indian Medicine*, Vol. 1, No. 1, 1966, published by Post-Graduate Institute of Indian Medicine, Banaras Hindu University, Varanasi, for the Central Council of Ayurvedic Research, Government of India.

Crataeva nurvala Buch.-Ham. (Sanskrit: *Bikwapatra*) have been studied. The drug is shown to exhibit both nicotinic and muscarinic actions. An aqueous soluble fraction from ethanol extract of the entire plant of *Selaginella rupestris* Spring (Sanskrit: *Sanjivini*) has been studied. Intestinal relaxant action and oxytocic action *in vitro* in some species of animals have been recorded.

In the field of toxicology, the toxicity of *Scnecarpus anacardium* (Sanskrit: *Bhallataka*) has been described and the depletion of ascorbic acid from adrenal glands by *Tamra bhasma* is mentioned. A study of the relation between dosage and toxicity of the oil extracted from *Bhallataka* nuts in rats and rabbits has been conducted. Given in doses recommended for clinical use, the oil is not toxic to liver and other organs. *Tamra bhasma* has also been reported to induce a depletion of the adrenal ascorbic acid in rats and guinea-pigs.

A paper entitled 'Therapeutic advances in Diabetes mellitus through ages' emphasizes the lacunae in our knowledge about this disease and briefly reviews the antidiabetic effect of some Indian medicinal plants.

Use of Indian medicines in surgical practice are welcome studies and they open up a new field of investigation. The feasibility of reducing the convalescent period after certain surgical procedures involving gastro-intestinal tract by premedication by herbal products, and the acceleration of healing time by *ghee* (butter fat) medicated with *Jasminum auriculatum* Vahl in experimental burns have been highlighted. The effect of *Purya karma* (pre-operative preparation on the convalescence of surgical patients) is a study of the influence of administering aqueous extracts of *Crataeva religiosa* syn. *C. nurvala* (Sanskrit: *Varuna*) and *Moringa oleifera* Lamb. (Sanskrit: *Shobhanjana*) during the preoperative period of gastrectomy or gastrojuenostomy, on biochemical changes and on post-operative recovery. Reduction in convalescence period and favourable metabolic alterations have been observed by the administration of the plant extracts.

A comparative study of healing in experimental burns has been carried out utilizing a technique

developed in the laboratory by which second degree burns can be produced in rats. The effect of application of *ghee* medicated with *J. auriculatum* has been studied. Mucopolysaccharide and collagen estimation of the burnt tissue during the process of healing and a comparative evaluation of healing time has clearly revealed a definite acceleration of healing time by the medicated *ghee*.

The varied topics and the wide coverage of the articles in the fields of pharmacognosy, experimental pharmacology, toxicology and clinical evaluation published in the journal are indicative of the intensive and coordinated research activity at the Post-Graduate Institute of Indian Medicine, Banaras Hindu University, Varanasi. These studies also reveal the intense desire of the investigators to obtain a scientific basis for the many therapeutic successes reported with Indian medicinal plants. However, many of these investigations are only of a preliminary nature. The foremost difficulty in replicating the results obtained with crude drugs is the standardization of the medicaments. Until quality control of manufactured drugs is established either by isolation and characterization of the active principles or by biological standardization of the crude drugs, therapeutic results obtained with indigenous drugs are liable to great fluctuations.

The limitation of the application of the results of animal experimentation to the human being has to be kept in mind. Since species variation is the rule rather than exception, the observations, particularly *in vitro* effects of drugs, cannot be translated *in toto* to the human beings. This is well recognized by all pharmacologists and clinicians engaged in chemotherapeutic studies, but still the reviewer wishes to emphasize this aspect in view of the wide conclusions drawn by many investigators on insignificant data.

Clinical trials pose another problem. In our enthusiasm to rejuvenate the ancient systems of medicine, one should not lose sight of the fact that there are now recognized procedures for clinical trials in international practice. These procedures should be adopted for establishing the efficacy of a drug, particularly when marginal benefits are claimed.

Symposium on Indian Ocean

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THE International Indian Ocean Expedition (IIOE), which is a multi-national project for the scientific exploration of the Indian Ocean and in which 19 countries took part with 38 ships, completed its field programme on 31 December 1965. India has been an active participant in the IIOE not only because of its geographical position but also because several phenomena occurring in the Indian Ocean directly affect the lives of the Indian people. During IIOE, a number of scientists of different countries belonging to different disciplines participated in the expedition and collected a vast amount of data. It was, therefore, considered necessary that the results of the studies should be brought to light either during the expedition itself or as early as possible after the conclusion of the field programme. During the expedition period itself a number of seminars and symposia were held by several participating countries where the preliminary results were discussed. In India also a number of seminars were held whenever any of the foreign participating ships called at our ports. In these seminars, which were more of the nature of informal discussions, an opportunity was provided for our scientists to come into contact with oceanographers of other countries and to discuss scientific problems relating to the Indian Ocean. In addition to these informal seminars, two symposia were held in India during the period of the expedition. The first was organized in December 1964 during the International Geological Congress in Delhi when group discussions were held on the geological and geophysical results of the IIOE and a number of interesting findings were brought to light. [Prior to this, in November 1964, the Royal Society, England, also held discussions on the Geological Results of the IIOE.] The second symposium was convened in July 1965 on the Meteorological Results of the IIOE in Bombay, and it was organized jointly by the Unesco and WMO. As the data collection and processing were still continuing, there was not much time for detailed studies on these data and hence the results presented in all the symposia should be considered as more or less tentative. During the Second International Oceanographic Congress held in Moscow during May-June 1966 a number of papers were presented on the scientific results of the IIOE.

In the Indian programme of the IIOE, 1962-65, scientists from several organizations and government departments in the country participated in the cruises of both the Indian as well as some of the foreign research ships, and collected a large amount of data under the various disciplines of oceanography. In order to provide a common forum for discussing the results of all the Indian workers, the Indian National Committee on Oceanic Research, at its meeting held on 3 April 1964, strongly recommended that a symposium on the results of

the IIOE be held jointly with the National Institute of Sciences of India (NISI).

The symposium, organized jointly by the National Institute of Sciences of India and the Indian National Committee on Oceanic Research (CSIR), was held from 2 to 4 March 1967 at the auditorium of NISI, New Delhi, under the following five sections: (1) Physical and chemical oceanography including geochemistry and radiochemistry; (2) Geology and geophysics; (3) Marine biology including productivity; (4) Fisheries; and (5) Maritime meteorology. One hundred and fifteen scientific papers were presented at the symposium.

Dr Panikkar, Director, National Institute of Oceanography (NIO) and Secretary, NISI, welcoming the delegates reviewed the work done in the Indian programme of IIOE where a number of young scientists from different organizations and government departments have participated and contributed to the scientific programme. He expressed satisfaction that most of these scientists who had participated in the Indian programme and some of the senior scientists have come to present their results. It was also gratifying, the speaker said, to find scientists from USA, USSR, West Germany and Japan, and also members of the Indian Ocean Biological Centre's Consultative Committee participating in the symposium on our invitation and giving us the benefit of their scientific experience. The Indian Ocean Expedition has brought about a general awareness and has created a great amount of enthusiasm for the study of oceanography in India.

Dr Atma Ram, Director-General, Scientific & Industrial Research, who spoke next, stated that the CSIR has deep interest in the development of oceanography as one of the scientific activities in the country. He expressed the hope that the science of oceanography would make material contribution to the country through the study of living resources and the mineral resources, and provide basic information of value in meteorology and oceanic transportation.

In his inaugural address, Dr D. N. Wadia, National Professor and Chairman of the Indian National Committee on Oceanic Research, stated that the International Indian Ocean Expedition, 1960-65, was a great event of the decade and said that everyone who had something to do with the expedition is looking forward to the publication of the results. Referring to the symposium Dr Wadia said that it was an important day in the history of oceanography in India, as more than a hundred young Indian disciples in this new science were taking part in collaboration with reputed foreign scientists. He also referred to two important cooperative projects that have been developed in connection with the expedition. The first was the International Meteorological Centre in Bombay which dealt with the large volume of meteorological

data collected during the expedition, and the second was the Indian Ocean Biological Centre in Cochin, established to handle the large amount of zooplankton collections taken with the Indian Ocean Standard Net. He also expressed satisfaction that the members of the Consultative Committee for the Indian Ocean Biological Centre were taking part in the symposium.

From the geologist's point of view, Dr Wadia said that the expedition work is very notable in revealing new features of the bottom topography of the Arabian Sea and the Bay of Bengal. The work during the expedition has brought to light several interesting bottom features such as submarine volcanoes, mid-oceanic mountain ridges, submarine valleys and canyons. But, according to the speaker, the most notable achievement would be the light it would throw on the vexed controversy of modern geology regarding the continental drift. Elaborating further on the problem of continental drift, Dr Wadia said, the bottom sediments and the cores obtained during the expedition's investigations is bound to throw some light on the question whether the subcontinent of India has been stationary, detached from Africa or Australia by the foundering of the portions of the old Gondwana continent, or whether after its separation from that continent, India has wandered some thousand miles from south of the equator into its present position in Eurasia. It is the belief of some geologists that India has come all the way from south of the equator and is, therefore, an intruder in Asia. Referring to the development which have taken place in oceanography since the start of the International Indian Ocean Expedition and comparing it with the earlier studies, Dr Wadia said that oceanography has now been put on the map of Indian science. From this small beginning it is yet to grow into a substantial national effort. He felt very happy that he has been associated with the oceanographic group since 1960 and he hoped that as a result of the discussions which would be taking place during the symposium much new knowledge would emerge out and would contribute to further development of oceanographic studies.

Prof. T. R. Seshadri, President, National Institute of Sciences of India, stated that he was very happy that this symposium on Indian Ocean has been organized under the auspices of the NISI. Apart from many benefits the study of ocean would bring to India, he said he would particularly emphasize on one aspect, viz. the study of organic chemistry of the ocean waters and the various plant and animal material contained therein, and he hoped that such studies would enable discovery of new types of biochemicals.

With the proposal of vote of thanks by Dr Ganguly of the Bhabha Atomic Research Centre, Bombay, the inauguration function concluded and the symposium was continued in different scientific sessions.

Physical Oceanography

The first session on physical oceanography was presided over by Dr E. C. LaFond (US Navy Electronics Laboratory), who in his paper dealt with

the oceanic circulation in the Bay of Bengal. He dealt mainly with the work carried out by the US research vessel, *Anton Bruun*, during her first IIOE cruise in the Bay of Bengal during March-May 1963, and stated that in the early part of the cruise the prevailing NE monsoon winds gave rise to upwelling along the Burmese coast, while in the latter part of the cruise there was upwelling along the east Indian coast. Influence of tides and internal waves on the circulation patterns was also discussed by him. The resulting effect of upwelling on the organic production and chlorophyll content based on the data of the *Anton Bruun* was also indicated in the paper.

Dr LaFond's paper was followed by four more papers on the Bay of Bengal. The first one by L. V. G. Rao and R. Jayaraman (National Institute of Oceanography), presented by Jayaraman, gave an account of the general hydrographical features of the central and southern Bay of Bengal based on INS *Kistna* data for 1962-63. The presence of certain typical water masses, particularly one of low density formed by the mixing of dilute waters from off the Burmese coast with those of the Pacific origin entering the Bay of Bengal through the Malacca straits was indicated, based on T-S relationships. The papers by Varadachari, Murthy, Thirupad and others from the Physical Oceanography Division, NIO, dealt with water masses, internal waves and thermocline features in the Bay of Bengal, and also the circulation patterns in the upper layers of the bay. The choosing of level of no-motion at 500 metres for dynamical computations, existence of long-period internal waves, of wavelengths varying from 150 to 500 km., and the effects of these waves on the dynamic computations of currents were discussed. The authors also discussed the methodology adopted by them in choosing the reference level. Variations in thermocline levels and the probable causes were also examined by these authors. Two interesting papers giving the results of direct current measurements were presented by scientists from Health Physics Division of the Bhabha Atomic Research Centre, Bombay. The first one by Nair, Neralla and Ganguly presented results of current measurements off Mormugao harbour in January 1967 and the second one by Nair and Bhattathiri on current measurements at the Angria bank late in 1965. An Ekman-Merz current meter was used in these studies. The current measurements off Mormugao showed that the currents were mostly towards the north-west with practically no southerly component. The speeds ranged from 0.04 to 0.60 knot. The tidal currents were also found to be very weak. The current measurements in the Angria bank region over a 26 hr period covering two tidal cycles showed current speeds ranging between 0.17 and 0.75 knot, in general, in all the three depths measured — surface, mid-depth and bottom. The directions were mostly west to west-south-west. The current measurement data were found to be in accordance with computations based on salinity-temperature measurements.

On Arabian Sea also there were a number of papers, the chief being one on water masses of the

Arabian Sea in the upper 500 metres by K. V. S. Ramam and coworkers from the Indian Naval Physical Laboratory, Cochin. Geostrophic currents in the Arabian Sea, and transparency measurements were also discussed by the same authors. There was a paper on the scattering layers over the continental shelf off Konkan coast by Rama Raju of the Physical Oceanography Division, NIO, wherein the author showed that the scattering layers are not due to the physical discontinuity (thermocline). One of the most interesting papers in the series was that presented by Balakrishnan of the Indian Naval Physical Laboratory, Cochin, on equipment and facilities designed for the calibration and checking of bathythermographs at the Naval Physical Laboratory.

Maritime Meteorology

The session maritime meteorology, which was held on the afternoon of 2 March 1967, was presided over by Dr K. R. Ramanathan of the Physical Research Laboratory, Ahmedabad. The major discussions were about the monsoons, theories in regard to their origin and their main features. The paper by B. N. Desai was on the air masses over the Arabian Sea during the south-west monsoon season and this discussed in great detail the earlier views held on the origin of the monsoon. According to the author one of the most favourable conditions for the onset of the vigorous monsoon on the west coast of India is the characteristic air mass stratification over the Arabian Sea with moist deflected trades in the lower levels and the dry unstable air from Arabian Sea and the neighbourhood. The strength of the deflected trades and their normal component to the Western Ghats govern the rainfall on the west coast of India. The observations by Pisharoty, which are somewhat different from those of Desai's, were presented in a paper by him entitled 'Cross-equatorial airflow over the Indian Ocean'. According to him, as the cross-equatorial flux is transported eastwards mostly south of 10°N, a significant part of the monsoon water vapour flux across peninsular India consists largely of water vapour evaporated from the Arabian Sea itself.

Y. P. Rao and Raghavendra (India Meteorological Department) discussed the variation of rainfall across the equator. The data are based on ship's reports in the Indian Ocean in the year 1964. The authors showed that there is no appreciable tendency for dry weather near the equator. Another interesting paper was by Rama of the Tata Institute of Fundamental Research on radon in the monsoon current. The paper gave an account of radon measurements in sea level air at Bombay, and also in surface air over the Arabian Sea and the Indian Ocean. Low values, characteristic of south-east trades, were observed up to a few degrees north of the equator. The implications of such measurements in terms of interaction between the south-east trades and continental air masses during the monsoon season were discussed. Another paper of special interest was by Ramamurthi and Jambunathan of the India Meteorological Department (Indian Ocean & Southern Hemisphere Analysis

Centre, Poona). This paper is based on the information collected by the use of automatic picture transmission (APT) sub-system installed at the International Meteorological Centre, Bombay, in December 1963. Interesting features were revealed of cloud developments associated with the first burst of the south-west monsoon over the Kerala coast of India. A paper presented by C. Ramaswamy on weather routing of ships gave an account of an important application of meteorology to navigational aspects in the Indian Ocean.

Chemical Oceanography Including Geochemistry and Radiochemistry

The session on chemical oceanography was presided over by Dr A. K. Ganguly of the Bhabha Atomic Research Centre, Bombay. Thirteen papers were presented at this session which included such varying topics as distributional studies on the various chemical factors such as oxygen, carbon dioxide and nutrients in the various areas of the Indian Ocean; geochemical, radiochemical and trace element studies on sea water and marine sediments; methods and techniques; application of radio tracers to the study of water and sediment movement, etc. The paper on the distribution of phosphorus in the northern Indian Ocean by R. Viswanathan and A. K. Ganguly of the Bhabha Atomic Research Centre, presented by Viswanathan, gave data on inorganic and total phosphorus in the upper 500 metres in the northern Indian Ocean and the Bay of Bengal. Valuable data were presented on the integral mean concentration values of phosphates in the upper 100-metre column (which is an index of available phosphorus for biochemical and biological activities and for organic production to take place) in the various areas and it was shown that there was considerable regional variations in the mean concentrations which could be used to characterize areas of high and low productivity. This paper was followed by papers giving the distribution and cycle of other nutrients like nitrates and silicates by C. V. G. Reddy and V. N. Sankaranarayanan (NIO). These authors presented data relating to nutrient chemistry collected from Arabian Sea, Bay of Bengal and northern Indian Ocean during the cruises of the INS *Kistna* and R.V. *Varuna*. The interesting variations in the pattern of distribution and the influence of upwelling and other types of circulation on the distribution in the upper layers was discussed. The nutrient enrichment due to upwelling was also pointed out by the authors. The patterns of distribution of oxygen discussed in the papers by Anand *et al.* and Garg *et al.* of the Directorate of Scientific Research (Navy) provided additional supporting data for the regional and seasonal variations in upwelling indicated earlier from other physical data. Krishnaswamy of the Tata Institute of Fundamental Research presented a paper on 'Trace elements geochemistry' by Bhat *et al.*, wherein he described a technique of concentrating cosmic-ray produced isotopes from sea water by dragging from a ship underway a container containing sponges impregnated with ferric hydroxide and subsequent elution of the adsorbed material.

The quantitative aspects of the technique were discussed and it was stated that the method has 95 per cent efficiency. In a paper on geochemical studies off Tarapore coast by Sarma and others of the Bhabha Atomic Research Centre, information regarding concentration and dispersal of radio-nuclides from the atomic reactor wastes and the role played by marine organisms and the circulatory and mixing processes in the sea were discussed. The paper on heavy water content of sea water concentrates and salt bitterns by Chaudhuri of the Central Salt & Marine Chemicals Research Institute, Bhavnagar, and the paper on osmium in sea water by Sharma and Parikh of the same institute provided interesting and valuable information.

Geology and Geophysics

Under the session geology and geophysics, 15 papers were presented. The session was presided over by Prof. Wolfgang Schott of Bundesanstalt für Bodenforschung, Hannover, West Germany. Prof. Schott first presented his paper on the 'Recent sedimentation in the Indian Ocean' (first results of *Meteor* in the Indian Ocean Expedition). In this paper he discussed the various aspects of the facial change of sediments from shore-line to the oceanic basin. According to him a number of different facies zones can be distinguished running parallel to the coast. Off East Africa five and off the Indo-Pakistan coast seven zones have been found. These first results are in agreement with observations in other shell areas, for instance, off the Indian east coast.

The paper by Prof. M. S. Krishnan on the geological evolution of Indian coastline dealt in detail with the origin of western coast of India up to the Kathiawar and Kutch regions. He brought out evidence to show that the island of Madagascar separated from India leading to the formation of Indian west coast in the Upper Cretaceous.

An interesting paper on the origin of the Indian Ocean by F. A. Ahmed (Aligarh Muslim University) discussed two hypotheses, one based on continental drift and the other which states that the continents have been where they are and only minor changes have taken place. According to the author, the fact that mountain ranges are continuous from Assam to Turkey shows that India has not drifted *independently* from Africa, as a linear translation of the Indian land mass would have resulted in a distinct break in the mountain ranges.

A paper by Varadachari, Nair and Murthy (NIO) on 'Submarine canyons off the Coromandel coast' was presented by R. R. Nair. This paper is based on echogram data obtained on board the *INS Kistna* during her cruise along the east coast of India during 1965. Three sets of submarine canyons on the continental slope and shelf between Cuddalore in the south and the mouth of Palar river were indicated in this survey and the *geomorphological* features of these canyons were discussed.

Another paper on the bathymetric features of the Bay of Bengal was presented by T. C. S. Rao of Indian Naval Physical Laboratory. Rao presented his analysis of echograms from the *INS Kistna* cruises in the years 1963 and 1964. The

main features revealed in the study are an oceanic rise along 83°E meridian between 11° and 15°N, a trench along the east coast of Ceylon and India (with the greatest depth of 4400 metres) and submarine valleys off the mouths of Mahanadi, Godavari and Krishna rivers on the east coast of India. The extensions of the Ganges submarine canyon in the Bay of Bengal basin down to 9°N were also indicated.

Four papers were presented on marine sediment characteristics off the east coast of India and three off the west coast. M. Poornachandra Rao's (Andhra University) paper was on oolites from the continental shelf sediments off the east coast of India. Subba Rao and Vedantam (Andhra University) presented a paper on distribution of foraminifera in the shelf sediments off Visakhapatnam, based on the data collected during the geological cruise (18th cruise) of the *INS Kistna*. Madhusudana Rao and Murthy (NIO) gave more detailed account of shelf sediments off the Madras coast. Papers on the characteristics of west coast marine sediments included one by Prabhakara Rao (Atomic Minerals Division, Department of Atomic Energy) on the nearshore sediments of the Neendakara-Kayankulam coast, Kerala, the second one by R. R. Nair and Pylee (NIO) on the size distribution and carbonate content of the sediments of the western shelf of India, and the third one by Chatterjee and Gururaja (Geological Survey of India) on the foraminifera of Mangalore coastal sediments. C. Karunakaran [Geological Survey of India (GSI)] presented two papers of more or less general interest, one bearing on mineral exploration possibilities on the Indian continental shelf, and the other on revision of the stratigraphy of the Andaman and Nicobar Islands. The paper on the mineral exploration possibilities dealt with in a general way the possible occurrence of different types of mineral deposits like phosphatic deposits, ilmenite and monazite, calcareous deposits and highlighted a proposed scheme of studies at the GSI on mineral exploration from marine sources. Most of the papers being more or less descriptive and in view of the relatively large number of papers, the discussions were mainly restricted to a few papers where some theories and hypotheses were put forward.

Marine Biology Including Productivity and Indian Ocean Plankton

The largest number of contributions were in the session on marine biology, the total number being 33. This session was, therefore, divided into two sub-sessions, one on Indian Ocean plankton and the other on marine biology (general) including productivity.

The sessions under Indian Ocean plankton and productivity were chaired by Dr M. Anraku from Japan. The first three papers were of an introductory character. Prof. Krey from West Germany presented a paper on plans and first draft for the atlas on chemical biology of the Indian Ocean. He discussed the type of projection used for this type of atlas and indicated the various steps leading to the preparation of these atlases. The atlas is

to consist of sections like primary production, chlorophyll and carotenoids, biomass of phytoplankton, seston, particulate carbon, etc. Prasad (IOBC, NIO) gave an account of the preparation of atlases on displacement volumes in respect of zooplankton at the Indian Ocean Biological Centre (IOBC), Ernakulam. The basic work leading to the preparation of the atlases was highlighted by the speaker. He also showed some atlases which have already been prepared, indicating the monthly distribution of zooplankton volumes for the Arabian Sea and the Bay of Bengal.

The paper by Prasad was followed by 11 detailed papers on the various aspects of specialized studies carried out on the international collection of zooplankton at IOBC. The introduction to this series of papers was given by E. Brinton, Unesco Curator at the centre. While introducing these papers, Brinton briefly summarized the sorting and research programmes at the IOBC and the specialist studies undertaken on the sorted samples. Following this introduction, he presented a paper by Vijayalakshmi Nair on the quantitative aspects of the distribution of chaetognaths in the Indian Ocean during both the south-west and north-east monsoon periods. The next paper was by Kasturirangan on 'Zooplankton atlas' with particular reference to copepods. He dealt with the processing of data relating to this large group of organisms with a view to incorporating them in the plankton atlases currently in preparation at IOBC. The special studies on the various sorted groups were indicated by a number of persons from IOBC. George Peter gave a paper on pelagic polychaetes, K. J. Peter on fish eggs and larvae, Jacob George on planktonic ostracods, Gopalakrishnan on decapod larvae, both a general survey and special studies on Penaeidae, Sakthivel on pteropoda, Aravindakshan on Carinariidae, and Balachandra Menon jointly with N. K. Panikkar on planktonic anthozoa (Coelenterata) — all from the IIOE collections. Apart from the papers by the group from IOBC, there were a few other interesting papers by Daniel and others based on the work carried out during the IIOE. The paper by A. Daniel and R. Daniel was on siphonophores collected during the 35th cruise of the Soviet research ship *Vityaz*, wherein the authors described a new genus and species of Physonectae. Daniel, Nagabhushanam and Daniel gave a very interesting paper on the organisms constituting the sonic scattering layer in the Bay of Bengal and eastern Indian Ocean, also based on *Vityaz* collections. The organisms were those sampled using an Isaacs-Kidd midwater trawl and the group consisted of siphonophores, pelagic tunicates, euphausiids, fishes, shrimps and medusae with a few squids, copepods and heteropods. The variations in the depths of the sonic scattering layer in relation to other oceanographic parameters were also discussed by these authors.

A few papers were also presented on phytoplankton pigments, primary production, and phytoplankton composition. Among these, mention may be made of one by Shah (Kerala University Oceanographic Laboratory) on the diurnal variations in chlorophyll content at a single station off Cochin

in the Arabian Sea, and the papers by Ramamurthy, Krishnamurthy and Venugopalan on primary production and phytoplankton composition in the nearshore waters off Porto Novo on the east coast of India. The only paper on marine bacteria was presented by Velankar of Central Institute of Fisheries Education, Bombay. The author, while reviewing the Indian work on the subject, dealt with qualitative and quantitative aspect of marine bacterial distribution in the Indian waters, the various physiological groups of marine bacteria, including those responsible for fish spoilage and also the role of bacteria in the ecology of the ocean with particular reference to bacteria-phytoplankton relationships.

In the next session, which dealt with papers on marine biology and productivity (general aspects), and which was presided over by Prof. P. N. Ganapati of Andhra University, Waltair, 12 papers were presented which included such varied topics as: Reproductive and nutritional cycles in a few vertebrates from the east coast of India by S. Krishnaswamy of Madurai University; Fouling organisms in Bombay harbour by Karande of the Naval Chemical and Metallurgical Laboratory, Bombay; Radioactivity and trace elements levels in marine organisms by Patel and Pillai of the Bhabha Atomic Research Centre, Bombay; and Seaweed drift on Indian seashore by V. Krishnamurthy of the Central Salt & Marine Chemicals Research Institute, Bhavnagar. Based on the work at the Zoology Department of the Andhra University, two papers were presented at this session. The first one was on the fauna of Kakinada Bay by Radhakrishna and Ganapati, and the second one was on quantitative studies on zooplankton of the Godavari estuary by Chandra Mohan. Benthic faunal studies in the nearshore regions off the south-west coast of India were discussed in two papers, the first one by Desai and Krishnan Kuty of the Biological Oceanographic Division, NIO, and the other by Kurian of the Kerala University Oceanographic Laboratory. Theodore Srinivasagam from Madurai University presented an interesting paper on a 'New approach to settlement studies' wherein he highlighted the role played by some nitrogenous substances including amino acids in conditioning sea water and making it favourable for the settling of some types of larvae, particularly the larvae of the serpulid, *Hydroides norvegica*. Although somewhat outside the scope of the symposium, the importance of the paper lay in the fact that studies of this type would help characterization of some of the dissolved organic constituents in the ocean, particularly of those described as 'ectocrines' which play an indirect role in the economy of the sea. Thus the marine biology sessions provided extensive coverage of scientific topics.

Fisheries

The last of the scientific sessions was on fisheries — both dealing with resources as well as special topics including methodology and techniques. There were 14 papers in this session which was chaired by Prof. T. S. Rassa of the Institute of

Oceanology, Academy of Sciences, USSR, Moscow. Prof. Rass presented first his paper on 'Ichthyological studies by Soviet participants in the IIOE'. According to Rass, deep sea fish fauna in the Indian Ocean seem to be under-investigated as compared with other oceans. He outlined the studies made by the Soviet group as a whole and stated that oceanic ichthyofauna of the pelagic and the deep sea realms formed the subject of investigations by a number of groups of workers. Reproduction and life history studies have also been undertaken by these scientists. The author has also listed the various groups of fishes which have both scientific as well as commercial importance in the Indian Ocean region. Panikkar's paper on the fishery resources of the Indian Ocean, Berry's on clupeoid resources and Dwivedi's on tuna resources were three important papers on the resource aspects of fisheries of the Indian Ocean. Panikkar discussed two broad patterns in the distribution, the south temperate fisheries represented along South African and Western Australian coasts and tropical and subtropical fisheries of the rest of the Indian Ocean. He indicated that there is considerable scope for the increase of production from the present yield of about 2.5 million tons to 10 times its value by intensive oceanographic studies to locate new resources and also newer techniques in fishing. The importance of the Arabian Sea as a region calling for special attention in increasing fisheries production and for intensive oceanographic studies owing to the unstable conditions was specially emphasized by the author in his paper and during discussion.

Berry's paper on the clupeoid resources and research in the Indian Ocean region laid stress on the need to improve our knowledge concerning the systematics of this important group. He gave an account of the work undertaken by him in collaboration with the research teams in Andhra University and the Porto Novo Marine Biological Station of the Annamalai University.

On the subject of fishery biology including techniques and methodology mention is made of the paper by Dwivedi (NIO) on the identification of fish populations with particular reference to the pelagic stocks of the Indian Ocean region; the one

by Alikunhi and George of Central Institute of Fisheries Education on 'Mark-recovery studies on commercially important marine fishes of India'; Gopalan's (NIO) paper on the silver pomfret, *Pampus argenteus*; and Pradhan's (Deep Sea Fishing Station, Government of India, Bombay) paper on the Indian Ocean flat fish, *Psettodes erumei*. Dwivedi's paper dealt with a new modification of starch gel electrophoresis method for the identification of populations in respect of clupeoid, scombroid and other pelagic fishes of the Indian Ocean. The paper by Alikunhi and George gave a description of the tagging experiments carried out by them on the sardines and mackerel in December 1966, conducted from Goa. In the same paper they have indicated the possibility of carrying out similar tagging studies on fishes like pomfrets and demersal fishes like scienids, etc. This has apparently been the first large-scale attempt at tagging marine fish in India.

The relationship between hydrographical factors and fisheries was given in the paper by Qasim and Sankaranarayanan with reference to Cochin region. In regard to studies on fishery yields, the theoretical yield studies on *Cynoglossus macrolepidotus* by Krishnan Kutty and Qasim and the more practical one based on trawling operations by Joseph (off-shore Fishing Station, Mangalore) deserve mention. On the subject of fish eggs and larval studies, K. J. Peter's paper on the larvae of *Rastrelliger kanagurta*, the paper by Balasubrahmanyam *et al.* (Porto Novo) on larval and juvenile stages of the flying fish *Exocoetus volitans* Linn. and *Hirundichthys coromandelensis* (Hornell), and the paper on distribution of fish eggs and larvae in Bay of Bengal by Solomon Raju and Ganapati deserve mention. A. G. K. Menon and Rama Rao (Zoological Survey of India) described in a paper the first occurrence of the flying fish, *Hirundichthys speculiger* (Valenciennes) in the Indian Ocean. The paper by Peter on the larval stages of the Indian mackerel was specially noteworthy as being the first account of these larvae from the Indian Ocean.

The scientific sessions were concluded with an appreciative reference by Dr Panikkar to the fine response to this symposium. The contributions will be issued as a special Symposium Bulletin of the National Institute of Sciences of India.

Symposium on International Upper Mantle Project

S. BALAKRISHNA & M. N. QURESHY

National Geophysical Research Institute, Hyderabad (AP)

A SYMPOSIUM on the International Upper Mantle Project was organized by the National Geophysical Research Institute, Hyderabad, India, during 4-8 January 1967. The symposium was jointly sponsored by the Geophysics Research Board, the Geological Survey of India, the Geological Society of India, the Indian Geophysical Union and the National Geophysical Research Institute. The main objective of the symposium was to take stock of the work done in the country so far and to draw up programmes of studies for the remaining period of the Upper Mantle Project. An organizing committee was formed with representatives of the sponsoring organizations to plan the working of the symposium.

The symposium was attended by over 200 delegates from all over the country. In addition, 12 foreign scientists also participated. The symposium was inaugurated by Dr S. Bhagavantam, Scientific Adviser to the Minister of Defence. Dr D. N. Wadia, National Professor of Geology and Geological Adviser to the Government of India, delivered the presidential address. Dr Atma Ram, Director-General, Council of Scientific & Industrial Research, and a number of other distinguished scientists were present at the inaugural function. Dr K. R. Ramanathan, Chairman, Geophysics Research Board, presided over the function.

Madame I. P. Kosminskaya and Dr Khitarov of USSR, Dr H. Closs of West Germany and Dr John Healy of USA were among the distinguished foreign scientists who participated in the symposium. A number of delegates from Geophysics Research Board, Indian Geophysical Union, Geological Society of India, Geological Survey of India, Indian Agricultural Research Institute, Defence Research & Development Organization, India Meteorological Department, National Mineral Development Corporation, Exploratory Tubewells Organization, National Geophysical Research Institute (NGRI), Oil & Natural Gas Commission (ONGC), Department of Mines & Geology, Gujarat, and the Universities of Roorkee, Banaras, Andhra and Osmania also participated in the symposium.

Dr Hari Narain, Secretary, Geophysics Research Board and Director, NGRI, welcomed the scientists and guests. In his report, he gave a brief history of the Upper Mantle Project studies in India and recalled the participating organizations and the studies which were in progress. He mentioned, in particular, the projects which have been undertaken at the National Geophysical Research Institute in connection with the Upper Mantle Project and the progress made in gravity studies, physical properties of rocks, geomagnetism and geoelectricity, seismology, theoretical geophysics, palaeomagnetism, heat flow measurements and integrated band studies in the Dharwar and the Cuddapah basin.

In his inaugural address, Dr S. Bhagavantam stressed the urgent need for geophysical and geo-

logical studies of the solid earth for the exploitation of mineral resources and for scientific enquiry.

In his presidential address, Dr Wadia pointed out that "modern geology, in spite of its advances in many spheres, is yet faced with the old problem, what caused the abrupt inequalities of the earth's surface". He emphasized that by virtue of her unique geodetic environments, India occupies a very special place in the field of geophysical studies and has many valuable geophysical data to contribute to the world body at large. He also pointed out the impact Upper Mantle Project may have on our insight of the processes leading to the formation and concentration of economic mineral deposits.

The deliberations of the symposium were divided into the following sessions (presidents of the sessions are given in parentheses): (I) Magmas and their relationship to tectonics of crust and mantle (Dr M. S. Krishnan); (II) Seismology and gravity studies (Dr A. N. Tandon); (III) Physics of the crust and mantle (Dr S. Bhagavantam); (IV) Geological, geophysical and geochemical studies on the Dharwar region (Shri B. Rama Rao); (V) Geological, geophysical and geochemical studies on Cuddapah basin, Gulf of Cambay and Andaman and Nicobar Islands (Shri W. B. Metre); (VI) Geological, geophysical and geochemical studies on Singhbhum and Aravalli regions (Shri A. K. Dey); (VII) Studies on continental drift (Dr F. Ahmed); (VIII) Special sessions: (i) Deep seismic sounding (Mme I. P. Kosminskaya); (ii) Dharwar, Aravallis, Singhbhum (Dr B. P. Radhakrishna); (iii) Cuddapah basin (Dr M. S. Krishnan); and (IX) Concluding session (Dr D. N. Wadia).

All the sessions began with the presentation of a key paper from one of the leading authorities in that particular sphere. These papers gave a critical appraisal of the present status of the studies and drew attention to some of the outstanding problems. Other papers dealing with the same or connected topics were presented later and at the end of each paper very lively discussions ensued. Informal discussions took place in the special sessions. Recommendations that emerged from the deliberations of the symposium were presented and approved in the concluding session which was presided over by Dr D. N. Wadia.

The following were some of the major recommendations of the symposium.

General — (1) There should be some means of communication among the geoscientists within the country. For this purpose a news bulletin on geosciences may be issued at least twice a year, which should report the work in geology, geophysics and geochemistry in progress at different institutions and universities; (2) There should be better co-ordination in granting research schemes by the Council of Scientific & Industrial Research, University Grants Commission and other government agencies on the one hand and different institutions engaged in

studies on earth sciences on the other. The research schemes should be oriented towards specific problems fitting in the overall framework of the broader problems of geosciences in India; and (3) In each of the four regions of combined geological, geophysical and geochemical studies, the three disciplines of geology, geophysics and geochemistry be kept under an Investigator-in-Charge. He should be in a position to coordinate the work for the respective region and also judge the work and compile it for sending for publication under the International Upper Mantle Project.

Cuddapah basin — (1) Regional gravity and magnetic anomaly map of the Cuddapah basin may be prepared jointly by the NGRI, Osmania University and Andhra University; (2) Representative rock specimen collection as far as possible for the gravity observation stations to be made for petrological and sedimentological work by all the parties; and (3) Geological Survey of India may be requested to carry out seismic soundings or profiles as required in areas where such work can be carried out in the Cuddapah basin.

Dharwar — (1) Recognition of the basement on which the Dharwar sediments were deposited; (2) Systematic geochronological studies by NGRI and Indian Institute of Science, Bangalore, in addition to GSI and preparation of stratigraphic time scale for the Precambrians of the different regions; (3) Preparation of gravity and magnetic anomaly maps of the region on 1:1 million scale; and (4) Deep seismic sounding along selected traverses.

Singhbhum region — (1) Integrated geological, geophysical and geochemical studies in the entire region; and (2) Detailed geochemical studies and trend of distribution of the major and trace elements up to a depth of 2500 ft to be undertaken with the help of samples obtained from various cores.

Magmas and magma tectonics — (1) Study of the Precambrian and the Post-Cambrian basic and ultrabasic intrusions; (2) Measurements of terrestrial mineral phases in the fresh and altered basic rocks including the amphibolites in order to get an idea of thermal gradients; and (3) Study of liquid inclusions occurring in these rocks in order to get an insight in the hydrothermal phase which will directly reflect on the composition of deep-seated substratum.

Crustal thickness studies — (1) Travel time curves and amplitude studies of existing data for similar areas in other countries pertaining to Indian conditions should be carried out; (2) Background noise

studies in the areas, where deep seismic sounding profiles are to be laid should be undertaken; (3) To start with deep seismic sounding profiles should be laid only in the shield area of India because it offers much simpler problems to be tackled; and (4) For the study of the shield area by deep seismic sounding method, shots can be fired much easily in the sea along the Indian coast and recorded on the land. Such a shooting programme will require much smaller charges for the same purpose. This will also enable reverse profile shooting on the land using shots in the sea both along the eastern as well as western coast of India.

In the concluding session, Dr H. Closs, Director and Professor-in-Charge, Bundesanstalt für Bodenforschung, West Germany, elaborated how Upper Mantle studies not only broaden our understanding of the earth's interior but also augment natural resources for the welfare of the human society. Dr Closs stressed that contrary to the common notion, the Upper Mantle Project is not only an important fundamental research programme but it also possesses strong utility bias, and will help in a better understanding of mineralization and exploitation of natural resources.

Madame I. P. Kosminskaya, Chairman of the Commission on Continental Margins & Island Arcs of the International Upper Mantle Project and a top-ranking Russian geophysicist, advocated the need of starting deep seismic studies in India. Technically known as 'deep seismic sounding', this method consists in experimental study of elastic wave propagation caused due to deep artificial explosions. In the USSR deep seismic soundings are being carried out along a number of profiles for delineating geological structures up to a depth of 40-50 km. and in some cases even up to 100 km. According to her, India has many features which may help in very effective utilization of this potential technique and the Deccan shield is an ideal place to make a start. The explosive for these investigations may profitably be detonated in the sea.

Dr John Healy of the US Geological Survey endorsed the views of Madame Kosminskaya. He expressed that various organizations in India such as the ONGC, NGRI, Atomic Energy Establishment, etc., should pool their resources for a successful execution of the project. A coherent integration of such regional surveys will enrich our knowledge of the crust and the upper mantle.

Cerium-141 & Cerium-144 in Ground Level Air at Bombay

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THREE major series of nuclear weapon tests were carried out during the period September 1961-December 1962. Most of these tests were of high yield and hence significant quantities of fission products were injected into the atmosphere. Studies on many of the important fission products were carried out at this centre. The two comparatively longer lived isotopes of cerium produced in fission are cerium-141 and cerium-144 having fission yields of 4.3 and 3.3 per cent respectively for 14 MeV. neutron fission of U-238 (Table 1). Due to their larger production in fission, study of these two isotopes of cerium provides a useful indication of the variations in fallout in the ground level air following high yield tests.

The quantities of cerium-141 and cerium-144 in the samples have been found by chemically separating cerium and analysing for the two isotopes by the decay of their gamma energy peaks in the gamma ray spectra of the samples. This is possible due to the large difference in their half-lives — 32.5 and 285 days for Ce-141 and Ce-144 respectively.

The measurements were carried out during the period 1961-65 following the three series of nuclear weapon tests, i.e. the Arctic test series of September-November 1961, the Pacific test series carried out during April-July 1962 and the Arctic test series from August to December 1962.

The air filter samples were collected by sucking 2.60×10^3 cu. m. air per month through HV-70 filters using blowers. These samples were ashed at 250°C. Twenty mg. of cerium carrier (10 mg. Ce/ml.) were added to each sample and then fused with sodium carbonate for about 4 hr. The fused mass was dissolved in nitric acid. Cerium and other rare earths, iron, etc., were separated from alkali elements and alkaline earths by hydroxide precipitation. The rare earths were precipitated as oxalates^{1,2} at pH 5.5, while iron remained in solution. Excess of ammonium oxalate dissolved zirconium and thorium.

Cerium and other rare earth oxalates were dissolved in 1:2 nitric acid. Cerium(III) was oxidized to cerium(IV) by potassium bromate and then precipitated as iodate^{3,4} by adding excess potassium iodate. Cerium was thus separated from the other rare earths.

The ceric iodate precipitate was dissolved in nitric acid. Cerium(IV) was converted to cerium(III) by hydrogen peroxide⁵ in acid medium. Zirconium was precipitated as iodate. Thorium and plutonium were co-precipitated with zirconium as iodate, while cerium(III) remained in solution.

Cerium(III) was oxidized to cerium(IV) as before and then precipitated as iodate. It was then converted to oxalate⁶ by heating with oxalic acid. The oxalate precipitate was transferred to a perspex tube of 0.4 in. diameter and 1.25 in. long.

The samples were counted using a NaI(Tl) crystal (2 in. diam. \times 1.75 in. thick, well type) coupled to a

single channel analyser. The sample counting times were adjusted to give an accuracy better than ± 5 per cent for all the samples. The samples were recounted after 30 days to determine the activities due to Ce-141 and Ce-144 separately. The precipitate was ignited after the second counting to determine the chemical yield. The activities of Ce-141 and Ce-144 in the air filter samples are given in Table 2.

Activity Data

The level of cerium-144 in air filter samples collected at Bombay during November 1961-June 1965 is given in Fig. 1. It is seen that the levels of cerium-144 are comparatively higher during late winter and early spring of each year. This periodic increase in activity is attributed to seasonal effects in the mixing between the stratosphere and the troposphere. Nearly similar variations have been

TABLE 1 — ISOTOPES OF CERIUM

Cerium	Half-life	Fission chain yield (14 MeV.)	Prominent radiation	Energy of prominent radiation MeV.
Ce-133	6.3 hr	—	β^+	1.3
			γ	1.8
Ce-134	72 hr	—	K-x	—
Ce-135	22 hr	—	β^+	0.81
Ce-136	Stable	—	—	—
Ce-137	9 hr	—	γ	0.445 (3*)
Ce-138	Stable	—	—	—
Ce-139	140 days	—	γ	0.166
Ce-140	Stable	—	—	—
Ce-141	32.5 days	4.3	β^-	0.442 (67)
			γ	0.145 (49)
Ce-142	Stable	—	—	—
Ce-143	33 hr	3.6	β^-	1.13 (40)
			γ	1.40 (37)
			γ	0.29 (43)
Ce-144	285 days	3.3	β^-	0.309 (76)
			γ	0.133 (10.9)
			β^-	2.0
Ce-145	3 min.	2.9	γ	—
Ce-146	14.6 min.	2.5	β^-	0.7
			γ	0.27
Ce-147	9 sec.	2.2	—	—
Ce-148	7 sec.	1.9	—	—
Ce-149	3.5 sec.	1.6	—	—
Ce-150	2.5 sec.	1.3	—	—
Ce-151	2 sec.	1.05	—	—
Ce-152	1.5 sec.	0.75	—	—
Ce-153	1.5 sec.	0.52	—	—
Ce-154	1 sec.	0.36	—	—

*Values within parentheses represent percentage yield for the given energy.

The isotopes Ce-133, Ce-134, Ce-135, Ce-136, Ce-137, Ce-138 and Ce-139 were not produced in fission; the rest of the isotopes were produced in fission.

Natural abundance of stable isotopes: Ce-136, 0.19; Ce-138, 0.26; Ce-140, 88.47; and Ce-142, 11.08.

TABLE 2—CERIUM-141 AND CERIUM-144 ACTIVITIES IN AIR FILTER SAMPLES COLLECTED AT BOMBAY

Sample No.	Period of collection	Cerium-141 activity on collection date ($\mu\text{C.}$)	Cerium-144 activity on collection date ($\mu\text{C.}$)*	Ce-141	Vol. of air sampled (m.^3)	Ce-141	Ce-144
				Ce-144		$\frac{\text{m.}^3}{(\mu\text{C./m.}^3)}$	$\frac{\text{m.}^3}{(\mu\text{C./m.}^3)}$
1961							
1	Nov.	—	814.0	—	1965	—	0.41
2	Dec.	—	1702.0	—	2500	—	0.68
1962							
3	Jan.	—	1775.0	—	2460	—	0.72
4	Feb.	—	1531.8	—	2220	—	0.69
5	March	—	2284.9	—	2870	—	0.80
6	April	—	2300.4	—	2500	—	0.92
7	May	310.0	998.0	0.31	4160	0.07	0.24
8	June	663.4	704.7	0.94	2430	0.27	0.29
9	July	70.5	240.3	0.29	2667	0.03	0.09
10	Aug.	159.6	271.99	0.59	2660	0.06	0.10
11	Sep.	57.05	317.35	0.18	2852	0.02	0.11
12	Oct.	1108.65	1138.20	0.97	2980	0.37	0.38
13	Nov.	543.68	1006.14	0.54	2760	0.20	0.36
14	Dec.	816.75	793.00	1.03	1815	0.45	0.44
1963							
15	Jan.	1016.40	2160.50	0.47	2479	0.41	0.87
16	Feb.	658.60	1773.10	0.37	2533	0.26	0.70
17	March	—	36035	—	21197	—	1.7
18	April	—	34710	—	19544	—	1.776
19	May	—	29426	—	19617	—	1.500
20	June	—	14347	—	19654	—	0.73
21	July	—	1504	—	9230	—	0.163
22	Aug.	—	1024	—	3200	—	0.32
23	Sep.	—	2388	—	3803	—	0.628
24	Oct.	—	1423	—	4326	—	0.329
25	Nov.	—	1433	—	5045	—	0.284
26	Dec.	—	3784	—	9298	—	0.407
1964							
27	Jan.	—	7109	—	19746	—	0.360
28	Feb.	—	10336	—	18793	—	0.55
29	March	—	12920	—	18330	—	0.705
30	April	—	17850	—	17850	—	1.000
31	May	—	11870	—	26378	—	0.450
32	June	—	6397	—	37635	—	0.170
33	July	—	7510	—	46936	—	0.160
34	Aug.	—	2140	—	35654	—	0.060
35	Sep.	—	2816	—	40224	—	0.070
36	Oct.	—	7517	—	53691	—	0.140
37	Nov.	—	4430	—	55370	—	0.080
38	Dec.	—	5630	—	67837	—	0.083
1965							
39	Jan.	—	3629	—	60478	—	0.06
40	Feb.	—	7027	—	63882	—	0.110
41	March	—	7668	—	47925	—	0.160
42	April	—	4189	—	38080	—	0.110
43	May	—	5528	—	55276	—	0.100
44	June	—	2484	—	49688	—	0.050

*Ce-144 activities were calculated on the basis of 10.9 per cent γ abundance for 0.133 MeV. (ref. 8).

observed at Bombay in the concentrations of cesium-137 in air during 1961-65 (ref. 7).

The high values of cerium-144 in 1963 compared to 1962 are due to the series of tests carried out during the second half of 1962.

Since Ce-144 decays with a half-life of 285 days, the decrease in activity during successive years is partly due to radioactive decay and partly due to the depletion of the stratospheric reservoir of fission

products. This is evident from Fig. 1, where Ce-144 values corrected to a common date, i.e. January 1963, are shown. The period January 1963 chosen as weapon testing was stopped after December 1962 and no fresh activity was introduced for several months as indicated in Fig. 2.

The ratio for May 1962 (Fig. 2) indicates that the activity is from 1961 tests. However, the arrival of fresh activity from Pacific tests is indicated by the

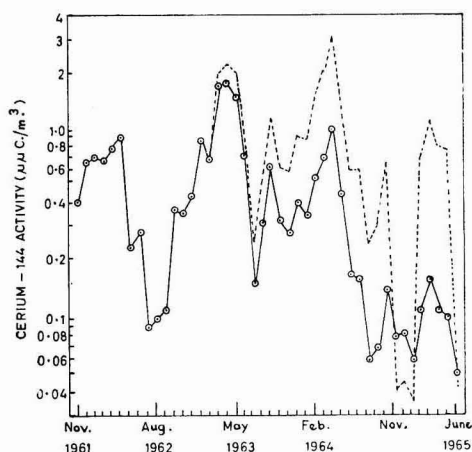


Fig. 1 — Cerium-144 activity of ground level air during 1961-65 at Bombay [The dotted line shows the values of cerium-144 activity corrected back to January 1963 for radioactive decay]

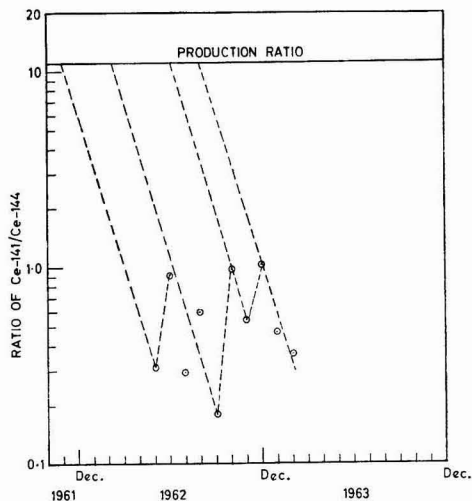


Fig. 2 — Ratios of cerium-141 to cerium-144 in ground level air at Bombay [The dotted lines indicate the theoretical decay of Ce-141/Ce-144 activity ratio with time. Production ratio gives the ratios of the activities of Ce-141/Ce-144 at the time of detonation]

ratios observed during the period July-September 1962. After September, the ratios again show an increase due to arrival of fresh activity from the polar 1962 tests. With the cessation of tests in December 1962, the ratios decrease with the approximate half-life of cerium-141, indicating the absence of further influx of fresh activity.

The high values in 1964 comparable to 1963 show the presence of large quantities of fission products in the stratosphere nearly a year after the cessation of the tests. Since the activity is fairly rapidly removed from the lower stratosphere with a half-life of 6-12 months, the high values in 1964 indicate the presence of debris in the upper stratosphere which descends slowly into the lower atmosphere. The levels in 1965, however, show a sharp decrease, indicating the depletion of the stratospheric reservoir of fission products.

Acknowledgement

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Plant Cell Wall Structure with Special Reference to Cotton Fibre*

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PLANT cell walls were traditionally considered the domain of plant anatomists. The earlier information on its physical structure was mainly obtained with the help of the polarization microscope. However, with the advent of X-ray diffraction analysis and the electron microscope, the biophysicist, biochemist and fibre technologist have been able to delve deeper into the fine and molecular structure of plant cell walls. The progress in the last two decades in particular has been spectacular and has been reviewed in an excellent manner by Preston¹, Frey-Wyssling² and Roelofs³. The abiding interest in this field, which apparently looks to be of academic nature, is not far to seek. The plant cell walls in the form of cotton, jute, hemp, coir, etc., provide us most of our clothes, sackings and cordages; the entire paper and rayon industry exclusively depends upon wood cells, and xylem vessels in trees make the timber almost irreplaceable by a man-made substitute.

Structure of Cellulose

Cellulose is all pervading in the plant kingdom. The botanist Payen, in 1844, coined this word to define the chief constituent of plant cell wall on the basis of certain staining reactions. Botanists still use the term in this limited sense. It was, however, Nageli, in 1858, who made real contribution to our knowledge of cellulose structure. It was he who observed the birefringent nature of plant cell walls and postulated its crystalline nature. This was later confirmed by X-ray analysis. To the fibre technologists, cellulose refers to a structural component which can be isolated almost in its original state by certain chemical treatments, from certain flowering plants, which are of commercial importance. The crystallographer from X-ray studies has interpreted it as a crystal lattice containing long chain molecules of β -1,4-anhydroglucose units associated with amorphous and paracrystalline regions of similar chemical constituents. The electron microscope studies have brought out yet another definition; the cellulosic material has revealed long, apparently endless thread-like bodies termed as microfibrils ranging 100-200 A. in diam. and are now regarded as a morphological unit of plant cell wall.

All the aforementioned viewpoints could be summarized in the definition that true cellulose is a polymeric substance which, on extraction from plants by standard chemical methods, consists solely of microfibrils and which in turn give X-ray diagram typical of cellulose I and yield only glucose on hydrolysis. Fig. 1 illustrates the β -1,4-anhydroglucose linkages of cellulose. The degree of polymerization, according to most investigators, could be between 5000 and 10,000 glucose units. The characteristic parallelization of cellulose microfibrils is illustrated in Fig. 2. From the X-ray diffraction pattern of

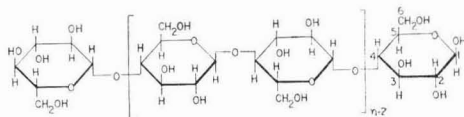


Fig. 1—Cellobiose unit and cellulose chain

cellulose I (Fig. 3) could be noted the strong lattice interferences 101, 10 $\bar{1}$ and 002 corresponding to the spacings of 6.1, 5.4 and 3.9 A. of which 002 is the most prominent. Each unit cell (Fig. 4) has the dimensions: $a = 8.35$ A.; b (fibre axis) = 10.3 A.; $c = 7.9$ A.; $\beta = 84^\circ$. Along the b axis, the glucose units of the chains are firmly held together by means of 1,4- β -glucosidic main valence linkages; along a axis, the adjacent chains, which run in alternate directions, are held by hydrogen bonding; and along the c axis, the lattice is held by weaker van der Waals' forces. In the unit cell, along the a axis, the anhydroglucose rings are separated by a distance of 2.5 A. which probably favours ready hydrogen bonding, while along c axis, the nearest distance between atoms is 3.1 A. However, with the exception of certain seaweeds like valonia and cladophora, microfibrils built up entirely of cellulose are rather rare.

Cell Walls of Algae and Higher Plants

The complexity of plant cell walls is well brought out by the data presented in Table 1 (Preston⁴). Apart from the amorphous cellulose, the incrusting materials contain xylose, arabinose, mannose, fucose, galactose and uronic acid. There are three different models of microfibrils proposed by Preston⁴, Rånby⁵

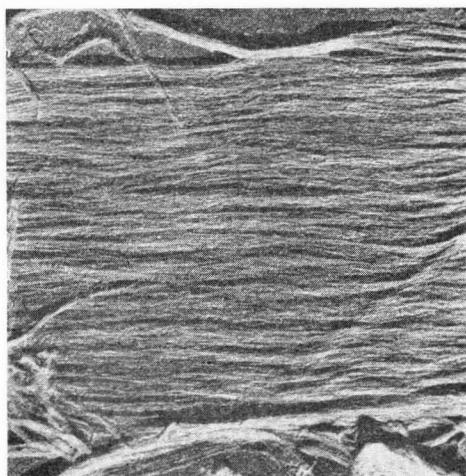


Fig. 2—Electron micrograph of secondary cell wall of cotton, shadowed with Au-Pd ($\times 21900$) [Note the characteristic parallelization of microfibrils]

*Based on a talk presented at the Session on Molecular Biology held at Banaras Hindu University, October 1966.

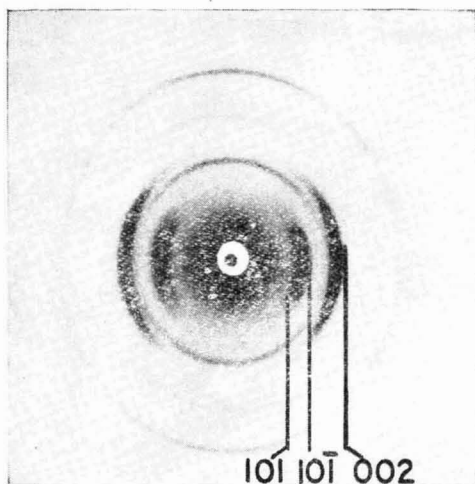


Fig. 3 — X-ray diffractogram of cotton; cellulose I [Note the 101, 101 and 002 interferences with the spacings of 6.1 Å., 5.4 Å. and 3.9 Å. respectively]

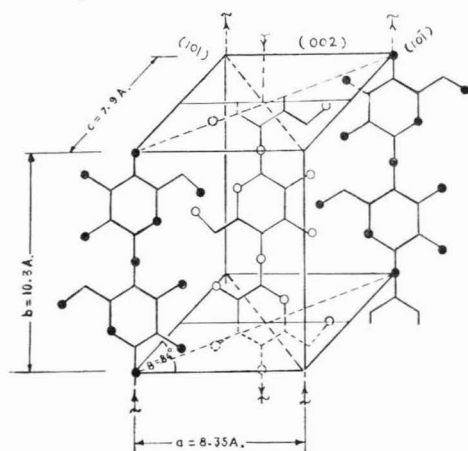


Fig. 4 — Unit cell of cellulose [Note the unit cell dimensions: $a=8.35$ Å.; b (fibre axis) $=10.3$ Å.; and $c=7.9$ Å.; $\beta=84^\circ$]

and Frey-Wyssling⁶. They differ in dimensions. However, they agree on the basic fact that there is a central crystalline core of glucose residues embedded in paracrystalline and amorphous region made of glucose residues and non-cellulosic sugars or sugar derivatives.

In higher plants, the composition of incrusting materials is still more complex. Apart from cellulose, many other substances like hemicelluloses, lignin, pectin, extraneous materials and even a small amount of inorganic matter are also present. Microfibrils can be extracted without any contamination of incrusting materials and viewed under an electron microscope.

The cell wall structure of elongated cells like tracheids, collenchyma cells, fibres, etc., in higher plants have been extensively studied. These are all

TABLE I — CHEMICAL CONSTITUENTS OF CELLULOSE MICROFIBRILS FROM VARIOUS SOURCES*

Source	Composition
1. <i>Valonia ventricosa</i>	Glucose
2. <i>Chaetomorpha mclagonium</i>	Glucose + arabinose
3. <i>Enteromorpha</i> sp.	Glucose + xylose + rhamnose
4. Fucales	Glucose + xylose + fucose
5. <i>Laminaria digitata</i>	Glucose + uronic acid
6. <i>Phyllo plumosa</i>	Glucose + galactose + xylose
7. <i>Rhodymenia palmata</i>	Glucose + xylose
8. Elm wood	do
9. Pine wood	Glucose + mannose + xylose

*After Preston⁴.

anisotropic and the microfibrillar architecture is basically the same whether in tracheids, valonia or cotton fibre. They pass helically around the cell. Most cells, in general, possess at least two such helically constructed layers differing in pitch or angle of inclination with respect to the axis of the cell. What is more, the phenomenon of spiral growth observed in seaweeds and some fungi has also been attributed to the helical growth of microfibrils by some investigators.

Till recently, it was taken for granted that, with the exception of fungi, plant cell walls are mainly cellulose. Depending on its origin, the cellulose structure was considered to be embedded in the matrix of hemicellulose and pectic compounds. Frei and Preston⁷, however, have shown that seaweeds belonging to the order Cauleriales have microfibrils made of β -1,3-linked xylan and in the case of Codiales, the microfibrils are made of β -1,4-linked mannan. There are many algae which contain wall made of two crystalline polysaccharides. These may be any two of the trio cellulose, xylan and mannan. *Halicystis*⁸ contains both cellulose II and xylan; *Hydrodictyon*⁹ contains cellulose I and mannan; and *Porphyra* has β -1,3-linked xylan mixed with β -1,4-linked mannan. Preston¹⁰ has very aptly summarized these findings. He states, "It is, therefore, clear that Nature has, as it were, 'experimented' with a variety of sugars in the formation of wall skeletal polysaccharides, and the range of sugars used may indeed be wider than is at present known. Only one of these experiments appears to have survived in higher plants."

Structure and composition of plant cell walls, both in growing and adult stage, have attracted the attention of biochemists and biophysicists, and yet there are very many fields not yet sufficiently explored and questions not yet satisfactorily answered.

Why certain species of timber are impermeable to preservatives while others apparently of similar microscopical characteristics can be treated easily? How exactly phloem transport takes place? What is the mechanism of cell differentiation and cell wall growth? These are some of the knotty problems still awaiting to be unravelled.

Growth and Development of Cotton Fibre

India is the original home of cotton and its antiquity dates back to Mohenjo daro period. The cotton fibres are seed hairs of plants belonging to genus *Gossypium*. The short staple Indian cottons

of commerce or *desi* varieties belong to *G. herbaceum* and *G. arboreum* species. However, in the last few decades many long staple Indo-American varieties belonging to *G. hirsutum* and even the fabled Sea Island cotton from West Indies belonging to *G. barbadense* are being cultivated in India. The problem of growing such diverse varieties of cotton under diverse climatic conditions could be well imagined. We have not yet been able to produce sufficient quantity of long staple cotton, economically spinnable to fine counts. Basically it is a problem of growing a long staple cotton with adequate secondary cell wall deposition on which to a considerable extent depend the fineness, maturity and strength of the fibre.

Cotton fibre is a unicellular hair some 1000 to 5000 times as long as it is wide (Fig. 5). For about 18-25 days after fertilization of the ovules, the fibres emerging from the seed coat grow merely in length. During the lengthening phase, the fibre is hollow, cylindrical, turgid and full of protoplasmic material enclosed in a thin primary cell wall sheath. Once the lengthening process more or less ceases, the secondary cell wall development and the process of thickening begins. A daily periodicity is observed in the deposit of these layers. A cross-section of a fibre would reveal the so-called daily growth rings analogous to annual rings in wood. The lamellar layers are laid inwardly (Fig. 6) with the result the diameter of the cell does not appreciably change. The secondary cell wall deposition continues further for about 25-30 days, depending on the variety, season and other factors. The extent of cell wall deposition is not uniform in all the fibres, even on a single seed. This results in large variations in what is called fibre maturity. If the thickening process has been

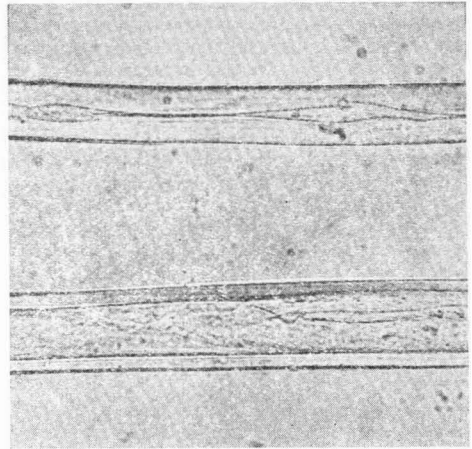


Fig. 7 — Mature (top) and immature (bottom) cotton fibres ($\times 350$)

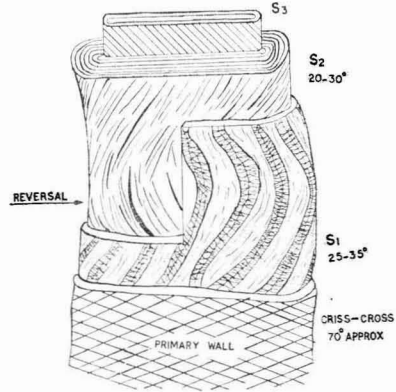


Fig. 8 — Microfibrillar structure of secondary cell wall of cotton fibre

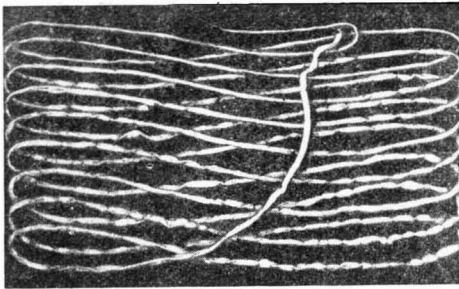


Fig. 5 — A single cotton hair ($\times 80$) [Note the enormous length as compared to width]



Fig. 6 — Cotton fibre swollen in cuprammonium hydroxide ($\times 250$) [Note the lamellar layers of cellulose and constrictions formed by broken primary wall giving ballooning effect]

inadequate in large number of fibres, such a cotton will have more of immature fibres as compared to mature ones (Fig. 7). These immature fibres are weak and create many difficulties in processing.

In Fig. 8 is presented schematically the microfibrillar structure of cotton fibre and in Table 2 is summarized the dimensions of various structural components of cotton fibre.

The thin primary wall, about 0.2μ , has criss-cross network of microfibrils laid about 70° to the fibre axis. In the network are embedded the non-cellulosic constituents like cutin, pectin, fats, waxes, etc. The secondary wall, $3-5 \mu$ thick, could be divided into S_1 , S_2 and S_3 layers. These are all made of microfibrils spiralling around the fibre axis in a helical manner, the inner layer being laid progressively steeper and steeper.

Broadly, S_1 layers are considered to have spiral angle between 25° and 35° and S_2 between 20° and 30° ; the spiral angle of S_3 is not well established. In S_2 layer are also present the

TABLE 2 --- DIMENSIONS OF GROSS AND FINE STRUCTURE COMPONENTS OF COTTON FIBRE

	Length, μ	Width, μ
Cotton fibre	30000	15.0
Primary wall	30000	0.2
Secondary wall	30000	5.0
Cellulose chain	1.8	0.0003×0.0008 (3 A. \times 8 A.)
Crystallites	0.015-0.150	0.005 (50 A.)
Unit cell of crystal- lites	0.00103 (10.3 A.)	0.00079×0.000835 (7.9 A. \times 8.35 A.)
Glucose anhydride unit	0.000515 (5.15 A.)	0.0003×0.0008 (3 A. \times 8 A.)

reversals, the most distinctive feature of cotton fibre secondary wall.

The average spiral angle or the angle which indicates the overall orientation of microfibrils has a great influence on the mechanical properties of cotton like strength, elongation, stiffness, toughness, etc. The orientation can be determined by X-ray or microscopy techniques. We shall be concerned here with the latter technique only.

Convolutions and Convolution Angle

Convolutions are the characteristic gross morphological features of cotton (Fig. 9). It is a natural twist imparted to cotton fibre during the desiccation process when the cotton bolls open up and turgid fibre cells begin to dry. Earlier workers were fascinated with this peculiarity of cotton and tried to correlate the number of convolutions with the spinning performance of cotton. These studies were not fruitful and Balls¹¹ had to remark, "Any cotton is convoluted enough and that none are convoluted too much". It was, however, shown by Meredith¹² that this natural twist or the convolution angle in cotton influences the strength of cotton. He reported from a study of 14 cottons that a high correlation coefficient (-0.87) exists between convolution angle and strength. It may be pointed out that out of these 14 cottons, 8 were fine hirsutums and

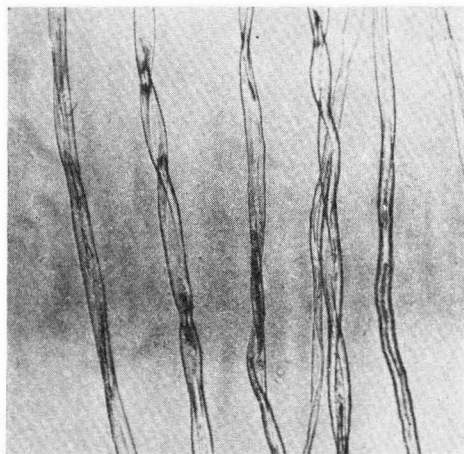


Fig. 9 --- Profile of convoluted cotton fibres ($\times 200$)

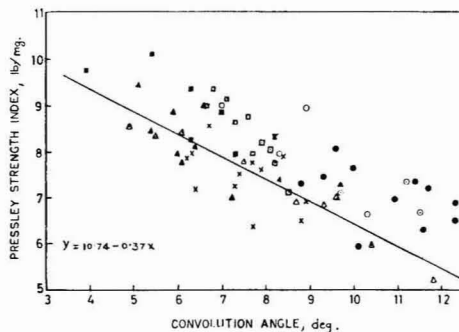


Fig. 10 --- Convolution angle in relation to Pressley strength index: \blacktriangle , *G. arboreum indicum*; \triangle , *G. arboreum bengalense*; \times , *G. herbaceum*; \bullet , *G. hirsutum* (Indian); \circ , *G. hirsutum* (American); \square , *G. barbadense* (Egyptian); and \blacksquare , *G. barbadense* (W. Indies)

barbadenses and 4 were the other extremes, representing very coarse Indian cottons. He had supported the view of Berkley and Barker¹³ that in so far as strength-orientation relation is concerned, different regressions hold good for different groups of cotton.

It was, therefore, felt that it would be worth while to ascertain how far the relationship between convolution angle and Pressley strength index (PSI) holds good for Indian cottons of varied strength and belonging to diverse species. Employing the quick method for the determination of convolution angle standardized by Betrabet *et al.*¹⁴, the convolution angle was derived by Meredith's formula

$$\tan \theta = \pi/2 \frac{D}{C}$$

where D is the ribbon width, C is the pitch of the convolution and \bar{D}/\bar{C} is the mean of D/C .

Convolution angle and PSI were determined on 67 cottons of Indian and foreign origin belonging to four botanical species: *G. arboreum*, *G. herbaceum*, *G. hirsutum* and *G. barbadense*¹⁵. The trend of relationship between strength and convolution angle for all the cottons is illustrated in Fig. 10. *G. barbadense* and *G. hirsutum* cottons are concentrated above the regression line, the former at the top and the latter at the bottom. On the other hand, *G. herbaceum*, *G. arboreum indicum* and *G. arboreum bengalense* cottons are predominantly concentrated below the regression line. Another point of interest is that cottons belonging to *G. hirsutum*, *G. herbaceum* and *G. barbadense* appear to group themselves species-wise. Despite these differences, a common regression line seems to hold good for the entire data. The correlation coefficient between convolution angle and PSI for all the cottons was highly significant at -0.73 .

Fig. 11 reveals the interspecific differences with respect to strength-convolution angle relationship. What stands out prominently is the identical behaviour of coarse Indian *G. arboreum bengalense* and fine Egyptian cottons. The correlation coefficient between the two parameters is highly significant at -0.97 and -0.93 respectively, thereby indicating a very close dependence of strength on fibrillar orientation in these two species.

No correlation between the two entities was observed in Indian hirsutums and herbaceums which indicates

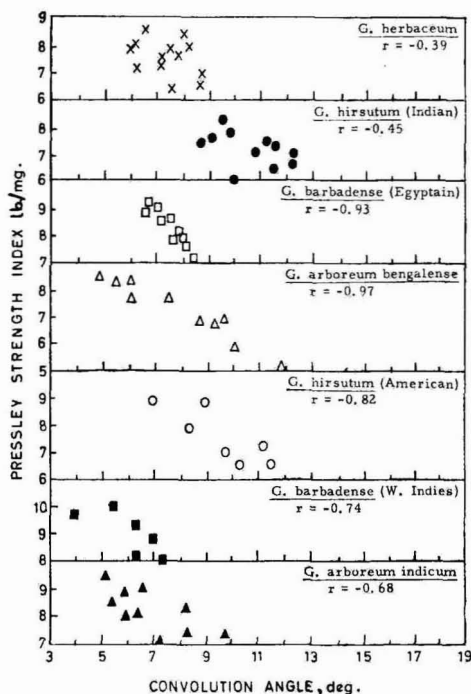


Fig. 11 — Species-wise relation between convolution angle and Pressley strength index

that factors other than fibrillar orientation influences the strength of cotton belonging to these species. It is of interest to note that the two entities are highly correlated at -0.82 in American hirsutums.

Lack of correlation between convolution angle and strength in Indian hirsutum and herbaceum may not be far to seek. These cottons, in general, suffer from immaturity and have poor strength which could be to a large extent due to improper cell wall development. Incidentally, most of the long staple Indian cottons called Indo-American varieties belong to *G. hirsutum* species.

Most of the earlier work on strength-orientation relationship in cotton was carried out mainly on American hirsutums or barbadenses. From our exhaustive studies, the fact emerges that no generalization could be made in strength-structure relationship for all cottons inasmuch as the type of cotton selected for investigation influences the trend of results to a great extent.

Birefringence and Spiral Angle

Birefringence or the optical anisotropy is well demonstrated by cotton fibres, under polarized light. The fibre as a whole behaves as a positive uniaxial crystal with optic axis parallel to the fibre axis. Cotton has higher refractive index for light vibrating along the optic axis of the fibre and a lower value for the light vibrating at right angles to the optic axis. If n^{\parallel} and n^{\perp} represent the refractive index respectively, $n^{\parallel} - n^{\perp}$ is the birefringence.

Meredith¹⁶ has reported that specific strength, measured at 1 and 10 mm. gauge lengths, and initial Young's modulus of cotton are highly correlated with birefringence. This lead Betrabet *et al.*¹⁷ to investigate how far birefringence is correlated with flat bundle strength and other mechanical properties. Twenty Indian cottons possessing a wide range of fibre properties and representing four chief botanical species were selected for this study. The Becke line method was used for the determination of refractive index and Stelometer strength tester was used to determine strength both at 0 and 1/8 in. gauge length. The stiffness and toughness were calculated from strength at 1/8 in. gauge and percentage elongation. The spiral angle denoting overall inclination of microfibrils spiralling around the fibre axis was calculated from Preston's formula which is deduced from the geometry of ellipsoid of the cellulose crystallite.

The n^{\parallel} values ranged from 1.568 to 1.578 and n^{\perp} values were more or less constant at 1.529. The birefringence value ranged from 0.0408 to 0.0481. The spiral angle ranged from 29.6° to 39.8° . However, on subtracting the convolution angle values (after correcting for the variation in ribbon width) from the respective spiral angle values, the difference was found to be approximately constant at $24.25^{\circ} \pm 0.37^{\circ}$, thereby strengthening the argument of Meredith that the spiral angle of fibrils in the original unconvoluted fibre may be about the same irrespective of the variety of cotton. In Table 3 are summarized the correlation coefficients between optical parameters and mechanical properties of cotton fibres.

Strength is related to a number of structural factors, chief among which are the molecular chain length and orientation. The data presented in Table 3 reveal that strength is highly correlated to n^{\parallel} , birefringences and spiral angle. It is of great interest to note that the correlation coefficients between spiral angle and bundle strength at 0 and at 1/8 in. gauge are more or less of the same order, being -0.72 and -0.74 respectively. This is in contrast to the observation of Rebenfeld and Virgin¹⁸. They reported a correlation coefficient as high as

TABLE 3 — CORRELATION COEFFICIENTS BETWEEN OPTICAL PARAMETERS AND MECHANICAL PROPERTIES OF COTTON FIBRES*

Optical properties	Fibre bundle strength		Fall in strength %	Toughness	Stiffness
	0 gauge	1/8 in. gauge			
Refractive index, n^{\parallel}	0.71 (0.1%)	0.75 (0.1%)	-0.36	—	—
Birefringence, $n^{\parallel} - n^{\perp}$	0.63 (1%)	0.74 (0.1%)	0.45 (5%)	0.50 (5%)	0.54 (5%)
Spiral angle, θ	-0.72 (0.1%)	-0.74 (0.1%)	0.35	-0.41 (5%)	-0.65 (1%)

*After Betrabet *et al.*¹⁷. Values in parentheses refer to statistical significance levels.

-0.92 between bundle strength and spiral angle as measured by X-ray diffraction method. The correlation coefficient, however, fell with increase in the test gauge length. It was -0.70 at 1.5 mm. gauge length and only -0.39 at 5.0 mm. gauge length. This once again supports the view put forward earlier that no generalization could be made on fibrillar orientation-strength relationship and that results are highly influenced by the varieties selected for investigation.

Toughness and stiffness are the other two important mechanical properties. The data presented in Table 3 indicate that these also appreciably depend upon the optical properties or fine structure of cotton cell wall. It could be concluded that higher the birefringence, stronger, tougher and stiffer are the fibres.

Structural Reversals

In cotton fibre the spiral structure in the secondary cell wall undergoes abrupt reversal in direction from left to right or vice versa along the fibre length. They are called structural reversals (Fig. 12) and can be located as dark bands when examined under crossed polarizer and analyser. Wakeham and Spicer¹⁹ have reported that with most cottons, tensile breaks occur preferentially at the structural reversal rather than in between reversals. Reversals are, therefore, considered as weak links in cotton fibre, and Radhakrishnan *et al.*²⁰ have demonstrated that swelling in alkali of mercerizing strengths removes the strains around the reversals and strengthens the weak links to a considerable extent. It was, therefore, of interest to know the distribution of reversals in various Indian cottons.

The cottons selected for the study were the same 20 cottons whose birefringence was determined earlier. In addition, 5 original barbadenses from West Indies were also tested. Two hundred fibres were scanned in the central 10 mm. region after irrigating with 18 per cent caustic soda¹⁷.

From the figures quoted in literature, it appears that the number of structural reversals in cotton is quite high. For instance, Meredith²¹ states that they are about 20 per cm. while Wakeham and Spicer¹⁹ report them to be about 100 per in. These results are mainly based on observations made on *G. hirsutum* and *G. barbadense* cottons.

Our investigation, however, established that distribution of reversals is a genetic character¹⁷. Their number is very low, between 2 and 6 per cm. in *desi* cottons, belonging to *G. arboreum* and *G. herbaceum* species and high, between 10 and 30 per cm., in *G. hirsutum* and *G. barbadense* species.

The number of reversals in cotton fibres did not show any relationship with mean fibre length,

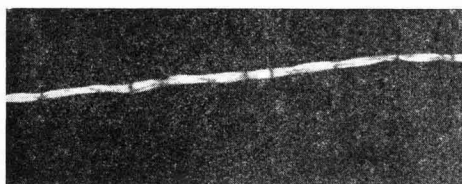


Fig. 12—Structural reversals in a cotton fibre observed between crossed Nicols (×200)

bundle strength or fall in strength due to increase in the test length. In the light of this, the weak link theory of Wakeham and Spicer¹⁹, and Radhakrishnan *et al.*²⁰ needs to be re-examined as it may not hold good for a large number of Indian cottons.

Structural reversals could at best be treated as only some of the sources of weak points in cell wall structure of cotton. Unfortunately, no practical methods have so far been evolved to locate other weak places in the cell wall of cotton fibre.

According to Meredith²¹, if it is assumed that cotton is effectively a series of cells of length equal to the average distance between reversals, the relation between cell length and cotangent of the standard angle at constant breadth is of the same form as that found in wood tracheids and bamboo fibres.

Preston² had shown that in wood tracheids and bamboo fibres the relationship $L = A + B \cot \theta$ holds good where L is the cell length, A and B are constants and θ is the standard angle calculated for a cell breadth of 24 μ . The values of θ for cotton were calculated from the equation

$$\sin \theta = (24 \pi / P) \sin 24.25^\circ$$

where P is the perimeter and 24.25° is the average spiral angle of the unconvoluted fibre.

The relation between L and $\cot \theta$ is shown in Fig. 13. The overall correlation observed was 0.60 for the two entities which was significant. But, on excluding five values for *G. arboreum indicum* cottons, the correlation vastly improved to 0.88. The striking feature of indicums to stand apart from the rest can be related to their having few reversals and a smaller perimeter. In contrast, bengalenses and herbaceums have few reversals and large perimeter and hirsutums as well as barbadenses have smaller perimeter and large number of reversals.

This peculiar behaviour of *G. arboreum indicum* cottons once again emphasizes the dominant part played by the types of cotton included in the study of structural properties of cotton.

Cell Wall Development in Two Problem Indian Cottons

It is the experience of spinners that the long staple cottons evolved in this country for spinning

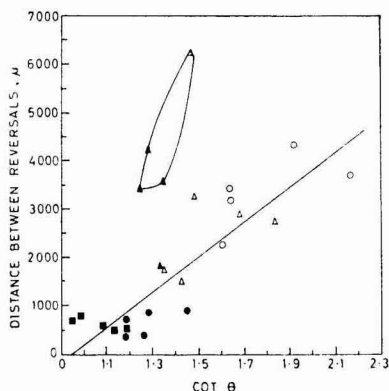


Fig. 13—Distance between reversals in relation to spiral angle: \blacktriangle , *G. arboreum indicum*; \circ , *G. herbaceum*; \triangle , *G. arboreum bengalense*; \bullet , *G. hirsutum*; and \blacksquare , *G. barbadense*

fine counts do not give the performance expected of them as overemphasis has been laid on the improvement of staple length alone. Importance of fibre maturity, strength, etc., is being realized of late. Hence, it was felt that acquisition of fundamental knowledge on the fibre development, especially during secondary thickening of these problem varieties, would be helpful in improving their maturity and strength. Deviraj belonging to *G. hirsutum* and Vijalpa belonging to *G. herbaceum* were selected for this study²². It may also be recalled that the study on structural properties had shown that Indian hirsutums and herbaceums do not have any close relationship between strength and orientation.

Green bolls of the two cottons of known age (from 24 days from the date of flowering to just prior to opening of the bolls) and collected at an interval of three days, were obtained in the preserved state. Degree of thickening, a measure of cell wall thickness, was determined on undried fibres. The representative dried fibres were tested for convolution angle, birefringence, reversals and tensile strength.

Degree of thickening showed linear relation with the age of development and was vigorous in herbaceum Vijalpa as compared to Indo-American Deviraj. The fibre from the side region of cotton seed in Vijalpa showed higher cell wall deposition as compared to fibre from chalazal region (Fig. 14). This difference was not observed in Deviraj.

Convolution angle increased with improvement in maturity. Just as degree of thickening, convolution angle was higher for side region fibres as compared to chalazal region fibres.

Birefringence values showed progressive increase with age, indicating improvement in orientation. Number of reversals was confirmed to be a genetic characteristic. They were negligible in herbaceum Vijalpa. However, in hirsutum Deviraj, about 8 reversals per cm. appeared in 30 days old samples. Their number increased at a higher rate and was about

25 per cm. in 51 days old samples and remained more or less constant thereafter.

The period of secondary cell wall thickening is about 24-27 days for the two cottons which seems to be inadequate especially for long staple Deviraj, resulting in high immaturity.

Efforts are called for to experiment and find out whether it would be possible to enhance the rate of cell wall deposition and/or prolong the vital phase of secondary cell wall development by any treatments or agricultural practice with a view to producing more mature and strong Indo-American cottons. Some experimental work in this direction has already been taken up at the Cotton Technological Research Laboratory.

Microfibrillar Morphology

Whether it is the structure-strength relationship, or distribution of reversals per unit length, or the average distance between reversals in relation to cotangent of spiral angle, species-wise behaviour of some of the Indian cottons has been rather peculiar. It was, therefore, felt that an electron microscopic examination of some typical cottons representing them may be fruitful. Hence, a very coarse herbaceum Wagad (28.65μ ribbon width), a fine Indian hirsutum Laxmi (17.20μ) and an American upland cotton (18.30μ) were selected for this investigation.

The fibres were cut into small fragments and subsequently disintegrated for 15 min. in a blender by beating in water. The slurry, after being dried on the specimen grid and appropriately shadowed with Au-Pd, was examined under an electron microscope both at low and high magnification for characteristic fibrillation pattern and distinctive texture of fibrillar mass.

Figs. 15-17 clearly reveal the coarse microfibrils ($230 \times 85 \text{ \AA}$) in herbaceum Wagad, in contrast to the fine microfibrils in Indian ($120 \times 30 \text{ \AA}$) and American ($110 \times 25 \text{ \AA}$) hirsutum cottons. This also demonstrates that microfibril dimensions vary

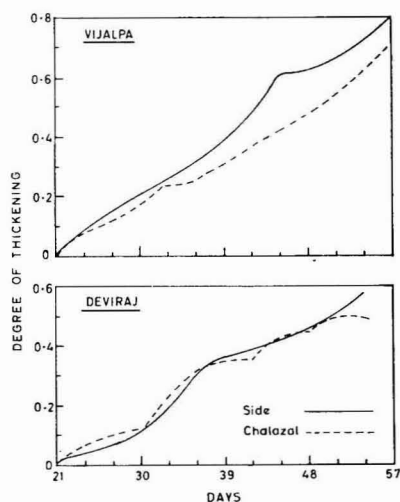


Fig. 14.— Degree of thickening during cell wall development in Vijalpa (*herbaceum*) and Deviraj (*hirsutum*) cottons

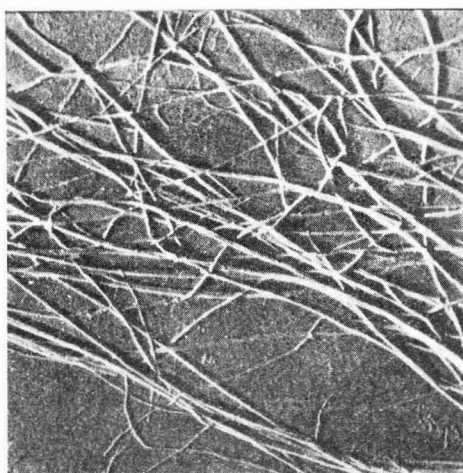


Fig. 15 — Electron micrograph of a coarse Indian herbaceum cotton, shadowed with Au-Pd ($\times 18500$) [Note the coarseness of microfibrils]

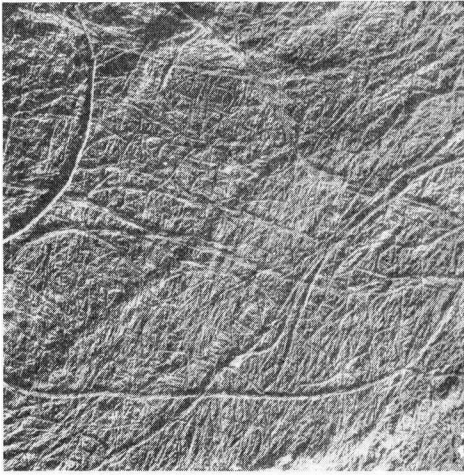


Fig. 16 — Electron micrograph of a fine Indian hirsutum cotton, shadowed with Au-Pd ($\times 16100$) [Note the fineness of microfibrils]

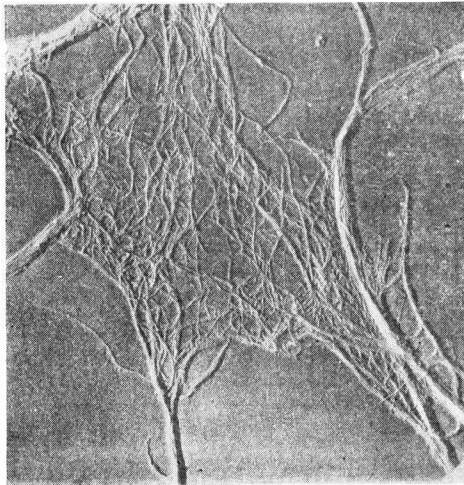


Fig. 17 — Electron micrograph of a fine American hirsutum cotton, shadowed with Au-Pd ($\times 18200$) [Note the fineness of microfibrils]

in cotton inasmuch as the gross fineness in cotton could be traced even to the microfibrillar level.

Summary

Biophysics of plant cell wall structure is reviewed in brief, summarizing the various viewpoints of the chemist, the crystallographer and the microscopist. Basic cell wall structure in algae and higher plants is dealt, in some details, with particular reference to cell

wall constituents and submicroscopic structure. The importance of this study has been emphasized in view of the neglect of this branch of science in India. With this background, the author's work carried out for about a decade on the structure of cotton fibre cell wall in relation to its important technological properties like strength and maturity is presented.

Beginning with convolutions, the gross morphological feature of cotton, which can be examined under an ordinary light microscope, the fine structure study on birefringence, structural reversals and microfibrillar morphology of Indian cottons, employing polarization and electron microscopic techniques are reviewed. The structure-strength relationship and structural reversals in cotton are dealt with in particular, and species-wise differential behaviour of Indian cottons with respect to structural characteristics is brought out. Fibre cell wall development in two typical Indian cottons prone to immaturity and poor strength is touched upon and how the fineness of cotton can be traced down even to microfibrillar level is illustrated by electron micrographs.

Acknowledgement

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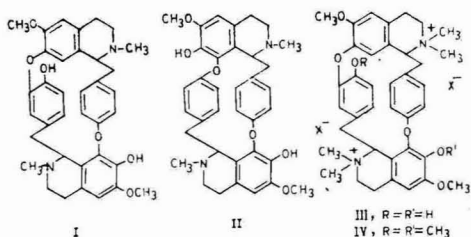
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Synthetic Investigations of Curare Alkaloids

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CURARE, the extract from *Chondrodendron tomentosum* and several species of *Strychnos*, has been used by South American Indians as an arrow poison¹. There are three varieties of curare, which are distinguished by their composition, as tubo curare, calabash curare and torf curare. Tubo curare contains *bis*-benzylisoquinoline alkaloids while calabash curare consists of indole alkaloids. The following two types of alkaloids have been isolated from tubo curare: (i) The tertiary bases, which do not possess a specific curare activity, but exhibit the general depressive action; alkaloids chondrodendrine (I) and isochondrodendrine (II) belong to this group. (ii) Ammonium salts, curarines, exhibiting a high and specific curare activity; the principal representative, tubocurarine chloride, or tubocurarine (III) is of considerable interest among these compounds.



The physiological action of tubocurarine, called the curarine paralysis, brings about complete relaxation of muscles, leading to immobility of the animals^{2,3}. Dimethyl ether of tubocurarine (IV) is 2-10 times as active as the parent substance and is used in complicated surgical operations, especially on the chest and the skull cavities^{4,5} in conjunction with narcotics. The use of curare alkaloids permits smaller doses of narcotics in surgical operations and as a result no post-operative sickness is observed.

Though the physiological activity of curare was well known even in the sixteenth century, the alkaloid (+)-tubocurarine chloride was isolated in pure and crystalline state in 1935 only⁶.

Low accessibility of these alkaloids has led to the search for their analogues, and the total number of these analogues known so far exceeds 100,000. Majority of them has no high activity, or advantages of curare alkaloids. These alkaloids are of great theoretical interest owing to their specific structure. The problem of their biosynthesis was also the subject of several investigations.

Synthesis of Tubo Curare Alkaloids

Macrocyclic molecules of tubo curare alkaloids can be divided into two fragments, benzylisoquino-

lines and diphenyl ethers, both of which can serve as starting materials for their rebuilding. Thus two different modes of their synthesis can be proposed depending upon the starting material used.

Synthetic Pathway Employing Benzylisoquinolines as Starting Materials

The oxidative coupling of benzylisoquinoline units (coclaurine or its N-methyl derivative and ammonium salt) seems to be the biogenetic route of their formation⁷⁻⁹. Some *bis*-benzylisoquinoline derivatives were recently obtained in this way¹⁰. An interesting point to note is that *bis*-benzylisoquinoline alkaloids are capable of splitting to the benzylisoquinoline units by means of sodium in liquid ammonia. This method is widely used for the elucidation of their structure. Japanese scientists have applied the double Ullmann condensation of brominated benzylisoquinoline unit with hydroxyl-containing component to produce the macrocyclic structure. But this method was shown to afford very poor yields of the macrocyclic structure. Besides, it does not give unambiguous results¹¹.

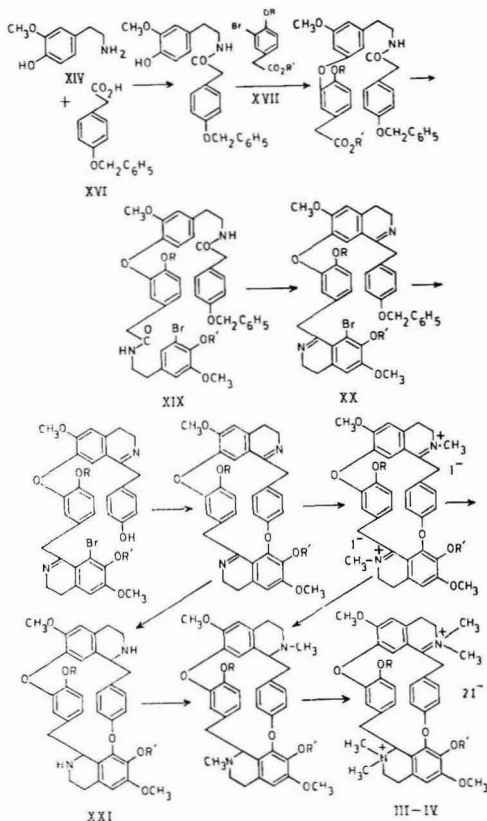
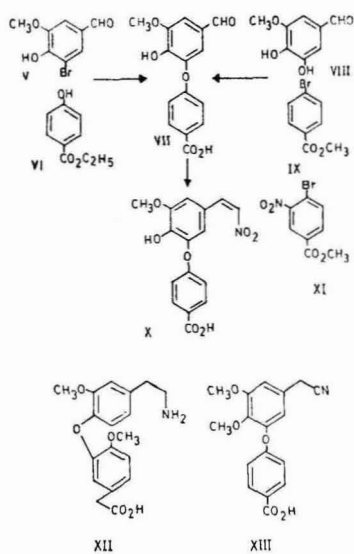
Synthetic Pathway Employing Substituted Diphenyl Ethers

The alternative synthesis of *bis*-benzylisoquinoline alkaloids, employing substituted diphenyl ethers, has been successfully used for building up alkaloids of oxyacantine, berbamine and magnoline types. The synthesis of the amino acidic diphenyl ethers, the structural units of tubocurarine and isochondrodendrine is difficult due to the unsuitability of the Ullmann reaction for their preparation. The most perplexing point to note is the presence of the hydroxy groups close to diphenyl ether linkage in these alkaloids. Even the simplest compounds of this type were obtained by means of Ullmann reaction in small yields¹². Such structural units are of definite importance owing to their potential physiological activity.

2-Hydroxy-3-methoxy-5-(β -nitrovinyl)-4'-carboxy-diphenyl ether (X) was the first substituted diphenyl ether which was synthesized in small yields from 5-bromovanilline (V) and 4-hydroxybenzoic acid ethyl ester (VI), or from 3-methylgallic aldehyde and 4-bromobenzoic acid methyl ester via the intermediate 2-hydroxy-3-methoxy-5-formyl-4'-carboxy-diphenyl ether (VII)¹³. The Ullmann reaction in the first case provides the desired compound (VII) in 10 per cent yield.

This method has been modified by introducing an active nitro group in one of the components, viz. the bromo component (XI). Even this modification does not increase the yield of the compound (VII) to any considerable extent owing to an increase in the number of steps, which are necessary to remove the activating group. Grundon *et al.*^{14,15} have published the synthesis of some similar amino acids

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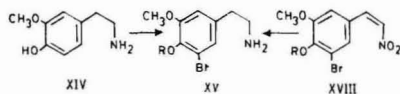
in this way, the most important one being the compound having the structure (XII).

The cyanomethyl diphenyl ether (XIII) corresponding to (X) was synthesized starting with aldehyde (VIII) via its O-methyl derivative, carbinol and chloride. The final product was also obtained employing Ullmann reaction between 3,4-dimethoxy-5-bromobenzylcyanide and 4-hydroxybenzoic ester¹⁶.

Some intermediate compounds and their homologues are useful for the elucidation of conformation of the diphenyl ethers. Thus, the spectral investigations have shown that diphenyl ethers have nonplanar configuration¹⁷.

Synthesis of Tubocurarine Iodide and Its Dimethyl Ether

These investigations finally led to the synthesis of racemic tubocurarine iodide and its dimethyl ether via the intermediate secondary and tertiary bases. The starting materials are β-(3-methoxy-4-hydroxyphenyl) ethylamine (XIV), *p*-benzyloxyphenylacetic acid (XVI), 3-bromo-4-alkoxyphenylacetic ester (XVII) and β-(3-methoxy-4-hydroxy-5-bromophenyl) ethylamine (XV, R = H), the latter being produced by bromination of (XIV) with dioxane dibromide¹⁸. The position of bromine in the molecule was established by comparison with a specimen, produced by lithium aluminium hydride reduction of the corresponding ω-nitrostyrene (XVIII, R = H).



O-Methyl and O-benzyl derivatives of the same amine (XV, R = CH₃, CH₂C₆H₅) were obtained from the corresponding ω-nitrostyrenes (XVIII, R = CH₃, CH₂C₆H₅) by Clemmensen reduction¹⁹.

Other starting materials were synthesized by usual methods. The total synthesis of tubocurarine

Chart 1 -- Synthetic pathway to tubocurarine iodide and its dimethyl derivative starting from β-(3-methoxy-4-hydroxyphenyl) ethylamine (XIV), *p*-benzyloxyphenylacetic acid (XVI) and 3-bromo-4-alkoxyphenylacetic ester (XVII)

(III) and its dimethyl ether (IV) is illustrated in Chart 1 (ref. 20-24).

This scheme is based on successive building up of the system, having the structural units of natural alkaloids, the final step being the formation of the second oxygen bridge.

This scheme (Chart 1) was chosen because of the relative stability of intermediate amides, the lower number of steps involved and the easy availability of the starting materials. The starting diphenyl ethers (XXII) were isolated chromatographically in two forms with the same molecular compositions but with different melting points²⁵. Their oxidation showed that both had the same skeleton, and the resulting compound was identified as 2,2'-dimethoxy-5,4'-dicarboxydiphenyl ether (XXIII) on comparison with an authentic specimen (Chart 2)²⁶. They are also interconvertible since on condensation with bromoamine they give the same amides (XIX). But the Bishler-Napieralsky reaction of the above diphenyl ethers results in the formation of the different dihydroisoquinoline derivatives (XXIV) and (XXVI), which on oxidation give different

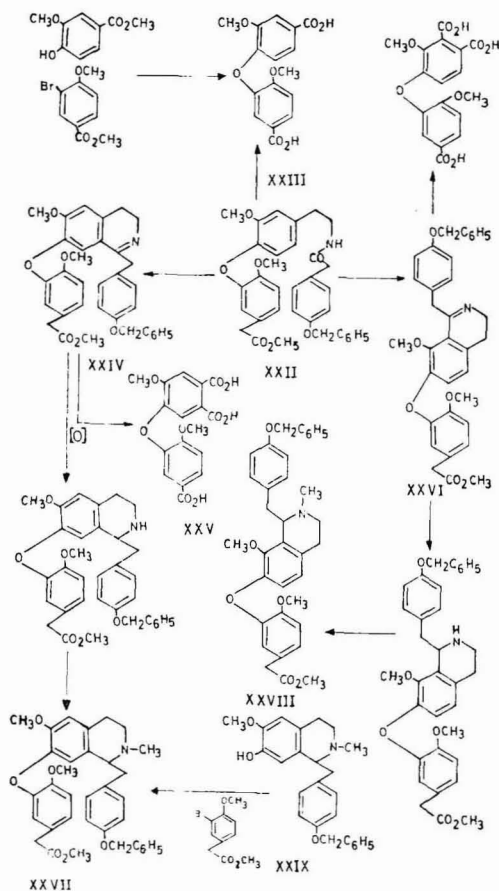


Chart 2—The formation of the same oxidation product (XXIII), and different dihydroisoquinoline derivatives (XXIV) and (XXVI) on cyclization from the two diphenyl ethers (XXII), and the transformation of the cyclization products to the tertiary bases (XXVII) and (XXVIII)

products (Chart 2). The lower melting material yielded the same tricarboxy-diphenyl ether (XXV), obtained from natural tubocurarine by King²⁷. Both the cyclization products, (XXIV) and (XXVI), were transformed into tertiary bases (XXVII) and (XXVIII) through a series of reactions as illustrated in Chart 2 (ref. 26).

The structure of the compound (XXVII) was confirmed by its synthesis from *N*-methyl-4'-*O*-benzyl-coclaurine (XXIX)²⁶. The data presented above point to the conclusion that the starting diphenyl ethers have different special configurations. The low melting diamide (XIX) and *bis*-dihydroisoquinoline base (XX) produced the desired final product. Ammonium salts were separated by means of crystallization in four racemic forms. This is in harmony with the suggestion that such molecules have two asymmetric centres and an asymmetric nonplanar structure^{20-22,24}.

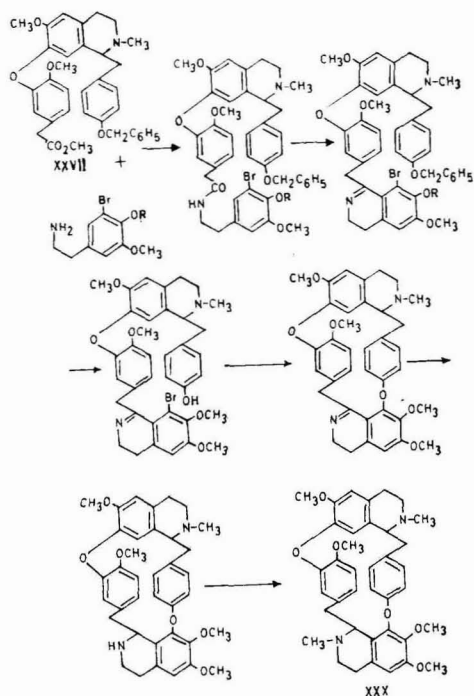


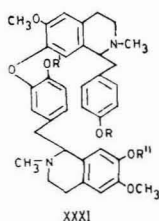
Chart 3—Synthesis of *O,O'*-dimethylchondodendrine (XXX) from 1-(4'-benzyloxybenzyl)-6-methoxy-7-(2''-methoxy-5''-carbomethoxymethylphenoxy)-*N*-methyl-1,2,3,4-tetrahydroisoquinoline (XXVII)

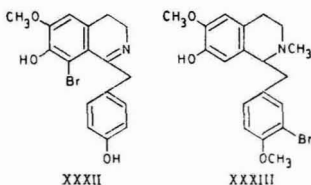
This route was also applied to obtain racemic monomethyl ether of *N,N'*-desmethylchondodendrine (XXI, $R = CH_3$, $R' = H$)²⁸, which was isolated from natural sources and was known as chondrofoline, the position of the hydroxy group in which was not elucidated before. The biogenetic proposals and colour reactions lead to conclusion that the most probable position of the hydroxyl was 2''.

The intermediate 1-(4'-benzyloxybenzyl)-6-methoxy-7-(2''-methoxy-5''-carbomethoxymethylphenoxy)-*N*-methyl-1,2,3,4-tetrahydroisoquinoline (XXVII) was also used to synthesize *O,O'*-dimethylchondodendrine (XXX) with different configuration at asymmetric centres²⁹ (Chart 3).

When homoveratrylamine was used instead of bromoamine, noncyclic derivatives (XXXI) were obtained, which are of great interest as the genetic chain between tubocurarine alkaloids and benzylisoquinoline alkaloids^{23,30}. Dimethyl derivatives of this substance (XXXI, $R = H$, $R' = R'' = CH_3$) and (XXXI, $R'' = H$, $R = R' = CH_3$) were recently isolated from natural sources^{31,32}, and are known as liensinine and isoliensinine respectively.

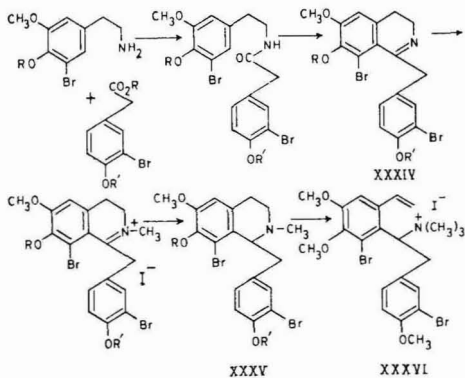
The Bishler-Napieralsky reaction was of special interest for bromine containing compounds





to obtain the starting material for the synthesis of other representatives of these alkaloids. Thus 1-(4'-hydroxybenzyl)-6-methoxy-7-hydroxy-8-bromo-3,4-dihydroisoquinoline (XXXII)³³ and 3-bromo-4'-O,N-dimethylcoclaurine (XXXIII)³⁴ were synthesized in the usual way.

Similarly, 2,7,4'-trimethyl-8,3'-dibromococlaurine (XXXV, R = R' = CH₃) was synthesized³⁵. We have shown, contrary to the earlier report³⁶, that Bishler-Napieralsky reaction can be successfully applied to benzyl derivatives as well as to methyl and acetyl derivatives. But in the former case the resulting 3,4-dihydroisoquinoline derivative (XXXIV, R = R' = CH₂C₆H₅) is a weak base, the hydrochloride of which is easily hydrolysed in acetone-aqueous solution with the liberation of the free base.



The final compound (XXXV, R = R' = CH₃) undergoes degradation to known Hoffmann base (XXXVI), obtained earlier¹¹ from natural N-methylcoclaurine.

Summary

A review of synthetic pathways to curare alkaloids of bis-benzylisoquinoline structure such as tubocurarine iodide and their derivatives, starting from benzylisoquinolines and diphenyl ethers is given.

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Impact of Coordination Chemistry on Leather Research & Technology*

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SCIENTIFIC pursuits in every field have not only enriched our knowledge in the respective field, but have also provided the basis for further technological advancement. Taking, for instance, natural and synthetic polymers, it is easy to recognize that compared to a few natural materials like cotton fibres, lignin, natural rubber, glass, etc., we have a whole range of synthetic fibres, rubbers of every kind, plastics and different kinds of leather. Two approaches are discernible in such advancement. To start with, certain building blocks like ethylene, isoprene, or a mixture of polybasic acids and diamines are taken and the building of chains deliberately induced by suitable polymerization techniques. Alternatively, the basic polymer chain is retained, but further reinforcement is effected with certain compounds which confer remarkable specific properties on the polymer. An example is natural rubber which is considerably improved by vulcanization wherein sulphur imparts the necessary stabilization. The building blocks in keratins, skins and similar proteins are made up of different amino acids and the links are of polypeptide (CO-NH) type. Further, the natural polymer is present in certain oriented and sequential structures with a helical form of high molecular weight (75,000-90,000) containing in certain cases as many as 3 individual chains. There is a high degree of order already present in the chain with hydrogen bonds stabilizing the structure and conferring strength to the fibres which one would like to preserve. However, the skin protein, collagen, is easily attacked by bacteria. Hence it is necessary that the protein should be stabilized to make it suitable for most of the end uses to which leather is put. This treatment, tanning, is brought about by a variety of substances of wide structural characteristics. Among these, treatment with metal salts is unique, in that the leather is made highly resistant to heat due to additional crosslinks at intra- and intermolecular levels.

Advent of Coordination Chemistry

Before the advent of coordination chemistry, the stabilization of the polypeptide chain by the metal salts was attributed to precipitation, salt formation¹, etc. From the simple postulates of Werner² that certain metal salts can possess auxiliary valency bonds, this field has made tremendous advances and even now holds the interest of chemists because of the lack of clear understanding of the forces between metal ions and ligands. Further, in several other fields, a knowledge of coordination chemistry has helped in understanding the reaction mechanisms and resulted in considerable improvement in technology. An example is

the stereospecific polymerization of ethylene, propylene, etc., in the presence of organometallic catalysts. Even in biological systems like haemoglobin, chlorophyll, etc., metal ion complexes are well known and have been characterized. Enzymes are known to possess a coordinated metal ion. However, in fibrous proteins like collagen, depending on the choice of metal ions and other factors, remarkably stable reversible structural entities can be formed.

Metal Ion-Protein Interactions

It can be logically argued that strongly interacting metal ions will form strong bonds and hence function as efficient tanning agents. But actually only a few metal ions behave as good tanning agents.

Proteins with their many reactive groups are capable of binding most metal ions, but the characteristics of metal-protein complexes vary widely. Among the great variety of protein-metal ion interactions the particular type in which metal ion is coordinated to specific sites in the protein forming an integral part in the structure and contributing to stabilization is of interest to the leather chemist. Collagen is made up of 19 amino acids with side chains of both acidic and basic character contributed by amino acid residues of glutamic and aspartic acids, arginine, lysine and histidine and polar groups of hydroxyproline, tyrosine, etc., in addition to backbone ketoimide group³. Even though several groups are available for interaction with metal ions, only a few of them, especially those of carboxyl groups, take part in coordination resulting in stabilization, due to factors like steric effect in collagen lattice, non-availability of reactive groups under the conditions of interaction and limitation to formation of bonding orbitals.

Most of the metal ions including some of the salts of isopoly and heteropoly acids like polyphosphates and silicates have been investigated⁴ for their tanning efficacy, but only the basic salts of chromium, aluminium and zirconium have been found to possess excellent tanning action. The salts of cadmium, iron, titanium, bismuth, beryllium and cerium together with silicates, tungstates and molybdates have been shown to possess only mild tanning action. It is one of the major unsolved problems in leather chemistry why certain metal ions alone exert tanning action. In this field, as in many others, practical technology has advanced greatly, whereas the theory has lagged behind considerably. During the last 25-30 years, the factors responsible for tanning action have been studied by different groups of workers⁵⁻⁹.

Factors Governing Metal Ion Coordination with Collagen

Neither the dried fibre nor the metal ion devoid of coordinated aquo group can tan. The metal

*Based on a lecture delivered by Dr Y. Nayudamma at Maharaja Sayaji Rao University of Baroda on the occasion of the award of Dr K. G. Naik Gold Medal.

ions which are solvated in water medium undergo substitution reactions, resulting in the formation of complexes in the presence of ligands. However, in order to possess tanning action, the complexes should have intermediate stability and should be capable of reacting further with available groups, in the protein. Thus trioxalatochromate and cyanide and EDTA complexes of metal ions cannot function as tanning agents. Extensive studies by the schools mentioned have shown the effects of anions, concentration, the charge characteristics of the tanning agent, pH , etc., on the effectiveness of the metal complex in coordinating with the reactive groups of the protein. Work carried out at the Central Leather Research Institute (CLRI), Madras, has contributed to the understanding of the metal complex formation with aluminium salts and optimum conditions for tanning with aluminium salts have been established¹⁰. The formation of a coordination complex with oxygen of the carboxyl group alone is no criterion for tannage to occur, because many of the transition metal ions and several other small sized ions do form stable complexes, but like copper are ineffective for tanning. A probable explanation offered is that the metal ion should also form polynuclear species.

Aggregation and Polynuclear Formation

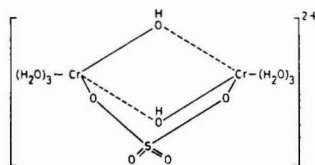
Many silicates hydrolyse rapidly and form large polynuclear species, whereas a few other metal ions like titanium hydrolyse with difficulty even to form binuclear species. Both these types are not quite suitable for tanning.

Other metal ions like zirconium, chromium and aluminium, which do tan, form polynuclear complexes in the presence of hydroxyl ion and certain organic and inorganic ligands like phthalate and sulphite respectively. However, quantitative data on the hydrolytic and complex formation constants of such complexes are restricted only to divalent species¹¹, whereas tripositive and higher charged ions have been ignored, except simpler species like iron, possibly due to the variety of products formed and the complicating factors. Potentiometric titration technique alone is applicable in a majority of cases¹², whereas spectrophotometry has been applied to some coloured and outer sphere (ion-pair) complexes¹³. The possible application of coulometric titration technique in studying hydrolysis and the related aggregation phenomenon is being explored. The optimum size of the complex and the concentration of hydroxyl ion, etc., seem, at the present state of knowledge, to be controlled and fixed by practical tanning tests rather than on theoretical grounds. The liquors formed themselves are complex mixtures and no single structurally uniform compound can be crystallized and its constitution and mechanism of interaction established, except very few like dioxalatochromate which do not have practical utility. Any separation procedure disturbs the equilibrium and modifies the complex in some manner. Recent investigations have shown that isotopic labelling coupled with ion exchange will prove to be a powerful technique at least from analytical and kinetic considerations, though not for characterization and structural determination.

However, the understanding of this subject suffers from many drawbacks. Cobalt ion has been known to form polynuclear species, yet it cannot function as a tanning agent. Iron which can form a variety of polynuclear species suffers from a great drawback as it reduces the strength of the protein fibres and defects occur in leather due to acid development, surface peeling, etc. Possibly the stability of intermediate forms of hydrolytic species may be one of the deciding factors¹⁴. However, quantitative data are lacking for arriving at any conclusion. Zirconyl chloride possessing 50 per cent basicity and polymerizing to discrete tetrameric forms does not exhibit good tanning effect, whereas sulphato-zirconic acid, which forms polynuclear species of indeterminate size, possesses excellent tanning property.

Preparative Methods Affecting the Nature of the Complex

In the preparation of the metal complex useful for tanning, the oxidation state of the starting materials, their availability, the acid used (especially the concentration and the nature of the anion), reducing substances used, if any, the competing reactions and the mechanistic pathways determine the nature of the products and their utility and commercial importance. Complexes derived from trivalent chromium salts, which account for more than 80 per cent of mineral tanned leather, are obtained from hexavalent chromium (dichromate) by reduction with sulphur dioxide, sugar or any other suitable reductant under optimum conditions of acidity. Several variations in the product are brought about by selecting the suitable reducing agent, whether it can effect one electron or multi-electron transfer or whether it can get oxidized and eliminated from the system or continue to be present in the system and modify the nature of the complex. Thus sulphur dioxide reduces dichromate easily giving rise to unstable sulphato basic chromium complex which gets stabilized to predominantly cationic chromium complex of the following empirical formula¹⁵:



With hypochlorite as the reducing agent, however, mononuclear species predominate¹⁶. The kinetics of many reduction steps are yet to be worked out and the intermediate formation of Cr^{3+} and Cr^{4+} species together with Cr^{2+} species has been postulated without much experimental support. Organic reducing agents have the advantage that the products of oxidation, if oxidative degradation is controlled, give rise to acids like acetic, formic, etc., which can form complexes with the metal ion by substitution of the aquo or sulphato group¹⁷. Several organic reducing agents like glycerol,

molasses, coconut pith, bagasse, vegetable tannins, oils, lac, etc.¹⁸⁻²⁰, have been investigated and the oxidation products identified by chromatographic and other techniques. Even in the presence of a simple organic reducing agent like sucrose, the material balance could not be obtained, nor all the products detected. Work is being undertaken using sucrose tagged with ¹⁴C. Conditions have been standardized for the preparation of powdered extracts which have industrial application. Apart from chromium salts, aluminium and zirconium salts are also used in tanning to a lesser degree. Since aluminium salts hydrolyse rapidly, the stabilization of the sulphates are accomplished by judicious addition of citric acid, so that a basic complex can be prepared²¹. With zirconium also the conditions for obtaining sulphato-zirconic acid from zircon sand have been standardized and released for industrial exploitation.

When more than one mineral tanning agent is present in solution, the nature of the complexes has been found to be different from that of the individual mineral salt. Potentiometric, spectrophotometric and electrophoretic techniques together with the reaction on collagen have provided evidence for the formation of complexes containing both the metal ions, especially with chromium and aluminium salts containing citrate and also with chromium and aluminium salts in the presence of gluconate and tartrate²².

Modification of the Complex and Its Effect in Tanning

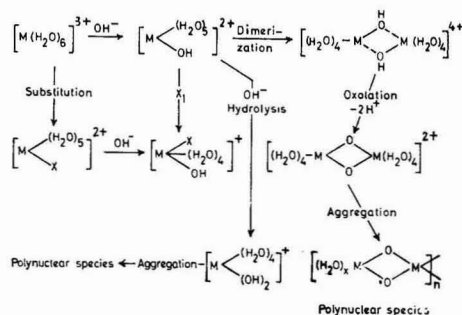
The salts present in the liquor used for tanning modify the tanning action in a number of ways, viz. dehydration of protein, buffer action and complex formation. The effect of neutral inorganic salts has been subjected to a great deal of study²³ and their complexing ability has been related to the concentration. However, controversy still exists whether the hindrance to tanning effect, especially at concentration beyond a molar ratio of 1:1, is due to complex formation or to the dehydrating influence on the hide protein²⁴. Spectrophotometric work done at CLRI has lent support to the formation of a complex^{25,26}. However, the effect of the changed environment on the stability of the sulphato complex has not been studied in great detail, though the complexes are known to be unstable and to get converted from negatively charged to positively charged ones easily²⁷. The problem is being investigated using labelled sulphate. Complex forming salts modify the tanning process to a greater extent than neutral salts²⁸. Monocarboxylic salts like formate, dicarboxylates like oxalate, tartrate and succinate, hydroxy carboxylates like phthalate, citrate and inorganic salts like sulphite have been recommended and used. Too stable a complex formation is detrimental for tanning action to take place. However, with certain complex forming metals like iron, best results are achieved only in the presence of optimum concentration of tartrate or sulphophthalate²⁹. Tulsī Ram and Nayudamma³⁰ have conclusively shown that cerium tanning is possible in the presence of phthalate as the complex forming ligand. Though the reaction

mechanism in the presence of such complexes has not been worked out, it has been established that bridged type of complexes are obtained in the presence of phthalate. However, different types of coordinating ligands behave somewhat differently with various metal ions. Citrate and other hydroxy acids show preferential complexing for aluminium and zirconium, assisting in the fixation and stabilization of the complex formed with protein, whereas in the case of chromium, formate and adipate are the preferred ligands. The function of the hydroxy acid as a ligand contributes to the co-ordination of both hydroxyl and carboxyl groups, since metal-oxygen bond is favoured. Some data have been obtained on the stability constants of metal-amino acid complexes. Shuttleworth and Sykes³¹ ruled out chelation with NH₂ group under the pH conditions obtaining in mineral tanning. The pK values of the ligands have also been correlated with the stability constants of the complexes. However, with α, β, γ and ε amino acids, the reverse behaviour was observed. Techniques have not yet been standardized for sorting out and systematizing the formation constants of individual complexes in solutions and extending them to heterogeneous systems. According to the complexing ability of the ligands and the ease of substitution in the co-ordination sphere, they have been arranged by Stiasny³² in the following order: nitrate < chloride < sulphate < formate < acetate < sulphite < oxalate. This order has been modified for aluminium and compared with zirconium and chromium by Selvarangan *et al.*³³ through pH titration studies with alkali at different temperatures in the presence of the complexing agent.

Separation, Characterization and Nature of the Complexes Responsible for Tanning Action

In a solution of basic mineral salt used for tanning, several complexing species having varying charges and sizes and different types of ligands in different positions exist in a dynamic equilibrium depending on free ligand concentration and pH, as illustrated in Chart 1.

Though all the reactions illustrated in Chart 1 are possible, some predominate, depending on the conditions like metal ion concentration, pH, ligand concentration³⁴, etc. The formation of highly



aggregated complexes is restricted only to a few complexes of high basicity.

Attempts to separate, crystallize and characterize these complexes have not succeeded so far with the exception of hexaquo salt and mono-substituted pentaquo salt which do not possess tanning action. This difficulty has been ascribed to the high hydrophilic nature of the hydroxyl and aquo ligands. Attempts to crystallize these complexes from non-aqueous solvents like methanol have failed. A few dioxane adducts have been crystallized with certain other metal complexes, but not with chromium complexes. The separation technique has necessarily been restricted to methods employed for characterizing differently charged complexes. Electrophoretic and ion exchange techniques have been used with some success. In electrophoretic techniques, though considerable overlapping of the charged components has been observed by a number of workers, Kawamura and Wada³⁵ and Devassy and Nayudamma³⁶ have succeeded in effecting separations with well-defined characteristic spots. Kawamura and Wada³⁵ obtained five well-defined complexes in nonaqueous conducting medium, whereas Devassy and Nayudamma³⁶ using acidic perchloric-nitric medium for electrophoretic separation, obtained three spots for cationic complexes. To prevent possible modification of the complexes in acidic medium, amine buffers have been suggested recently.

The separated spots could at best give a quantitative estimate of chromium and possibly of sulphate, but further characterization was not possible. Microcoulometric titration is being developed for determining the hydroxide content of the complex. Mean effective charge of the complex has been found by making use of ion exchange technique³⁷; but several assumptions like binuclear nature of the species present³⁸ have been made.

The alternate ion exchange method suffers from the drawback that elution procedures, especially those involving acids, disrupt the nature of the complexes and has so far been useful for obtaining analytical data only. Separations involving differently cross-linked ion exchange resins³⁹ and possibly membranes have been suggested, but no tangible results have been reported. Recent attempts have shown that by using radioactive isotopes of chromium and sulphur, better separations can be achieved with ion exchange procedures using metal perchlorates as eluting agents.

Kinetics and Mechanism of Mineral Tannage

The affinities of different complexes for an ion exchange resin are widely different and polynuclear species resist elution even by 3M perchloric acid^{40,41}. Gustavson first suggested that with chrome complex, a small quantity, viz. 10 per cent, of the complex is taken up initially by the resin in cross-linked form, and the rest of the complex is linked unipointly. Gustavson^{42,43} employed pyridine treatment technique to determine ionically bound sulphate only and suggested that the crosslinked chromium complex may not contain any residual charge and hold ionic sulphate. This view has been questioned by German research workers and

also by Bowes⁴⁴. Though the affinity between the complex and ionic sulphate depends on the nature of the complex, the real difficulty seems to be in adducing experimental support for this hypothesis. Methods for determining differently held sulphate groups have been critically reviewed⁴⁵ and a new method based on nonaqueous titration technique for finding acidic groups has been proposed⁴⁶. Here also labelled liquor with both chromium and sulphate should be capable of giving conclusive evidence, since the lability of the complex is always associated with fast and rapid exchange. Further work in this direction should be of considerable value.

Theories of crosslinking have been generally accepted for explaining the physical characteristics and thermal stability of mineral tanned leather. Though there is unequivocal evidence for the carboxyl group of the collagen taking part in chrome tannage, it is not so with other mineral tanning agents like zirconium and aluminium. The fixation of zirconium has been ascribed by different workers to basic groups of collagen and polypeptide backbone⁴⁷⁻⁴⁹. Ranganathan and Reed⁵⁰, by electron microscopic investigations, found considerable deposition of aggregated polyzirconates within the fibre. Recent investigations have shown that carboxyl groups may also contribute to zirconium tannage⁵¹. Selvarangan⁵² explained aluminium tannage to fall primarily in line with chromium tannage except for the weaker nature of Al-COO link. An attempt has been made to treat all mineral tannages from the same standpoint and to evolve some sort of unified theory⁵³. However, there are many gaps in such a treatment and far too many simplifications have to be resorted to in order to provide a reasonable understanding of the reactions involved. Yet another consideration in the treatment of chrome tannage, especially of cationic type, is to ascribe coordination only to carboxyl group and limiting crosslinking between two carboxyl groups at favourable positions of steric orientation. X-ray investigations have shown that only side chain groups are involved in coordination. At the pH obtaining in mineral tannage (3.5-4.0), the possibility of free amino groups getting uncharged and coordinating has been considered remote by Shuttleworth⁵⁴. Other possible sites are substituted amide and groups where lone pair of electrons of nitrogen atom may provide some overlap. Since no technique is available for investigating the type of metal-ligand linkage in tanned leather, information about the groups responsible for chemical bond formation has been obtained from a study of the complexes in solution. No evidence has been found for chelation of the amino group, when present in α -position to carboxyl group, with chromium up to pH 5, though differences exist between spectrophotometric curves obtained with acetate and amino acetate ligands⁵⁵. Another ionizable site involving nitrogen is the NH group in imidazole ring in histidine amino acid residue. Several imidazole complexes of other elements like zirconium and also some transitional elements are known. However, the pK value of NH in imidazole group is around 6 and hence it may contribute

negligibly to coordination. Nevertheless, the activation of the ionization by other side groups as well as by coordination of other neighbouring groups may possibly lower the pK value, in which case there is no reason why it should not coordinate as well as crosslink. Evidence is being sought for the presence of coordinated and crosslinked imidazole groups in chrome tanning by conventional potentiometric and similar techniques. Controversy exists also in anionic type of tannage in the mechanism of chrome tannage. One group of workers maintain that in this case, fixation is restricted to basic groups⁵⁶, whereas Shuttleworth⁵⁷ envisages coordination to carboxyl groups as in case of cationic chrome tannage. The argument advanced is analogy to solutions where high ligand concentrations lead to further coordination giving rise to maximum coordination number and negative charge with the ligand. However, restrictions on the available concentration of carboxyl groups together with the alternate method of fixing negatively charged complexes has been overlooked. The repulsion or attraction of the neighbouring group in the protein network has been emphasized recently⁵⁸. The mechanism of formation of stable nonionic complexes of chromium with hexametaphosphate has been studied by Nayudamma *et al.*⁵⁹ and the part played by side chain polar groups like hydroxyl during fixation of the complexes has been brought out, confirming the earlier studies by Gustavson and Holm⁶⁰ and Gustavson⁶¹ on noncationic complexes based on phthalate and sulphite. These liquors are unique in that they give negligible increase in shrinkage temperature.

Stability and Factors Preventing Rupture of Metal-Ligand Bond

Mineral tannage under a variety of conditions is considered reversible, since by treatment with strong complex forming ligands like oxalate, fixation is reversed and the metal ion displaced from the metal-protein complex almost completely. However, in practice tanned leather is subject to only limited variations and the ability of the metal-protein complex to withstand these conditions determines its application. Moisture, heat, repeated mechanical flexings, sweat, etc., are the main agents causing damage. The difficulty in determining the nature of the complex inside the collagen fibres has already been referred to. It is all the more difficult if one has to follow the changes and modifications of the complex inside the leather. It has been estimated that the bond energy along the polypeptide chain is 70,000-90,000 kcal./mole for C-N-C bond and the intermolecular cohesive force per 5 Å. chain length is 6,000-10,000 cal./mole for silk fibroin and polyamide⁶², although exact thermodynamic data for collagen are not available. The contribution to thermodynamic stability by the tanning agent in terms of energy values is being investigated. However, another approach is to determine the bond dissociation energy for simple systems containing bonds of the type Cr-OOC, Al-OOC, Zr-amino acid, etc., and correlate it with the stability of the complex. The poor stability of aluminium tanned leather is perhaps associated

with the weaker nature of the complex, though quantitative results are not available. ΔF values, calculated from stability constant values, could be employed for correlation. However, the slow breaking up of the bond causing deterioration and rupture is difficult to study. Bowes and Raistrick⁶³ studied the deterioration of chrome tanned leather and compared it with the deterioration of other combination tanned leathers and showed superiority of chrome-protein complex in withstanding deterioration. The criteria for analysis were visual observation, stripped tanning agent, lowering of shrinkage temperature and, sometimes, acidity. The deterioration is ascribed to many causes, chief among them being further hydrolysis of the complex to liberate acid which breaks down the protein. Even organic acids cause damage. The stabilization of the complex to withstand this damage should await detailed study of the fixed complex and its modification in changed environment. One of the other chief deteriorating agents is sweat. Lactic acid is known to complex directly with the metal-protein complex and break it down causing deterioration and detanning. Recent studies⁶⁴ have shown that glutaraldehyde combination tanning with chrome tannage overcomes this defect and makes the tanned leather sweat resistant. Though the mechanism of sweat resistance is not yet established, the modification of the complex by aldehyde has been suggested. Specific results show no change in chrome complex as far as the formaldehyde in solution is concerned⁶⁵. It remains to be seen if a complex with built-in sweat resistance and capable of retaining its tanning action can be successfully prepared. Hydrophobic complexes like fatty acid complex of chromium in solvent medium have been prepared and used successfully for shower-proofing and waterproofing of gloving and clothing leather⁶⁶. The ability of aluminium salts to complex with phenolic hydroxy acids is well utilized by retanning myrobalan tanned leather with basic aluminium sulphate resulting in high shrinkage temperature⁶⁷. Recent investigations have shown that a polymerized built-in complex formed by treating chrome liquor with acrylic acid possesses some lubricating properties in addition to filling⁶⁸. Acrylate polymerized complex with aluminium has also been reported.

Thus tailoring the mineral tanning complex to suit various end uses with specific ligands by the application of principles of coordination seems to have a bright future.

Summary

The role of coordination chemistry in stimulating and promoting the growth of leather research and in helping the understanding of protein-metal interactions is reviewed. The progress made in this field in general, with particular reference to the contributions made at the Central Leather Research Institute, Madras, has been brought out. The problems remaining to be solved are highlighted.

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REVIEWS

IONOSPHERIC RADIO PROPAGATION by Kenneth Davies (Dover Publications Inc., New York), 1966. Pp. xiv+470. Price \$ 2.25

This is the Dover edition of the National Bureau of Standards Monograph No. 80, originally published in 1965 by the US Government Printing Office. It replaces the previous NBS publication (Circular 462) with the same title, incorporating the results obtained during the two great international scientific ventures: the International Geophysical Year (1957-58) and the International Quiet Sun Year (1964-65). Meant primarily as a handbook for radio communication engineers, the book mentions only briefly the origin, formation and morphology of the ionospheric layers and deals more exhaustively with the theory and techniques of radiowave propagation. There is an excellent introduction to the magneto-ionic theory of radiowave propagation (including a short note on the generalized magneto-ionic formulae), a brief description of the various ionospheric sounding techniques (with emphasis on the ionosonde), the principles and mathematics of oblique propagation, and a useful description of the factors affecting signal strength. These are followed by a chapter describing in some detail ionospheric propagation prediction systems, including a description of the method of numerical mapping of ionospheric characteristics developed by Gallet and Jones, and chapters on VHF scatter propagation from ionospheric irregularities and from meteors and propagation of low and very low frequency waves.

This is an extremely valuable handbook to radio communication engineers, and to many of the ionospheric physicists concerned with ionospheric soundings.

A. P. MITRA

THE DEVELOPMENT OF HIGH ENERGY ACCELERATOR edited with commentary by M. Stanley Livingston (Dover Publications Inc., New York), 1966. Pp. xi+317. Price \$ 2.50

The book under review deals with particle accelerators which by projecting a highly concentrated beam of ions and electrons cause the disruption of atomic nuclei enabling an analysis of fundamental particles from which the atoms are formed. The 28 papers brought together in this book comprise the prewar innovative principles, concepts as well as advances of the development of high energy accelerators.

The first section dealing with direct voltage acceleration consists of an exposition of Cockroft and Walton's voltage multiplier and five papers by van de Graff, Tue, Barton, Herb and others on the belt-charged electrostatic generator.

The second section on resonance acceleration deals with the initial working models of the cyclotron, the principles and mechanics of linear accelerators and the betatron in papers by Wideroe, Lawrence, Sloan, Alvarez, Ginzton, Kerst and

others. The third section dealing with synchronous acceleration collects together the papers by Veksler, McMillan, Bohm, Brobeck, Livingston and others. These papers describe the electron synchrotron, the synchro cyclotron and the proton synchrotron. Section four presents a description of the principles of alternating gradient focusing by Courant, Christofilos, Regenstreif, Blewett, Livingston and Thomas. Thus this collection covers the basic reports on the origin and development of the technique and the science of high energy accelerators which enable scientists to fathom the structure of the atomic nucleus.

All the publications dealing with the growth and development of high energy accelerators employed for effecting nuclear reactions are brought together in this volume. The editor of this work is to be congratulated for bringing out this work which will be of immense value to the nuclear physicist as well as to the students of nuclear science and nuclear engineering.

SWAMI JNANANANDA

ACOUSTICS: DESIGN AND PRACTICE: Vol. 1 (Asia Publishing House, Bombay), 1966. Pp. xxviii+539. Price Rs 50.00

The reviewer took time to go through this exquisite volume of over 500 pages claimed by the publisher to be written "from the standpoint of the practical engineer".

The work stems from the author's active planning and design work of 30 years in the All India Radio where he is the Deputy Chief Engineer. But unlike other high officials who have necessarily to handle from time to time diverse aspects of radio engineering, the author has had the uncommon privilege of continuously concentrating on a single subject throughout. He has planned and designed, among other things, 300 studios all over the country. He has also scrutinized and critically analysed works of his own design and gives to the reader of the book the benefit of this extensive study. The author's attachment to the subject and his eagerness to share his experiences and to guide others in the line is obvious throughout the book.

While the approach followed in the book makes it a splendid treatise for the student of advanced building acoustics, the sound guidance given and the exhaustive information presented in it make it an invaluable reference book for the practising engineer.

The book is broadly divided into six chapters bearing the titles: (i) Introduction and history, (ii) Speed and hearing, (iii) Reverberation formulae, (iv) Absorption coefficient, (v) Acoustical material, and (vi) Noise. At first sight the titles appear to be a list of topics commonly dealt with in a work of this nature. The unusual part is the skilful presentation and coverage of the subject. The text presents generally the basic theoretical picture using only the minimum mathematical treatment essential for the

purpose. The subject matter chosen for discussion under each head has a strong practical bias. Difficulties commonly encountered in noise control, acoustical design and acoustical measurement are discussed very frequently with the obvious objective of helping the field engineer in this task.

The subject of reverberation, absorption and absorbing materials is given the priority, prominence and attention it deserves. All relevant topics are discussed at length in three consecutive chapters followed by elaborate appendices. The chapter on noise, covering over 200 pages, is comprehensive enough to be an independent monograph. Its inclusion in the book makes it a fuller guide on noise control and acoustical design which are closely linked topics. This section deals with measurement and control of noise in buildings and control of shock and vibration in machinery. Sections dealing with noise abatement in relation to town planning and control of noise in air-conditioning systems are very useful additions.

A special feature of the book is that all this material occupies only two-thirds of the volume. Then follow four important appendices covering 114 pages. The appendix on sound absorbing materials gives details about the absorption properties and mounting methods for various products, including proprietary materials, not only of Indian origin but also those from UK, USA, Germany, Japan and many other countries of the world. These elaborate and exhaustive data make the book a reference work of immense value. Maintenance and renovation of acoustically treated rooms is a problem which receives scant attention in text-books. This book incorporates a special appendix on this topic. This is followed by an acoustical terminology on fundamental propagation, transmission systems, instruments, music and architectural acoustics as well as an additional appendix on design and layout of acoustical laboratories.

The treatise includes a number of useful tables, diagrams and nomograms required for frequent reference in acoustical work as also 29 full-page plate illustrations of acoustical materials, methods of installation and acoustical instruments. Bibliography of the literature cited is included at the end of each chapter. Pictures showing 16 different Indian musical instruments will be of considerable interest, particularly to the readers abroad.

Noise and acoustical problems in buildings are now receiving more prominence and it is necessary to take them into account at the design stage. This book will prove to be a valuable guidebook to the senior student and the professional man. It will be an asset to any technical library and is sure to be appreciated as a standard reference book by prospective readers in India and abroad.

M. PANCHOLY

APPLIED OPTICS AND OPTICAL ENGINEERING—
A COMPREHENSIVE TREATISE: Vol. 3, edited by
R. Kingslake (Academic Press Inc., New York),
1966. Pp. xiv+374. Price \$ 15.00

This is an excellent compilation of information in the field of optics in a digested form. The need for a handy reference book on optical components in the English language has long been felt and this

work fills this gap. Written in parts by specialists in each field and edited by R. Kingslake, the volume may be considered as a must for those engaged in the design, production and use of optical instruments.

The volume consists of nine chapters of which four are devoted to general description of production techniques, viz. lens design, optical manufacturing, and the testing of complete objective and mirror coatings. Each chapter gives an excellent survey of the field in the style of the respective author. An average reader finds in these chapters things of his interest. The rest of the chapters are devoted to specific details of optical components, viz. photographic objectives, microscope objectives, spectacle lenses, mirror and prism systems and eyepieces and magnifiers.

What a reviewer would have liked to comment has been stated by the editor himself in the preface. The level of academic sophistication varies considerably from chapter to chapter; this is inevitable when many authors having different interests and backgrounds are involved. Rapidly developing topics such as the lasers have largely been omitted because anything written would probably be out of date by the time it is published. One does not find any mention in this volume of projection or telescope objectives, not to say of several other items like components of polarizing equipment, medical optical instruments, scale reading microscopes of surveying instruments, and so on. It will perhaps be worth while to revise, in the next edition, the chapter on photographic objectives to include also the projection objectives and add at least two more chapters, one on telescope objectives and the other on miscellaneous optical components.

Notwithstanding these remarks, the book should be of immense value to all those associated with optical instruments—designers, producers and users.

RAM PRASAD

ELECTRON PROBE MICROANALYSIS by L. S. Birks
(Interscience Publishers Inc., New York), 1963.
Pp. ix+253. Price \$ 9.25

Electron probe microanalysis is one of the most recent techniques developed for specialized chemical analysis. The above is the seventeenth monograph published on 'Analytical chemistry and its applications'. The author, in the first chapter, initiates the reader into the subject by describing its scope and later on he develops the subject in different chapters dealing with the historical background, electron optics and circuit system, mode of specimen observation and their preparation, X-ray crystal optics, detectors and energy dispersion, the theory and the applications of the instrument to various fields, etc. It also includes several appendices dealing with excitation efficiency, intensity function, mass absorption coefficient, etc., useful for the electron probe microanalysis technique. The author has written the book admirably well and it will be useful to chemists, metallurgists and others who are interested in this new powerful tool.

A.G.

SYMPOSIUM ON ADVANCES IN ELECTRON METALLOGRAPHY AND ELECTRON PROBE MICROANALYSIS (American Society for Testing & Materials, Philadelphia), 1962. Pp. v+207. Price \$ 6.00; \$ 4.80 (Members)

This is the third publication by ASTM on the techniques of electron metallography dealing with thin films of iron, stainless steel, aluminium and other non-ferrous metals, their characteristics, microstructure, etc. This publication also includes a good review article on the technique and applications of electron microscope by Bigelow, a paper on the use of electron probe microanalysis in metallographic problems by Heise and also a classified bibliography on electron probe X-ray microanalysis.

A.G.

FUNDAMENTALS OF CHEMISTRY: A MODERN INTRODUCTION by F. Brescia, J. Arents, H. Meislich & A. Turk (Academic Press Inc., New York), 1966. Pp. xv+816. Price \$ 8.95

The authors have attempted to present a modern approach to the introduction of the subject matter of chemistry at the freshman level. The book consists of 29 well-written chapters and five appendices, of which the first one is especially useful to students. Each chapter is divided into neat compact sections, dealing with specific topics. The language used throughout the book is easy to read and follow for a freshman student, and involves clear statements without ambiguity and circumlocution. The figures in the book are extremely well presented and add to the ease of understanding of the subject matter; for example, the illustrations in the sections dealing with crystal structure, space lattices, unit cell dimensions and ligancy. Bold-face print is consistently employed in the chapter to distinguish between the text and the data presented or tables or numerical examples solved in the text. Sometimes this has resulted in several contiguous pages being printed in bold-face print, e.g. pages 571-573, where a numerical problem has been solved.

The book presents a unified approach to the teaching of chemistry at the basic level. The atomic and molecular structures and bonding, thermochemistry and thermodynamics, kinetics, analytical aspects of chemistry, chemistry of 'organic' molecules, electrochemistry, metallurgical aspects, nuclear and polymer chemistry, all these and other areas of the subject receive a well-balanced attention, without singling out anyone for special treatment. The abstruse ideas of quantum chemistry or band theory of metals are presented with the same ease as the ordinary gas laws. Numerical examples have been judiciously introduced as a part of the text to enable students to gain confidence in their understanding of the subject. As far as possible, the authors have attempted not to give a sense of finality to conclusions drawn from data; the students are made aware of other possibilities — for example, the 'epilogue' at the end of Chapter IX on 'Types of chemical bonds' is extremely interesting, starting with the sentence "Our discussion of the nature

and stability of compounds has significance only with the familiar reference frame of temperature and pressure".

The problems given at the end of the chapters add greatly to the value of the book by serving two purposes: (i) to let the student practise on what he has learnt in the text; and (ii) to arouse the curiosity of the student for the subject matter of chemistry. For example, the very first problem at the end of Chapter I asks, "Refer to the table of contents of a recent issue of *Chemical Abstracts* in the library and list the sections you would expect to scan if you were... a chemist employed to develop missile fuels".

There are a few typographical errors: for example, on page 142, Table 7-10, HO_2O_3 should be H_2O_3 ; on page 143, Table 7-11, element Gr should be Cr, BK should be Bk. But these are minor mistakes and do not detract from the general merit of the book. I have used this book for a course in general chemistry at the freshman level and found it extremely useful. The authors have not claimed to have arranged the subject matter in any order with finality. The numbering of sections in each chapter affords the individual instructor a great deal of flexibility to conduct the course in his own manner. I recommend the book strongly for adoption as a basic text for a one-year course in chemistry at the freshman level.

V. RAMAKRISHNA

EXPERIMENTS IN GENERAL CHEMISTRY — A LABORATORY TEXT by C. N. R. Rao & U. C. Agarwala (Affiliated East West Press Ltd, New Delhi), 1966. Pp. v+222. Price Rs 9.50 or \$ 2.50

About 50 per cent of a student's time at the degree level in most Indian universities is spent in laboratory work and yet it is generally agreed that the educational value that the students derive from performing the present laboratory exercises is not commensurate with the time devoted. It is being felt that the syllabi for the laboratory work should be revised to include more of the experiments which illustrate the basic principles of chemistry and which aim at developing the laboratory skill of the student to enable him to handle more complex experiments later. In this context the publication of this book is a step in the right direction. A set of 45 experiments are given from which a suitable choice could be made for using this as a text for the first chemistry course in general chemistry. It is felt, however, that the portion dealing with basic concepts, the laboratory, and laboratory techniques (23 pages) is a bit sketchy; some of it could have been left out without impairing the value of the book.

H.C.G.

THE BIOCHEMISTRY OF COPPER edited by J. Peisach, P. Aisen & W. E. Blumberg (Academic Press Inc., New York), 1966. Pp. xvi+588. Price \$ 23.50 This book contains the papers presented at the Symposium on Copper in Biological Systems held at Harriman, New York, during 8-10 September 1965. There are 40 articles, each by an outstanding biochemist, biologist, chemist, clinician or physicist,

with a summary at the end of each chapter. The book is divided into six parts dealing with structural problems of copper protein chemistry, a study of the role of copper in electron transport and other biological activity, cytochrome oxidase, polyphenol oxidase and laccase, amine oxidases and hemocyanin, and ceruloplasmin. There are up-to-date reviews of cytochrome oxidase, laccase, amine oxidases, Wilson's disease and ceruloplasmin.

The book is well documented. The chapters on ceruloplasmin are particularly commendable and there is one chapter exclusively devoted to discussion on ceruloplasmin. An excellent index adds greatly to the usefulness of the book. The papers presented cover every angle of the study on copper proteins. The book is highly recommended for any biochemist and as a necessity for any researcher working in this field.

T. RAMAKRISHNAN

HORTULUS by Walafrid Strabo; translated from the German by Ralf Payne; commentary by Wilfrid Blunt, Hunt Facsimile Series No. 2 (Hunt Botanical Library, Carnegie Institute of Technology, Pittsburg, Pa, USA), 1966. Pp. xi+91, 28 linoleum-cut page decorations by Henry Evans, 10 double-page facsimile plates 26.5×17 cm. Price \$ 12.00

This is a book, the sort of which one often dreams about but seldom encounters. The printing, binding and general presentation are of the highest order, in every way up to the very high standard set up by the Hunt Facsimile series.

The subject of *Hortulus* is a treatise on garden plants, their appearance and cultivation, their medicinal virtues, etc., described in beautiful easy-flowing Latin hexameters; the original of this *Hortulus* does not seem to have been preserved; the present edition is a reproduction of a manuscript of 849; the MS. was discovered in 1509, and from that time the *Hortulus* has been considered one of the landmarks in gardening literature. The present edition contains an account of the life of the author (pp. 1-18), the manuscript of 849 in facsimile from the original in the Vatican Library with a transcription in classical Latin form and an English translation in free verse (pp. 24-65).

Walafrid, the author, known by the nickname of Strabo ('the squint-eyed'), was born in 809 in South-west Germany; as a boy he was put under various tutors in the Benedictine order, which he joined as a monk; eventually he was elected Abbot of St Gall's monastery. It was during his tenure of this office that he wrote the twenty-seven poems, which a later scribe grouped under the name of *Hortulus*, or 'Little Garden'.

The *Hortulus* is a "down-to-earth practical but very artful manual by a man who had a garden of his own, who loved it and who himself cultivated it". The garden was mostly a kitchen garden, where both medicinal plants and vegetables and a few fruit trees were grown. The titles of the various chapters of the *Hortulus* will give an idea of the contents of the same: On the cultivation of gardens; the difficulty of the undertaking; the gardener's perseverance and the fruits of his labour;

poems on Sage, Rue, Southernwood, Gourd, Melon, Wormwood, Horehound, Fennel, Iris, Lovage, Chervil, Lily, Poppy, Clary, Mint, Pennyroyal, Celery, Betony, Agrimony, Tansy, Catmint, Radish, Rose. The *Hortulus* closes with a dedication to Father Grimald, an old tutor of the author.

To give a sample of the treatment of the various subjects I shall quote (in translation) a few lines on the Lily:

Now the lily, and ah! what lines can my
simple Muse
Lean and meagre as she is,
find to praise
The shining lily? Its white is the white of
glistening snow,
Its scent the scent of sweetest frankincense,
Not Parian marble in whiteness, not spikenard
in fragrance
Surpass our lily.
If a snake, treacherous and wily
As it is by nature, plants with deadly
tongue its parcel
Of venom in you, sending grim death through
the unseen wound
To the inmost vaults of the heart — then
crush lilies with a weighty
Pestle and drink the juice in wine. Now
place the pulp
On the top of the livid spot where the
snake's tongue jabbed;
Then indeed you will learn for yourself
the wonderful power
This antidote has. Nor is that all: this
same pulp
Of crushed lily is good for limbs that are
twisted awry.

Pages 69-78 discuss the various editions of the *Hortulus* from 1510 to 1957; then follows a list of plants with the English and scientific names; the book closes with three pages of references and five of index. The colophon states: "Printed by Joh. Enschede en Zonen, Haarlem. Typefaces: Romulus and Cancelleresca Bastarda. Bound by Proost en Brandt, Amsterdam. Paper used for book: Superior quality woodfree offset. Paper used for cover: Linson vellum . . . Edition limited to 1500 copies."

To summarize, I find the book one that is a pleasure to a botanist, a treat to a Latin scholar, and a feast to the eye for a lover of good books.

H. SANTAPAU

THE PEPTIDES by Eberhard Schröder & Klaus Lübke (Academic Press Inc., New York). Vol. I: METHODS OF PEPTIDE SYNTHESIS; 1965. Pp. xxix+481. Price \$ 20.00. Vol. II: SYNTHESIS, OCCURRENCE AND ACTION OF BIOLOGICALLY ACTIVE POLYPEPTIDES; 1966. Pp. xxvii+632. Price \$ 30.00

Since the first synthesis of oxytocin by du Vigneaud and his colleagues in 1954, there has been a tremendous upsurge of work in the synthesis of polypeptides. The recent total synthesis of insulin, a polypeptide consisting of 51 amino acids, by three independent schools is no small achievement. This success has been due mainly to the developments during the last decade in the methods of peptide

synthesis and selective protection of amino and carboxyl groups. *The Peptides* in two volumes, in which Schröder and Lübke have set out to review the present status of the synthetic aspects of peptide chemistry and synthesis, occurrence and action of biologically active polypeptides, is most welcome. Although addressed to the specialist, these volumes will also be useful to those who desire to have a general knowledge of the basic principles of peptide chemistry, and would be particularly valuable to those who are just entering this rather specialized field and wish to get acquainted quickly with the available information in the field.

Vol. I starts with a valuable section on nomenclature, followed by chapters on amino- and carboxyl-protecting groups, the formation of the peptide bond and special problems of polyfunctional amino acids. Following this presentation of the general techniques of peptide synthesis, there are chapters dealing with certain special areas of peptides, the synthesis of cyclic peptides, depsipeptides and peptoids, the plastein reaction, solid-phase peptide synthesis and finally a chapter on the problems of racemization. There is a comprehensive bibliography of over 2700 references, covering the literature up to the end of 1964. Almost every method that has been used in peptide chemistry has been dealt with in this volume and, therefore, the whole armamentarium of technique is made available in this volume. The only lacunae that one can find are that the treatment of the subject is not critical and it is left to the reader to assess the usefulness of different methods in a particular situation (which may not be very helpful to a fresh entrant to this field), very little attention has been paid to the mechanistic aspects of the reactions mentioned, and adequate justice has not been done to the problem of racemization, which is of immense importance in the synthesis of polypeptides.

In Vol. II, the synthesis and biological activity of important natural peptides and their analogues are described; where necessary the synthetic routes are schematically described, and comparative biological activity tabulated. This volume again starts with a chapter on nomenclature with a view to making this volume an independent reading. The main part of the book is divided into three sections. Section I deals with linear peptides and covers tissue hormones like bradykinin, angiotensin and related hormones, glandular hormones like MSH, ACTH, glucagon, insulin and synthetic enzyme models. Section II deals with heterodetic cyclic peptides and covers the field of oxytocin, vasopressin and depsipeptides. Section III deals with homodetic cyclic peptides covering both homomeric and heteromeric cyclic antibiotics and the toxic principles of *Amanita phalloides*. As the authors have stated in the introduction, "the biological aspects are discussed from the chemist's point of view and are intended to provide him primarily with a source of condensed information on the multiplicity of the biological arsenal of activity display", the activity data are thus easily comprehensible to those who are not too well versed in the jargon of pharmacodynamics. This volume covers the field almost up to the middle of 1965

and has a comprehensive bibliography of almost 2800 references.

There are some typographical mistakes, e.g. acidic on page 296, 3rd paragraph, line 9 should read acetic, but these are of a minor nature. The language at places is also involved, but this is understandable judging that the book is a translation.

These two volumes indeed give a very comprehensive review of the field and would be most useful to those who are interested or engaged in peptide research.

NITYA NAND

SOME PROBLEMS IN THE THEORY OF CREEP IN CONCRETE STRUCTURES — International Series of Monographs in Civil Engineering, Vol. 1, by N. Kh. Arutyunyan (Pergamon Press Ltd, Oxford), 1966. Pp. xi+290. Price 80s.

Creep effects in materials, especially metals at elevated temperatures and other construction materials such as concrete, wood and plastics, can be quite significant. Creep in concrete is a complex phenomenon dependent on many variables, such as humidity and the maturity of concrete at the time of loading. Moreover, the effects of shrinkage and creep often interact on each other. Although voluminous analytical and experimental investigations have been carried out on creep on concrete structures, a unified and clear presentation of this complex problem has not been attempted so far. This timely translation from Pergamon Press provides scholars in the English-speaking world with a window on the valuable work done by Russian scientists. The merit of the work is that it presents an integrated picture starting with a theoretical analysis of the elastic-creep problem and going on to applications to concrete, reinforced concrete and prestressed concrete structures. Hence the book will have an appeal not merely to the research scientist but also to the design engineer.

Chapters I and II are devoted to the development of the basic theory. In Chapter III, the effect of creep on thermal stresses in concrete structures is considered. The important problem relating to the influence of creep on shrinkage is considered in Chapter IV. The analysis of structures undergoing foundation settlement and creep simultaneously is presented in Chapter V. Examples of a two-span continuous beam and a railway tunnel are discussed to illustrate the application of the theory developed to practical situations. The effects of creep on reinforced concrete members — beams, pipes and frames — are considered at length in Chapter VI. Creep effects on prestressed concrete beam and pipes are dealt with in Chapter VII. In the last chapter, some nonlinear creep problems are briefly discussed.

Integral equations are extensively used in the presentation.

G. S. RAMASWAMY

BOOK NOTES

IMDA SOUVENIR (All India Instrument Manufacturers & Dealers Association, Bombay), 1966. Pp. ix+97. Price Rs 5.00

The All India Instrument Manufacturers & Dealers Association has brought out a souvenir in connection

with the decennial celebrations held in November 1966. The souvenir presents survey of various instrument industries in India such as those making glassware, laboratory equipment, optical, surgical and clinical, electrical, electronic, material testing and process control instruments, and engineering measuring tools and gauges. Besides listing the Indian standards for the various instruments, the souvenir provides data on exports and imports of instruments. The industrial licences issued for the manufactures of tools and equipment are also listed. The names and addresses of member firms of the association and a directory listing their products, a note on the training facilities in instrument technology, and information on foreign collaboration in the industry make the souvenir a useful reference book for both manufacturers and users of instruments.

JOURNAL OF MINES, METALS AND FUELS, MINING TECHNIQUES AND EQUIPMENT—Special Number 1966 (Books & Journals Private Ltd, Calcutta), 1966. Pp. xiv+214. Price Rs 20.00

This collection of 25 feature articles on various aspects of mechanization of the mining industry attempts in a limited way a global survey of the present status of the industry as well as the trends and developments in mining techniques and equipment. But for an article on the electrical equipment in the Liberian iron ore mines and another on gold mining in South Africa, the volume in general emphasizes the recent progress made in open pit and underground coal mining industries in the following countries: USA, UK, USSR, France, Germany, Sweden, Poland, Belgium, Czechoslovakia, Japan and India. The techniques discussed include automation and remote control systems, besides the improvements on the less sophisticated conventional methods.

The technical and management personnel of the Indian mining industry will find this reasonably priced and attractively got-up volume useful.

PUBLICATIONS RECEIVED

PROCEEDINGS OF THE SIXTH REGIONAL CONFERENCE ON WATER RESOURCES DEVELOPMENT IN ASIA AND THE FAR EAST (United Nations, New York), 1965. Pp. ix+400. Price \$ 4.50; Rs 27.00

MODULAR COORDINATION IN BUILDING—ASIA, EUROPE AND THE AMERICAS (United Nations, New York), 1966. Pp. v+67. Price \$ 1.00; Rs 6.00

REPORT OF EXPERT GROUP ON SECOND-HAND EQUIPMENT FOR DEVELOPING COUNTRIES (United Nations, New York), 1966. Pp. vi+24. Price \$ 0.50; Rs 3.00

WORLD ENERGY SUPPLIES, 1961-1964 (United Nations, New York), 1966. Pp. 99. Price \$ 2.00; Rs 12.00

REPORT OF THE UNITED NATIONS INTERREGIONAL WORKSHOP ON TEXTILE INDUSTRIES IN DEVELOPING COUNTRIES (United Nations, New York). Pp. iii+92. Price \$ 2.00; Rs 12.00

AN EXAMINATION OF SOME ASPECTS OF THE UNIT-LOAD SYSTEM OF CARGO SHIPMENTS: APPLICATION TO DEVELOPING COUNTRIES (United Nations, New York), 1966. Pp. vi+96. Price \$ 2.00; Rs 12.00

HOUSING IN AFRICA (United Nations, New York), 1965. Pp. vii+221. Price \$ 3.50; Rs 21.00

DEMOGRAPHIC YEARBOOK, 1965 (United Nations, New York), 1966. Pp. viii+808. Price \$ 11.00; Rs 66.00 (paper) and \$ 15.00; Rs 90.00 (cloth)

ECONOMIC ASPECTS OF IRON-ORE PREPARATIONS (United Nations, New York), 1966. Pp. xiv+280. Price \$ 4.00; Rs 24.00

WORLD POPULATION PROSPECTS (United Nations, New York), 1966. Pp. vii+149. Price \$ 2.00; Rs 12.00

ECONOMIC BULLETIN FOR LATIN AMERICA, Vol. XI, No. 1 (United Nations, New York), 1966. Pp. iv+156. Price \$ 2.50; Rs 15.00

FOREIGN TRADE STATISTICS OF AFRICA (United Nations, New York), 1965. Pp. 325. Price \$ 4.50; Rs 27.00

THE DIGITAL COMPUTERS by K. C. Parton (Pergamon Press Ltd, Oxford), 1966. Pp. 125. Price 17s. 6d.

PRINCIPLES OF INDUSTRIAL MICROBIOLOGY by Allan Rhodes & Derek J. Fletcher (Pergamon Press Ltd, Oxford), 1966. Pp. xviii+320. Price 35s.

ELECTRONIC AUTOMATIC CONTROL DEVICES by A. A. Bulgakov (Pergamon Press Ltd, Oxford), 1966. Pp. xxiv+549. Price £ 6

THE MEASUREMENT OF AIR FLOW by E. Ower & R. C. Pankhurst (Pergamon Press Ltd, Oxford), Fourth Edition, 1966. Pp. viii+367. Price 65s.

Use of ascorbic acid as an indicator for heavy metals

In an effort to decide the optimum amount of the chelating reagent, e.g. EDTA, etc., required to react with the offending heavy metal ions which often find their way into the solutions as contaminants of water or other laboratory reagents, Dr McNair Scott of the University of Pennsylvania, Philadelphia, has developed a simple method of titrating contaminated water and solutions using ascorbic acid as an indicator.

The new method is based on determining the amount of the chelating reagent just sufficient to stop the catalytic oxidation of ascorbic acid which is related linearly to the concentration of the metal ion, and consists in following the oxidation rate of the acid (5.8×10^{-5} molar in double distilled water) added to a test sample by the decrease in absorption at 2650 Å. in a spectrophotometer followed by addition of the chelating reagent until there is no further decrease in absorption [*Nature, Lond.*, **212** (1966), 606].

Electroviscous fluids

Some fluids which thicken and even solidify instantly and reversibly at high electrical field strengths have been developed. A typical example of such a fluid is a dispersion of silica in a naphthenic vehicle with a nonionic surfactant. Scientists have proposed an 'induced polarization mechanism' which explains most of the experimental observations.

The surface charges over the dispersed particles attract a layer of oppositely charged ions from the medium. These ions forming the fixed portion of an electrical double layer attract a more diffuse layer of ions. The applied electric field polarizes and distorts the double layer, which tends to elongate towards the electrode having charge opposite to that of the diffuse layer. Electrostatic interaction between the distorted double layers in a naphthenic vehicle, which has a low dielectric constant, requires more energy to stir the fluid. This extra energy manifests as electroviscosity.

NOTES & NEWS

The electroviscosity of a fluid has been found to be proportional to the square of the field strength and inversely proportional to the shear rate. Also, electroviscosity increases with temperature. Both these facts are in tune with the polarization mechanism. If this mechanism is correct, then the dielectric constants of the fluids should vary as electroviscosity does, since dielectric constant is a measure of the ease of polarization. This has been found to be true with the fluids tested.

The unusual properties of electroviscous fluids are of theoretical importance to rheologists and physical chemists, and it would lead to a better understanding of the liquid state. Among the applications which can result from research in this field are motion control and detection instruments, separation and purification methods, catalysis and control of chemical reactions, solid state electronic components, and devices for selective transmission of electromagnetic and mechanical radiation [*Chem. Engng News*, **44** (1966) (No. 26), 46].

Determination of minimum energy for a chemical reaction

A direct measurement of the minimum energy required for a chemical reaction to take place has been made for the first time. Scientists at the California Institute of Technology, Pasadena, USA, employing a new technique of studying covalent reactions as a function of energy have determined the threshold energy of the reaction $D + H_2 \rightarrow DH + H$ to be 0.33 eV. [*Chem. Engng News*, **44** (1966) (No. 15), 23].

The factors governing the kinetics of elementary gas phase reactions are the reaction cross-section (σ) which varies with varying values of the relative translational energy of the reagents (E), the threshold energy (E_0), and the Boltzmann thermal distribution function. Knowledge of the energy dependence of the

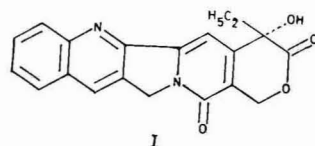
reaction cross-section is important for understanding the details of chemical reactions on a molecular level. As rate constants are not too sensitive to cross-sections, a direct method of measuring $\sigma(E)$ is necessary. The only such technique known, that of reactions in crossed molecular beams, is limited to a few ionic reactions only because of insurmountable difficulties.

The Caltech scientists photolysed a mixture of DI and H_2 with monochromatic light of different wavelengths in the range 3660-3030 Å. The DI absorbed light and dissociated giving monoenergetic D atoms of known energy. The translationally hot D atoms formed DH by reacting with H_2 molecules; the D atoms escaping this reaction became cold and formed D_2 by reaction with DI. The concentration ratio $[DH]/[D_2]$ is directly related to the energy difference of the energy cross-section. When E equals the threshold energy, E_0 , this ratio and cross-section vanish simultaneously.

The new technique can be used to study a whole family of reactions and will prove useful in testing the validity of various models proposed for them.

Camptothecin, an alkaloid with antitumour action

Camptothecin, an alkaloid with a novel ring system, showing antitumour activity has been isolated from the Chinese tree *Camptotheca acuminata*. From high resolution mass spectrometry the compound was assigned the molecular formula $C_{20}H_{16}N_2O_4$. The structure (I) consisting of five fused rings has been proposed and the absolute configuration of the asymmetric centre established



by X-ray analysis. Leukemia-inoculated mice administered with doses of camptothecin have been found to live longer than infected but untreated mice. The National Cancer Institute of USA has chosen this compound for tests in the cancer chemotherapy programme. The activity of this compound is ascribed to the presence of a hydroxyl in proximity to a lactone ring—an α -hydroxylactone ring is fused to an α -pyridine ring [*Chem. Engng News*, **44** (1966) (No. 28), 19]

Spectrochemical method for the identification of compounds

The effectiveness of the semi-quantitative spectrochemical procedure has been extended to include identification of simple chemical compounds by recording the voltage fluctuations of the d.c. arc during sample consumption. The recorded voltage fluctuations differ sufficiently between compounds to permit identification by comparison with reference patterns. A specially designed cored graphite cathode, filled with a 1:2 mixture of BaCO_3 and graphite powder, has been used to increase arc stability so that the observed fluctuations are attributable primarily to effects originating from the anode. Reference patterns of over hundred compounds have been made and found to be functions of both the analytical conditions under which they are made (arc gap and current, electrode design and material, etc.) and the properties of the sample material (volatility rate, ionization potential, molecular weight, decomposition products in the anode and their reactivity with the electrode material). Under standardized conditions, voltage fluctuation patterns are characteristic of the compound. All the reference patterns recorded are characterized by a voltage as a function of the amount of sample material, and the lowest voltage drop for compounds of the same elements is approximately the same as determined by the ionization potential of that element. Compounds with boiling points between 1000° and 3500°C. are suitable for identi-

fication because of their reproductive patterns, while compounds with boiling points less than 1000°C., with their short consumption periods (<20 sec.), make it difficult to resolve small time differences. Compounds with boiling points above 3500°C. give erratic patterns because of uneven and erratic distillation [*Analyt. Chem.*, **38** (1966), 1372].

Ecdysterone, a new metamorphosis hormone of insects

From the whole body extracts of *Bombyx mori* a new metamorphosis hormone, ecdysterone, with moulting activity has been isolated. The aqueous extract of *Bombyx mori*, free from the already known ecdysone, was exhaustively extracted with ethyl acetate. After evaporation of the solvent, the residue was fractionated on an alumina column with gradient elution using methanol and benzene. Repeated layer chromatography on silica gel of the hormone containing fractions yielded ecdysterone. The new hormone crystallizes in large anhydrous plates (m.p. 226°C.) from ethyl acetate-methanol and is three to five times as active as ecdysone in the Calliphara test. It has the molecular formula $\text{C}_{27}\text{H}_{44}\text{O}_6$, with an unsaturated α,β -keto group, $-(\text{CH}_3)_2\text{C}-\text{OH}$ group of the steroid side chain and two steroid methyl groups at C-10 and C-13. The IR spectrum (KBr) of ecdysterone is similar to that of ecdysone, but carbonyl and ethylenic bonds lie at 1645 and 1612 cm^{-1} respectively. Ecdysterone is probably a C_{27} -steroid with a cholesterol side chain [*Angew. chem. internat. Edn*, **5** (1966), 248].

Rapid estimation of very small amounts of proteins

The observation that a linear relationship exists between areas of the spots obtained on chromatograms of serum proteins on UFS nitrocellulose membrane filters and concentrations of the protein solutions has led to the development of an accurate, simple and rapid method for the quantitative determination of soluble proteins in amounts as small as 1 $\mu\text{g}/\mu\text{l}$.

The method which consists in measuring the areas of the spots obtained after circular chromatography of the proteins on HUFs nitrocellulose membrane filters can be used both for micro-determinations and routine protein determinations. It can also be used in following the course of various column fractions of proteins with minimal loss of protein material.

For calibration, a droplet of the acetate buffer pH 3.7 (developer) is applied on the glossy side of the membrane with a glass capillary to form a circular spot 5-8 mm. in diam. The standard protein sample (bovine serum or bovine serum albumin) is then applied into the centre of the wet spot by touch with a capillary (internal diam. 0.02-0.03 mm.) calibrated to 1 μl . and gently blowing out the solution. After drying the spots at 80°C. for 5-10 min., the membranes are placed with the glossy side down on the surface of the staining solution (Amido black 10 B or azo-carmin B in acid solution). The areas of the protein spots are then plotted against the corresponding concentrations of the standard solutions of the protein [*Nature, Lond.*, **212** (1966), 75].

Cytochrome c from *Bacillus megaterium* and *B. subtilis*

A method for isolating cytochrome c from *Bacillus megaterium* and *B. subtilis* has been reported by Tsutomu Yamaguchi and his coworkers of the Department of Agricultural Chemistry, University of Tokyo, Japan [*Biochim. biophys. Acta*, **124** (1966), 413]. The method consists in preparing protoplasm of *B. megaterium* strain KM and *B. subtilis* IFO 3026 with phosphate buffer using 15-h nutrient broth cultures grown at 37°C. and with lysozyme at 100 $\mu\text{g}/\text{mg}$. dry weight of organism; the stabilizing agent is 0.5M sucrose.

The cytoplasmic fraction, a pink pellet obtained from the protoplast preparations, constituting about 17 per cent (wt/wt) of the initial dry weight of the organism, is suspended in distilled water (120 g. dry wt/3 litres) and dialysed against 200 volumes of distilled water at 5°C. for 48 hr, changing the distilled water every 12 hr. To the dialysed suspension 0.02M NaOH is added

up to pH 8.0. After stirring for 20 min. at 5°C., the suspension is centrifuged at 105000 *g* for 30 min.

The clear supernatant is collected and the pH adjusted to 6.0 with 0.02*M* HCl. The yellowish precipitate is centrifuged off, and a clear pink supernatant obtained, to which trichloroacetic acid (final conc. 2 per cent) is added and allowed to stand for 10 min. in a refrigerator. The red precipitate formed is resuspended in distilled water and dissolved completely after addition of concentrated ammonia (pH 7.0). The solution is chromatographed on a Sephadex G-50 (fine) column and eluted with distilled water. The red fractions are collected and lyophilized. The yield is about 0.005 per cent of the cytoplasmic membrane.

Cytochrome *c* from *B. subtilis* is prepared using dialysis and alkali treatment to release the cytochrome from the cytoplasmic membrane.

A new diabetic strain of mouse

A new inbred strain (C57BL/Ks) of mouse with hereditary diabetes, that can be used in the study of human diabetes, has been developed by Drs Katharine P. Hummel, Margaret M. Dickie and Douglas L. Coleman of Jackson Laboratory, Bar Harbor, Maine.

To have diabetes in full form the mice must inherit the gene (*db*) from both parents. Although *dbdb* females do not breed (infertile), their ovaries function normally when transplanted into a normal female. Ten out of 23 offsprings resulting from cross between female having *dbdb* ovaries and *+db* males were of the diabetes phenotype and they consequently develop the disease.

The inbred diabetic mice appear to be normal at first, but soon get fat with a rapid increase in body weight during the first few weeks. The blood sugar of all diabetics had concentration of at least 200 mg./ml. of blood by 8 weeks of age and all reached or exceeded a level of 300 mg./ml. by 10 weeks, whereas the blood sugar of control did not exceed 200 mg./ml. of blood at any age. Apart from blood sugar rise they have other symptoms like

polyuria, polydipsia, polyphagia and glycosuria.

In spite of fasting and losing weight with lowered blood sugar they soon regain weight and blood sugar levels after the free availability of food is restored. Attempts to control weight by restriction of food as has been successful with obese mice have failed. As in the case of human diabetes, this disease, when rampant, causes a drastic loss of weight in mice also. Between 3 and 6 months of age the animals enter a terminal phase and usually die.

Other ways in which the animal disease parallels that in humans include sensitivity to stress, excretion of sugar in the urine and strikingly abnormal changes in the islets of Langerhans. Some of the diabetic mice have responded to insulin treatment, but the proper dosage remains to be worked out [*Science*, **153** (1966), 1127].

British Non-Ferrous Metals Research Association

The annual report of the British Non-Ferrous Metals Research Association for the year 1965 records the progress made during the year in over 50 research projects concerning development of new materials, melting, casting and fabrication and corrosion studies.

A new major experiment — production scale study of the continuous casting process applied to copper and copper alloy billets and rolling slabs — has been launched satisfactorily, with the object of examining the influence of mould design and operating conditions on the surface finish, soundness and internal stress of the castings. A horizontal continuous casting machine for smaller sections including strip for use as cast or after cold rolling or drawing has also been constructed, and graphite dies are used to study the casting of high conductivity copper and such copper alloys which are difficult to hot work. Tests carried out with hard impregnated graphite dies for gravity die-casting of Cu alloys for obtaining longer mould lives and better surface finish than could be obtained with metal dies have indicated their lack of toughness.

A wrought cupro-nickel alloy has been produced with hot workability better than that of 70-30

cupro-nickel; the material can be extruded and drawn into tubes, forged into bends and has adequate weldability. An Al-Zn-Mg alloy has been developed with improved stability in ductility and resistance to stress corrosion than 10 per cent Mg-Zn alloy for use in aircraft castings. Another new material prepared is a zinc base die-casting alloy with high creep resistance (Zn-Cu-Ti alloy with minor Al additions) for use up to 150°C. An attempt at developing two-phase alloys with one of them being fibrous has led to the development of an interesting new type Cu base alloy with unusual longitudinal strength. An examination has been made of the limitations of various rapid shop-floor tests for melt quality in the bronze industry. The precautions necessary during melting of complex brasses, to avoid formation of iron inclusions, have been established. For assessing the suitability of lead clad steel structure for architectural applications, the effect of thermal cycling on such structures has been studied. The influence of the variation in grain structure in medium strength Al-Zn-Mg alloys having adequate resistance to stress corrosion and acceptable weldability and extrusion properties has been tested. Work has been initiated in the study of oxidation and mechanical behaviour of certain alloys of chromium which are largely unexplored so far. An investigation is underway to determine the interphase energies of dispersion hardened alloys, the results of which would be useful in the choice of the right kind of dispersed particle. Transmission electron microscopic studies of quench sensitive alloys have indicated premature precipitation of hardening constituents during slow quenching of some high strength Al-Zn-Mg alloys.

The project on lubrication in copper wire drawing has been successfully completed and a large improvement in die life has been achieved. A study of time-temperature relationship in annealing both fire-refined and electrolytic high conductivity copper has shown that fully soft wire could be obtained with ultrashort annealing time under suitable control, and a commercial high speed strand annealing unit has been adapted

for this purpose. Ultrasonic vibrations have been employed during wire drawing operations and the mechanism involved is under investigation.

A theory of pitting has been developed which can explain within a single mechanism the effects of a number of distinct factors, such as the presence of brazing alloy or carbon and other types of surface films. An investigation of the high temperature oxidation of zirconium and the 'breakaway' phenomenon with electron probe microanalyses has been completed. The development of accelerated tests for assessing the quality of anodized coatings on aluminium, a clear lacquer for copper and its alloys in outdoor architectural applications, and a surface treatment for non-porous thin gold electrodeposits for use in printed circuitry are other notable achievements.

Central Electrochemical Research Institute, Karaikudi

Among the major achievements of the institute recorded in its annual report for 1965 are: a fluidized bed technique for obtaining uniform, hard and adherent deposits of lead oxide on graphite, carbon and titanium electrodes; a method for the treatment of cyanide effluents; successful reduction of *p*-phenetidine employing a rotating amalgamated cathode; and an additive to water for laying concrete which inhibits reinforcement corrosion. The sixth seminar on electrochemistry was held during the year.

A direct method developed for the estimation of nickel sulphate and nickel chloride in electrolytic baths consists in extracting the nickel salts with isopropyl alcohol and estimating nickel with EDTA using murexide indicator. Nickel plating from chloride-free nickel baths using insoluble anodes has been attempted and the effect of various variables on the current efficiency and nature of deposit has been studied. The chloride-free bath has been found to have certain advantages over Watt's bath for interior plating. A bath with a higher current efficiency and bath life, and which can

control the composition of the deposit better has been developed for iron-nickel alloy plating.

Electrochemical reduction studies of *o*-nitrophenol, nitrobenzene, maleic acid, nitrourea, nitroguanidine, *p*-nitrobenzoic acid and citral, and electrochemical oxidation studies of *p*-nitrotoluene and γ -picoline have been carried out. The electrodeposition of lead dioxide on graphite electrodes of different shapes and sizes has been carried out and the applicability of these electrodes in the preparation of chlorates and perchlorates of alkali and alkaline earth metals is being examined.

Salt water activated magnesium cells (5 amp. hr/1.4 V.) using locally developed silver chloride electrodes have been fabricated. Silver oxide-zinc cells have been fabricated for low temperature performance (-10° to -20°C). The cells have a capacity of 10-11 amp. hr/1.5 V. at subzero temperatures and 20 amp. hr/1.5 V. at normal temperatures. Activated carbon, prepared by heating a slurry of carbon-platinum chloride at 800°C . in hydrogen atmosphere, on a graphite plate support has been used to make a hydrogen-chlorine fuel cell. The cell gives a voltage of 1.3 V. and current densities of 10 m. amp. and 40 m. amp. at 1.05 and 0.52 V., with 10 per cent hydrochloric acid.

The behaviour of a number of metals and alloys in 30 per cent KOH in the potential range between hydrogen evolution and oxygen evolution has been investigated and it has been observed that 321 stainless steel has better corrosion resistance than 304 and 347 types. With a view to replacing tin in packing industry, the relative corrosion behaviours of sprayed and aluminized aluminium and tin have been studied. Aluminium sprayed steel sheets have been found to compare well with tin in all the electrolytes. It has been observed that vapour phase inhibitors, when incorporated in hard film solvent deposited coatings, which are used for the temporary corrosion prevention of engineering stores, increase the inhibition of corrosion.

The mechanisms of reference electrodes, Ag/AgCl, Ag/AgBr and

Ag/AgI, are under investigation. The Faradaic impedance of Ag/AgI electrode in potassium iodide and silver nitrate solutions of various concentrations in 5M sodium nitrate supporting electrolyte have been measured in the frequency range 400-2000 Hz. The bipolarization induced due to stray current on the face of the metal plate kept in a plating bath away from d.c. lines has been studied. The absence of the effect has been noticed at a critical distance; at high currents the anodic and cathodic regions merge into each other. The adsorption of formaldehyde, cyclohexane, benzene, naphthalene, decalin and formamide at mercury-solution interface has been studied.

Announcements

■ *Prof. C. N. R. Rao*—The Faraday Society, London, has awarded the Marlow Medal and Prize for 1967 to Prof. C. N. R. Rao, Head, Department of Chemistry, Indian Institute of Technology, Kanpur, for his original research contributions in physical chemistry. Prof. Rao has to his credit over 75 original papers and reviews in the fields of chemical spectroscopy, molecular structures and solid state chemistry. He is also the author of two books on spectroscopy (Butterworths, London, and Academic Press, New York), one of which has been translated into Russian and Japanese.

■ *Raja Ravi Sher Singh of Khalsia Memorial Cancer Research Award*—The Indian Council of Medical Research has invited applications or nominations for the award of the above prize of the value of Rs 900 to an Indian national for outstanding research work in the experimental or clinical aspects of cancer carried out in 1966 or outstanding work in the organization and conduct of any service or service-cum-research programme in the cause of cancer prevention during the year 1966. Full details of the work carried out, reprints of published papers, and a biographical sketch of the worker should be sent to the Director-General, Indian Council of Medical Research, P.O. Box 494, New Delhi, before 31 August 1967.

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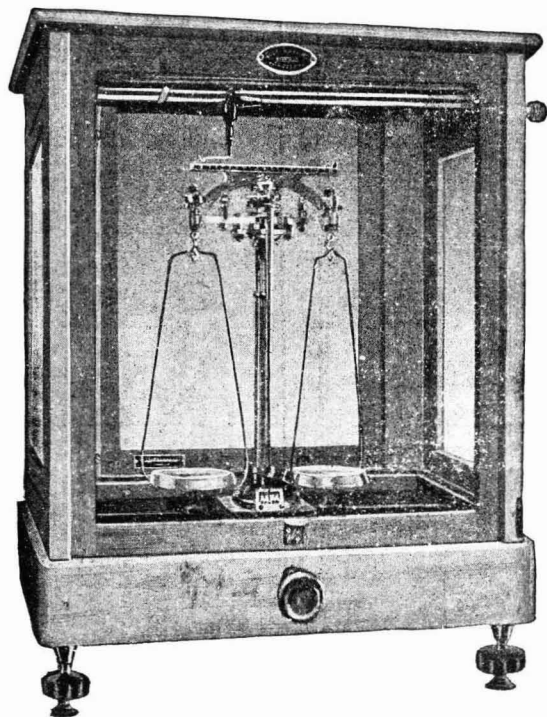
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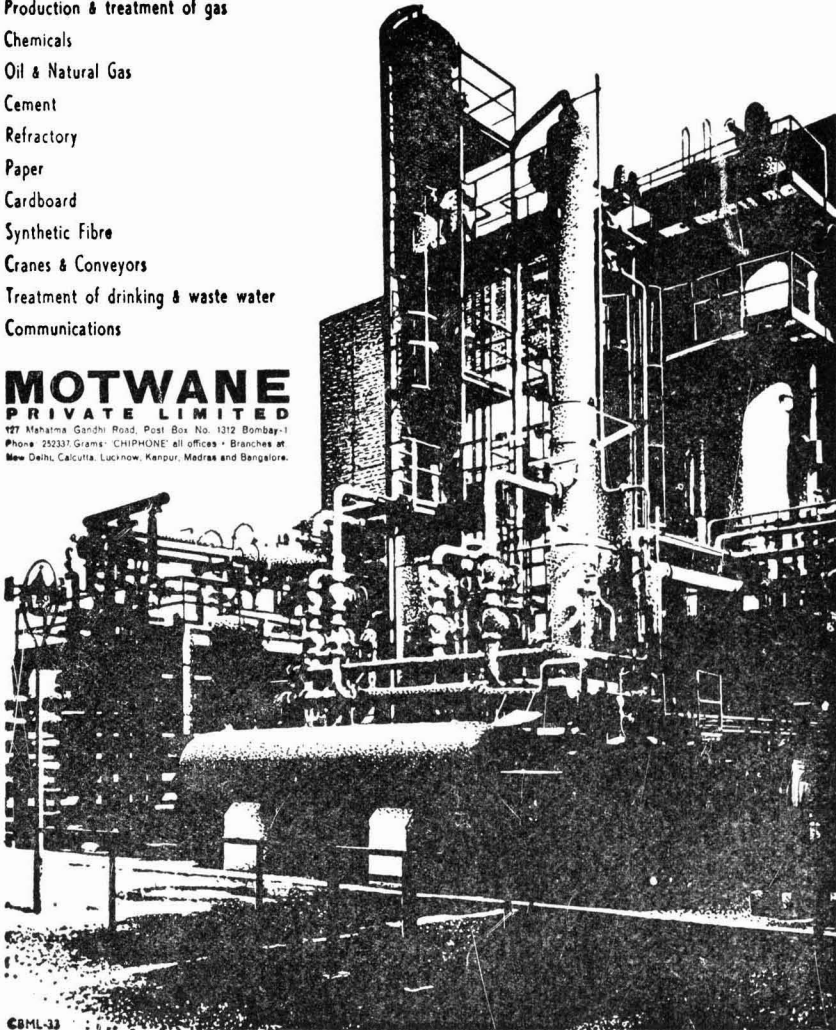
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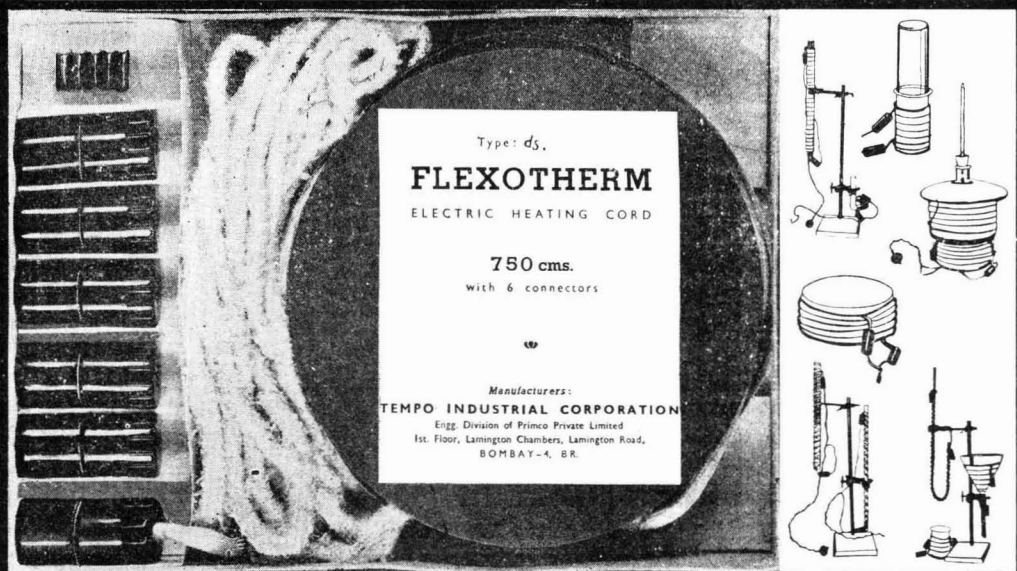
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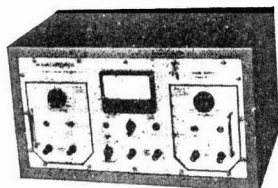
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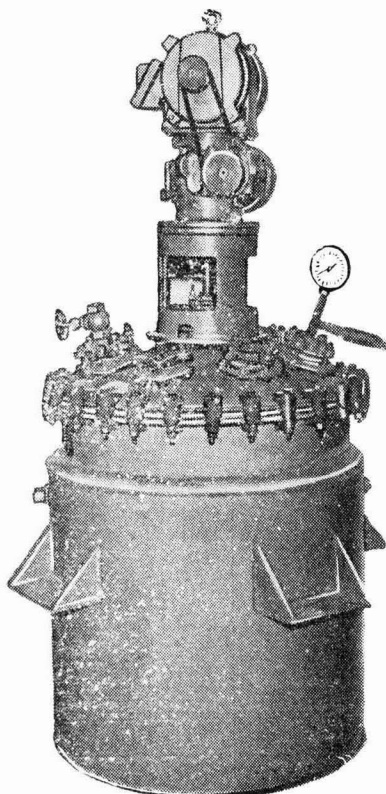
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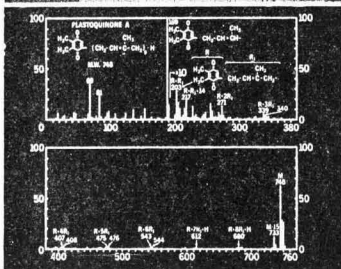
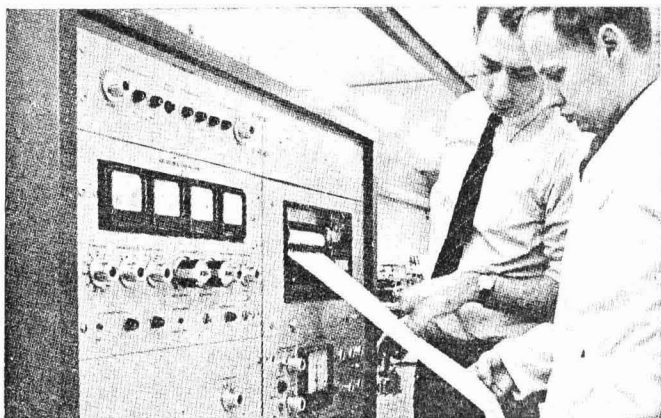
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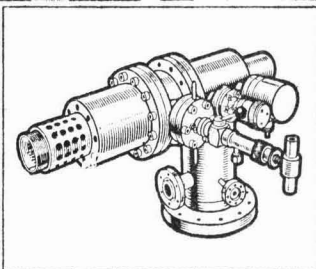
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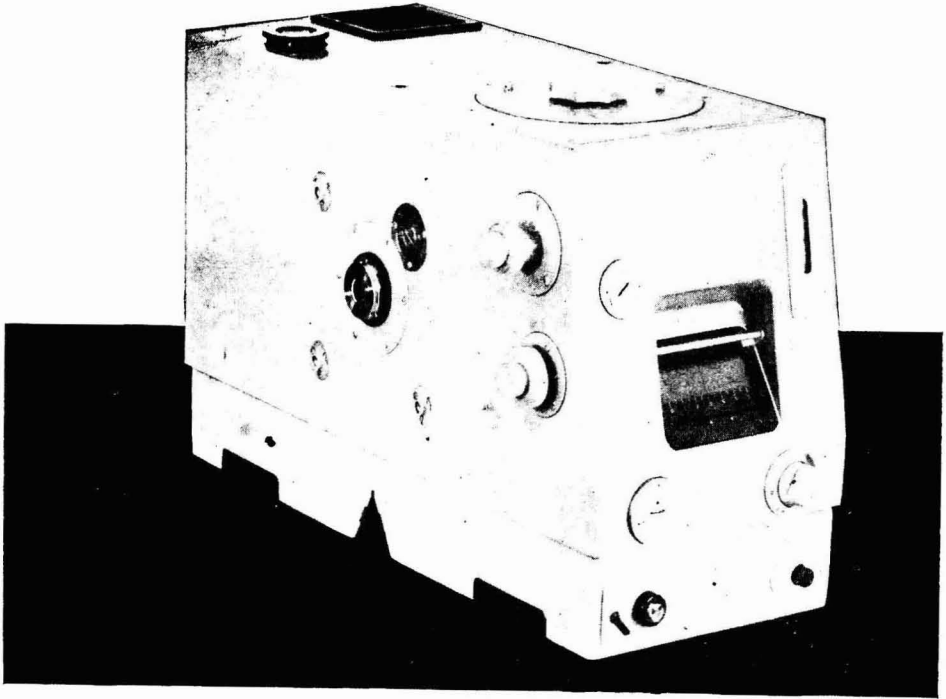
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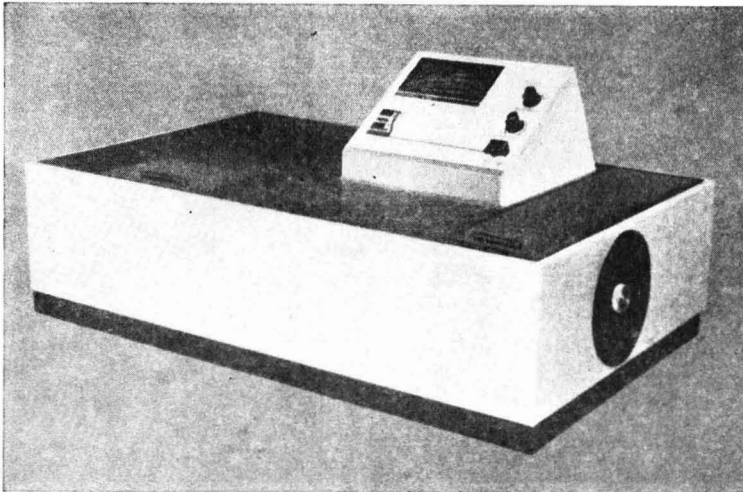
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