Journal of Scientific & Industrial Research

Vol. 13, No. 12, DECEMBER 1954

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- Grading of sugar
- House construction and thermal comfort
- Polymerization of vinyl monomers
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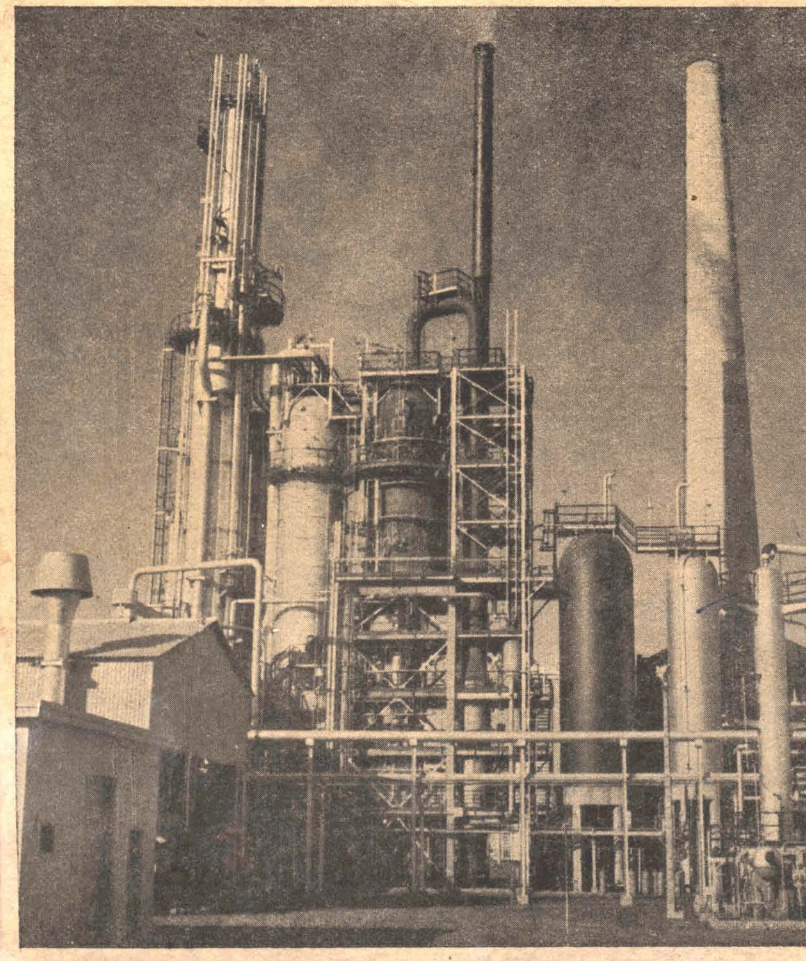

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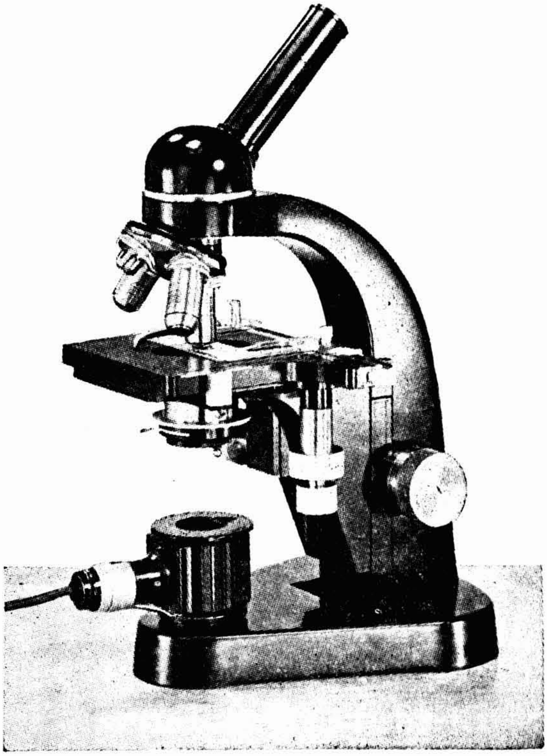

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COVER PICTURE

India's first modern oil refinery — the Stanvac refinery — at Trombay Island (Bombay) was formally declared open by the Union Minister for Production on 19 November 1954. The picture on the cover shows the refinery after it went into operation.

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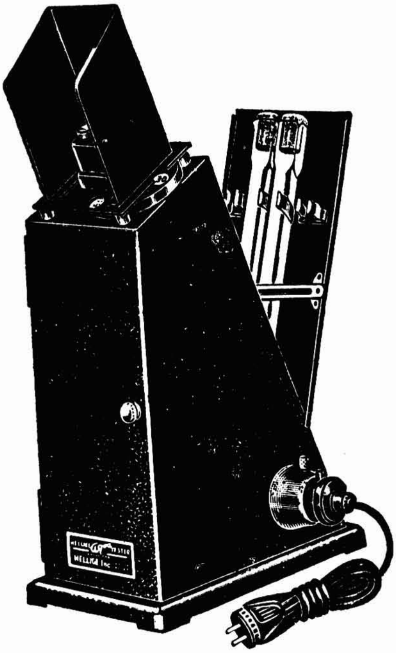

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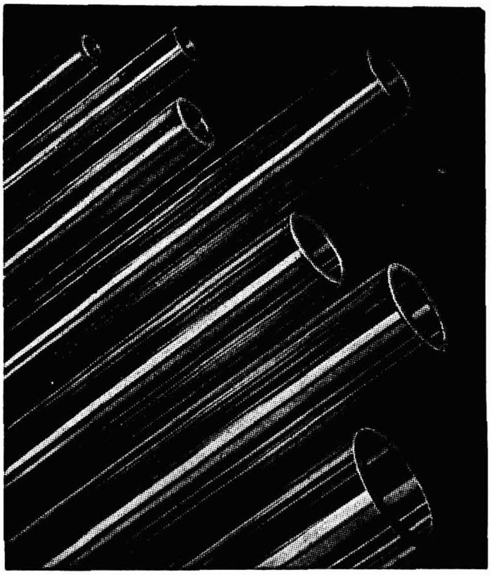

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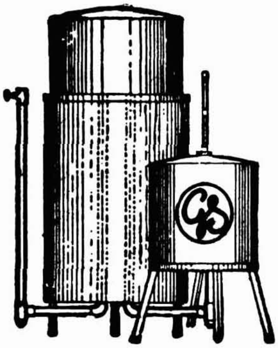

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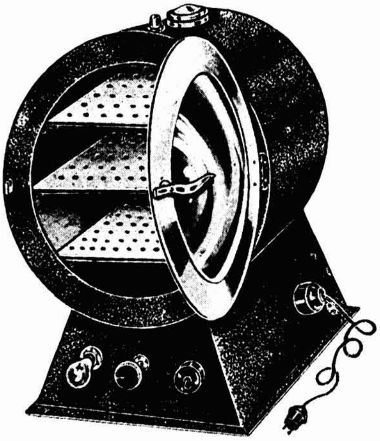

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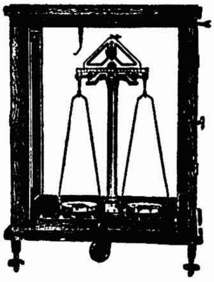

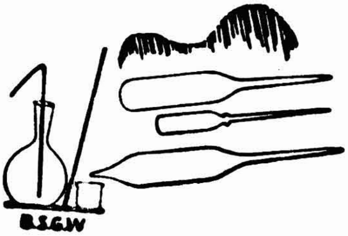
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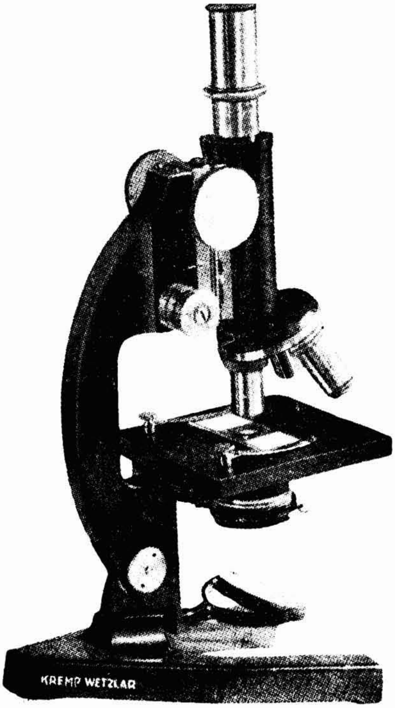
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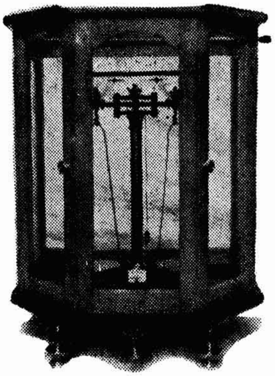

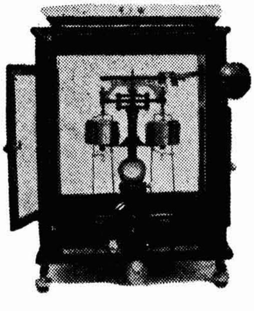

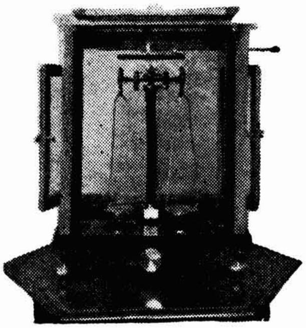

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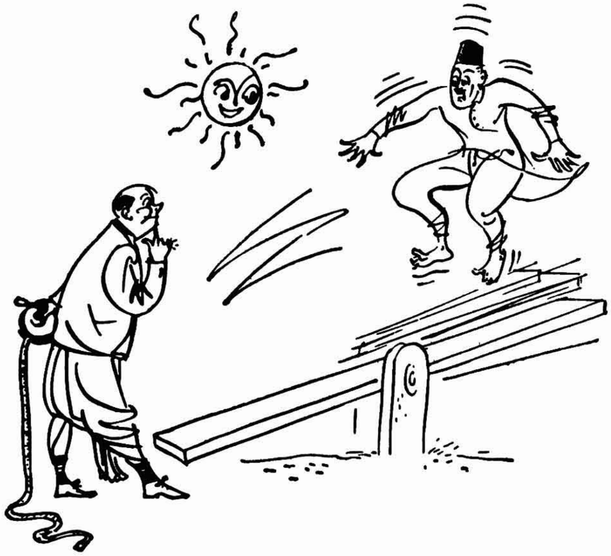

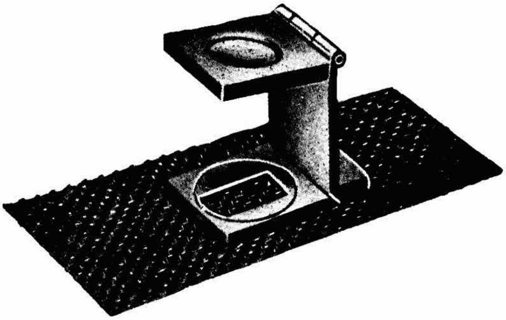

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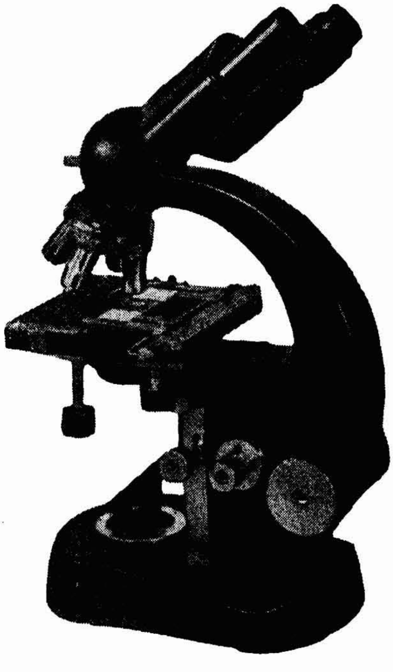

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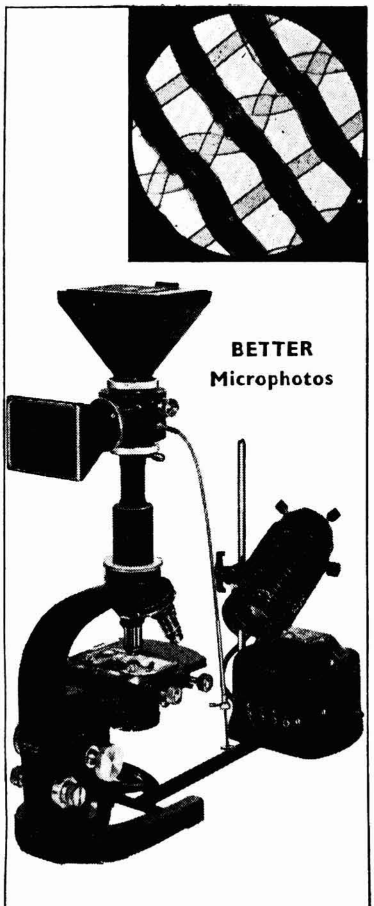
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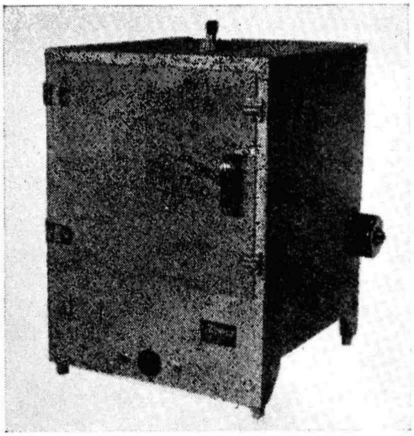

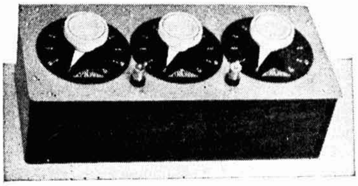

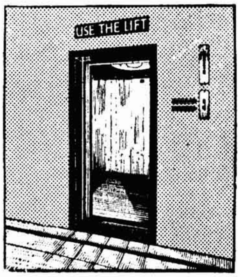
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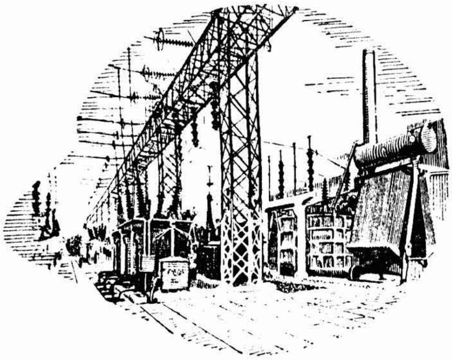

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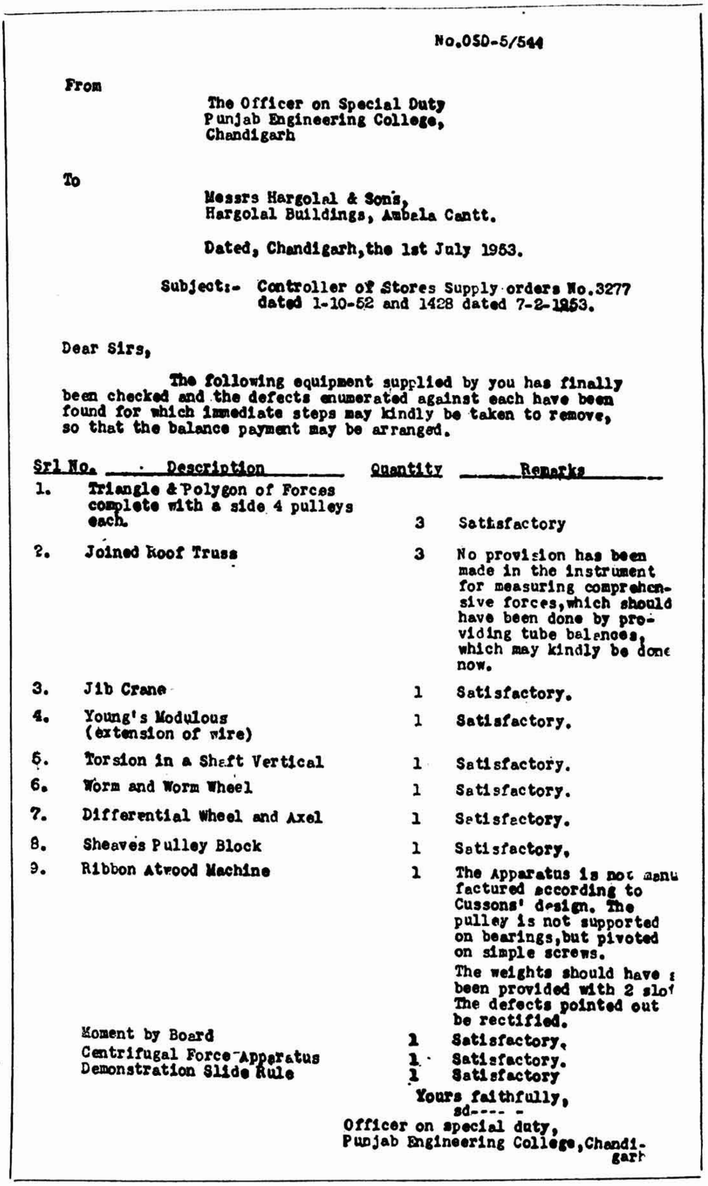

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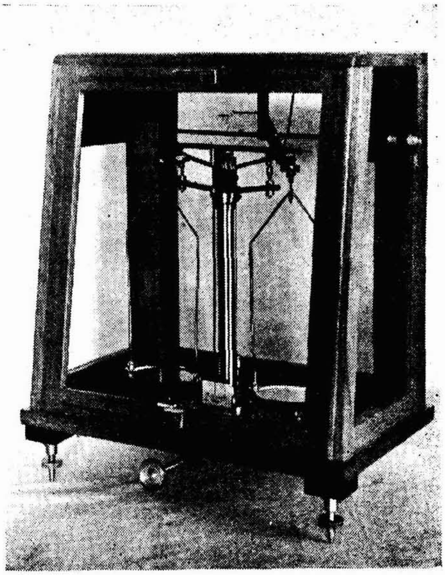

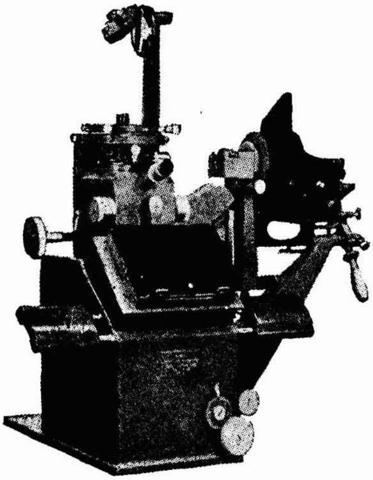

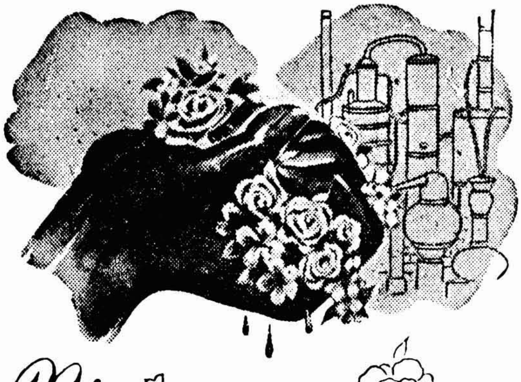


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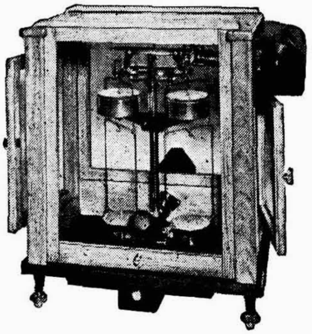

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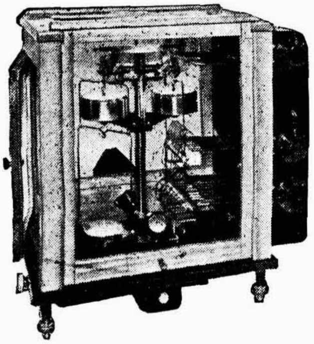

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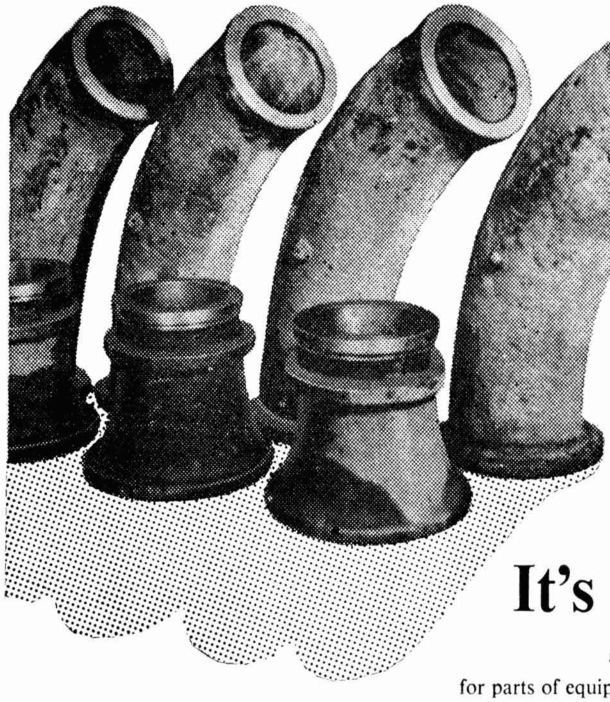

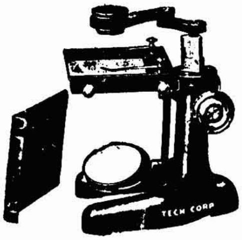
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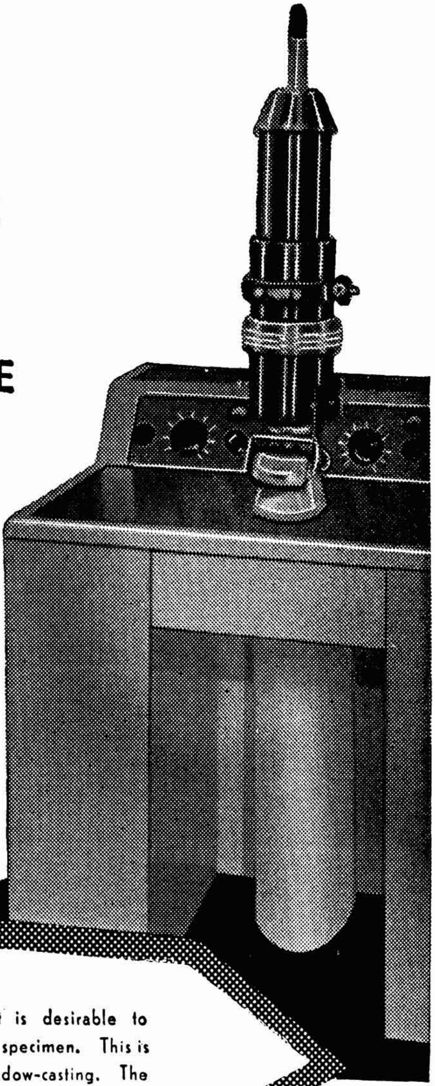

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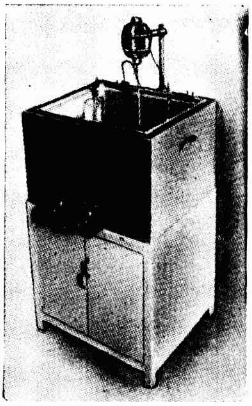

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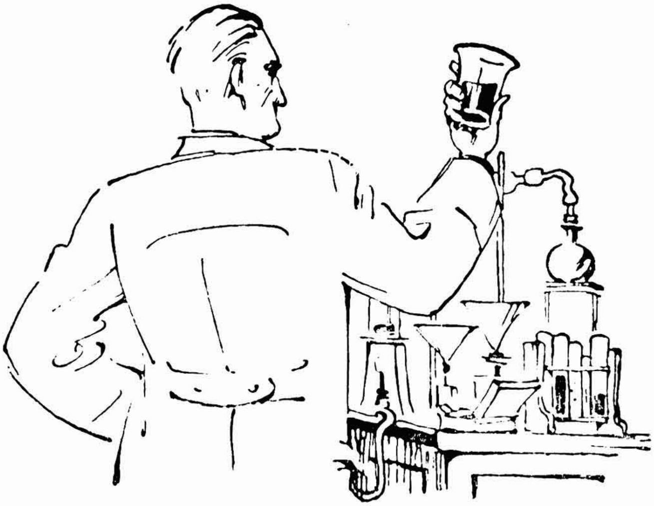

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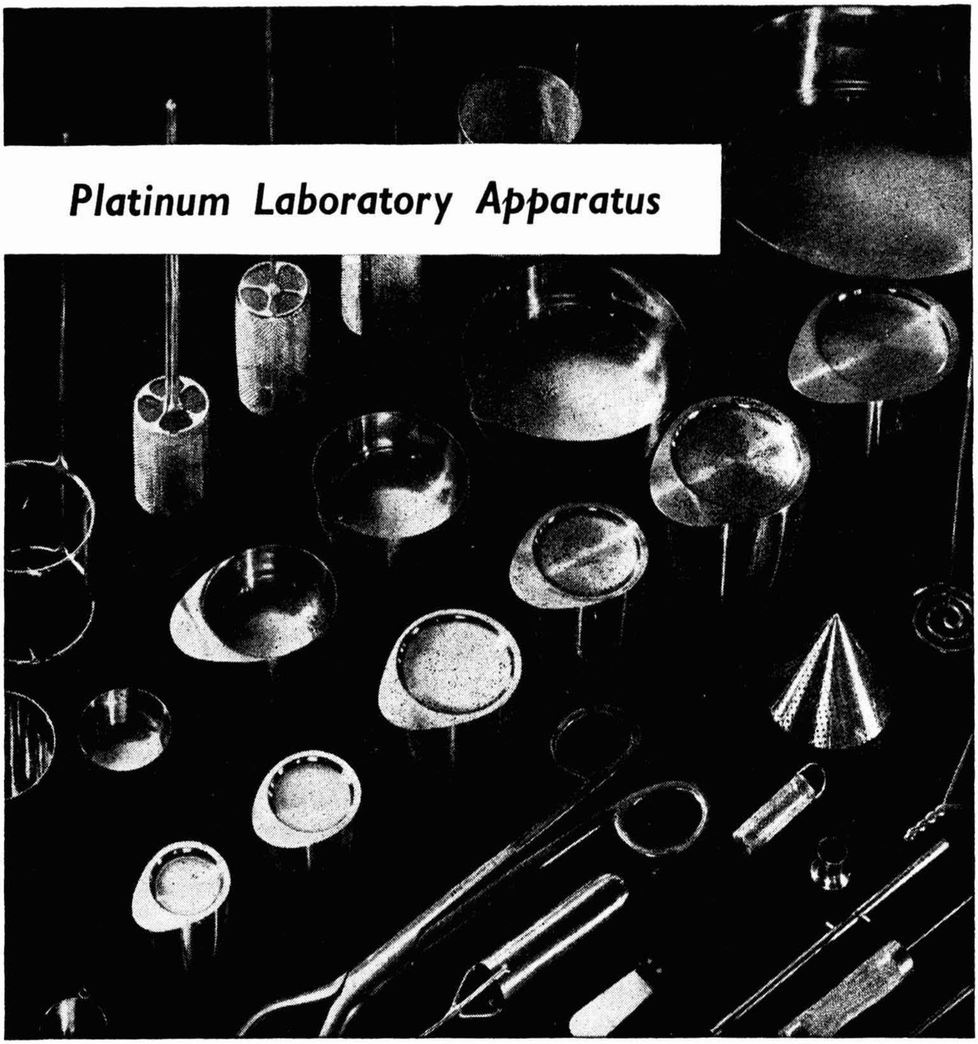

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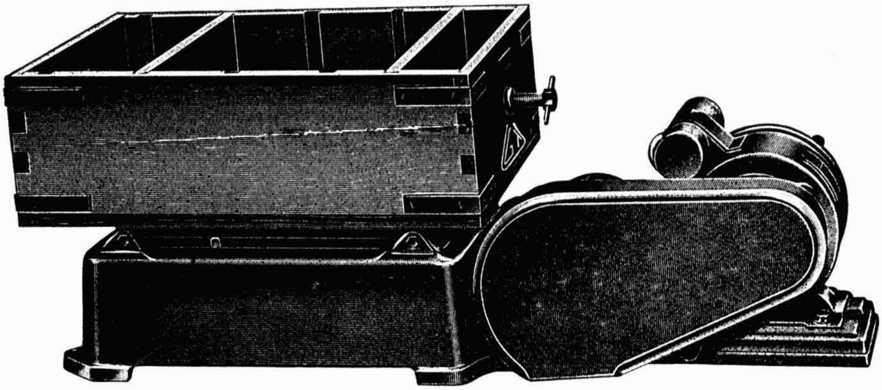

Technical Education—Development Programmes

PROBLEMS relating to the training of technical personnel for meeting the requirements of an expanding industry were discussed by the All-India Council for Technical Education, which met in New Delhi on 30 October 1954. A five-year programme for the development of technical education and training was considered and a seven-man committee, with Dr. S. S. Bhatnagar as Chairman, was appointed to formulate detailed proposals.

The Council for Technical Education has examined and assessed the need of existing institutions preparing students for the first degree and diploma courses and initiated a programme of development. Postgraduate courses in engineering and technology have been started in various institutions and facilities have been created for research in different fields. New courses in management studies have also been instituted. The experience gained in operating the development schemes will prove valuable in launching more ambitious projects to meet the increased demand for technicians and technologists under the Second Five-Year Plan (1956-61), which is expected to be an " industrial plan ". Since it takes three to four years to train the technical personnel required, the task before the Council has to be executed with urgency and with a precise appreciation of the needs and requirements.

The schemes considered at the recent meeting and recommended to the Government include apprentice training and technical education for artisans and craftsmen in the age group 14-17 and for supervisory personnel in the age group 16-21; part-time technical education facilities for adult workers and sandwich courses for technical education and training; provision of facilities for the training of technical teachers; and practical training to graduates and diploma holders.

Apprenticeship training

In his address to the Council, Maulana Abul Kalam Azad, Minister for Education, referred to the importance of apprentice training schemes. He observed: " I feel that greater activity, both in intensity and scope, is necessary in the field of co-operative projects with industry. Apprenticeship training schemes at all levels have not yet received the attention they deserve. In this, the active interest and co-operation of industry are the forerunners of any successful schemes. Government has already accepted the recommendations of the Secondary Education Commission to provide diversified courses at the secondary level. Such courses can be useful only if opportunities are available to young school leavers to go into industry as learner-workers or apprentices, having at the same time facilities for part-time instruction in technical schools. Such schools could be set up by industry. Provision should also be made in existing engineering colleges, which are at present doing mostly full-time work.

" I am glad to note that in so far as graduate apprenticeship training is concerned, it has been possible to secure fairly good response from industry. All the same, what has been done is not enough. Much more will have to be done at all levels. I take this opportunity of making a special appeal to the representatives of industry and commerce on the Council and to industrialists outside to participate fully in the apprenticeship schemes, which must be worked out and put into effect."

Technical training involves not only institutional training but also training in industry, and the success of any scheme of training will be measured not by the number of certificate, diploma, or degree holders, but by the number of trained personnel absorbed by industry or participating in productive enterprises. It may be mentioned in this context that the Scientific Man-Power Committee (1949) reported that industries set great value on pre-employment training and that only students who have been " conditioned ", after passing out of technical institutions, can find employment in industrial concerns. The " conditioning ", which is prescribed as a qualification for employment in industry, is the supplement to institutional training and this is a responsibility which industry has to shoulder. The technical and technological institutions instruct the students of today to make them skilled workers and managers in industry tomorrow. In the great task of training a competent working force and managers for industry, both educational institutions and industry have a vital common concern.

Several measures have been suggested from time to time to augment the facilities for practical training in industry. The Scientific Man-Power Committee recommended that " suitable legislative measures should, if necessary, be introduced to make it obligatory on the part of every industrial concern to provide industrial training facilities ". It has also been suggested that the co-operation of foreign firms operating in India, State-sponsored industries, and industries enjoying tariff protection, should be enlisted to expand the facilities for apprentice training. Some industrial concerns are indeed offering apprentice facilities for students passing out of technical institutions. For instance, the Sindri Fertilizer Factory affords training for engineering graduates and trade apprentices; the factory has also made provision for short-term training of engineering students from universities. Considering the magnitude of the problem, however, the facilities now available in industry for practical training are totally inadequate. A comprehensive and enduring system of works training on a much greater scale should be formulated.

The role of industry

This is possible only if industry assumes the responsibility as an interested partner in technical education programmes. Without such partnership, the programme of technical education may miss the touch of reality and clear purpose. The identification of young people who have shown capacity to profit by technical training and the formulation of programmes of study which will develop their best potentialities is a joint task of technical institutions and industry. This has been recognized in all highly advanced countries. In U.K., for instance, representatives of the Federation of British Industries, Industrial Co-operative Research Associations, and technical institutions frequently meet to discuss and exchange information on problems of education and practical training. Movement of staff from technical schools to industry and vice versa is encouraged. Professors are frequently appointed as consultants in industries allied to their fields of specialization. Technical institutions provide part-time or full-time instruction facilities for workers in industry and technical staff from industry are called upon to give lectures in technical institutions. The identity of interest between technical institutions and industry in the training of technical personnel is clearly manifest. Industry realizes that co-operation with educational institutions is necessary in its own interests.

The formulation of realistic plans for technical education in India has been rendered difficult by the paucity of data on the requirements by industry of technical personnel. The estimates of the Scientific Man-Power Committee do not appear to be valid under the present conditions. These estimates were based on " Production to Personnel Ratio " and reliance was placed on targets of production suggested by the Industries Panels set up by Government. In view of the changed conditions, a fresh assessment of the requirements is called for. Quantitative estimates of personnel needs of industry should be correlated with the output of students from technical schools and colleges and provision should be made for in-industry training in programmes of technical education.

The All-India Council of Technical Education is confronted with two major problems in formulating the plans for the development of technical education. First, securing the collaboration of industry and second, assessment of demand for trained personnel at all levels. The effort of the educator is primarily to equip the students so that after leaving the school or college they may find full opportunities to develop their activities as workers in industry. In the great task of making the effort of the educator effective, industry has a part to play. The number of students to be trained and the type of training to be imparted should be based on realistic estimates of the present and future needs of industry. It is only on the basis of such data that ideas and projects can be shaped to correspond to reality and the needs of the situation. The Council composed of leaders of education, industry and administration may be confidently expected to tackle the various problems of technical education with expertness and vision.

Symposium on Solar Energy & Wind Power

A FOUR-DAY symposium on Solar Energy and Wind Power, jointly sponsored by the Government of India and the Unesco, was held in the National Physical Laboratory, New Delhi, from 22 to 26 October 1954. Delegates from various countries, including Australia, Burma, Ceylon, Denmark, France, Holland, India, Israel, Pakistan, Russia, South Africa, U.S.A. and West Germany, participated in the symposium. Dr. K. S. Krishnan, F.R.S., presided.

The symposium was inaugurated by Shri K. D. Malaviya, Deputy Minister for Natural Resources and Scientific Research, on 22 October 1954. Shri Malaviya referred to the arid and semi-arid conditions prevailing in some parts of India and the possibility of utilizing wind power and solar radiation for bringing prosperity to the regions. He observed: Scientists and engineers are meeting here to consider how best to utilize wind power and solar radiation to supplement the energy we derive from coal, oil or waterfalls. It is important that we should derive energy from these abundant and inexhaustible sources at economic and competitive rates. Our scientists are aiming, therefore, to effect economy in the processes of utilization of wind power and solar energy.

Wind power — The discussion on wind power opened with a paper by Prof. D. Dresden (Holland) who outlined the progress achieved in the harnessing of wind power. Two questions arise for consideration: (1) Applications for small power in places where the only alternative source would be such small prime-movers as diesel or gasoline motors; in these cases wind power, once selected, would have to be relied upon as the only available source; (2) applications for large blocks of power with the main purpose of conserving fossil fuels during the time the wind blows with enough force. The technical problems involved in the two fields of application have been analysed and suitable designs have been worked out. Successful wind-driven generators of capacities up to 70 kW. are now operating in Denmark. Two 100 kW. installations, embodying new technical features suggested by recent aeronautical research, are under test in U.K. These are looked upon as prototypes for units of 1,000 kW. or more, to which class belongs the Smith-Putnam experimental plant at Grandpa's Knob, Vermont, U.S.A. A study of the information published in U.K. points to the possibility of generating electricity competitive with that of steam plant.

Following the review by Dr. Dresden, papers relating to wind regime studies, economics of wind power, utilization of wind, solar radiation and other local energy resources for the development of communities in arid and semi-arid areas were discussed. Surveys in India, U.K. and Israel show the necessity for seeking favourable sites before installing wind power machines. Dr. L. A. Ramdass (India) reported that there were many regions stretching from Saurashtra to Travancore where wind power could be effectively harnessed. Mr. K. M. Shankaran (India) suggested the installation of a large machine to capture winds at high altitudes.

Mr. Golding (U.K.) said that his researches showed that it was possible through careful search to discover places where the wind speed would be higher than the surrounding areas. He described the methods followed in Britain for estimating wind energy. He suggested that rural populations should be educated in the use of wind power; this would encourage the demand of wind power plants.

Dr. Hütter (Germany) discussed the design of wind power plants of medium size and emphasized the need to study load requirements, especially for water pumping, before designing a wind machine.

The possibility of combining wind power and bullock power was discussed by Mr. P. V. Ramiah (India). Mr. V. J. Bhatt discussed the possibility of utilizing wind power in Saurashtra to supplement thermal power generation in the electricity grid.

Solar energy — In a general review of developments in the harnessing of solar energy, Dr. Farrington Daniels (U.S.A.) observed that the devices available at present cannot compete with coal and petroleum in industrialized countries. The first developments will have to come in small isolated units where electrical power is not available and where transportation costs for oil or gasoline are excessive. Under such conditions, inexpensive solar engines are needed, even if they are not efficient. Among the more promising applications of solar energy are the heating and cooling of houses and demineralization of salt water. Photochemistry offers much hope for long-range development and intensive photochemical research may yield promising results. Important progress has been made in the direct conversion of sunlight into electricity by the use of crystalline semi-conductors.

Solar engines, the delegates agreed, could not effectively compete with electricity, coal and gasoline, but they could compete with animal power. The difficulties of using sunlight were its low intensity and the fact that the sun's radiation would have to be collected over a large area. The cost of operation accordingly would increase.

Several types of solar heaters were described in detail. They included heaters with large parabolic mirrors focussed on a cooking vessel or the boiler of a steam engine. Mr. Gardner described a new and simple arrangement of adjustable flat mirrors mounted on rows in a simple frame. Prof. V. A. Baum (U.S.S.R.) showed pictures of large parabolic collectors which generated steam at pressure. He also described a refrigeration machine which, with a parabolic mirror 80 sq. metres in area, had daily produced 250 kg. of ice.

The solar cookers were regarded as particularly important because they could be made cheaply and help to save cowdung and plant materials which are now used as fuel — the first essential to increase food production and the second to check soil erosion. It was, however, agreed that solar cookers would have to be made cheaper — say, Rs. 20 each — before they become popular.

Some delegates described the application of solar energy for heating houses. The heat could be stored in hot water, in beds of small rocks or in chemicals such as hydrated salts Thin plastics offered cheap materials which could be used as collectors. It was disclosed that applications for heating houses would become popular in cold climates.

Prof. Trombe (France) said it was an anomaly that although solar energy was difficult to use because it was weak, nevertheless, it was used at many places for experimental furnaces of the highest temperatures.

Exhibition — An exhibition displaying charts, maps, photographs, working models and technical publications was arranged by the organizers of the symposium.

The exhibits on solar energy utilization included solar cookers, domestic solar water heaters, hot air solar engines for pumping water and steam cookers. The Indian solar cooker, developed by the National Physical Laboratory, attracted much attention. This cooker formed the subject of a BBC television science programme in October 1954. The commercial model was demonstrated in Somaliland and in a trial run three-fourth gallon of water was boiled in less than an hour from an initial temperature of 72°F. The overall utilization efficiency was 33 per cent; with better anodized reflectors, the performance of the cooker could be considerably improved.

The domestic water heating arrangement had an auxiliary tank of 100 gallon capacity for storing hot water. The hot air engine, installed in a paraboloidal mirror, develops about $\frac{1}{16}$ h.p. and is capable of pumping water from a depth of 15 ft.

An arrangement for concentrating solar energy by plane mirrors had been set up by Dr. A. L. Gardner. The heat gathered from 200 individual mirrors was brought to a common focus and concentrated on a boiler for raising steam.

Outstanding exhibits on wind power utilization were put up by the British Electrical

Industries Research Association, U.K., Messrs James Alston & Sons, Melbourne, and Allgaier-Werke, Uhingen, Wurt (Germany). Numerous photographs, survey maps and graphs on wind energy data were also exhibited.

A working model of Comet-C pattern, direct action, Australian windmill attracted wide attention. Mills of this pattern have given satisfactory results in areas with a wind velocity of 4 miles per hour and above and they require little or no servicing.

Charts showing the constructional details of the governor, power transmission system and direction control of the Allgaier wind power plant system were also displayed.

Ionospheric Data—September 1954

CHARACTERISTICS OF THE IONOSPHERE OVER CALCUTTA

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FIG. 1 shows the monthly average diurnal variations of the ordinary ray critical frequencies of regions E and F_2 (f^oE and f^oF_2) and also similar variations of the heights of maximum ionization (hpF_2) and bottom ($h'F_2$) of the F_2 layer during September 1954. The f^oF_2 variation curve has been compared to that predicted three months before. The percentages of the total number of occasions during routine observations when the critical frequency for the sporadic E layer (fE_s) was greater than 3, 5 and 7 Mc/s. have been plotted for the different hours in Fig. 2. Table 1 gives the median values for the different ionospheric parameters.

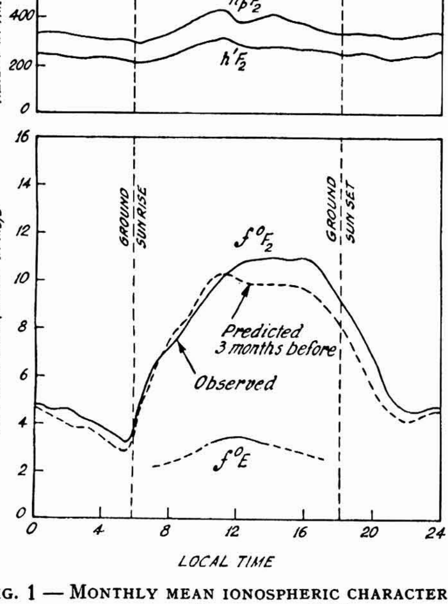


FIG. 1 — MONTHLY MEAN IONOSPHERIC CHARACTERISTICS FOR SEPTEMBER 1954

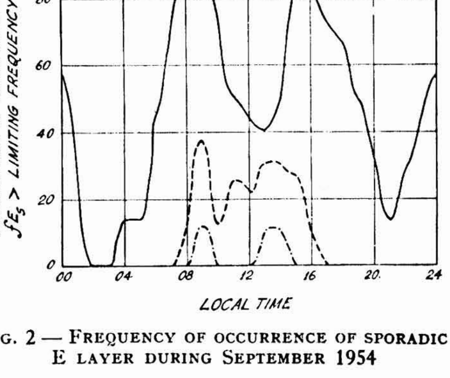


FIG. 2 — FREQUENCY OF OCCURRENCE OF SPORADIC E LAYER DURING SEPTEMBER 1954

Fig. 3 gives the mean M.U.F. predictions for transmissions to different distances via F_2 region over Calcutta during December 1954.

The intensity and frequency of occurrence of sporadic E layer during September 1954 were less than in the previous month. The behaviour of the F_2 region was normal.

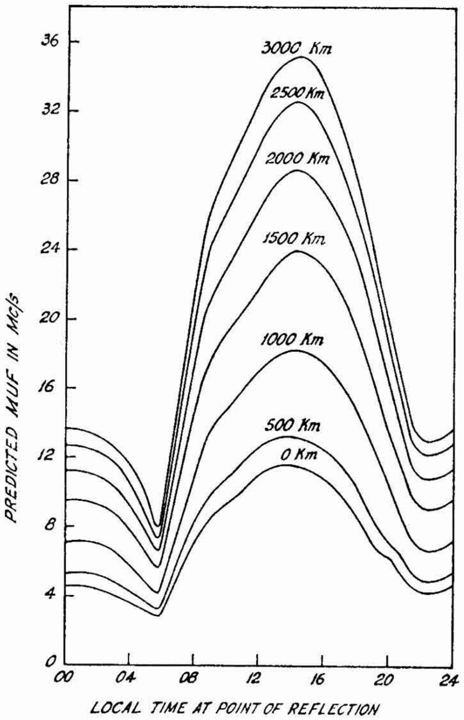


FIG. 3 — PREDICTED M.U.F. FOR TRANSMISSION VIA F_2 REGION OVER CALCUTTA DURING DECEMBER 1954

CHARACTERISTICS OF THE IONOSPHERE OVER AHMEDABAD

K. M. KOTADIA, R. G. RASTOGI & R. M. SHERIFF

Ionospheric Research Station, Physical Research Laboratory, Ahmedabad

FIG. 1 shows the diurnal variations of the monthly median critical frequencies of the ordinary waves reflected from E, F_1 and F_2; Fig. 2 shows the variations of the height

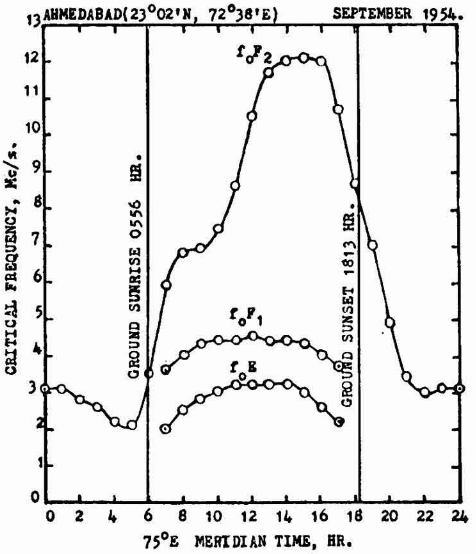


FIG. 1 — DIURNAL VARIATION OF CRITICAL FREQUENCIES OF ORDINARY WAVES REFLECTED FROM E, F_1 AND F_2 REGIONS

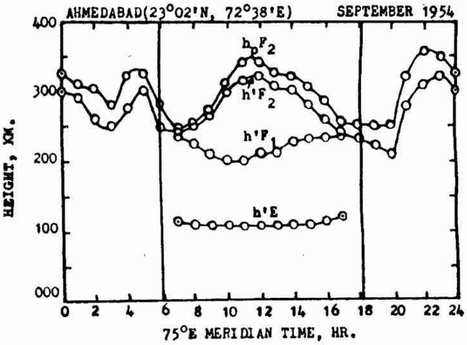


FIG. 2 — DIURNAL VARIATION OF VIRTUAL HEIGHTS OF E, F_1 AND F_2 REGIONS

TABLE 1 — MONTHLY MEDIAN HOURLY VALUES

(*September* 1954)

TIME*	$f^{\circ}F_2$ Mc/s.	hpF_2 km.	$h'F_2$ km.	$f^{\circ}E$ Mc/s.	fE_S Mc/s.	$(M3000)F_2$
00	4·60	330	240	—	3·20	2·85
01	4·60	330	240	—	—	
02	4·55	330	240	—	—	
03	4·15	315	240	—	—	3·00
04	3·80	300	240	—	—	
05	3·40	300	225	—	—	
06	4·25	300	210	—	2·80	3·05
07	6·40	300	225	—	3·45	
08	7·10	330	240	—	3·85	
09	8·40	360	270	—	4·60	2·70
10	9·00	420	300	—	4·70	
11	10·00	420	300	3·40	—	
12	10·75	390	300	3·50	—	2·65
13	10·80	390	300	3·35	—	
14	11·10	390	270	3·30	4·10	
15	11·05	390	270	—	3·45	2·60
16	11·00	360	270	—	3·50	
17	10·40	345	270	2·70	3·90	
18	9·15	330	240	—	3·30	2·85
19	7·70	330	240	—	3·40	
20	6·55	322	240	—	—	
21	5·10	300	225	—	—	3·05
22	4·70	315	240	—	—	
23	4·60	330	240	—	—	

*Time: 90° East Meridian Time (U.T. + 6 hr.)

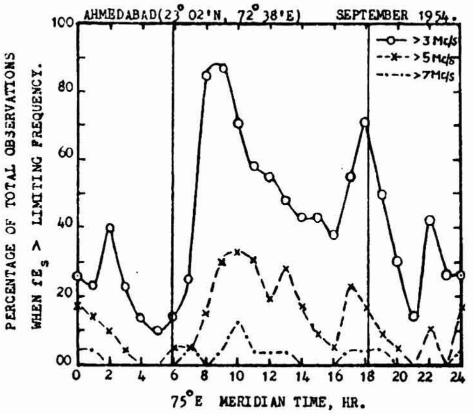


FIG. 3 — DIURNAL VARIATION OF OCCURRENCES OF SPORADIC E LAYER WHEN fE_s WAS HIGHER THAN 3, 5 AND 7 Mc/s.

of maximum electron density and of the minimum virtual heights of the different regions; Table 1 gives the monthly median values of the various parameters for E, E_s, F_1 and F_2 regions and the frequencies of occurrence of E_s during hourly observations when fE_s was higher than 3, 5 and 7 Mc/s. and the diurnal variation of the percentage occurrences of E_s is shown in Fig. 3.

The median critical frequencies of F_2 in September 1954 were higher than those in August except from sunset to midnight. There is an overall decrease in maximum electron density of the ionosphere compared to that in September 1953.

The intensities and frequencies of occurrence of sporadic E layer were appreciably lower than in the previous month, but higher than in September 1953.

TABLE 1 — IONOSPHERIC DATA, AHMEDABAD, SEPTEMBER 1954

(*Tabulated hours 75°E. Meridian Time*)

TIME hr.	MEDIAN VALUES								NO. OF OCCURRENCES OF E_S WITH			TOTAL NO. OF DAYS FOR WHICH E_S DATA ARE AVAILABLE
	f^oF_2 Mc/s.	h_pF_2 km.	$h'F_2$ km.	f^oF_1 Mc/s.	$h'F_1$ km.	f^oE Mc/s.	$h'E$ km.	fE_S Mc/s.	$fE_S>$ 3 Mc/s.	$fE_S>$ 5 Mc/s.	$fE_S>$ 7 Mc/s.	
00	3·1	325	300	—	—	—	—	4·7*	6	4	1	23
01	3·1	310	290	—	—	—	—	3·1*	5	3	1	22
02	2·8	302	260	—	—	—	—	4·1*	8	2	—	20
03	2·6	280	250	—	—	—	—	3·2*	5	1	—	22
04	2·2	322	275*	—	—	—	—	3·0*	3	—	—	22
05	2·1	325	300*	—	—	—	—	2·9*	2	—	—	20
06	3·5	283	250	—	—	—	—	2·8*	3	1	—	21
07	5·9	250	245	3·6	235	2·0	115	3·6*	5	1	1	20
08	6·8	255	250	4·0	225	2·5	110	4·2	17	3	—	20
09	6·9	273	267	4·3	210	2·8	107	4·2	20	7	1	23
10	7·4	310	300	4·4	203	3·0	107	5·0	17	8	3	24
11	8·6	340	315	4·4	200	3·2	107	5·5	15	8	1	26
12	10·5	342	320	4·5	210	3·2	107	4·4	15	5	1	27
13	11·7	325	305	4·4	212	3·2	107	5·3	12	7	1	25
14	12·0	320	300	4·4	227	3·2	110	3·7	10	4	—	23
15	12·1	305	280	4·3	233	3·0	110	4·3	10	2	—	23
16	12·0	285	260	4·0	233	2·6	115	3·8	8	1	—	21
17	10·7	255	242	3·7	235	2·2	120	4·6	12	5	1	22
18	8·7	250	230	—	—	—	—	4·1	17	4	1	24
19	7·0	250	223	—	—	—	—	3·2	11	2	1	22
20	4·9	250	207	—	—	—	—	3·1	6	1	—	20
21	3·4	320	275	—	—	—	—	2·9	3	—	—	21
22	3·0	355	307	—	—	—	—	4·7*	6	2	—	19
23	3·1	350	320	—	—	—	—	3·9*	5	—	—	23

*Median based on observations less than ten.

Continuance of the Desert Locust Active Cycle

K. B. LAL
Director, Locust Control, New Delhi

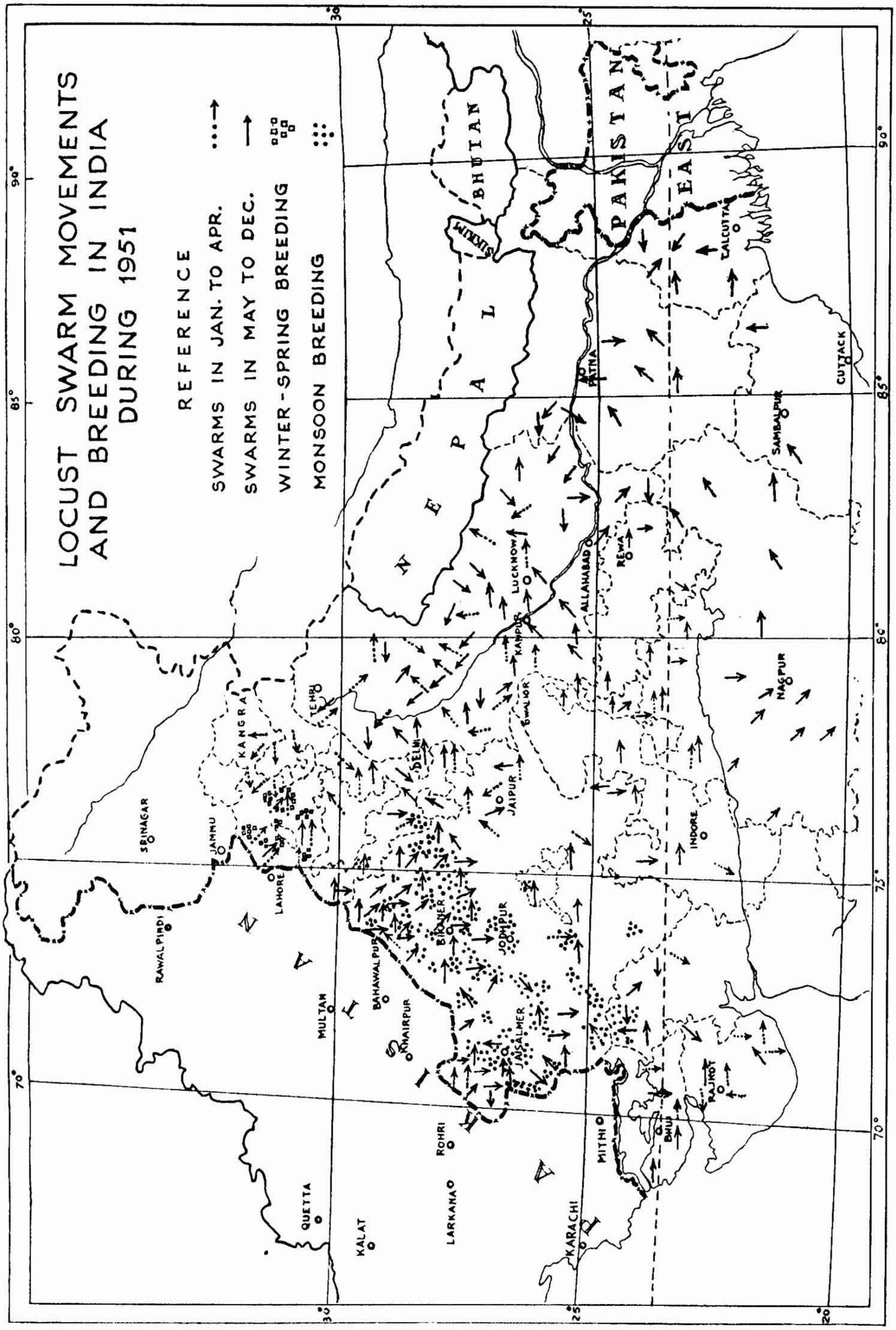
IT is now well known that outbreaks of the desert locust, *Schistocerca gregaria* Forsk., occur periodically and fairly authentic records of such outbreaks in India are available from 1812 onwards. The two other locusts of the Indian region, namely the migratory locust, *Locusta migratoria* Linn., and the Bombay locust, *Patanga* (*Cyrtacanthacris*) *succincta* Linn., have not been very active of late, though hopper concentrations of the former species were observed in Ramanathapuram district of Madras State in February 1954. Subsequently, on 2 June 1954, an aeroplane pilot observed a small locust swarm at a height of 1,000 ft. from the ground about a mile from Bangalore. Since there was no possibility of any swarm of the desert locust having flown that far south in June 1954 and since no adults or hoppers of the Bombay locust were observed in any appreciable numbers during the year, it was presumed that the locust swarm over Bangalore seen by the air pilot could only be that of the migratory locust. Some details about these observations have been published by Ramachandra Rao[1].

Pruthi[2] gave an account of the outbreak of a fresh cycle of the desert locust which started in 1949 and is still continuing. Since there are as yet no indications of this cycle coming to an end and since Pruthi's account dealt with the first two years of the outbreak only, it may be useful to take his account further and discuss the nature and the course of the outbreaks as they developed in 1951, 1952, 1953 and 1954. In describing the initial stages of the present desert locust outbreak, Pruthi gave a fairly detailed account of the biology, phase characteristics, breeding habits and swarm migrations and also of the organizations for locust control in India. The background information for the present paper is, therefore, already available and need not be repeated. Likewise, since the organizations for locust control in India have remained substantially the same as they were in 1950, remarks about them would be confined only to the improvements in the organizations and in the techniques of locust control as they have occurred during the past three or four years.

Locust situation in 1951

Unlike in 1950, there was a fair amount of locust activity in the winter and spring of 1951. During the preceding autumn in 1950, about half a dozen swarms had developed in Banaskantha and Mehsana districts of Bombay State and the adjoining cultivated districts of Rajasthan. To these were added some immature swarms which came over in October from Pakistan and did not return westwards as may have been expected. All these swarms moved generally in the eastern and north-eastern directions during the winter of 1950-51. During the second and third weeks of January 1951, widespread rains occurred in the Punjab and Uttar Pradesh and neighbouring areas, when the swarms moving towards such areas concentrated at the bases of the Punjab hills and the adjoining Kumaon hills in Uttar Pradesh. Two swarms also entered Punjab (India) from the adjoining districts of Punjab (Pakistan). Egg-laying started about the middle of February in Hoshiarpur district and extended to Ferozepur, Amritsar, Jullundur and Kapurthala districts. A couple of swarms, which were at that time present in Uttar Pradesh, moved actively towards east in the last week of February and, after crossing Bihar, reached Bengal in the first week of March and entered Assam soon after.

Most of the swarms broke up into small swarmlets and were destroyed by control operations undertaken in the Punjab and Uttar Pradesh. Likewise, the eggs or the hoppers emerging from them were also destroyed in large quantities so much so that no swarms developed from them.


LOCUST SWARM MOVEMENTS AND BREEDING IN INDIA DURING 1951
REFERENCE
SWARMS IN JAN. TO APR.
SWARMS IN MAY TO DEC.
WINTER-SPRING BREEDING
MONSOON BREEDING
NEPAL
BHUTAN
SIKKIM
EAST PAKISTAN
PAKISTAN
CALCUTTA
CUTTACK
PATNA
SAMBALPUR
NAGPUR
REWA
ALLAHABAD
LUCKNOW
KANPUR
GWALIOR
TEHRI
DELHI
KANGRA
JAIPUR
INDORE
SRINAGAR
JAMMU
LAHORE
RAWALPINDI
BIKANER
JODHPUR
BAHAWALPUR
MULTAN
KHAIRPUR
JAISALMER
RAJKOT
BHUJ
MITHI
ROHRI
LARKANA
QUETTA
KALAT
KARACHI
30°
25°
20°
70°
75°
80°
85°
90°

Meanwhile, heavy locust breeding was continuing on a large scale in the winter-spring breeding areas of Pakistan, Iran and countries of the Middle East, which provided sources for subsequent swarm incursions into India.

During April and the first week of May, India was free from locust swarms, eggs or hoppers, but soon after, swarms from the west began to come in, the first of which entered India across the Bahawalpur border and was observed on 13 May in Ganganagar district of Rajasthan. The incursion of swarms from the west continued till mid-August and was heaviest during June. During this period of 3 months, about 54 swarms entered India through Punjab and Rajasthan. The swarms during May-July were pink, yellow or mixed, but in August they were predominantly yellow.

The swarms arriving in India in May and June found conditions very dry and temperatures high and continued their flights eastwards with the prevailing winds. During June, the swarms moving east and south-east reached West Bengal and one of them even crossed into East Bengal. Swarms had also moved into the States of Madhya Bharat, Madhya Pradesh, Saurashtra, Bombay and Kutch, from where they generally flew towards north-east resulting in heavy infestations in Rajasthan, southern Punjab, southern and eastern parts of Uttar Pradesh and adjoining districts of Madhya Bharat.

Due to scattered but localized rainfall during June, there was some light breeding in two areas of Jodhpur Division. However, with the setting in of the monsoon in full force in the last week of July, heavy and extensive egg-laying occurred in Banaskantha district of Bombay State, in several parts of Rajasthan, in Hissar district of Punjab and in Ajmer State during August and first week of September. The total gross area infested by hoppers was about 45,000 sq. miles. In all cases, the eggs or the hoppers emerging from them were completely destroyed and no swarms formed as a result of the monsoon breeding. However, swarm incursions from the west continued during September and October and about 13 of them were traced as having come into India through Rajasthan and Punjab. The last swarm of the year coming into India was observed on 5 December in Bikaner Division. In the course of their movements, these swarms reached as far as PEPSU and the western districts of Uttar Pradesh, south-western districts of Madhya Bharat and Ajmer State. Many of these swarms were destroyed.

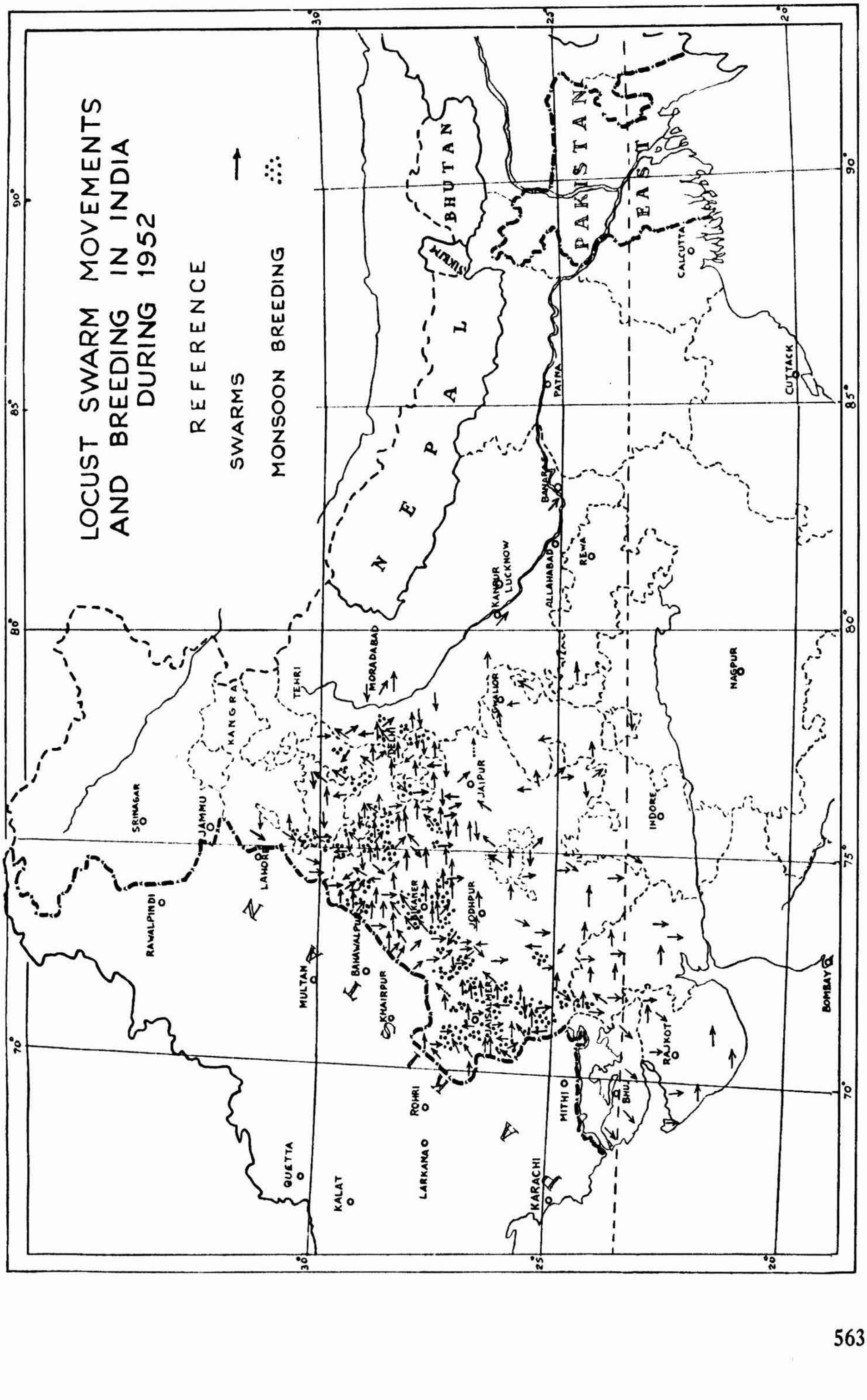
Locust situation in 1952

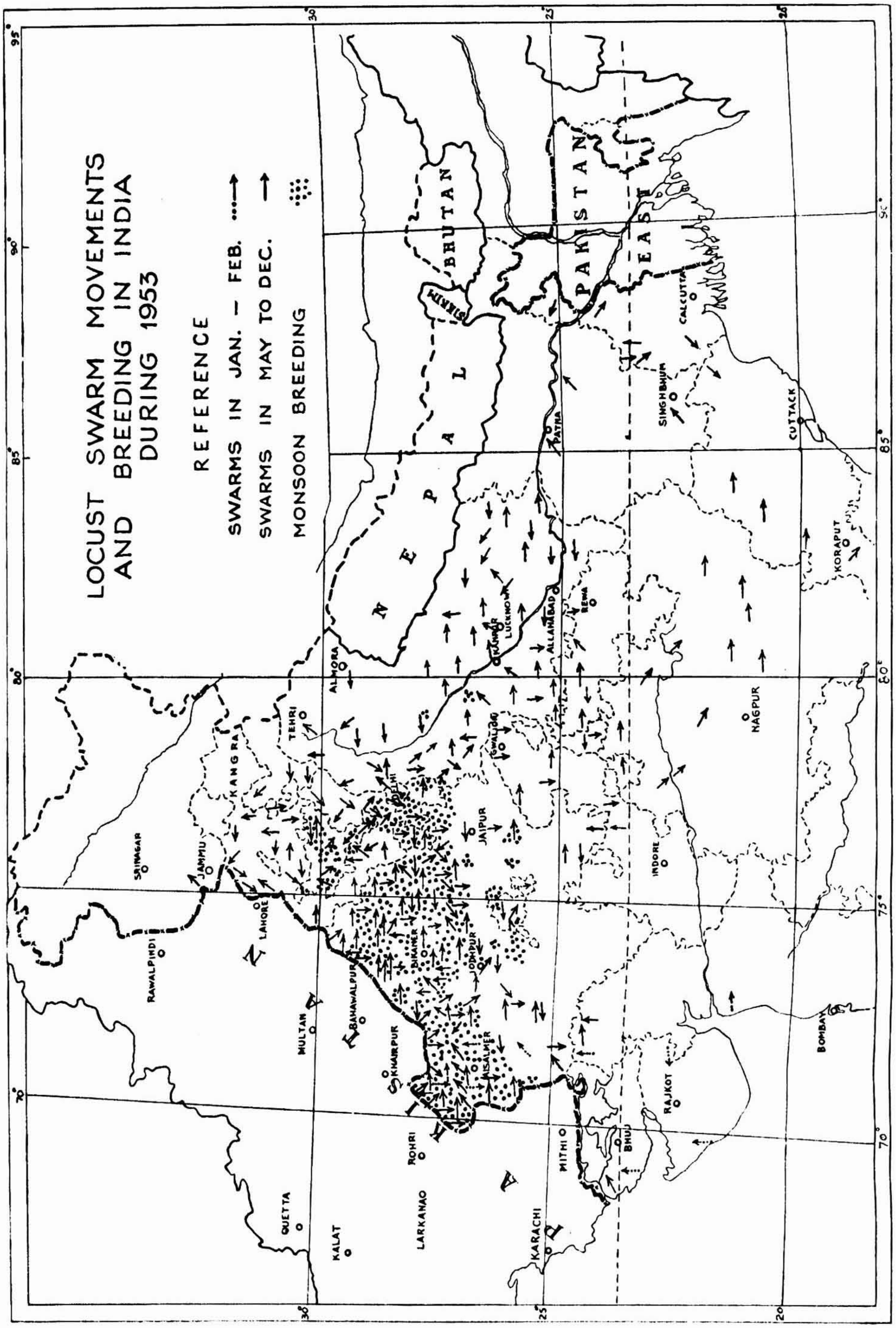
There was no locust activity in India during the winter-spring of 1952, except for a small pink swarm reported from Bharatpur tehsil (Rajasthan) on 13 February and in the adjoining areas of Agra district soon after. Nothing was heard of this swarm and presumably it got scattered and perished. The population of individual locusts also was practically nil in India till the end of April.

A sudden rise in the population of scattered locusts was observed in the western parts of Rajasthan from 3 May onwards and these proved to be the forerunners of a swarm which came into India from Pakistan and was observed on 15 May in Barmer district of Rajasthan. No more swarms entered India during the next three or four weeks but the population of scattered locusts continued to rise in Rajasthan, presumably due to the influx of loose swarms from the west. From 19 May onwards till the end of August, the main swarm incursions into India from the west continued, a total of 69 swarms having been traced during this period. Again, from about the first week of September to the end of the year, about 40 swarms entered India through Bikaner and Jodhpur Divisions across Sind-Bahawalpur border. As before, the swarms received during the monsoon season moved eastwards up to Banaras district. However, these swarms as well as those received during the post-monsoon period, continued roaming about in Rajasthan, PEPSU, Punjab, Uttar Pradesh, Ajmer, Delhi, Madhya Bharat, Vindhya Pradesh, Kutch, Saurashtra and Bombay States.

Breeding occurred heavily and extensively from 6 July to 6 September in Rajasthan, Punjab, PEPSU and Uttar Pradesh and also in Palanpur district of Bombay State. The total area infested by locust eggs and hoppers during this period was estimated to be over 80,000 sq. miles.

Control operations were organized all over the areas infested against settled swarms as well as eggs and hoppers and were successful to the extent that hardly any swarms were allowed to form on Indian soil.


LOCUST SWARM MOVEMENTS AND BREEDING IN INDIA DURING 1952
REFERENCE
SWARMS
MONSOON BREEDING
NEPAL
BHUTAN
SIKKIM
PAKISTAN
EAST
CALCUTTA
CUTTACK
PATNA
BANARAS
ALLAHABAD
REWA
KANPUR
LUCKNOW
MORADABAD
TEHRI
KANGRA
DELHI
GWALIOR
JAIPUR
NAGPUR
INDORE
SRINAGAR
JAMMU
LAHORE
RAWALPINDI
MULTAN
BAHAWALPUR
BIKANER
JODHPUR
KHAIRPUR
JAISALMER
ROHRI
LARKANA
QUETTA
KALAT
KARACHI
MITHI
BHUJ
RAJKOT
BOMBAY
30°
25°
20°
70°
75°
80°
85°
90°


LOCUST SWARM MOVEMENTS
AND BREEDING IN INDIA
DURING 1953
REFERENCE
SWARMS IN JAN. - FEB.
SWARMS IN MAY TO DEC.
MONSOON BREEDING
NEPAL
BHUTAN
SIKKIM
EAST PAKISTAN
PAKISTAN
SRINAGAR
JAMMU
RAWALPINDI
LAHORE
KANGRA
TEHRI
ALMORA
DELHI
MULTAN
BAHAWALPUR
KHAIRPUR
BIKANER
JODHPUR
JAISALMER
JAIPUR
GWALIOR
CAWNPUR
LUCKNOW
ALLAHABAD
REWA
PATNA
SINGHBHUM
CALCUTTA
CUTTACK
KORAPUT
NAGPUR
INDORE
ROHRI
QUETTA
KALAT
LARKANAO
KARACHI
MITHI
BHUJ
RAJKOT
BOMBAY
30°
25°
20°
95°
90°
85°
80°
75°
70°

Locust situation in 1953

During the winter-spring of 1953, locust activity was low in India, only a couple of swarms having been observed roaming about in Kutch and Banaskantha district of Bombay State during January and two or three small swarms in Rajasthan and Ajmer States in the first week of February. Presumably, these swarms got scattered and perished so that India was free from swarm activity after 8 February and till the middle of May. There was no winter-spring breeding in any part of India.

From about the middle of May, locust swarms began coming into India again from the west and these incursions continued till the middle of November. The number of swarms coming into India during May was 26, during June 33, during July 35, during August 15, during September over 21 and during October and November 6.

During May and June, swarms were actively moving towards east. During the first fortnight of June, swarms visited Uttar Pradesh, Madhya Bharat, Bombay, Vindhya Pradesh, Bihar, Orissa and West Bengal States in addition to eastern Rajasthan, Punjab and PEPSU wherein the main concentrations occurred. Swarm movements continued in July in several of these States, but by the end of August not many swarms were left in India. However, the incursions from the west were still continuing and the last swarm of the year was observed in Nagaur district of Rajasthan on 25 December.

Early in July, egg-laying started in nine districts of Rajasthan, three of Punjab and one of PEPSU. Hoppers emerged for the first time in the year on 14 July. Another wave of egg-laying occurred in the second fortnight of July over large parts of Rajasthan, Punjab and PEPSU and also in Uttar Pradesh, Ajmer and Delhi States. During August, hopper infestations covered extensive areas and during September, patchy, post-monsoon breeding occurred in a few districts of Rajasthan, PEPSU and Punjab. The infestations were controlled completely.

Locust situation in 1954

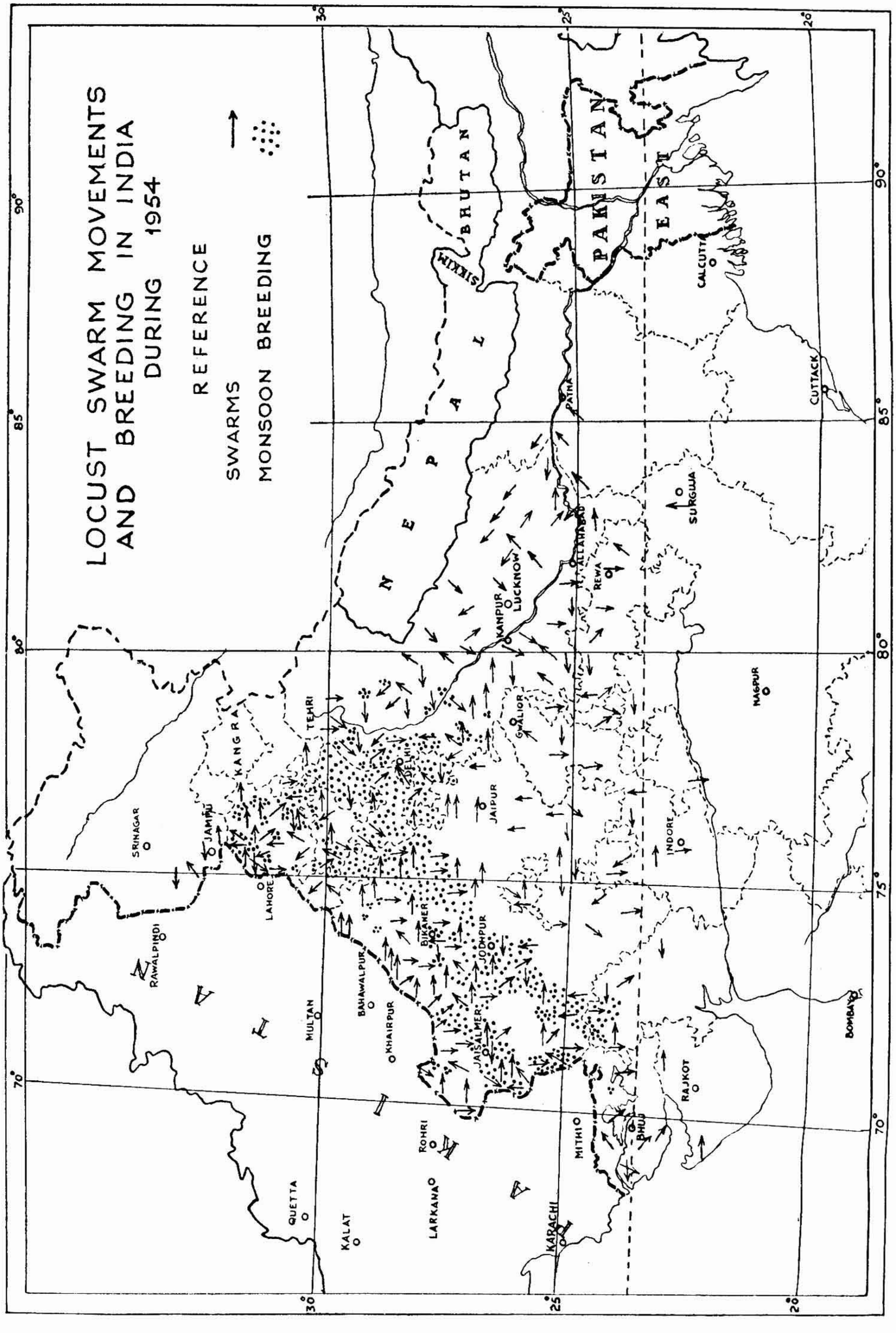
No swarm over-wintered in India and no breeding occurred during winter-spring of 1954. The population of scattered locusts in the desert areas was very low during January, February and March 1954. However, the first swarm of the year was observed in Jodhpur Division on 11 April and by 20 April three more swarms had entered through Rajasthan. These swarms, which were mostly of yellow locusts, got dispersed, thereby raising the population of the scattered locusts in Rajasthan.

Swarm incursions from the west commenced again on 15 May and continued till nearly the end of October, the total number of swarms having been traced to have come into India being 8 during May, 32 during June, 25 during July, 24 during August, 8 during September and 6 during October. These swarms moved from Rajasthan and Punjab into the States of Delhi, PEPSU, Ajmer, Bombay, Uttar Pradesh, Madhya Bharat, Madhya Pradesh, Vindhya Pradesh, Saurashtra, Kutch, Jammu and Kashmir and Bihar. Most of the swarms that came in were of mature locusts but during June the swarms were mostly of pink and grey locusts.

Locust breeding occurred mainly in four waves. In the first wave in June, eggs were laid in several areas of Rajasthan, Hissar and Gurgaon districts of Punjab, Sangrur district of PEPSU and Meerut district of Uttar Pradesh. The egg-laying in July was on a very extensive scale and affected practically the whole of Rajasthan and Punjab States, Banaskantha district of Bombay State, four districts of PEPSU, 14 districts of Uttar Pradesh, some parts of Ajmer State and very large areas in Delhi State. During August, the third wave of egg-laying occurred in practically all the areas mentioned above except Banaskantha district of Bombay State. There was not much egg-laying during September but towards the end of this month and in October, extensive egg-layings occurred in Rajasthan, PEPSU, Punjab and Delhi States. The total area infested with eggs and hoppers in the desert areas as well as in the States has been estimated to be about 50,000 sq. miles.

Organizations for locust control in India

The basic structure of the organizations for locust control in India has remained the same as that described by Pruthi (loc. cit.) but have been greatly strengthened, especially the Central organization of the Government of India, by the addition of vehicles, dusting and spraying machines, wireless stations and various other types of equipment.



LOCUST SWARM MOVEMENTS AND BREEDING IN INDIA DURING 1954

REFERENCE

SWARMS →

MONSOON BREEDING ⁘

In the States also, which have the responsibility of controlling locusts in their cultivated areas, the State Plant Protection organizations, which also undertake locust control work, have been improved and strengthened. A major development was the employment of fixed-wing aeroplanes for spraying locust hoppers and settled swarms from the air. During the years 1951, 1952 and 1953, three aeroplanes, obtained from the U.S. Government on loan under the T.C.M., operated for 1-2 months each year in Rajasthan during July, August and September. During 1954, three Piper Cub Super-Cruisers, obtained under an agreement with the Hind Provincial Flying Club of Uttar Pradesh, have done the same job during August and September in Rajasthan. The spraying equipment used on these aeroplanes were received from the U.S. Government under the T.C.M. However, spraying from air by aeroplanes is not by any means adequate or suitable to replace the ground organization for locust control to any appreciable extent. Their value has been chiefly in providing supplementary assistance for locust control in special cases, when large concentrations of locust hoppers at a stretch had to be destroyed in a very short time.

A new technique, increasingly adopted since 1951, has been to spray egg-infested grounds with Aldrin, with a view to killing the hoppers as they emerged and came in contact with the poisoned surface. Incidentally, it may be stated that the only other place this modern technique has been employed is East Africa where the sprayings were done by the Desert Locust Control Unit of the United Kingdom Government. Another notable development in locust control has been the increasing use of aldrin spray in addition to the dusting with benzene hexachloride. For a variety of reasons, poison baiting has not been used in India on any appreciable scale.

Although the principle of international collaboration in locust control has been well recognized for over the last ten years, the translation of this principle into action, at any rate, as far as India is concerned, has been greater since 1951 than before. During 1953, India sent a team of technical men and equipment to Iran to assist the Government of that country in fighting locusts during spring. In the same year, India also offered to assist an international campaign against the desert locust in the Arabian peninsula with six technical officers, and during 1954, proposals are under the consideration of the Government of India for sending a more or less self-contained team with equipment to Arabia to assist in destroying locusts there during the winter and early spring of 1955.

References

1. Ramachandra Rao, Y., *Indian J. Entomol.*, **16**(1) (1954), 84.
2. Pruthi, H. S., *J. sci. industr. Res.*, **9** (1950), 358.

Photoelectric Measurements on Grading of Indian Sugar

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IN India, for the purposes of commercial transactions, crystal sugar has been divided into 15 grades, the distinction depending upon crystal size and colour (degree of whiteness). The grain size series has five grades designated by A, B, C, D and E, A being sugar of the biggest grain size and E the smallest. The colour series consists of three colours designated as 29, 28 and 27, the grade 29 being the whitest. Thus, there are 15 inter-combinations. Grain size group is determined by sieve test, while the colour is judged only visually. The estimation of colour visually introduces personal judgement and, thus, considerable uncertainty. Though photoelectric methods are employed in foreign countries they have not been applied so far in India. It was, therefore, thought worth while by the Sugar Sectional Committee of the Indian Standards Institution to examine the possibilities of grading Indian sugar by photoelectric methods and the problem was referred to the National Physical Laboratory. The results of the investigation are given in this paper.

It was found that in foreign countries, apart from visual estimation, there were at least three different methods for evaluating the grades of sugar photoelectrically. At the National Bureau of Standards[1], America, diffuse reflectance from sugar placed at the centre of a hemispherical enclosure, which is uniformly illuminated, is analysed spectrophotometrically. Keane and Brice[2] as well as Gillett and Meads[3], both in America, measured only the reflectance from granulated sugar with photoelectric cells leaving out colour measurements. Another method which is extensively used abroad is the measurement of transmittancy of dissolved sugar.

In the first instance, it was necessary to know the degree of variation of both colour and reflectance among the 15 grades of sugar. For this preliminary work it was not considered worth while to incorporate all the refinements of spectrophotometry and hence in the initial stages observations were taken with a single monochromator. And these were later confirmed by repeating the observations with a double monochromator and a commercial type of photoelectric instrument — Lumetron.

Spectral reflectance of sugar

Spectral reflectance of sugar was measured by means of photoelectric spectrophotometer built round a Hilger constant deviation spectrometer (FIG. 1).

A symmetrical slit (S_1) replaced the eyepiece of the telescope of the spectrometer and a short distance behind this slit was placed a photomultiplier tube (P_c) inside a light-tight housing which was attached to the exit slit (S_2) by means of a demountable coupling. The photomultiplier tube used was I.P. 22 (R.C.A.) and 800 V. was supplied to it from a stabilized electronic power supply similar to that described by Miller *et al.*[4]. The circuit diagram of the power supply is shown in Fig. 2. About 1,000 V. obtained from the secondary of a step-up transformer are subjected to half wave rectification and smoothened as usual. Any variation in the output voltage with respect

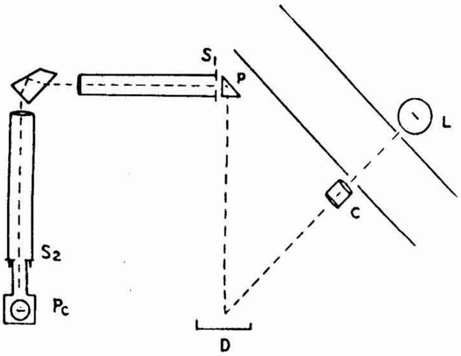

FIG. 1 — SINGLE MONOCHROMATOR: OPTICAL ARRANGEMENT

to the voltage across two VR 105 tubes is amplified with a difference amplifier consisting of two VR 91 tubes and applied to the grid of 807 tube in proper phase which helps in stabilizing the output. The potentiometer P_1 helps to adjust the negative feedback properly.

It was found later that the voltage stabilization was not enough for very accurate work, so dry batteries were used for observations with the double monochromator.

The photoelectric current was measured by a sensitive (500 mm. μA) galvanometer and the maximum current drawn was kept below 0·5 μA so as to avoid fatigue effects of the photo-tube. The width of the exit slit (S_2) of the spectrometer was adjusted to transmit a band 7 mμ wide in the wavelength region of 500 mμ and reflectance measurements were taken at interval of 10 mμ.

Fig. 1 also shows the optical arrangement used for collimating the light reflected from the sugar surface into the spectrophotometer. The sugar was kept in a 9 cm. diam. and 2 cm. deep glass dish, D. Reflection was obtained from the sugar surface flattened and made flush with the edge of the dish by pressing the sugar under a slight rotary motion with a glass plate. An area of about 4 cm. diam. at the centre of the sugar surface was illuminated by a beam of light condensed from the lamp, by the achromatic condenser C. The light beam was incident on the sugar surface at an angle of 45°. The lamp, L, a 500 W. projector lamp, was fed by a constant voltage transformer. Suitable blackened shields were placed to cut off extraneous light from the sugar surface and the spectrophotometer. The dish, D, was placed with the sugar surface horizontal and vertically below the right angle prism P placed immediately in front of the spectrometer slit S_1, so that only the light scattered by the sugar surface in a small solid angle around the direction normal to the surface entered the spectrophotometer after total reflection in the prism P. No difficulty was experienced in preparing the sugar surface so as to get reproducible reflectance values.

The standard surface used was that of fine magnesium oxide (A.R. quality) powder pressed to a flat surface and its reflectance was measured in exactly similar manner as that of sugar. However, magnesium oxide was placed in a silvered watch glass of 7·5 cm. diam. instead of in the larger glass dish.

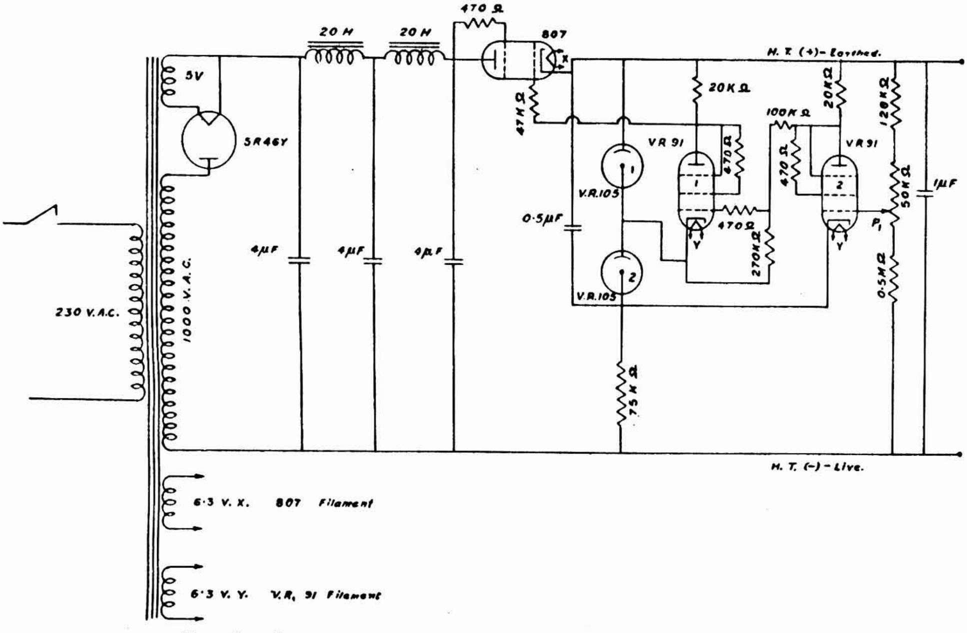

FIG. 2 — STABILIZED POWER SUPPLY FOR THE PHOTOMULTIPLIER

Colour evaluation

In order to express colour on C.I.E. trichromatic system the data required are the values of galvanometer deflections for the sample of sugar and the magnesium oxide at successive wavelengths at intervals of 10 mμ. The ratios of these deflections are multiplied by the energy distribution of the illuminant and the tristimulus values of different colours which correspond to the sensitivity of the eye to these colours. The products are added up, separately for each primary, and each of them is expressed as a fraction of the total. These fractions are the trichromatic coefficients and the coefficient of Y co-ordinate expressed as the percentage is the brightness.

In the present instance the colour co-ordinates have been calculated for the illuminant C and the results are given in Table 1.

When the values of the colour co-ordinates were plotted on the chromaticity diagram it appeared that the degree of variation of colour was rather small for the 15 grades of sugar, though the values of reflectance showed appreciable variation among the 15 grades. For example, the value of reflectance for A27 is 44·6 per cent, while it changes to 52·2 per cent for A28 and 64·0 per cent for A29; thus, there is a measurable variation in reflectance values in the three sugars, which are of the same grain size but differ in whiteness. Similar variation in reflectance is observed among other grades. Bigger grains, however, show greater variation than the smaller grains, as will be obvious by comparing the changes in reflectance values for samples A27, A28 and A29 with those for E27, E28 and E29.

When it became clear from the results obtained with a single monochromator that there was sufficient variation in the 15 grades of sugar in reflectance values, it appeared worth while to check the results with double monochromator, which has a greater accuracy on account of better purity of spectrum. Other refinements were also introduced with a view to greater accuracy.

Measurements with double monochromator

The optical arrangement in the double monochromator will be clear from Fig. 3. General view of the assembly is shown in Figs. 4 and 5.

Light from 500 W. projection lamp is focussed with an achromatic lens on sugar placed in a small dish and the light beam falls at an angle of 45°. Reflected light within a narrow cone round 90° is reflected by a suitable prism on to the entrance slit S_1; the beam is then reflected by the concave mirror M_1 and is then dispersed by a constant deviation prism P_1. The resultant spectrum falls on the concave mirror M_2, from where it falls on slit S_2. The slit S_2 selects a small portion of the spectrum, which then falls on the concave mirror M_3, which reflects it on another constant deviation prism P_2, which further disperses the incident beam. After this dispersion the beam falls on the concave mirror M_4, which reflects it on the final exit slit S_3, where is located the receiving system. By dispersing the light beam twice, the purity of spectrum is improved owing to the diminution of scattered light.

TABLE 1 — MEASUREMENTS WITH SINGLE AND DOUBLE MONOCHROMATORS

SAMPLE	CHROMATICITY CO-ORDINATES			REFLECTANCE %				
	x	y	z	I	II	III	IV	V
A27	0·342	0·354	0·304	44·6	37·0	41·1	41·7	38·6
A28	0·334	0·350	0·316	52·2	46·8	52·8	53·2	50·6
A29	0·308	0·332	0·360	64·0	—	—	—	—
B27	0·339	0·345	0·316	47·5	41·2	44·3	43·1	42·6
B28	0·333	0·343	0·324	56·6	46·9	53·4	50·2	49·5
B29	0·315	0·328	0·357	65·9	55·1	61·7	60·1	59·2
C27	0·340	0·349	0·311	54·0	48·2	50·3	49·2	48·8
C28	0·327	0·335	0·338	58·5	52·6	56·9	54·0	54·1
C29	0·311	0·322	0·367	67 7	57·4	68·0	63·5	65·8
D27	0·336	0·346	0·318	61·3	56·5	61·2	56·8	57·7
D28	0·326	0·336	0·338	64·4	61·5	64·5	61·0	62·4
D29	0·325	0·332	0·342	64·6	61·9	—	—	—
E27	0·335	0·344	0·321	61·3	59·3	62·3	59·3	58·0
E28	0·334	0·345	0·321	64·3	61·5	62·5	59·4	59·5
E29	0·327	0·337	0·336	70·5	68·4	69·6	68·3	68·1

I, single monochromator — 37 wavelengths; II, lumetron; III, double monochromator — 37 wavelengths; IV, double monochromator — 10 wavelengths; V, double monochromator — 10 wavelengths.

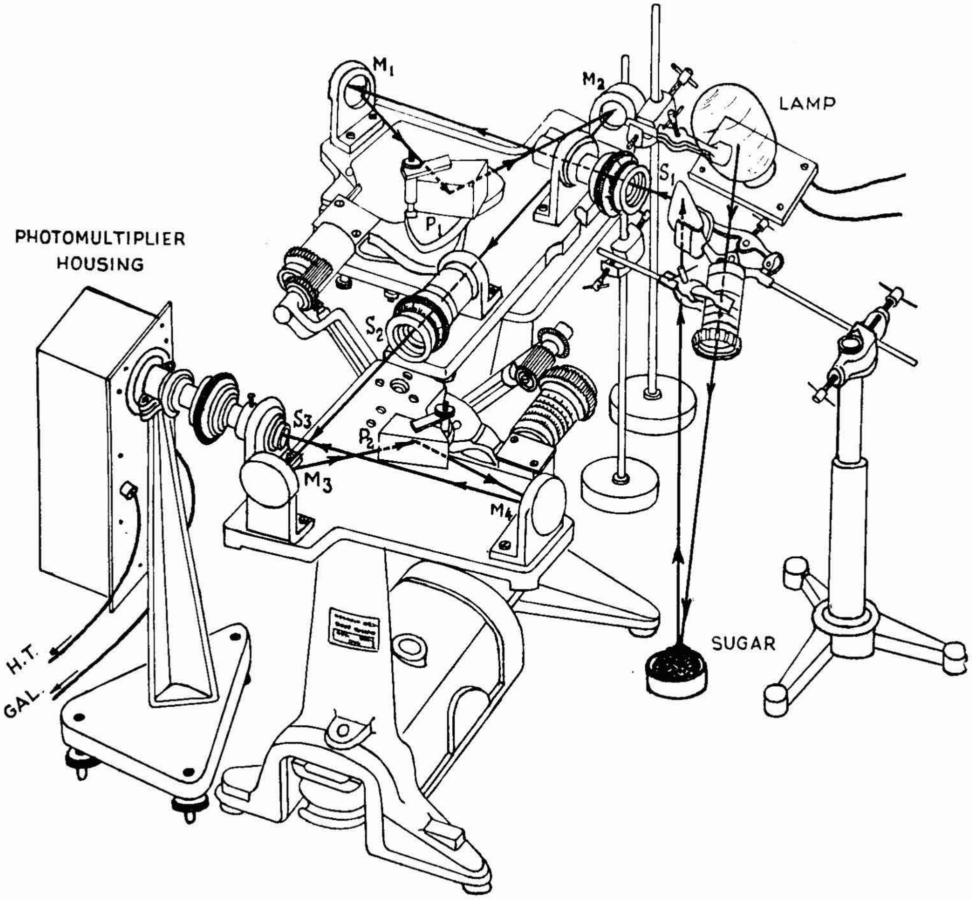

FIG. 3 — DOUBLE MONOCHROMATOR: OPTICAL ARRANGEMENT

Reflectance values

Values of reflectance as obtained with the double monochromator are given in columns III, IV and V in Table 1. The values in the column marked III have been obtained by utilizing 37 wavelengths, while those under IV and V by utilizing 10 wavelengths, a procedure which is generally accepted in colour calculations for economy of labour without sacrifice of much accuracy[5]. The new set of reflectance values confirm the order of variation of reflectance for the 15 grades of sugar as obtained with the use of single monochromator. The values in columns III, IV and V also show the degree of reproducibility which appears to be quite good, considering that frequent handling of sugar in the course of measurements necessarily contaminates the sugar to some extent.

From these observations it appeared that it would be possible to distinguish between the 15 grades of sugar by reflectance values. There are still sources of error in the methods described above; they will have to be eliminated in any standard method.

After it was found that the apparatus built in the laboratory was able to distinguish between 15 grades of sugar by reflectance measurements it was of interest to see if any instrument available commercially could do the same. For this purpose, Lumetron made by Photovolt Corporation, America, was utilized and the

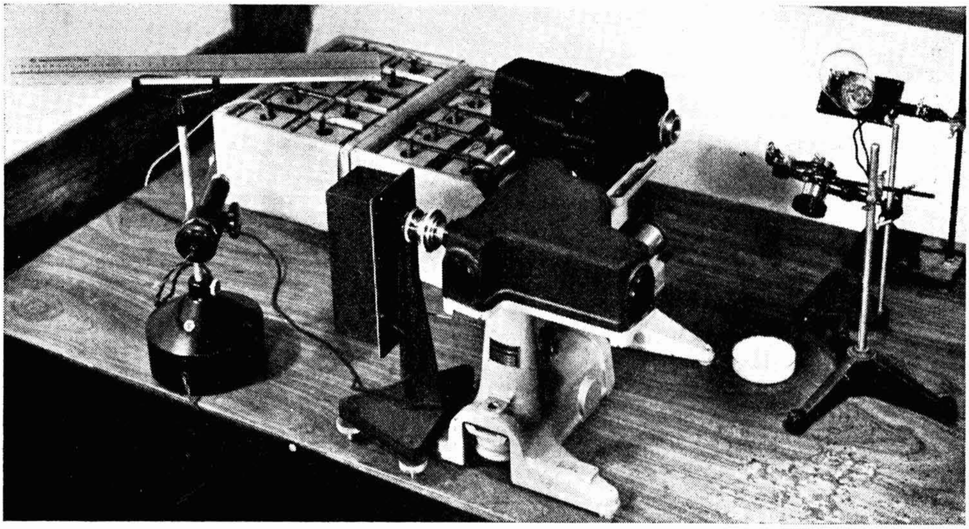

FIG. 4 — DOUBLE MONOCHROMATOR: GENERAL VIEW

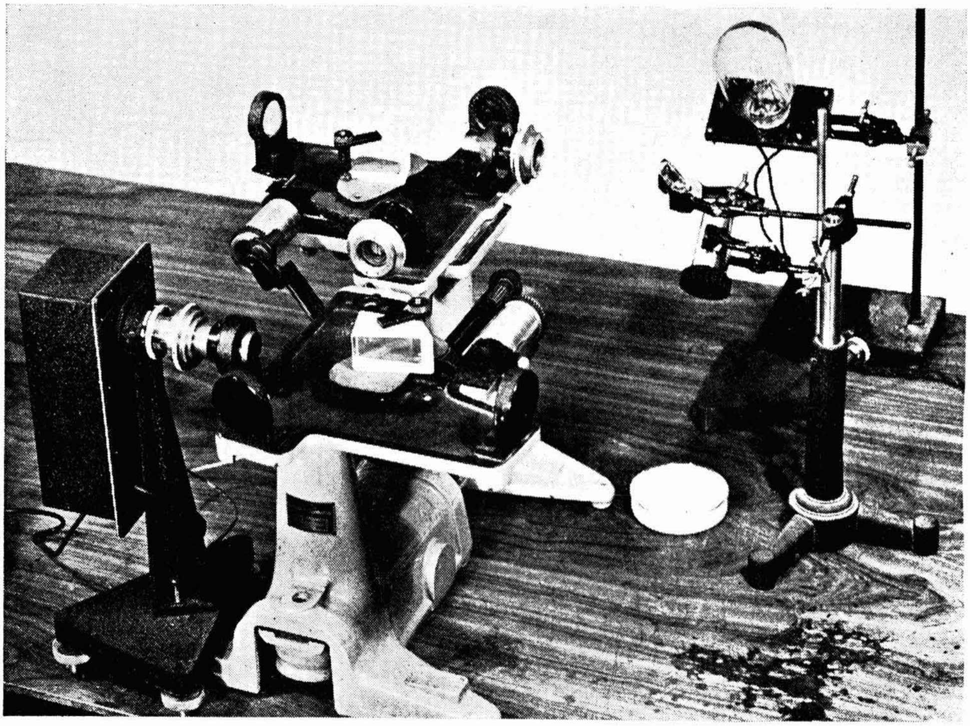

FIG. 5 — DOUBLE MONOCHROMATOR: OPTICAL LAYOUT

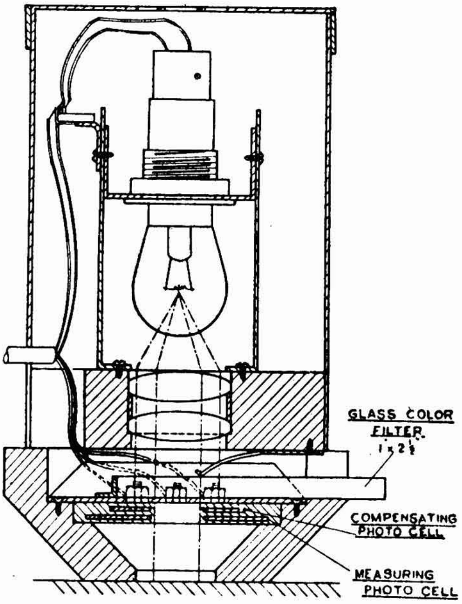

FIG. 6 — LUMETRON: GENERAL VIEW

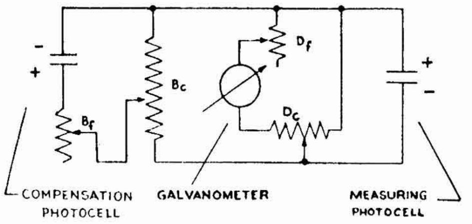

FIG. 7 — LUMETRON: SIMPLIFIED ELECTRIC CIRCUIT

results obtained are given under column II in Table 1.

Measurements with Lumetron

The construction of the Lumetron will be clear from Figs. 6 and 7. There are two photocells of barrier layer type, termed the compensating photocell and measuring photocell. The latter is illuminated with diffuse reflectance from the sample, while light from the source falls directly on the compensating cell. The two photocells are connected in opposition and the difference current is measured with a galvanometer. To give colour values, three filters are provided; from the readings with the green Y filter the reflectance percentage can be calculated.

Reflectance values for the 15 grades of sugar are given in Table 1; colour co-ordinates have not been measured since the instrument did not appear to be accurate enough to differentiate between the colour values of the sugar samples.

Colour specifications

For a commodity like sugar, subjective visual judgement of a customer is the final arbitrator. Photoelectric measurements only attempt to give results with as close a correlation with this visual judgement as is possible. Thus, though depicting the colour point on a chromaticity diagram is of great scientific significance, it depicts little to correlate closely with the visual judgement.

TABLE 2 — MEASUREMENTS WITH DOUBLE MONOCHROMATOR

SUGAR	COLOUR CO-ORDINATES			DOUBLE MONOCHROMATOR, DOMINANT WAVE-LENGTHS mμ	SINGLE MONOCHROMATOR, DOMINANT WAVE-LENGTHS mμ
	x	y	z		
A27	0·342	0·356	0·302	570	575
A28	0·343	0·357	0·300	570	573
A29	—	—	—	—	545
B27	0·329	0·348	0·323	571	578
B28	0·350	0·366	0·384	575	575
B29	0·320	0·336	0·344	568	568
C27	0·341	0·355	0·344	575	576
C28	0·333	0·343	0·324	575	576
C29	0·318	0·336	0·346	566	557
D27	0·337	0·360	0·303	571	575
D28	0·332	0·338	0·330	578	575
D29	—	—	—	—	577
E27	0·340	0·346	0·314	577	576
E28	0·342	0·350	0·308	576	575
E29	0·333	0·336	0·331	580	575
Source C	0·310	0·316	0·374	—	—

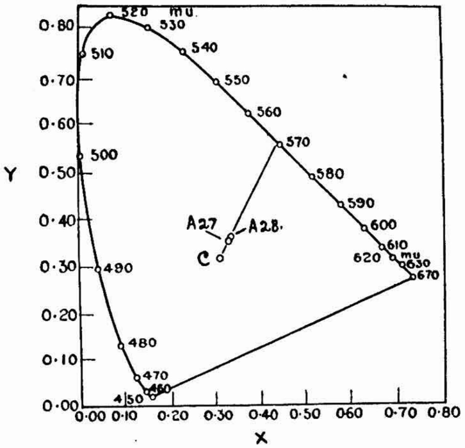

FIG. 8 — CHROMATICITY DIAGRAM WITH DOMINANT WAVELENGTH: SUGAR SAMPLES A27, A28 AND A29

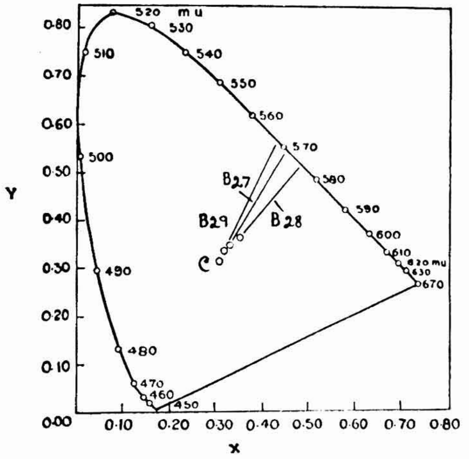

FIG. 9 — CHROMATICITY DIAGRAM WITH DOMINANT WAVELENGTH: SUGAR SAMPLES B27, B28 and B29

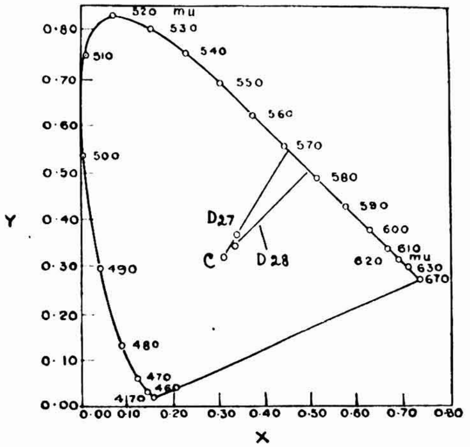

FIG. 11 — CHROMATICITY DIAGRAM WITH DOMINANT WAVELENGTH: SUGAR SAMPLES D27, D28 AND D29

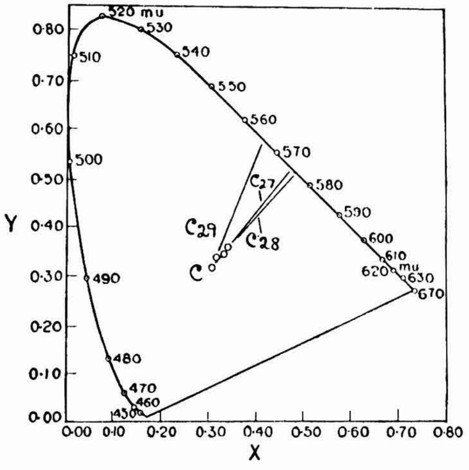

FIG. 10 — CHROMATICITY DIAGRAM WITH DOMINANT WAVELENGTH: SUGAR SAMPLES C27, C28 AND C29

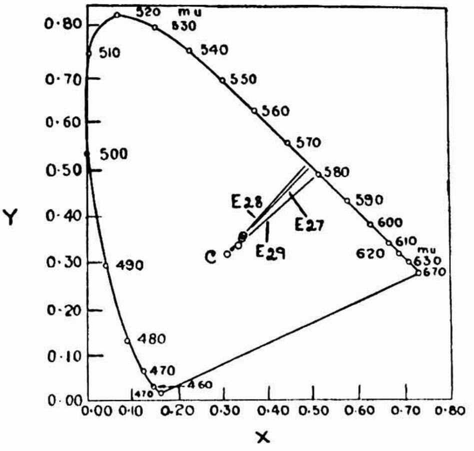

FIG. 12 — CHROMATICITY DIAGRAM WITH DOMINANT WAVELENGTH: SUGAR SAMPLES E27, E28 AND E29

For such purpose, another method is adopted — namely the specification by dominant wavelength. The latter is of course calculated from the tristimulus values, but the representation of colour on the basis of dominant wavelength gives a better correlation with the visual judgement. Dominant wavelengths have, therefore, been calculated for the 15 grades of sugar. For this purpose, observations were taken with the double monochromator and the tristimulus values were calculated using 37 wavelengths (TABLE 2). The dominant wavelengths can be seen from the graphs in Figs. 8-12. For comparison, dominant wavelengths calculated with the use of a single monochromator are also given in Table 2.

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House Construction & Thermal Comfort in the Subtropics

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(*Continued from November* 1954 *issue*)

High ceilings

THE idea that high ceilings contribute towards keeping the houses cool in summer is so widely accepted — even by builders and engineers — that specifications relating to minimum ceiling heights are commonly included in building bye-laws. If this view is correct, we should have some explanation for it which will stand the test of scientific study.

The choice of a method of approach to the study of this problem is not easy. To judge whether houses with high ceilings are cool in summer or not, mainly on facts associated with building practice and experience, is not likely to lead to satisfactory conclusions, particularly when we have to deal with millions of houses and many different ways of building them. A statistical approach to the problem is, therefore, ruled out.

The method of experimentation has also its drawbacks. The direct testing of the thermal effect of high ceilings would involve the comparison of temperature in two houses, one with a low ceiling and the other with a much higher one, but otherwise built in exactly the same way and exposed to exactly the same weather conditions — including solar radiation and wind. Such an experiment would be expensive. To select a suitable pair of test houses from an existing group of houses would be difficult, for floor plans and surroundings are not likely to be identical, and various modifying factors come into play, rendering the conclusions questionable.

A more profitable way of getting at the problem is to list all the reasons commonly put forward for the cooling effect of high ceilings and add to the list other plausible ones, and examine them individually in the light of known physical laws and facts. This method of attack needs less elaborate preparations than those required for other methods and is likely to provide more information.

Using this approach to the problem, we may list the following plausible reasons for the cooling effect of high ceilings and classify them under four general heads: (a) *Air-layer theories* — (1) warm-air-layer theory and (2) humid-air-layer theory; (b) *ceiling radiation theory*; (c) *ventilation theories* — (1) the chimney effect and (2) effect of night breezes at high levels; and (d) *volume theories* — (1) storage of cool night air and (2) slow humidification with large air volumes.

According to the first explanation under (a), if the ceiling is high, the hot air has a good chance to rise to the upper reaches of the room and out of the way of the occupants. Another way of putting it is to say that the air near the ceiling protects the occupants below from the effects of heat. We may call this, in either form, the warm-air-layer theory.

The above theory can be easily tested. Temperature measurements made at different levels in closed rooms of a bungalow in summer show very little difference. If the ceiling is significantly warmer than the rest of the room, there will be a sharp temperature gradient in the air film adjacent to the ceiling. However, observations of near-ceiling temperatures show that the relatively steep temperature gradient in this film lies within 2 or 3 in. of the masonry surface. We are hardly concerned with this almost negligibly thin air film in the present discussions†.

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†The starting of a ceiling fan in a previously undisturbed room can, under favourable circumstances, result in an initial downward gust of sensibly warm air coming from this film. This effect is, of course, transient.

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So far as the great mass of air in the room is concerned, the temperature difference found at different heights is usually of the order of 1°F. — perhaps 2° — under favourable conditions. A large number of such observations made during summer in the rooms of a masonry bungalow indicate that the supposed layer of warm air-layer is largely imaginary*.

The actual air temperature is, of course, not the only factor determining the temperature we *feel* or the " effective temperature " of air. Other factors which come into play are humidity and velocity of air. By means of suitable charts†, the effective temperature of the air can be determined from these three factors. In addition, the net exchange of radiation with the surroundings will affect the effective temperature. The sun, for instance, is a very significant item in the " surroundings " on a clear day out of doors. Clothing affects the effective temperature, but we should note that it is fundamentally an artificial device used to maintain near the skin more desirable air conditions than are provided by the weather.

These considerations lead us to the second air-layer theory. Perhaps the air on the upper reaches of rooms in summer is more humid than it is below. Breathing and perspiration both tend to moisten the air around us, and since moistened air is slightly less dense than dry air, this suggestion is plausible. Tests with a psychrometer, however, indicate no perceptible difference in humidity at different heights in the rooms.

The switching on of a ceiling fan will throw any air-layer theory into serious difficulties, for the effect of the circulation is to mix up the air.

Under (b) we have a popular belief which suggests that warmth received by direct radiation from the ceiling will be reduced if the distance from the ceiling to the occupant is increased. What do physical laws and tests tell us ? The law of radiation within a hollow enclosure shows that no one interior surface such as a ceiling can add to the warmth of a room by radiation unless it is warmer than other interior surfaces. Calculation of the radiant heating effect of a ceiling 9° warmer than the rest of the room, which is a rather large difference in practice, indicates that it is insignificant. For instance, if such a ceiling were 200 sq. ft. in area, and 4 ft. above the head of an occupant and 9° warmer, the net radiation exchange between the ceiling and the occupant would be that of a 550 W. heater at a distance of about 2 ft., radiating equally in all directions.

A simple test with a 550 W. electric flat iron showed that the radiant warmth could not be felt at 2 ft. from its flat surface. Therefore, the effects of direct ceiling radiation need not be taken seriously, and in passing we may further note that the raising of the ceiling by, say, 6 ft. from the usual height would certainly not eliminate this warming effect — negligible as it is.

Some heat is of course transferred from the ceilings of masonry houses to the rooms, but this is mostly by air currents. The small amounts of heat that are transferred by direct radiation are of no practical importance to thermal comfort.

Under (c) we consider how high ceilings effect ventilation in the rooms. The theory of the chimney effect is that, just as a tall factory chimney creates a draft, a tall house should perform similarly and thus be well ventilated, the warm air leaving by ventilators near the roof.

To begin with, let us remember that the draft of the factory chimney requires not only the chimney but also the heated air within it. Without any interior source of heated air in a bungalow in summer, we can hardly expect such a chimney effect. As we have seen, greater changes in day and night temperature are found outside the house rather than inside it. We should, therefore, expect the greatest positive chimney effect well into the night, when the heat of the day has penetrated through the walls and when the outside atmosphere has cooled down to its minimum. During the hottest part of the day, we should expect a reverse or negative chimney effect — the air tending to pour in through the ventilators. However, in view of the relatively mild temperatures we are concerned with, the chimney effect — whether positive or negative — should be far less in bungalows than in a factory chimney.

Tests made on a night following a hot June day (1941) in Lahore were significant. A

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*The author's repeated observations leading to this conclusion are confirmed by those of Mr. Mason Vaugh of the Allahabad Agricultural Institute to whom he is indebted for his interest in this field of investigation.

†*American Society of Heating and Ventilating Engineers' Guide*, 1946, Ch. 12.

simple breeze-measuring instrument was used close to an open ventilator near the roof of one of the bungalows of the Forman Christian College. The doors below were open. It was a calm evening, but now and then there were gentle puffs of breeze to which the instrument responded readily. In contrast, no steady air current arising from the chimney effect was detected. Common experience again verified these findings. On a calm, warm evening one feels no immediate cooling on opening a ventilator high above one's head. However, if there is any breeze blowing, the cooling effect of opening a door or a window for " fresh air " is noticed at once.

Of course the chimney effect exists, and we must not conclude that ventilator openings are of no value. The evidence indicates, however, that drafts arising from this effect in our bungalows in summer are quite insignificant in practice compared to the ventilation provided by natural breeze through well-placed windows of liberal area.

The second ventilation theory is suggested naturally by the conclusions of the first. Should we not expect overnight cooling of the ceilings of a house to be more thorough if these ceilings are high above the ground, where swifter breezes and perhaps cooler temperature prevail?

To verify this theory wall temperatures were measured at three different heights on the shady side of a tall building at sundown, and again early the following morning. From the readings the overnight cooling was determined at three different levels. At a height of 40 ft. there was an overnight temperature drop of 11·7°F., at 22 ft. it was 10·8°F. and at 4 ft. above the ground it was 10·2°F. It is to be noticed that these tests were on an outside wall where exposure to natural breeze was most favourable. Yet for even 36 ft. increase in height, the increase in overnight cooling was only a degree and a half. The corresponding effect indoors for a change in ceiling height from 8 to 16 ft. could be only a fraction of a degree at best. Observations made inside the rooms showed that the differences in overnight cooling at different levels were not great enough to be detected with any certainty. It is, therefore, clear that in practice the benefit of a high ceiling is insignificant compared to the effects of other and more obvious arrangements for good ventilation.

Under (d) we consider the theories which postulate that what we need for comfort in hot weather is a large volume of air. Possibly we do. Just how does large air volume help to keep us cool?

That a large room volume makes possible the storage of a liberal amount of cool air is a popular theory. Admitted at night, this air is supposed to be kept confined for the benefit of the occupants during the hot part of the following day when the house is kept closed.

Let us accept the benefit of overnight ventilation in summer. It is not the air, however, that stores the night coolness. This has been indicated earlier. A little calculation will show that the thermal capacity of a single brick is nearly as much as 100 cu. ft. air. It is the interior masonry which functions basically as the repository of coolness stored by overnight ventilation. In comparison, coolness stored by the confined air is insignificantly small and in the practice this " confining " of the night air is not very effective.

The temperature of air in a closed masonry room is substantially controlled by the thermal capacity of the masonry. If no artificial aids are employed to keep the air warmer or cooler, its temperature will closely approximate that of the walls. Clearly, therefore, the maximum benefits accruing from overnight cooling are to be realized by means of effective ventilation of the interior masonry surfaces of the house and not by making the static air volumes large.

The second volume factor is of interest. If there are occupants in a small closed room, their breathing and perspiration should increase the humidity of the air around them, making them feel progressively warmer as the degree of saturation is increased. Experiments to test this effect were carried out in Lahore in the summer of 1941. In one test, three young men stayed in a small closed room for 20 min. In another, the author sat in a small car with closed windows for 10 min. The results were similar. On closing the doors for the start of the experiment, in each case, the temperature of the confined air rose quickly to that of the enclosure and remained constant thereafter. The relative humidity, however, rose steadily. Dry and wet bulb temperatures were noted at regular intervals on an Assamann psychrometer. From each pair of readings the relative humidity and the effective temperature were ascertained.

The accompanying graphs (FIG. 7) show clearly why small rooms tend to become uncomfortably warm in summer if they are not well ventilated. Evidently, therefore, lack of adequate ventilation is one reason why many conventionally built small rooms tend to become " stuffy " in hot weather. Thus, while these results do emphasize the need for liberal ventilation or change of air for small rooms, they do not indicate any need for large rooms or high ceilings.

It should be pointed out here that the practice of closing up a house during a summer day does not necessarily call for large individual rooms in order to avoid progressive increase in humidity. All that is needed is that the air in the rooms be changed reasonably often, perhaps once an hour. Unless the outisde atmosphere is very stagnant, this rate of air change will usually be provided, especially if there is easy air-communication between rooms within the house by the infiltration of air through the cracks around the outer doors and windows. At the same time such a slow rate of air change will not itself significantly alter the temperature of the walls which have been cooled by overnight ventilation.

Summarizing our findings, we find that of the seven theories discussed, only the last one reveals any space-dimensional factor which is significant in making small rooms uncomfortably warm in summer, and even this one is not necessarily associated with small rooms or rooms with high ceilings. With the evidence we now have, we may conclude that there is no fundamental need of building residences with ceilings more than two or three feet higher than the height of a man. The resulting economy of construction and convenience is obvious.

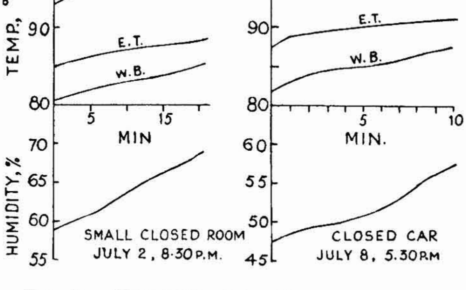

FIG. 7 — HUMIDIFICATION OF CLOSED SPACES

The experience of the author's family living at Lahore in a residence with ceilings not over nine feet high has amply verified this conclusion. True, the lowered ceilings do not directly make the rooms cooler. Nevertheless, liberal facilities for natural ventilation, controllable window shades and liberal shade by neighbouring trees made the house comfortable, both in summer and in winter. This result is fundamentally the outcome of the basic constructional features of the house.

Discussion

In perusing what follows, the reader should keep in mind that the topic of this paper is the bearing, on thermal comfort, of the constructional features of residences, i.e. those features which are a part of the design of the house and those items of basic equipment which do not call for the consumption of fuel or power. At the same time, it is necessary that artificial aids should also be considered. Thus, while the subjects of heating and cooling loads, the methods of dehumidification and other technical aspects of air-conditioning are largely outside the scope of our discussion, consideration will also be given to possibilities of improving comfort by artificial means.

The first important outcome of our study arises ultimately from the climatic and economic conditions discussed earlier. The indication is that, so far as comfort in buildings is concerned, the study of overall and continuous methods of heating and cooling cannot be satisfactorily applied to the problems on hand. This is because continuous heating and cooling methods are based, fundamentally, on the assumption of a steady flow of heat which is not characteristic of masonry residences in the subtropics of Asia. Instead, our study should be based on the principles of varying heat flow, and our emphasis should be on methods of temporary and local heating and cooling — so far as artificial aids are used. That is, the artificial aids used should be "space" heaters or coolers, employed only when and where they are wanted.

The second finding is the need of ample facilities for controlled ventilation, including natural ventilation. This can hardly be overemphasized. The effectiveness of overnight cooling also calls for liberal window areas, particularly near the ceiling levels, so that interior walls and ceilings may be cooled easily by night breeze.

A thickness of 1 ft. or more of masonry is effective in protecting the interior of a house from the extremes of the outdoor diurnal temperature variations, particularly if the house is kept closed. Further, the benefits of overnight cooling, which are due to the storage of " coolness " in the interior of a masonry house, cannot be as effective in the case of houses where light, insulating construction materials are used.

Shading a part of a house will help in keeping that part cool. If a feasible and economical method is available for controlling shade, such a feature of design is highly desirable.

The shading of windows, otherwise exposed to the sun, is to be considered first, for the effect of sunlight is felt most where it enters directly. Shades should be placed outside glazed windows rather than inside. Arrested sunlight produces heat and it is certainly preferable to dissipate this heat in summer outside the windows rather than to the room air within.

In the absence of any heating or cooling system operating nearly continuously, the use of insulating materials on the walls of a masonry house is practically useless. This applies to solid materials as well as to confined air spaces. It is a mistake to think that lightly constructed outer walls, even if made of good insulating material, will " keep out " summer heat. Unless artificial cooling equipment is installed, such a house will not be satisfactory during the hot months in the subtropics.

There is no evidence of any relation between ceiling height and summer coolness for masonry residences. The economics and conveniences which are possible with lowered ceilings and more compact designs are, therefore, developments much to be desired.

Lines of further development

It is evident that increased use of artificial aids for improving thermal comfort can hardly be expected for the masses of India and Pakistan. Even improvements in the constructional features of houses have their limitations in scope, principally on account of the increased costs they are likely to involve. The improvements thought of, therefore, must be applicable in the main to middle-class groups.

One line of development worthy of study for extension and improvement is the cooling of air directly by the evaporation of water. This method of cooling has been discussed earlier. As yet there has been almost no commercial development of cooling units based on this method and designed for private homes in India. In the arid south-western regions of the United States, on the other hand, " desert coolers " have gained considerable acceptance. They have been experimented with at some places in India*.

Another experiment worth mentioning is that of Mr. Abdul Ghafoor, Chief Engineer, Irrigation Branch, P.W.D., Lahore, who successfully used a carefully laid pile of bricks in place of *khus* matting. The bricks laid with their depressions up and with liberal air spaces between the rows, function effectively both as a water absorber and as a storage for the " coolness " resulting from evaporation. Though the ventilating fan is kept running, the wetting of the pile of bricks needs to be done only once or twice a day. For periodic wetting, water from a small tank above the brick pile is distributed evenly by soaking slowly through a porous mat of gravel concrete covering the pile. Each wetting is complete within a few minutes.

The fact that direct cooling by evaporation is gained at the cost of increase in humidity raises the question of the practicability of cooling air indirectly by the evaporation of water. Under favourable conditions the wet-bulb temperature can be many degrees below the dry-bulb temperature. If the heat taken for evaporating water into one air stream can be extracted, through the walls of suitably arranged channels or ducts, from another air stream, then this second air stream would be cooled but not moistened and would presumably be more desirable for the occupant than the first. The principle of this method of cooling a medium is employed in the evaporative condenser, which has enjoyed increasing favour for industrial power plants in the West†. Study and experi-

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*United Christian Schools, Jullundur and also Allahabad Agricultural Institute, Allahabad.

†*American Society of Heating and Ventilating Engineers' Guide*, 1946, pp. 709.

mentation with this method of cooling would be worth undertaking, though it must be remembered that the effectiveness will still be limited by the initial dryness of the atmosphere just as in the case of direct evaporative cooling. The value of non-addition of moisture to the air ultimately used will have to be balanced against the losses involved in the heat transfer between the two air streams and also the increased costs of equipment involved.

A second general line of desirable development is that of improving the facilities for controlled shade. The advantages of "solar house" construction have been discussed earlier and might well be explored further for these regions. However, the limitations mentioned need to be kept in mind, and the substitution of a very large area in glass for a south masonry wall needs to be considered with caution.

Some standardized construction providing adjustable shutters or shades outside windows would be a most desirable development. In the case of the author's experimental residence, the suspension of shutters in the first instance by hinges proved highly unsatisfactory, both on account of the inconvenience of their operation from within the house and also because of the serious damage that was being done to these hinged shutters by sudden dust-storms. Both these difficulties were overcome by operating the shutters on rails as described earlier.

Again, there is need for convenient design and construction of removable roof shading, fulfilling the function of light thatching.

A third direction of development is that of using the heat and cold stored in the earth for the comfort of the residents in a house. The temperature of the earth some 15 or 20 ft. below the ground tends to approximate the all-year mean above quite closely and in large areas of the subtropics this mean is a "comfortable" temperature. In Lahore, for example, it is not far from 76°F. It is possible to use this desirable temperature to make the occupants in a house a little more comfortable during the extremes of summer and winter.

One simple and obvious method of accomplishing this is to build houses 15 or 20 ft. underground where temperatures vary very little throughout the year. It would certainly be worth trying in the subtropics for certain special purposes, such as hospital surgeries, where comfortable and dependable temperatures are important. The local conditions should be favourable for the experiment. In particular, the underground water table should be low enough to be well out of the way.

Another method of using earth-stored heat and coolness is a basic feature of the experimental residence built at the Forman Christian College, Lahore. Outside air is drawn into the windows of the cellar and then down an air-well to an underground tunnel which makes a rectangular circuit of 120 ft. of running length along its centre line, which is about 14 ft. below the surface ground level. It is then drawn up through a central air duct by means of a single fan, and distributed through adjustable grilles, one of which opens to each of the ten rooms of the house. The air paths from tunnel to occupants were made as short as the design would allow, and in order to minimize losses on the way, the ducts were made of wood. The fan is of low power and, following the first finding given in the summary of findings, the system is not expected to be used for more than about two rooms at a time. The earth-tempered air is shut off from unoccupied rooms by damper valves, one located suitably behind each grille, which are ordinarily kept closed.

Exploratory studies and experiments indicated that the benefits of using earth-stored heat and cold would be limited, and the best that could be expected is that the system might obviate the use of ceiling fans. This has substantially turned out to be the result; for, though occasionally the help of a table fan has been found desirable when a group of people is present on a humid summer evening, ceiling fans have not been installed. The earth-cooled air stream has provided reasonable comfort in summer weather. The benefits in winter have been less marked, though the warm air stream has certainly helped to the extent of removing the chill from a room on winter days. It was found desirable to use the only fireplace in the house during the coldest evenings for two to four weeks.

As expected, ventilation with the ground-warmed air in winter called for using the adjustable grilles to direct the air stream away from occupants in a room, whereas summer cooling favoured projecting the stream directly towards the occupants.

Another outcome, not quite expected, was the tendency of cool air to stay down in the tunnel when the fan was not running. This causes no difficulty in summer. In winter, however, a natural circulation results, for the ambient air tends to sink down through any available opening and displaces the warm air in the tunnel, even when the fan is at rest. The result is that the tunnel tends to keep a little cooler than if it were solid earth. Furthermore, the difficulty of keeping warm air down until it is wanted contrasts sharply with the situation in summer when no such difficulty arises. Probably this phenomenon is one reason for the greater success of the system in summer than in winter.

Finally, we may consider a line of development which first interested the great pioneer in thermodynamics, Lord Kelvin, but which has only recently found practical application, and which is as yet not a serious competitor of radiators and fans — the " heat pump ". The heat pump in theory is a special case of the mechanical refrigerator which is, thermodynamically, a heat engine working in reverse. A heat engine takes a quantity of heat (Q_1) from a hot source, converts a part of it into mechanical work (W), and rejects the remainder (Q_2) as unavailable heat energy to the cold (or cooler) sink. The overall efficiency of a heat engine is usually low — ranging from 8 to 30 per cent. The refrigerator, on the other hand, takes heat (Q_2) from a cold region by the assistance of an input of mechanical work (W). This work converted into heat is added to (Q_2) and the total heat (Q_1) delivered to the hot region. In practice, the heat (Q_2) extracted from a cold body represents considerably more energy than the work (W) which transfers it to the hot region. The ratio Q_2/W, called the coefficient of performance (COP) of the refrigerator, is considerably greater than unity. Even commercially, values as high as five or six are quite possible.

It may be shown theoretically that the efficiency of an ideal or " reversible " heat engine is given by $E_{\text{rev.}} = \frac{T_1 - T_2}{T_1}$ which is the same as $\frac{Q_1 - Q_2}{Q_1}$ where Q_1 and Q_2 are the quantities of heat taken from and rejected to the source and sink which are at temperatures T_1 and T_2 respectively. Correspondingly the COP of an ideal refrigerator is given by $\text{COP}_{\text{rev.}} = \frac{T_2}{T_1 - T_2}$ which is the same as $\frac{Q_2}{Q_1 - Q_2}$. Thus a small temperature difference or range of $T_1 - T_2$, which is the basic reason for a low engine efficiency, is also the basis for a high coefficient of performance in a refrigerator. Advantage is taken of this relationship in the heat pump which, working within a comparatively small temperature range, can be used for both summer cooling and winter warming. In summer it "pumps" heat from the inside of the house to the outside and vice versa in winter.

It would seem, therefore, that where only a few degrees of heating or cooling is required, a suitably designed heat pump should call for very little power input. To be specific, if we take as an all-year-mean temperature 75°F. and suppose that the range within which our heat pump is to operate is $\pm 20°$, we find that this range is less than 4 per cent of the absolute temperature, and that the ideal COP would be over 25. It may be worth while to note that since (Q_1) is always greater than (Q_2), the heating (COP) is always greater than the cooling (COP) for the same system operating in the same temperature range. This difference becomes less significant as the operating temperature range is reduced.

We cannot expect a (COP) of anything like 25 in practice, for there are losses due to friction and the presence of heat-transfer temperature differentials. If we designate the extra work done to cover these losses by L, then the actual COP would be given by $\text{COP}_{\text{act.}} = \frac{Q}{W_i + L}$, where Q stands for either Q_1 or Q_2 and W_i the work input required for an ideal heat pump. This may also be written as $\frac{T}{\Delta T - \frac{L}{Q} T}$ where T stands for either T_1 or T_2, according to whether we are heating or cooling the rooms, and ΔT is the operating temperature range. Remembering that the losses always function in such a way as to hinder the operation of the machine, the corresponding actual efficiency of the same apparatus, used as an engine after making necessary mechanical alterations, would be $\text{Eff.}_{\text{act.}} = \frac{\Delta T}{T} - \frac{L}{Q}$.

A reasonable practical assumption is that at least half the input power to the heat pump should be consumed usefully in pumping heat. In such a case the losses L should at most be equal to W_i or $\frac{\Delta T}{T}$ should be at least as much as $\frac{L}{\underset{\sim}{Q}}$. This assumption would call for a heat pump whose actual (COP) would be not less than half the ideal value. If it were operated as a heat engine, its actual efficiency would be almost zero.

This analysis indicates that in order to achieve the most advantageous heat pump, we should try to design and construct a heat engine with the lowest possible Carnot or ideal efficiency. This ideal efficiency depends of course on the operating temperatures only.

A reasonable question for investigation, therefore, presents itself: within how small an operating temperature range ΔT is it possible to make a heat engine which can continue to run itself at an operating speed representing a reasonable requirement ? The desired heat pump should then be such an engine working in reverse.

In Europe and North America, the function of the heat pump has been chiefly that of winter warming, and the overall operating temperature range is much more than 20°. The equipment employed use liquid-vapour refrigerants — " Freon 12 " in particular — and a considerable part of the operating temperature range for the refrigerant must necessarily be assigned to the heat transfer differentials at both the heating and cooling ends of the system.

In large plants, the ready availability of an adequate outside source of heat (or a sink in summer time) has constituted a major problem. Usually well-water is used. In small plants for private homes this problem is apparently less acute, and even collection of heat from the ground around the house has proved quite feasible. The relative cheapness of coal, oil and gas, nevertheless, have discouraged the widespread adoption of the heat pump as a heating device.

Since it is air that we wish to cool or warm, the question arises as to whether or not the use of the room air itself as the " refrigerant " is a practical possibility. Air compression systems have been used to produce ice, but have generally not been as practical or as efficient as vapour compression systems. The large air volumes and the extensive metal-to-air transfer surfaces involved have called for rather bulky equipment.

Theoretically it should be possible to compress room air nearly isentropically, cool it to ground temperature by passing it through a conduit buried in earth, and then in the process of returning it to the room expand it isentropically again, thus cooling it below ground temperature. For winter warming, the compression and expansion would be interchanged, so that the air delivered to the room would be warmer than ground temperature. For the suggested 20°F. or roughly 4 per cent temperature change, these operations would involve approximately a 10 per cent change of density and 14 per cent change of pressure, the latter amounting to about 2 lb./sq. in.

The equipment called for would be a compressor and a slightly lower capacity air motor working together and involving large volumes of air with small pressure differences. How nearly the suggested small temperature range of 20° can be achieved with a self-operating air machine working as an engine is a matter of design and experimentation. Points in favour of an air heat pump are: (1) it is admirably suited to the practice of non-continuous operation, and (2) the losses of cooling range due to heat transfer differentials should be very little indeed — being practically restricted to the transfer, in the conduit, to or from the ground. If such a system could be developed which could run with reasonable economy on the power of a 100 or 150 W. motor, it should be a boon to many homes in the subtropics.

REVIEWS

ROCKET PROPULSION, by Eric Burgess (Chapman & Hall Ltd., London), 1954, pp. 235. Price 21*s*.

This book provides a concise and fascinating account of a very live subject. Almost every aspect of the rocket propulsion has been covered. Most of the unnecessary mathematical and engineering details have been profitably kept to a minimum. The possibility of the application of atomic energy for inter-planetary travel has also been dealt with. There are four useful appendices provided in the book. Of these, the first three give the salient points regarding the internal ballistics of the rocket.

This book will be useful to those who contemplate a serious study of rockets and rocket propulsion.

KARTAR SINGH &
K. R. KARMARKAR

SPOT TESTS, by F. Feigl (Elsevier Publishing Co., Amsterdam; Distributors: Cleaver-Hume Press Ltd., London), 1954, pp. xii + 518. Price 45*s*.

First published in 1931 under the title *Spot Tests*, this book, now in the fourth edition, has expanded into two volumes. The study of intermediate successive editions and of companion volumes dealing with " Specificity, Sensitivity and Selectivity of Reactions " by the same author indicates the tremendous growth the subject has undergone. The author points out in the early chapters of the book that spot reactions are conducted with micro-drops, i.e. in volumes from 0·03 to 0·001 ml. and the identification limit is of the order of 0·2 (dilution limit 1: 250,000). This places in the hand of the analyst an extremely valuable and powerful tool for conducting analysis of a bewildering variety of materials that he is called upon to carry out in the course of his professional work. Feigl has shown that identification and dilution limits obtainable with spot tests are comparable with the classical methods of qualitative microanalysis, e.g. the technique of identification of crystals under the microscope.

A successful spot test technique employs the medium of spot plate or filter paper followed by a series of reactions which may involve masking, adsorption, or catalytic effects. These, if diligently and intelligently carried out, can lead to the indication for absence or presence of a particular ion, which may have to be shifted from amidst a large variety of materials present; some of these may be capable of interfering with the course of the reactions. It is, therefore, necessary to be clear about the physico-chemical processes and theoretical considerations involved. In the present edition, as in the previous editions, the first two chapters have been devoted to the theory and working technique. These chapters also include a description of the range of apparatus (all this can be easily built up in a laboratory), that is usually employed for spot test work. The next two chapters are devoted to the tests for cations and anions. Under each ion, specific methods and limits of identification and theory of the reactions along with possible sources of interference are given. Three further chapters give the tests for free elements, analysis of mixtures by spot tests and application of these reactions to various technical materials. However, the scheme of analysis for alloys and steel evolved by late Dr. B. S. Evans and his colleagues of the British Armament Research Department does not find a mention in the book.

Thus anybody seeking the aid of a suitable technique for analytical problems in hand will receive through this book a clear guidance to avoid the pitfalls. The more enquiring minds will find a fascinating vista in the companion volume *Specific, Sensitive and Selective Reactions* by the same author.

The book is well printed and bound in a flexible and durable cover.

M. R. VERMA

DER ULTRASCHALL UND SEINE ANWENDING IN WISSENSCHAFT UND TECHNIK, by Prof. Ludwig Bergmann (S. Hirzel Verlag, Stuttgart), Sixth Edition, 1954, pp. 1114

The treatise under review is the sixth revised and enlarged edition of Prof. Bergmann's celebrated work on ultrasonics. The previous edition published in 1949 covered 748 pages and incorporated a bibliography of 2322 references. The present work covers 1114 pages and incorporates 5162 references.

The subject of ultrasonics has grown so fast during the last two decades that workers in the field have had to refer to voluminous original references even for ordinary details. This work fulfils the keenly felt need for a comprehensive and up-to-date treatise on the subject. The author has included in the text most of the important advances made in the field of ultrasonics during recent years. The book has been brought up to date (March 1954) by including in the bibliography a list of about 600 papers published during the period the book was under print.

During the past twenty years, Prof. Bergmann, who has himself contributed largely to the subject of ultrasonics, has, through these treatises, raised the subject of ultrasonics from an unknown and obscure position to the present prominent place it occupies.

This book is a treatise of outstanding merit and will be welcomed by research workers in the field. It is also a useful work of general reference since there are several pages devoted to the applications of ultrasonics in several fields, e.g. medicine, agriculture, etc. The book should find a place in the libraries of all research institutions and universities.

S. PARTHASARATHY

ANNUAL REVIEW OF BIOCHEMICAL AND ALLIED RESEARCH IN INDIA, Vol. XXIV for 1953 — Society of Biological Chemists, India (Sheile & Co., Bangalore), 1954, pp. vi + 202. Price Rs. 6

The Society of Biological Chemists, India, has been bringing out a useful publication every year in the form of an annual review. The first issue was brought out in 1930 and consisted of 20 pages only, as compared to the present volume for 1953 which consists of about 200 pages. The present volume comprises 14 chapters, written by specialists in their respective fields, reviewing in a succinct manner the progress of biochemical and allied research in India during 1953 in the domains of microbial, plant, animal and human biology. The work carried out by Indian workers in foreign laboratories is also included in the review.

This volume follows, more or less, in the footsteps of its predecessors, with a few welcome additions like the special reviews on " Chromatography " and " Food Technology ". Notable omissions are the chapters dealing with plant animal pathology and public health aspects of food adulteration and deterioration. It is hoped that the above fields of work (at least their biochemical aspects) would be reviewed in the next volume.

The section on " Vitamins " could usefully be broadened to include work carried out in relation to animal hormones which are assuming increasing importance from day to day. The work relating to plant hormones is already being reviewed in the section on " Plant Physiology ".

Under the section " Food Technology ", a sub-section could be added to deal with the nutritional and biochemical aspects of processed products prepared from oils and fats, by hydrogenation or otherwise. Some scientific work in this line is being carried out at a number of nutrition laboratories in India.

The volume has succeeded in reviewing the work of about 900 Indian authors published in about 1,140 papers, and would doubtless form a useful addition to the reference library of workers in the field both in India and abroad.

C. N. ACHARYA

COTTONSEED AND ITS PRODUCTS (Council of Scientific & Industrial Research, New Delhi), 1954, pp. 64. Price Rs. 2

This booklet brought out by the Vanaspati Research Advisory Committee of the Council of Scientific & Industrial Research reviews the progress made in the utilization of cottonseed during the past fifty years, and gives much valuable information on the use of cottonseed and its products in food technology.

Though India is one of the major cotton growing countries of the world, and her ginning industry produces about one million tons of cottonseed, only 5 per cent of this quantity is being utilized for the production of oil and the rest is used mostly as cattle feed. The target of cotton seed oil production envisaged by the Planning Commission at the end of the first five-year period is 12,500 tons representing about 12·5 per cent of the total estimated capacity of production of 1 lakh tons of cottonseed oil. Scientific and technological information on the utilization of cottonseed is extensive but scattered.

The booklet deals with the role of cottonseed in Indian economy, composition, storage and processing of cottonseed, nutritional aspects of products from cottonseed, refining of cottonseed oil and examination of cottonseed and its edible products. It also contains an appendix giving a list of apparatus, and agents used for the examination of cottonseed and its products, a classified list of manufacturers and of suppliers of equipment for processing cottonseed and list of cottonseed oil mills in the Indian Union.

The publication should prove useful to technologists and research workers interested in the processing and the utilization of oilseeds and oilseed products.

SURVEY OF RESEARCH IN PLASTICS WITH SPECIAL REFERENCE TO THE DEVELOPMENT OF PLASTICS INDUSTRY IN INDIA (Council of Scientific & Industrial Research, New Delhi), 1954, pp. 156. Price Rs. 5

The report compiled under the auspices of the Plastics Research Committee of the Council of Scientific & Industrial Research deals with all the problems of research in the various fields of plastics. It follows, in the main, the method of classification followed in the *Annual Reports on the Progress of Applied Chemistry*. Besides a chapter on fundamentals of high polymers, one chapter is devoted to natural resins and resin-like substances, a second to naturally occurring polymers, such as cellulose and allied products, proteins and casein, and rubber and its derivatives, a third to synthetic polymers built from materials with etheroid unsaturation. Later chapters are devoted to methods of processing, machinery and equipment, auxiliary materials for plastics, raw materials, analysis and testing, education in plastics and plastics industry in India. The report also contains a special appendix devoted to a review of the work done under the Plastics Research Committee during the period 1940-53 and a comprehensive bibliography of the recent books relating to high polymers.

The research problems suggested are grouped under five categories: (1) *Fundamental* — fields of research as may be said to be fundamental in character; (2) *Extension* — fields of research in which some work has been done elsewhere, but which requires adaptation to Indian conditions and raw materials; (3) *Educational* — primarily intended for giving training to student investigators to enable them to understand the basic principles of a given process, and to equip them for guiding industrial development; (4) *Developmental* — fields of investigation in which only the basic principles are known; and (5) *Process* — includes such pilot-plant work as may be required for the industrial development and processes found to be successful on a laboratory scale.

The report is a handy reference volume and should prove useful to the research worker and the technologist engaged in plastics research and development.

PUBLICATIONS RECEIVED

ELSEVIER'S ENCYCLOPAEDIA OF ORGANIC CHEMISTRY — SERIES III — CARBOISOCYCLIC CONDENSED COMPOUNDS, Vol. 12B, Edited by F. Radt (Elsevier's Publishing Co., Amsterdam, London, New York; Distributors: Cleaver-Hume Press Ltd., London), 1954, pp. 4561-4840, price: Single Vol. £10 15*s*. Series Subscriber £9 10*s*. Complete subscriber £ 8 5*s*.

NUCLEAR SPECIES, by H. E. Huntley (Macmillan & Co. Ltd., London), 1954, pp. xix + 193, price 21*s*.

ELECTRONIC MEASURING INSTRUMENTS, by E. H. W. Banner (Chapman & Hall Ltd., London), 1954, pp. xiv + 395, price 45*s*.

MODERN CERAMIC TECHNIQUE APPLICABLE TO INDIAN INDUSTRIES AND OTHER INDUSTRIAL PAPERS, by N. V. Raghunath (The Bangalore Printing & Publishing Co. Ltd., Bangalore), 1953, pp. 65, price Rs. 3/8

GAS DYNAMICS OF THIN BODIES, by F. I. Frankl & E. A. Karpovich (Interscience Publishers Inc., New York; Agents in India: Asia Publishing House, Bombay), 1954, viii + 175, price $ 5.75

Development of Atomic Energy

A TWO-DAY conference on the development of atomic energy for peaceful purposes was inaugurated by the Prime Minister at the National Physical Laboratory, New Delhi, on 26 Nov. 1954. Among those who attended the conference were distinguished scientists, industrialists, ministers and senior officials of the Central Government and two observers from Burma, Dr. F. Ba. Hliand Mr. V. Hli Nyunt.

The subjects discussed at the conference included measurement of nuclear data, choice and design of atomic reactors, instrumentation for reactor control, extraction of uranium and thorium, and role of chemistry and metallurgy in atomic energy.

In his inaugural address, the Prime Minister expressed the view that development of atomic energy even for peaceful purposes should be the exclusive responsibility of the State not only because of the dangerous character of the work but also on account of the high costs involved in it. There were two aspects of the problem: technological and scientific. While the State would undertake the development of technology, the study of nuclear science and basic research in the subject should form part of the curricula of studies of the Indian universities.

India's plan for the development of atomic energy was outlined by Dr. H. J. Bhabha. The plan, directed at harnessing atomic energy for the generation of power, is based on the utilization of thorium, of which India has the world's largest deposits, as the ultimate source. The rate at which this can be done depends, however, on the answers to several technological problems, some of which are known and some yet to be obtained.

Heavy water is an essential part of an atomic energy programme and any country which desires to become self-sufficient must make provision for manufacturing it. Dr. Bhabha disclosed that Government had decided to set up a fertilizer cum heavy water plant in the Bhakra Nangal area where large amounts of cheaper power will be available, and where there is an adequate supply of cooling water. The plant will produce some 250,000 tons per annum of fertilizer in the shape of nitro-limestone and from 5 to 6 tons of heavy water per annum.

The basic raw materials required for atomic energy production are minerals and ores containing uranium, thorium, beryllium, lithium and zirconium. There are besides, a number of accessory natural mineral substances required for production and utilization of atomic power. The papers read at the conference revealed that India's resources in zirconium and lithium are ample while in respect of beryllium, the Archaean crystalline rocks of India carry this mineral in quantity sufficient to last for many years. The demand for beryl, both for commercial and strategic purposes, is growing and fresh deposits are being discovered, but India is likely to preserve its lead as one of the world's most important producers. Monazite, which occurs in the black sand deposits of Malabar and Madras coasts, is the principal ore for thorium metal. The monazite at Travancore constitutes the largest single deposit of thorium in the world. Revised quantitative estimates of India's resources in monazite are being made.

The papers dealing with the part played by chemistry in the atomic energy programme emphasized considerable research work on developing methods for extraction of uranium, the only naturally occurring fuel, from very low-grade ores which occur in India. Since thermal reactors require the fuel, the moderator and the reflector in a high state of purity, work must be done on preparation of materials of high purity, and also on methods for rapid and accurate estimation of small traces of impurities. In order that a self-sustaining chain reactor may function, it is necessary to remove products produced as a result of fission, recirculate uranium and isolate plutonium produced. The chemist must provide suitable processes for the efficient separations involved. In order that cheap atomic power becomes possible the chemist must also provide cheaper methods of producing the pure fuel and of recirculating it. Thorium is also of importance because it can breed nuclear fuel and problems similar to those for uranium must be tackled for this element as well. The chemist must also study the effects of radiation and the chemical and structural changes it brings about.

In the field of metallurgy, the problems requiring immediate attention are improvement of the existing metallurgical processes for uranium and thorium, development of raw materials and devising suitable methods for fabrication. Fundamental work will also have to be done in subjects such as diffusion, alloy formation, power metallurgy, etc. Though in the initial stages of development the aim would be to make the reactor elements in as short a time as possible, at a later stage, emphasis would be on improving the existing processes from the point of view of cost and efficiency.

Preservation of Fruits & Vegetables — A Symposium

SIXTY-SEVEN papers dealing with problems of the fruit and vegetable preservation industry were read and discussed at a two-day symposium inaugurated by Dr. S. S. Bhatnagar at the Central Food Technological Research Institute, Mysore, on 4 Oct. 1954. Over a hundred delegates representing the fruit and vegetable preservation industry and allied industries, Government departments and research institutions from all over India participitated in the symposium.

The proceedings were conducted under the following 11 sections: (1) Raw materials including minor fruits and vegetables, their survey, quality, etc.; (2) Advancement in scientific and technical knowledge of the Indian fruit and vegetable preservation industry; (3) Quality control of manufacturing processes; (4) Sanitation and microbiological problems in relation to the quality and shelf-life of processed fruit and vegetable products; (5) Additives and preservatives; (6) Nutritive value of preserved products; (7) Application of refrigerated storage of fruits and vegetables for the benefit of the preservation industry; (8) Containers for fruit and vegetable products; (9) Plant and equipment in the processing of fruits and vegetables; (10) Technical information service and publicity for the Indian fruit and vegetable preservation industry; and (11) General.

To provide the industry with improved varieties of fruits and vegetables throughout the year, systematic research work on horticulture was emphasized. Such work should be undertaken by horticulturists and food technologists under the joint auspices of the Indian Council of Agricultural Research and the Council of Scientific & Industrial Research.

Papers dealing with recent advances in India in fruit and vegetable preservation dealt with such developments as pre-cooked and dehydrated soup powders, utilization of cashew apples, preservation of dried fruits and vegetables, technology of fruit wines, ciders, beers and liquors, brining and pickling of fruits and vegetables, canning of baked beans in tomato sauce, pectin jelly powders, etc.

A vegetable soup powder which can be readily dehydrated in boiling water has been developed using a combination of ingredients such as tomato, potato, peas, starch, onions, sugar, salt and spices. Soup powders containing 5-10 per cent hydrogenated fat have been found to be more palatable than those made without added fat. The fat used was stabilized by the addition of butylated hydroxy anisole (BHA). Soup powders keep well for a year under ordinary conditions of storage.

Cashew apples are an important byproduct of the cashew-nut industry in India. The fruits do not, however, find any important industrial use at present. They are not used for table purposes because of their highly astringent and acrid taste. Nevertheless, they are very juicy and rich in sugar and vitamin C. Recent investigations at the Central Food Technological Research Institute have resulted in the development of palatable products such as cashew-apple juice, syrup, candy, chutney, jam canned fruit in syrup, curried vegetable, and pickles. Suitable methods of brining different materials like mangoes, bitter gourd, raw papaya, karonda, amla, onion, cabbage, carrots and Indian hog plums have been developed. A solution containing salt, turmeric powder and acetic acid gives better curing and longer storage life.

The canning of baked beans in tomato sauce, with or without meat, is a very important industry in the U.S.A., Canada and several European countries. Special varieties of bean like the Canadian pea bean, the European pearl bean and the Japanese Ohtenashi bean are used for this purpose. In the course of an investigation at the C.F.T.R.I., a local red variety of field bean (*Dolichos lablab*), grown over large areas in Mysore State and the Deccan, has been found suitable for canning as baked beans in tomato sauce. This bean has, however, a slightly bitter beany flavour, the removal of which requires extra care. Search for other types of beans suited for the purpose has shown that a variety of fresh bean from Kashmir known as "earliest of all" gives excellent results. The canned product is free from any bitter or beany flavour and compares well with products imported from abroad. Attempts are being made to grow this variety of bean to help in the development of the canning of baked beans in tomato sauce.

Investigations conducted at the Punjab Agricultural College & Research Institute, Lyallpur (Pakistan), on the pectin content of fruits have shown Valencia Late sweet orange, King mandarin, Thompson grape-fruit, Meyer lemon and Galgal (*Circus limonia* Osbeck) to have the pectin content. Pectin derived from citrus fruits has proved a good substitute for gelatin for use in jelly crystals. Recipes for a number of products, such as high-solids jelly powders, 15 per cent sugar jelly powders, non-sugar jelly powders, etc., have been standardized.

Studies on micro-organisms causing spoilage of canned products have resulted in the isolation of the following strains: *Bacillus cereus* var. *mycoides* and *Microcus candidus* from potato; *Bacterium Zopfi* and Zenkeri from beet; *Alacligenes viscous* and *Alacligenes marsheltie* from carrot; *Aerobacter cloacae* from *patal* and squash; and corynebacterium helvolum from radish. A heat-resistant strain of *Bacillus coagulans* was isolated from spoiled cans of cauliflower. The organism grows in salt concentrations up to 6 per cent and in sucrose concentrations up to 60 per cent, and can withstand 110 min. heating at 100°C. Besides, strains of *Bacillus subtilis* and *Bacillus polymyxa* have been isolated from cauliflower and peas respectively. A correlation observed between maximum growth temperature and thermal resistance suggests the probable existence of even more resistant strains among the facultative and obligatory thermophiles.

Many of the common fruits and vegetables cannot be grown without the use of insecticides. Insecticides that are being used at present, persist as residues, even after the fruits and vegetables are washed and cooked. It was pointed out that the indiscriminate use of DDT on potatoes and other fruits and vegetables is likely to affect the health of the consumers. There is need, therefore, for vigilance on the part of the manufacturers. Methods to detect contamination by injurious insecticides have been developed at the C.F.T.R.I.

Additives have been looked upon as food adjuncts or accessories having but a meagre role in nutrition and useful only in flavouring otherwise bland foods. Recent studies have, however, shown their importance in nutrition and their effect on digestion.

Saffron, nutmeg and asafoetida, used in Indian homes as flavouring agents, were tested by specially designed methods. Whereas saffron and nutmeg have been found to prolong the generation time of some spore-forming bacteria, asafoetida does not appear to possess any " preservative " action. Saffron activates pancreatic amylase in its digestion of starch but its effect on proteolytic and lipolytic enzymes is negligible. Nutmeg has been proved to be generally depressing whereas asafoetida does not appear to exert much influence on digestive enzymes.

A stable vitamin C concentrate has been prepared from the juice of amla (*Emblica officinalis*) by spray drying juice containing 20-25 per cent sodium chloride. The product does not absorb moisture when exposed and is fairly stable, the loss in vitamin C after 6 months storage being only 20-25 per cent.

Fortification of fruit juice beverages with synthetic ascorbic acid not only improves their nutritional value but also helps in the case of some juices like those of grape and apple, better retention of colour and flavour and vitamin. Work at the C.F.T.R.I. on the fortification of jack-fruit squash has shown that the temperature of storage is an important factor influencing the retention of ascorbic acid. At a fortification level of 50-150 mg., per 100 g. the percentage retention, during a storage period of 57-60 weeks, was 50-75 per cent at room temperature, 6-13 per cent at 37°C. and 88-98 per cent at 2°-5°C. The retention is higher in the case of samples preserved with SO_2 as compared to those preserved with sodium benzoate. The apparent ascorbic acid content in squash stored at room 'temperature and at 2°-5°C. was 5·5-12·2 per cent and 3·6-11·9 per cent respectively. Addition of 100-150 mg. of ascorbic acid per 100 g. of squash is recommended for jack squash.

Studies have been conducted at the Institute of Science, Bombay, on two commercially important varieties of mangoes, *Badami* and *Raspuri*, to determine the influence of canning operations on the overall nutritive value. The samples were analysed for carotene, ascorbic acid, proteins, acidity, sugars (reducing, non-reducing and total), ash, calcium, iron and phosphorus. The retention of carotene and ascorbic acid has been found to be excellent, while in the case of other nutrients no material change has been noticed.

Refrigerated storage of fruits and vegetables and problems dealing with their refrigerated transport were discussed in several papers. Although much data has been collected on the cold storage behaviour of several varieties of fruits and vegetables, information on potential market life is not readily available. Quick freezing of fruits has been found to yield relatively more juice. Studies carried out with amla, mangoes, cashew-apple, lemon and oranges have shown that 14-20 per cent more juice can be obtained by quick freezing these fruits at −20°F.

The problem of evaporator design was discussed in relation to the need for the most economical units for production of particular kinds of products. At present, evaporator improvement is particularly directed at economies in manufacture and operation. It was pointed out that although evaporation forms the most important operation in the production of fruit juice concentrates, the evaporator must be considered in relation to the complete process. The tremendous strides made in controlling processes have invariably had a bearing on evaporator design. But, the production generally envisaged in India is far below what is usually considered an " economic operation " in America and Europe.

In addition to chemical and biological factors, the method of drying adopted and the type of dryers used affect the quality of the dehydrated product and economies of operation. The selection of dryers depends on the maintenance of the most suitable conditions of drying for the material handled and also on the scale of operations. There have been improvements in the design of dryers to secure economies in drying cost. These, however, are mostly manufactured for outputs which it is not always possible to obtain in widely scattered localities in India. Tunnel drying has been the usual practice and some improvements have been effected in the design of dryers for this purpose. The use of modern turbo-dryers presents great advantages in economy and quality of production though not in initial cost. The design and construction of modern types of dehydrators with a wider range of flexibility and with a lower output for economic operation, to suit Indian requirements, was stressed.

High production costs and low profits have been the main problems of the fruit and vegetable preservation industry. Several suggestions were put forward for the extension of fruit and vegetable preservation in India and to place the industry on a sound footing. These include: (1) creation of a development fund by levy of a cess; (2) setting up of a development board to administer this fund for effective advancement of the industry; (3) import of duty-free machinery, tinplate and other requirements of the industry; (4) exemption from sales tax for a period of five years; (5) availability of sugar at world market rates; (6) improvement of conditions of rail transport and concessions in freight charges; and (7) inducing the army and the canteen stores to purchase indigenous products.

NOTES & NEWS

Coal-tar oil as denaturant for power alcohol

THE MAIN CONDITIONS WHICH A denaturant should fulfil for use in power alcohol are: (1) It should be soluble in alcohol and petrol; (2) impart a taste and smell which are sufficiently disagreeable to render alcohol unfit for drinking even on dilution and flavouring; (3) should be easily detected; (4) should not be highly poisonous; (5) it should be of indigenous origin, cheap and available in sufficient quantity; (6) it should not corrode metals during storage of power alcohol in metal containers and its products of combustion should not be corrosive; and (7) it should not be easy to separate it from alcohol.

No denaturant satisfies all the above conditions. Different substances have been used as denaturants for alcohol. In Bihar and U.P., kerosene oil (1 per cent v/v) is employed. But it is not quite satisfactory. Coal-tar oil is being employed in France and Australia for denaturing alcohol but details as to its suitability and the amount required for denaturation are not known. It was, therefore, considered of interest to see if distillates from Indian coal-tar can be used for the purpose.

A sample of light creosote oil obtained from Messrs Shalimar Tar Products Ltd., Lodna, Bihar, was used in these studies. The oil was made neutral by repeated washing with 10 per cent (w/w) caustic soda solution and distilled. Four fractions, i.e. distilling between 165° and 230°, 230° and 270°, 270° and 300° and 300° and 330°C., were collected. Different proportions of these fractions, varying from 0·1 to 2 per cent (v/v), were dissolved in alcohol and the solutions examined for colour, turbidity and smell. The denatured alcohol was distilled till 50 per cent of the amount taken distilled over and the distillate examined as before.

These tests showed that the optimum amount of any of the fractions to be used for effectively denaturing alcohol was 0·3 per cent (v/v). At this level, the denaturant imparts a distinct yellow colour and sufficient disagreeable smell to alcohol which on dilution becomes turbid. It is difficult to remove tar oil by distilling denatured alcohol as the disagreeable smell persists in the distillate. The distillate also turns turbid on dilution. The presence of denaturant can be easily detected by the violet colour of the solution when a few drops of concentrated nitric acid are added to a small amount of denatured alcohol.

Since the denaturant is used in power alcohol, it is advisable to use the lower boiling fraction of neutral creosote oil, i.e. the fraction distilling between 165° and 230°C. As kerosene with a boiling range up to 280°C. is employed, tar oil fractions distilling up to 280°C. may be employed.

The various coal-tar oil distillate fractions are being examined for their sulphur content. The maximum permissible amount of sulphur in gasoline and motor spirit, according to U.S. Government specifications, is 0·1 per cent. In Bihar, petrol and power alcohol are mixed in the proportion of 80:20. If the percentage of denaturant used is 0·3-0·5 per cent on the weight of alcohol, the sulphur content of the fuel may be within the permissible limits.

The author is thankful to Dr. K. R. Krishnaswamy, formerly Director of Industries, Bihar, for suggesting the problem and for his interest in the work.— S. M. PRASAD, *Provincial Industrial Research Laboratory, Patna University, Patna.*

Durability of sandstone

INDIA HAS LARGE RESERVES OF sandstone and in localities it occurs, it is preferred to bricks in building construction on account of its cheapness, comparative strength and stability, and attractive appearance. The output of sandstone in the country rose from 232,445 tons valued at Rs. 899,028 in 1939 to 350,477 tons worth Rs. 4,466,668 in 1951, but there is still scope to develop this building material and increase its utilization.

A knowledge of the durability of sandstone is important in the design, construction and maintenance of buildings built with them. Sandstone is porous, and as a result of repeated soaking and drying, absorbs salts from soil, mortar, backing material and other sources which get crystallized in the pores. This is accompanied by volume changes in the stone, and if the cementing material is weak, these changes cause disintegration of the stone.

The Central Building Research Institute, Roorkee, is at present engaged in formulating tests for evaluating the durability of sandstone. The investigation includes the determination of chemical composition, bulk density, porosity, water absorption and saturation coefficient, and crystallization of soluble salts. The crystallization test affords a useful means of differentiating between good, moderate and poor quality sandstone and reveals potential sources of weakness.

A systematic study of the various properties of sandstone, i.e. resistance to weathering, strength, durability, etc., will help in increasing its use for building purposes and relieve to some extent the scarcity of traditional building materials such as brick and concrete.— N. K. PATWARDHAN & C. A. TANEJA, *Central Building Research Institute, Roorkee.*

New nuclear particles

TWO FUNDAMENTAL DISCOVERIES in nuclear physics have been reported recently — one by Marcel Schein of the Chicago University, the other by Dr. G. S. Shrikantia from the Sydney University. Prof. Schein's discovery relates to the anti-proton, the existence of which was predicted by Dr. Enrico Fermi. The new event was recorded in a special film pack carried in a " Skyhook balloon " to an altitude of 101,000 ft. A cosmic particle struck a proton in the aluminium covering the film pack. The picture that resulted shows a cascade of very narrow V-shaped streaks of paired electrons, positive and negative, travelling away from the collision. Since no charged particles were observed, Prof. Schein assumes that it is due to an annihilation process of an anti-proton from the outer space. The energy of the new particle has been calculated to be at least 10^{15} to 10^{16} ev.

Working with plates also exposed to cosmic radiation, Dr. Shrikantia found a track which indicates a new type of meson or meson decay. A charged heavy meson resting in the photo emulsion was found to decay into three charged particles, of which no more than one can be a light meson. One plausible interpretation of the nature of the decay is via a two-stage process: the charged heavy meson decays into two light mesons, one of which is neutral. The neutral light meson then decays into two electrons and a gamma ray which escapes detection [*Chem. Engng. News*, **32** (1954), 3045].

Synthesis of puromycin

TOTAL SYNTHESIS OF THE ANTIbiotic puromycin has been achieved by research workers at the Lederle Laboratories, U.S.A. Crude methyl D-xylofuranoside reacts with acetone in the presence of copper sulphate and sulphuric acid to give a readily separable mixture of methyl 3, 5-*O*-iso-propylidene-α-D-xylofuranoside and its β-anomer. Each anomer is then used separately in the synthesis until *O*-methyl is removed. 2-*O*-Mesylation, deacetonation in acetic acid, and oxide formation with sodium methoxide give methyl 2, 3 - anhydro - D - xylofuranoside. Treatment with ammonia at 100°C. causes ring opening of the anhydro sugar, with Walden inversion. The product is methyl 3-amino-3-deoxy-D-arabinofuranoside, isolated as the crystalline *N*-isopropylidene derivative.

Acetylation with acetic anhydride forms methyl 3-acetoamino-3 - deoxy - D - arabinofuranoside; mesyl chloride in pyridine gives methyl 2, 5-di-*O*-mesyl-3-acetamino-3-deoxy-D-arabinofuranoside. Sodium acetate in boiling 95 per cent methyl cellosolve displaces the 2-mesylate with the neighbouring 3-acetamino group (with inversion) and the 5-mesylate by acetate.

Acetylation isolates methyl 2, 5 - di - *O* - acetyl - 3 - acetamino- 3-deoxy-D-ribofuranoside. *O*-Deacetylation of either anomer of this latter compound, *O*-benzoylation, and the removal of *O*-methyl group give 2, 5-di-*O*-benzoyl-3-acetamino-3-deoxy-α-D-ribofuranose. This compound, when acetylated with acetic anhydride-pyridine, gives an anomeric mixture of 1-*O*-acetyl-2, 5-di-*O*-benzoylacetamino-3-deoxy-D-ribofuranosides.

When this anomeric mixture is combined with titanium tetrachloride, the chloromercury derivative of 2-methyl-mercapto-6-dimethylaminopurine and ethylene dichloride in a 20-hr. reflux, a crude nucleoside is obtained. Raney nickel desulphurization and *O*-debenzoylation give a compound which is identical in all respects with the *N*-acetyl derivative of 6-dimethylamino-9-(3′-amino-3′-deoxy-β-ribofuranosyl)-purine which can be easily converted to puromycin [*Chem. Engng. News*, **32** (1954), 3259].

Magnesium from sea water

A NEW PROCESS BASED ON ION exchange for extracting magnesium from sea water has been patented (*U.S. Pat.* 2,671,714). The resin which is used in a granular form is a sulphonated copolymer of styrene, ar-ethylvinylbenzene and divinylbenzene. In the first of the two exchange columns sea water enters at the bottom; in the second column a regenerant solution of over 10 per cent sodium ion concentration and 0·007 per cent magnesium concentration (sp. gr. 1·192) also enters at the bottom. The resin is continuously circulated in both columns. In the first, the sea water by cation exchange is depleted of magnesium ions, and the resin from this column is picked up in a fresh water jet and sent to the top of the second column, where it falls by gravity. In this column dilution of the ultimate product is controlled by spaced electrodes, a difference in electrical resistance between water and the product solution enabling the interface between the two liquid layers to be controlled. The magnesium removed from the sea water is steadily transferred to the second solution until it reaches a concentration of 2·7 per cent, a forty-fold concentration from the initial level of 0·0685 per cent [*Chem. Age*, **71** (1954), 165].

Synergist action

IN A STUDY ON THE RELATION OF synergists to antioxidants in fats, it was observed that citric and ascorbic acids substantially delayed the rate of peroxide accumulation during the induction period of lard which contained prooxidant levels of α-tocopherol or N.D.G.A. While low levels (0·025 per cent) of both acids showed effective synergistic action with α-tocopherol, higher levels were proportionately less effective. Neither citric nor ascorbic acid showed any substantial effect on peroxide development when added to lard alone. Tocopherol was found to have a markedly protective effect on ascorbic acid, its oxidation being substantially reduced in the presence of tocopherol.

On the basis of the present study and previous evidence, a theory has been postulated regarding the mechanism of synergist action. A reduced form of free radical formed by, but not destructive of, tocopherol probably would change rapidly in contact with air to forms destructive of the antioxidant and synergist alike. Only an inhibitor for the catalysis of peroxide decomposition would save the antioxidant from indirect self-destruction in a system involving chain reactions. It is presumed that the real function of synergist is that of an inhibitor in the decomposition of peroxides induced by the antioxidant [*J. Amer. Oil Chem. Soc.*, **31** (1954), 321].

Effectiveness of insecticides

PRELIMINARY STUDIES BY THE United States Department of Agriculture have shown that addition of chemical extenders to some insecticide sprays increases the time they remain lethal against insects. Applied as an oil-base spray, DDT does not form long-lasting residues on foliage because the oil penetrates into the leaf. However, when a highly volatile solvent such as methyl ethyl ketone is used instead of oil, it quickly vaporizes when sprayed, leaving a residue of DDT on foliage surfaces. In comparative tests, a DDT-oil solution sprayed on foliage of spruce and pine trees was effective against flies for less than 15 days, while it was more than 60 days for methyl ethyl ketone sprays. With relatively volatile aldrin and lindane, improvement was effected by the addition of non-volatile solvents like chlorinated terphenyls. In this case effectiveness was prolonged from 10 days to more than 100 days [*Chem. Engng. News*, **32** (1954), 3259].

Anti-tubercular compounds

ABOUT 50 ETHYLMERCAPTO COMpounds have been found to afford protection to mice infected with human type tuberculosis, when 0·2 per cent or less is added to their diet. One of them — S-ethylcysteine (L and DL) — is at least as effective as pyrazinamide and several times more effective than *p*-aminosalicylic acid. Another, S-ethyl-L-cysteine, was equally effective against isoniazid-resistant strains. Some may be used to enhance the activity of isoniazid or streptomycin. Clinical tests are now under way to determine their value in treatment of human tuberculosis.

The present study grew out of the observation that growth of certain nitrifying bacteria was inhibited by several alkylmercapto acids. A systematic investigation has also been undertaken of the relationship of structure to *in vitro* anti-tuberculosis activity of derivatives of β-ethylmercaptopropionic acid. Substitution of various terminal alkyl groups (methyl through octadecyl) on the sulphur atom gives activity only with the C_2H_5 homologue. Varying the distance between sulphur and carboxyl to give mercaptoacetic through mercaptovaleric acids indicates that the β-relationship between sulphur and carboxyl is essential. Replacing carboxyl by $-CH_2OH$, -CHO, -COOR does not destroy activity. In general, structural modifications which decreased the tendency for cleavage of the C_2H_5-S-R homologue decreased anti-tuberculosis activity [*Chem. Engng. News*, **32** (1954), 2964].

Maintenance of cultures by freeze drying

A DISCUSSION ON THE MAINTENANCE of Cultures by Freeze Drying was arranged in London in September 1953 by the Permanent Committee of the British Commonwealth Collections of Micro-organisms. In some respects the discussion formed a natural sequence to the symposium on " Freezing and Drying " arranged in 1951 by the Institute of Biology. Papers presented before the meeting together with a full record of the discussion have been published (H.M.S.O., London, 1954, price 5*s*.). The papers submitted included: (1) Maintenance of Cultures in U.K.; (2) Outline of Drying Method Used in the National Collection of Type Cultures (1950-53); (3) Notes on the Freeze Drying of *Brucella abortus* S. 19 Vaccine; (4) Concentration Effects during Freeze Drying of Suspensions containing Phenol; and (5) The Determination of Moisture in Culture.

The discussion centred round a number of problems relating to freeze drying. Beginning with the designers problem, the subjects covered included: Effect of culture age and growth medium on the material to be dried; effect of the drying process on viability; effect of the suspending fluid on viability; effect of drying on the organism; survival of organisms in the dried state; conditions of storage; moisture content and its measurement; and effect of moisture content on viability.

The young cultures are more susceptible to drying than the older ones and all available evidence suggests that organisms in the stationary and decline phases are much less susceptible to chemical reactions than those in the logarithmic phase. The medium of growth, surprisingly enough, had little effect on drying. The residual moisture seems to have vital effect on the survival rate of an organism, 4-7 per cent moisture content appearing to be optimum.

Of all the suspending media tested, nutrient gelatin was found to be the most satisfactory, and the incorporation of ascorbic acid or sodium ascorbate produced an additional protective effect. The main value of the gelatin-ascorbic acid technique seemed to lie in the relatively slow deterioration which occurred on prolonged storage even in the absence of a vacuum. The relative impermeability and small surface area of the gelatin pellet and the presence of reducing substances might help to inhibit process of oxidation which appeared to be concerned in bringing about the death of the organisms during and after drying. High survival ratio has been observed with a number of organisms when 5-10 per cent glucose or lactose is incorporated in the suspending medium. It is presumed that the beneficial effect of sugars is due to their automatic control of residual moisture.

The problem of drying vaccinia differ from those encountered with bacterial cultures. Small-pox vaccine and some other vaccine seem to preserve well when 5 per cent bacteriological peptone is incorporated in the medium.

In the preservation of micro-organisms it is not only necessary that the cultures should maintain their viability over prolonged periods, it is equally important that the cultures should show stability of their metabolic and morphological characters. Freeze-drying is as efficient or superior to other soil and sand culture methods for the preservation of micro-organisms. However, in spite of good viability, a loss in ability to produce certain metabolic products has been observed, especially with highly selected and unstable strains.

Dried cultures keep perfectly well at room temperature if they are kept in the dark, but die quickly if exposed to daylight. Cultures keep best when stored in ampoules under vacuum.

Orange juice concentrates

A NEW METHOD OF PRODUCING concentrated orange juice that retains about 93 per cent of the flavour has been announced. The " Hi-ester Retention Process " involves the continuous freezing out of the unwanted water. The juice is frozen to a sherbet consistency at 27°-27·5°F. under constant agitation. The mixture is then centrifuged. The ice phase contains about 85 per cent of the original juice, while the liquid phase or supernatant contains about 15 per cent. The supernatant liquor containing 93-95 per cent of the volatile flavour esters and 30 per cent sugars is stored in a vapour-proof cold-wall tank, under nitrogen. The ice phase which contains only a trace of flavour oils and about 8·4 per cent sugars is evaporated under vacuum and the evaporator residue containing about 57 per cent sugars is combined with the flavour-rich supernatant to form a 3: 1 orange juice concentrate of 42°Brix. Since efficiency gains are made in the evaporation step, the increased operating costs of the process are not appreciable, the difference being less than 0·0015 cent additional per six-ounce can [*Chem. Engng. News*, **32** (1954), 3132].

New aluminium paints

TWO NEW TYPES OF ALUMINIUM paste pigments have been recently introduced which, although similar in respect to fineness and covering power, gives a specular reflectance that is 50-200 per cent greater than was available with previous aluminium pigments, although total reflectance is approximately the same. The increased specular reflectance of paints made with these pigments results from the fact that the individual flakes are smoother and more polished than those of the regular products which have a thickness of 0·1-1·5 μ and are 100 μ or more in diameter. The amount of polished aluminium pastes used per gallon of vehicle is less than the unpolished grades.

It is probable that with flat surfaces, the coarser, diffusely reflecting pigments will continue to be preferred. Like enamels, the polished pastes tend to accentuate imperfections in the surface which would not ordinarily appear with diffuse-type pigments.

Another aluminium paste is the non-leafing type which fills the need for aluminium pigments for use in polychromatic and other textured finishes. The non-leafing feature also promotes excellent adhesion when used as a primer. Non-leafing paints find many applications where the outstanding moisture impedance and protective properties of aluminium paint are desired without the aluminium colour [*Aluminium News*, **7** (1954), July].

Phosphorus pentoxide

PHOSPHORUS PENTOXIDE IS IN considerable demand as a catalyst in the production of water-resistant paving asphalts. It is also in wider use as a drying agent, in the production of organic esters and polyphosphoric acids and as a condensation and polymerization agent, etc. To meet the growing demand the Virginia Carolina Corporation has recently started up a special plant at Charleston, South Carolina. Basically the process used consists in burning of phosphorus in dry air and combustion and condensation stages, the critical step being the complete drying of the air used for the oxidation.

The feed air is blown through a two-stage activated alumina dehumidifier, reactivation of the alumina in the first stage taking place continuously. The water content of the air is reduced to not more than 0·0011 lb. per 1,000 cu. ft. of air. With more moisture in the air, serious corrosion problems are encountered owing to the formation of polymers. The first stage dryer is divided into four horizontal stationary sections each having an upper and lower bed of alumina with an air space between the beds. A rotary valve directs steam-heated air to the spent beds while delivering wet air feed to the reactivated sections. The flow of air is through the beds and out of the air space. Air leaving the first stage has a dew point of −5°F. The second stage has two absorbers which are used alternately and reactivated in a batch operation. The air leaves the second stage with a dew point of −70°F. and is metered with a rotameter.

The molten phosphorus direct from an adjacent furnace is run into a feed tank. Hot water is then metered into the tank displacing the phosphorus into the combustion chamber. By means of an automatic ratio controller the air-phosphorus ratio is strictly maintained to ensure that no lower oxide of phosphorus is formed. In practice the amount of air is maintained at 8 per cent above the theoretical amount to produce the pentoxide.

Combustion of the phosphorus is effected at 3,000°F. in a chamber 10 ft. long by 4 ft. diameter, some of the heat developed being removed by water circulating in a jacket. The gases leave the chamber at 1,200°C., this also being a critical point since the temperature drop between the chamber and the condenser directly affects the crystal size of the pentoxide [*Chem. Tr. J.*, **135** (1954), 726].

Iron oxide from copperas

A PROCESS IS DESCRIBED FOR THE production of iron oxide and ammonium sulphate from copperas, a waste product from the titanium dioxide industry. Copperas in the form of fine crystals or as a slurry with filtrate from the process is added to concentrated ammoniacal liquor obtained by steam stripping of gaswork ammoniacal liquor in such quantity that the total ammonia (free and combined) represents up to 10 per cent excess by weight of the quality of total ammonia required theoretically to react completely with the copperas. The mixture is agitated and heated by direct steam to the desired temperature, preferably between 60° and 100°C., though it is possible to operate at room temperature. The process can be controlled by controlling the *p*H of the mixed solution. The precipitate is removed by means of a rotary vacuum filter and washed with warm water. An additional 15 per cent of the concentrated ammoniacal liquor is then added to the filtrate without further heating and the mixture again filtered. The filtrate substantially free from iron is stripped with live steam to remove excess ammonia, and the ammonium sulphate concentrated and crystallized.

The combined precipitates are mixed with burnt oxide or with solvent extracted spent oxide, adjusted to the desired moisture content and spread in the air to complete the oxidation of iron to ferric state. Alternately the combined precipitates may be mixed with peat or saw dust in the ratio 2: 1 and used for the purification of coal gas [*Chem. Age*, **71** (1954), 286].

New process for carbon blacks

INCREASED YIELDS AND OTHER advantages are claimed for a new process for carbon black production — termed the Lynn Furmatic method — developed by the Lynn Carbon Black Co. Designed to operate entirely on natural gas, or a mixture containing as much as 50 per cent oil, the process makes a black composed of channel, furnace, and a catalytically cracked type of carbon black. Key engineering features include specially designed burners, a zoned furnace, and two-stage air cooling of the product gases. The type and amount of carbon black recovered are a function of the air-gas ratio and temperature-pressure relationship, all of which are automatically controlled and may be varied as required. In general, two types of products will be made per run.

Product gases containing carbon black are cooled to 1,000°F. in the primary air cooler, pass through four cyclone separators in series, and leave the secondary air cooler at 275°F. Dust tube collectors catch the final product for pelletizing, although a fluffy product can be manufactured. Part of the total production comes from the initial cyclone separators. Furnace temperature may be controlled precisely, leading to formation of carbon black above the burners in the lower region of the furnace, by dissociation, requiring a somewhat lower temperature than pure thermal cracking.

Thermal cracking occurs in the upper zone of the furnace, which contains a hood which also acts as a catalyst for cracking the unburned gas.

Average yields have been estimated at 12 lb. of carbon black per 1,000 cu. ft. of gas, compared with about 7·4 lb. for the furnace process, and 1·9 lb. for channel plants. Operating costs have been estimated at 60 per cent of the conventional furnace type process. Capital investment for large-scale plants has been forecast as 30 per cent less than for the furnace process [*Chem. Engng. News*, **32** (1954), 3294].

Determination of morphine

MORPHINE FORMS A STABLE GREEN complex when iodic acid is added to its acidified solution followed by the addition of an ammonium bicarbonate-nickel chloride reagent. This iodic acid-ammonium carbonate-nickel salt reaction has been adopted for the routine spectrophotometric determination of morphine; the method is sensitive down to about 0·005 per cent of morphine in solution and 0·03 per cent of morphine can be determined with an accuracy of ±2 per cent. The advantages of the method are its specificity and the low absorption intensity of any background colour in the region of maximum absorption of the stable green complex. The pH for the iodic acid reaction should be below 1·6, and the optimum pH range of the absorption intensity is 8·00 ± 0·05. Of the bases occurring with morphine in nature only pseudomorphine interfered weakly. The method has been used for the rapid determination of morphine in opium and poppy capsule [*J. Pharm. Pharmacol.*, **6** (1954), 590].

High-temperature X-ray camera

A X-RAY CAMERA CAPABLE OF operating at temperatures up to 2,200°C. is described. It consists of three parts: the base, the top cover and the film holder. All the facilities and working parts are in the base with the exception of the thermocouple vacuum gauge at the top window. The top cover is mounted on the base with an O-ring seal and the film holder slides over the top cover into its correct position. The camera is water cooled with coils mounted on the base and the top cover. It can be used with vacuum or an inert atmosphere of helium or argon.

The X-rays pass through a tube guide mounted on the film holder and then through a small beryllium disc and a collimator, strike a rotating sample and are diffracted through a beryllium window. The camera gives an unobstructed picture from 8° to 172°.

The heaters are two 0·005 in. tantalum strips bent into a shape resembling an old-fashioned keyhole, their ends fitting into slots in two parallel vertical tantalum power leads.

The X-ray beam is collimated by passing through a 0·025 in. diameter hole drilled through the lead-filled end of a stainless steel tube and emerging through a 0·025 in. hole on the other end. The film holder is made of a brass cylinder with top and bottom rings which hold a black paper-covered strip of X-ray film on its surface.

Before operating, the camera is purged and filled with helium or argon. Water is allowed to pass through the cooling coils and the power fed to the heaters. The film holder is then slid into place and exposures made. A number of successive exposures can be made at different temperatures without disturbing the camera by simply removing the film holder and changing the film. Temperature is read with an optical pyrometer. A number of metallic oxides and a metal have been examined, and room temperature parameters calculated from their patterns agree well with those obtained in standard cameras [*J. Amer. ceram. Soc.*, **37** (1954), 360].

First oil refinery opened

INDIA'S FIRST ONE MILLION TON per annum petroleum refinery erected by the Standard Vacuum Oil Co. at Trombay Island (Bombay) was formally declared open by the Union Minister for Production, Shri K. C. Reddy, on 19 Nov. 1954. The refinery went on stream in July this year, six months ahead of schedule. The Stanvac Refinery is the first modern refinery of this magnitude in India. It is the outcome of the largest single foreign investment in India after her independence.

The refinery will turn out every year more than 300 million gallons of six different fuel products by processing crude oil which will come mostly from the Persian Gulf area. These are (in million gallons): gasoline, 90; kerosene, 40; automotive diesel oils, 59; industrial diesel oils, 40; industrial fuel oils, 55; and bunker fuel, 45.

The project, it is estimated, will result in an annual saving of more than Rs. 120 lakhs in India's foreign exchange, and provide, in addition, employment for about 500 technicians and workers.

Development of the Indian sugar industry

THE RECENTLY CONSTITUTED Development Council for Sugar Industry held its first meeting in Delhi on 9 August 1954. Among the subjects discussed at the meeting were: (i) revision of the target of production and the establishment of new factories; (ii) shifting of unsuitably located sugar factories; (iii) investigation into the factories lying idle; (iv) fixing sugarcane price on the basis of quality; (v) revision of Indian sugar standards; and (vi) revision of price differentials.

After the substantial increase in the consumption of sugar following complete decontrol in 1952-53, it was felt necessary to revise the original target of 15 lakh tons set in the First Five-Year Plan to 18 lakh tons. Though the existing installed capacity of the sugar industry is capable of producing 15·5 lakh tons, licenses for increasing production by *c.* 50,000 tons have already been granted and applications for a capacity of 430,000 tons have been received by the Government. Of these, 24 are for effecting substantial expansions in existing plant, 27 for establishment of new plants and 2 for setting up of sugar refineries. The establishment of sugar refineries did not receive much support from the members, and it was suggested that the present factories might be asked to utilize their plants for refining sugar when they remain idle during the off-season.

The Government felt that besides setting up new factories there was urgent need for utilizing the existing capacity of the industry to the fullest extent. The Council has accordingly agreed to the setting up of a Committee to: (1) prepare a plan for shifting unsuitably located sugar factories to suitable sites; and (2) investigate into the affairs of 16 factories at present lying idle for the past several years, with a view to bringing them back into operation.

An important decision taken by the Development Council was to set up a Committee of growers and millowners for a detailed examination of the proposal for the introduction of a system of payment of price for sugarcane on the basis of its quality.

The Indian Central Sugarcane Committee decided in December last to adopt 15 new combined standards for colour and grain for crystal sugar as recommended by the Indian Standards Institution, from November 1955. The Indian Institute of Sugar Technology, Kanpur, has prepared a standard set for the 1954-55 season. In view of the differences between the sugar mills and the growers about the correct interpretation, and impartial application of the standards, Government proposed that a system of inspection for enforcing correct grading may be adopted. The Council decided to set up a Committee of millowners and trade to examine the question.

Considering that the existing state controls over molasses were an impediment to the planned development of the power alcohol and sugar industries which were centrally administered, the Council recommended central control over molasses. The Council also approved of a grant of Rs. 3·5 lakhs as subsidy to the Saraya Distillery for conducting large-scale experiments on a new process for the extraction of sugar from molasses. The Committee have also decided to set up a body to consider the possibility of establishing byproduct industries of sugarcane.

Protection to calcium chloride industry

THE QUESTION OF CONTINUANCE of protection or assistance to the calcium chloride industry was discussed at a recent meeting of the Tariff Commission. Shri M. D. Bhat, Chairman, observed that the present difficulties of the calcium chloride industry seem to arise mainly from lack of sufficient demand for its product. Protection can be of little assistance under such circumstances and the future prospects and stability of the industry would depend largely on the measures which the industry would adopt to stimulate the demand by improving the quality of its product and reducing the cost of its production.

The present capacity of the industry for the manufacture of calcium chloride of commercial quality is estimated at 1,500 tons per annum, while the actual production during the last four and a half years was 1,345 tons in 1950, 959 tons in 1951, 913 tons in 1952, 733 tons in 1953 and 305 tons during the first half of the current year. Since the last inquiry in 1949, the domestic demand for the chemical has considerably declined and it may be estimated at between 700 and 750 tons for 1954 and at about 900 tons per annum for the future.

Heavy electrical equipment in India

THE GOVERNMENT OF INDIA HAVE appointed a committee to enquire into the manufacture of heavy electrical equipment in the country. The committee will enquire into the exact requirements of the country in the matter of heavy electrical equipment and the extent to which the requirements can be met by current production in India and by its possible expansion in the immediate future. The committee will take into account the unused capacity available in Government establishments and workshops including State Government workshops. It will investigate the extent of the remaining requirements and how this could be met speedily and economically and the agency through which it should be met.

Fertilizer Production Committee

THE GOVERNMENT OF INDIA HAVE appointed a committee to consider and make recommendations on various questions relating to increasing the production of nitrogenous fertilizers. The committee will consist of Shri B. C. Mukharji, Chairman; Dr. A. Nagaraja Rao, Chief Industrial Adviser to Government, Dr. M. D. Parekh, Chairman of the Development Council for Fertilizers and Heavy Chemicals, and Shri K. C. Sharma, Sindri Fertilizers & Chemicals Ltd. (Members); and Shri P. M. Nayak, Deputy Secretary, Ministry of Production, Secretary.

The need for expanding the capacity for fertilizer production in the country has been felt because the current capacity is insufficient to meet the internal demand which is expected to rise steadily during the coming years. It has been estimated that additional capacity for producing 2·5 lakh tons of nitrogenous fertilizers per year will have to be set up by 1961. It is proposed that as a first step immediate action should be taken of planning and creating additional capacity for 1·7 lakh tons of nitrogen per year.

Rice milling

THE GOVERNMENT OF INDIA HAVE set up a committee to examine the working of different rice milling methods now in vogue in the country, with Shri C. P. Karunakara Menon as Chairman. The committee will inquire into the various types of rice milling methods with respect to technical, nutritional, consumer preference, economic and employment aspects and make recommendations regarding the future policy to be adopted, indicating the administrative, financial and legislative measures which should be taken by the Central and State Governments to give effect to them.

Arecanut development

THE FOLLOWING PROPOSALS WERE approved by the Indian Central Arecanut Committee which held its sixth annual meeting in Bombay: (1) Establishment of a research sub-station in West Bengal; (2) better utilization of the byproducts of arecanut conducted at the Gauhati University; (3) collection of yield data of coconut and arecanut in Mysore; and (4) establishment of an arecanut nursery in Andhra State.

Duty on scientific instruments

THE GOVERNMENT OF INDIA HAVE announced that they would, on an *ad hoc* basis, exempt customs duty on re-importation of such scientific instruments and apparatus sent abroad for repair provided that no drawback of duty is admissible at the time of export. To qualify for exemption, it will be necessary for a certificate to be obtained before export of the instruments and apparatus in question from the Development Wing of the Ministry of Commerce and Industry, to the effect that the repairs to be done to the instrument/apparatus are such as cannot be carried out within the country.

Solvent extraction plants

THE GOVERNMENT OF INDIA HAVE decided to invite fresh applications for the installation of solvent extraction plants for the extraction of residual oils from oil cakes and expansion of the units which are already operating or which have been granted licences under the Industries (Development & Regulation) Act. Interested parties should send their applications in the prescribed form to the Ministry of Commerce and Industry.

Small-scale Industries Board

A SMALL-SCALE INDUSTRIES Board has been set up by the Government of India to frame and implement programmes for the development of small industries in the country.

The Board will co-ordinate the activities of the four Regional Institutes of Technology for Small-scale Industries which will be set up in terms of the recommendations on small industries by the International Planning Team of the Ford Foundation. These Institutes are to be located in Calcutta, Bombay, Faridabad and Madurai. The Institutes are to assist small-scale industries in improving their technique of production and management, in obtaining credit and finance and securing important raw materials, in marketing their goods to the best possible advantage and in promoting patterns of development for bringing about co-ordination in production programmes between small and large-scale industries.

The Board will also co-ordinate the activities of the proposed Marketing Service Corporation which would later integrate its activities with those of the Regional Institutes of Technology and of the Small Industrial Corporation which is to be set up to organize production by small industries for meeting Government orders.

In addition to the four Regional Institutes the Government of India have also sanctioned four Branch Units of these institutes to be located in Hyderabad, Travancore-Cochin, Bihar and the U.P.

National Industrial Development Corporation

THE NATIONAL INDUSTRIAL DEVELOPMENT Corporation was registered as a private limited company on 20 Oct. 1954 under the Indian Companies Act. The Corporation has a share capital of Rs. 1 crore, of which Rs. 10 lakhs have been subscribed.

Indian Rubber Bulletin

THE SPECIAL NUMBER OF THE *Indian Rubber Bulletin* (No. 68, Sept. 1954) published by the Association of Rubber Manufacturers in India carries articles presenting an account of the development and progress of the rubber industry in India in the fields of mechanical rubber goods, rubber insulated cables, footwear and waterproof fabrics. There are also articles dealing with raw materials and rubber machinery design as well as on the important subject of standardization and quality control.

The bulletin, a monthly, is published from 57-B Free School Street, Calcutta 16.

Scientific Publications in South Asia

THE INDIAN LIBRARY ASSOCIATION, with the assistance of Unesco, has published Vol. 1 of a *Union Catalogue of Learned Periodical Publications in South Asia* (Principal Editor: Dr. S. R. Ranganathan, Indian Library Association, Delhi, 1953, price Rs. 25) covering the physical and biological sciences. The catalogue covers 175 libraries in India and 74 in Indonesia, Malay, Burma and Ceylon. The catalogue is arranged according to the Colon Classification, and indicates the status or subject of specialization of the library, as well as the holdings. The catalogue is the first of its kind published in South Asia and should prove useful to research workers in the region.

Announcements

Nobel Prize Awards, 1954 — The Royal Swedish Academy of Science has announced the following Nobel Awards for the year 1954:

Chemistry — Prof. Linus Carl Pauling (53) of the California Institute of Technology for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances. This refers chiefly to his work into the structure of protein, the key component of living matter.

Prof. Pauling began his career with research into the nature of the chemical bond which led to a study of metal bonds and the nature of metals. In 1925, Prof. Pauling received his doctorate from the California Institute of Technology. He took postgraduate courses at the Universities of Munich, Copenhagen and Zürich. Since 1937 he has been Director of the Gates and Crellin Laboratories of the California Institute of Technology and has been Chairman of the Division of Chemistry and Chemical Engineering since 1931.

Physics — Prof. Max Born (72) for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wave function and Prof. Walter Bothe (63) for the coincidence method and his discoveries made with this method. Professors Born and Bothe belong to the generation of German scientists who during the years 1920-30 laid the foundations of modern nuclear physics.

Prof. Born studied at the Universities of Breslau, Heidelberg, Zürich, Goettingen and Cambridge. He became a British subject in 1939 and until recently held a Chair in Mathematical Physics at Edinburgh University.

Prof. Bothe, born in Oranienberg, Germany, was educated at the University of Berlin. Since 1934 he is the Head of the Institute for Physics of the Max Planck Institute for Medical Research in Heidelberg.

Medicine & Physiology — Dr. John Franklin Enders of the Harvard University Medical School and his collaborators, Drs. Thomas H. Weller of the Harvard School of Public Health, and Frederick Robbins of the Western Reserve Medical School, Cleveland, Ohio. The three doctors were honoured for their discovery of the ability of the poliomyelitis virus to grow in cultures of different tissues.

Dr. Enders, Dr. Weller and Dr. Robbins discovered that the virus could be grown in test-tubes on bits of human testicular or money tissue. The technique has made possible the preparation of a safe and effective polio vaccine and has provided a rapid and simple method for identifying the different types of polio virus.

The technique marks a new landmark in medicine in as much as it has revolutionized virus research. Since it was first announced in 1949, it has become one of the most effective weapons in the fight to eradicate not only polio, but a host of other virus infections.

A symposium on *Recent Advances in the Biochemistry of Vitamins* will be held during the Easter of 1955 under the joint auspices of the Society of Biological Chemists, India, the Royal Institute of Chemistry (Deccan Section), the Indian Medical Association (Bangalore Branch) and the Indian Dairy Science Association. Abstracts of paper relating to original contributions on: (a) methods in vitamins research, (b) biological role of vitamins, (c) vitamins in nutrition and medicine and (d) vitamins in food technology may be sent to the Hon. Secretary, Society of Biological Chemists (India), Indian Institute of Science, Bangalore 3, to reach him by the 31st January 1955.

Rewards for Discovery of Uranium Deposits — The Government of India have announced awards ranging from Rs. 100 to Rs. 1,000 to persons discovering new deposits of uranium and bringing sample of the ore or ore-bearing rocks to the notice of the Department of Atomic Energy. The amount of the award will be determined by the extent of ground covered by the new deposit, the grade or value of uranium contained in it, and the distance from the nearest deposit of uranium ore already known to the Department of Atomic Energy. Samples (at least 1 lb.) with applications for rewards should be addressed to the Secretary, Department of Atomic Energy, Government of India, Bombay 1, or to the Geological Adviser, Department of Atomic Energy, Government of India, New Delhi.

International Congress of Pure and Applied Chemistry, Zürich, 1955— In response to a request from the Executive Committee of the International Union of Pure and Applied Chemistry, the Ministry of Natural Resources and Scientific Research have assigned to the Council of Scientific & Industrial Research the work of scrutinizing and forwarding scientific papers received from contributors in India for the forthcoming XIV International Congress of Pure and Applied Chemistry to be held in Zürich from 21 to 27 July 1955. The papers together with their abstracts (*c.* 250 words) will be received by the Secretary, C.S.I.R., Old Mill Road, New Delhi, up to 15 January 1955.

Obituary: *Dr. Enrico Fermi* — By the death on 28 Nov. of Dr. Enrico Fermi at the age of fifty-three, nuclear physics has lost one of its most distinguished research workers.

Dr. Fermi was born in Italy where he received his education and spent the first years of research. In 1938 he was awarded the Nobel Prize in Physics. He went to the United States the following year where he carried out early research on atomic bomb at the University of Chicago and built United States' first nuclear reactor. In November this year he was awarded a special prize of $ 25,000 by the American Atomic Energy Commission.

At the time of his death Dr. Fermi was Professor of Physics at the University of Chicago's Institute for Nuclear Studies.

INSTRUMENTS AND APPLIANCES

Biological Assay Apparatus

The automatic biological assay apparatus developed in the Pharmacological Department of University College, London, and manufactured by Casella (Electronics) Ltd., London [Agents in India: Associated Instrument Manufacturers (India) Ltd., New Delhi] is designed to improve the accuracy, speed and convenience of measurement of the activity of drugs on isolated organs.

The principle consists in controlling the flow of drug and washing the solution into and out of the isolated organ bath using electromagnetic valves which compress rubber tubing. The cycle has been divided into several stages. The time required for each of these operations is independently variable over a thousand-fold range by adjusting the relevant controls on the panel which regulate the time interval between the pulses sent out by the timer to the uniselector switching device. The wide range of times has been introduced to make the apparatus adaptable enough to be used with any isolated preparation likely to be encountered in bio-assay work.

Some typical examples of the use of the apparatus are standard assay of posterior pituitary extract on guinea-pig uterus, test of activity of an antispasmodic drug on rabbit intestine, four-point assay of histamine on guinea-pig ileum, potentiation or antagonist experiments, etc. The apparatus as supplied is described as particularly suitable for three or four-point assays involving the repetitive addition of a limited number of drug solutions.

New Sample Counter

A new completely sealed automatic flow counter has been introduced by Tracerlab Inc., U.S.A. The new unit, which accommodates up to 25 samples, makes possible the obtaining of automatic radio-assays with a windowless Geiger or proportional counter.

The unit keeps all samples under gas flow at all times, and accepts samples up to $1\frac{7}{8}$ in. diam. and $\frac{5}{16}$ in. high. Because of this unique feature, excellent accuracy and reproducibility are obtained without long pre-flush and excessive gas usage. The instrument may be set so that each of the samples is counted one, two, three or four times, or so that the cycles are repeated indefinitely. A switch on the control panel makes it possible to bypass any desired number of samples and to advance the index accordingly.

The results of the radio-assays are printed on the tape of the SC-5D Tracergraph, along with the sample number in terms of elapsed time for the predetermined number of counts measured by the scaler. Either the SC-18 Superscaler or the CS-51 Autoscaler may be used with the new counter.

The unit has an overall accuracy of *c.* 1 per cent, a resolving time for Geiger counting of *c.* 150 microsec.; and is limited only by the resolving time of the scaler and/or amplifier for proportional counting.

P.V.C. Exhaust Fans

In the extraction of acid fumes from various zones of a chemical plant it is necessary that the exhaust fans should be inert to the fumes in the air passing through them. Oxythene rigid P.V.C. exhaust fans made by Horwitch Smith & Co. Ltd., Birmingham, are reported to satisfy this requirement for they are quite inert to acid and other corrosive fumes. They are available in a full range of sizes for use in inlets from 6 to 27 in. wide and up to 4 in. W.G. The fan housing is made from unbreakable oxythene " Duo-Ply " P.V.C. sheet if required. It consists of two strong side pieces joined together with welded strengthening rods. There is a rectangular outlet and a round inlet for the fan although the latter can be converted to rectangular section if required. The hub of the fan runner is made of steel and the rigid blades are slotted to it. The hub is finished with a complete covering of rigid P.V.C. and the blades are welded in their positions.

The motor and the fan are mounted on a fabricated steel stool which is itself coated with oxythene vinyl base plant protecting paint or, if specified, the stool can be fully insulated with oxythene "G" plastisol. This protects it completely from chemical attack of any kind.

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Corrigendum

Dr. K. Venkataraman has asked us to state that in the paper entitled "The Fries Reaction: Part VI — The Rearrangement of Aryl p-Toluene-sulphonates & a Convenient Method for the Synthesis of Hydroxy-diarylsulphones" published in this Journal, **13B** (1954), 181, his name as one of the authors should be deleted.

Progress Reports

TEA RESEARCH IN INDIA

THE TOCKLAI EXPERIMENTAL STATIONS' ANNUAL Report for the year 1953 records all-round progress in its research activities. The following are some of the investigations carried out in the different departments of the Station.

Agricultural and botanical research — Analysis of data obtained on the yield of tea under varying light intensities has shown that when light intensity is reduced to between 50 and 70 per cent of full light, the yield of tea is significantly greater than for unshaded tea. It was also seen that when efficient nitrogen fixing trees are used for providing shade, the effect is even more pronounced. Of the seven shade trees tried, *Albizzia stipulata* (green), *A. stipulata* (red) and *A. odoratissima* were found to be most efficient. It was found that the effect of the application of nitrogenous manure persists till the year after application of the manure both in shaded and unshaded tea plants. This effect, however, was observed for an extra year in tea that was under a more efficient species of shade tree.

Experiments on the effect of nitrogen under shade on the characters and valuation of made tea have shown that the application of 100 lb. per acre of nitrogen slightly reduced the strength and colour of liquors, and caused a slight deterioration in the infused leaf, but the actual valuation of the tea was not affected. The quality, briskness, colour of tip, dry leaf and infused leaf were not significantly affected by shade, but the strength and colour of the liquors were greatly improved at reduced light intensity. This improvement was significant even at 0·1 per cent level.

Several media were tested to find out a standard potting medium and it was found that a medium consisting of sub-soil 7 parts, sand 2 parts, coconut fibre as organic matter 3 parts, and a fertilizer base (made up of hoof and horn meal 2 parts, superphosphate 2 parts and potassium sulphate 1 part) 5 lb./cu. yd. gave the best results.

Further work carried out to elucidate the nature of acidity in the tea soils and the effect of manuring on soil conditions has shown that ammonium sulphate not only makes the soil acidic but is also responsible for decrease in total exchangeable metal cations and exchangeable calcium in the soil.

The average amount of hair on the under-surface of the leaf has been found to bear a relation to agrotype index. It has also been shown that the weight and thickness of the stem and the density of the wood in the leaf petiole are also related to the density of hair. The quality of tea is found to be associated with both high stem weight and density of wood in the leaf. The best populations of plant appear to be those in which hair is associated with anthocyanin pigment in the leaf petiole. In full light no relationship exists between hair and yield, but under shade increasing hair is associated with increasing yield. The dry weight of the stem on the plucked shoot increases with shade and on the best *jats*, the percentage of stem in the made tea is increased by shade from 24 to 30 per cent.

Entomological research — Laboratory and field trials with new synthetic insecticides, acaricides, and fungicides have been continued. Aramite W.P. 9-(p-tert-butylphenoxy)-isopropyl 2-chloroethyl sulphide at 1 lb. to 50 gal. of water kills a high percentage of active forms and eggs of red spider. The migrating red spiders from the treated levels do not survive long, but die without depositing eggs. Aramite was also found to affect a high percentage of quiescent forms.

Tea aroma and flavour — Ether extracts of tea leaf have been fractionated for determining the chemical substances responsible for tea flavour and aroma by chromatography on alumina. Clones with China characters gave on ether extract a crystalline material which on chromatographic analysis revealed the presence of a substance with the characteristics of an aldehyde. Clones of Assam type without any China characters when treated similarly gave either no crystalline substance or an exceedingly small amount of it. Phenylethyl alcohol, citronellol and hexenol (*cis*-m-hex-3-en-1-ol), whose occurrence has been reported in tea, produced a rawness in tea when used in small amounts. In slightly larger quantity the aroma was totally different from the natural aroma of tea, which shows that these substances can form no more than a very small part of the blend.

Withering of tea — An apparent increase in caffeine during withering has been noticed. Metabolic studies have revealed that caffeine influenced the extent of condensation of oxidized catachins which is found to be greatest when tea leaves are subjected to withering for a long time. Differences in the extent of condensation are partly responsible for determining the characteristic liquoring properties of teas withered for different lengths of time.

Withering carried out in an air-conditioned chamber has shown that it is possible to wither tea in 3 hr. and at greatly increased thickness of leaf spread. The experiments indicate that teas made from rapidly withered leaf give an inferior liquor in comparison with teas made from naturally withered leaf unless rapid withering is preferably preceded by a period of storage. Temperature of withering was not found to have any significant effect on the quality of tea. It was found, however, that during flavoury periods, i.e. the second flush and autumnal seasons, flavour may be conserved by withering at a low temperature (70°F.). The same holds good for tea grown in Darjeeling and at higher altitudes, where flavour is of paramount importance.

INDUSTRIAL RESEARCH IN HYDERABAD STATE

THE ANNUAL REPORT OF THE CENTRAL LABORATORIES for Scientific & Industrial Research, Hyderabad (Dn.), for the year 1952 records considerable research activity, the emphasis being mainly on industrial utilization of the processes evolved in the laboratories. A brief account of the activities of some of the sections is presented here.

Oils and fats — Sitaphal seed (*Annona squamosa* Linn.) oil in benzene and kerosene was found to be highly toxic to soft-bodied insects like cabbage aphids, pumpkin beetles and saw-fly larvae. Spraying wood with 8 per cent solution of the oil in kerosene oil gave up to 50 per cent mortality of termites. The insecticidal character of the oil is destroyed by alkali refining, the soap-stocks obtained from two-stage alkali refining being non-toxic. Soaps obtained from sitaphal oil and its blends with groundnut and coconut oils gave profuse and steady lathers; more elaborate studies on the degree and persistence of foam indicated that the lathers were steadier in non-alkaline than in alkaline media. Sitaphal oil, being available at one-third the price of groundnut oil, can profitably replace it in soap-making.

From the studies related to the manufacture of dehydrated castor oil (DCO) it was found that of the several bleaching earths tried (in combination with active carbons), outstanding bleach was obtained with "Tonsil"— a brand of German fullers' earth. Dehydration of light-coloured material was best obtained using sodium bisulphate-sodium bisulphite mixture as catalyst, adding zinc oxide or slaked lime immediately after dehydration and before cooling and working at high vacuum. For bodying DCO to a material conforming to Indian Government specifications, bubbling of carbon dioxide through the oil during bodying did not suppress darkening. Addition of 0·8 per cent zinc oxide just after dehydration and subsequent bodying for *c.* 16 hr. at 240°-60°C. and at a vacuum of 4-6 mm. Hg gave a bodied DCO of viscosity 17-25 poises, low acid value and a set-to-touch time much lower than demanded by specifications.

The isolation of triricinolein from castor oil using light petroleum was conveniently effected in a liquid-liquid extractor, it being expedient to mix the oil and the solvent outside than in the extractor.

A systematic study of the reaction between halogens in solution and ricinoleic acid showed that bromine was added instantaneously and quantitatively with very slight substitution; with chlorine the reaction is instantaneous, but addition occurs to only about half the theoretical extent side by side with a similar amount of substitution. The concentration of halogen in solution had no effect on the pattern of halogenation, nor had catalysts like hydrochloric acid, nitrobenzene and iodine. Pyridine, however, withheld both available chlorine and hydrogen chloride produced by substitution.

Aca-catechin, obtained by ethyl acetate extraction of *katha* was found to possess outstanding antioxidant properties. Using the Swift stability test and raw fresh groundnut oil as substrate, raw *katha* conferred protection factors of 2·5 and 2·6 at 0·05 and 0·1 per cent concentration respectively, while aca-catechin at concentrations of 0·05, 0·1 and 0·2 per cent exhibited factors of 2·4, 4·0 and 6·0. These compare favourably with the protection factor of 1·3 shown at 0·1 per cent concentration by ethyl gallate. Synergistic combinations with carboxylic materials, particularly phosphoric and oleic acids, were very effective. Outstanding response was obtained in alkali-refined groundnut oil of low natural stability.

Fuel — A self-supporting continuous process of briquetting coal fines was developed and is being tried on a pilot-plant scale. When coal fines are mixed with suitable amounts of low temperature tar and lime and briquetted, the tar acids react with lime forming a complex compound which increases the viscosity of tar a thousand-fold. The briquettes increase in strength on storage. On carbonization, an amount of tar equivalent to the original is recovered leaving a smokeless briquette.

Investigations on the weathering properties of Kothagudium and Tandur coals showed that while the top coal layers exposed directly to atmosphere was markedly affected and considerably weakened in strength so as to crumble on handling, the inner layers remained unaffected.

Oxidation of Hyderabad coals in a fluidized bed for 23 hr. at 220°C. gave alkali-soluble coal acids in yields exceeding 90 per cent and oxidation products similar to humic acid in yields amounting to 80 per cent of the original coal.

A 4 lb. capacity electrically heated still was designed and fabricated for investigations on the distillation of low-temperature tar obtained by the carbonization of Hyderabad coals in 15 lb. capacity externally heated laboratory plant.

It has been shown that by taking suitable steps such as preheating, use of higher temperatures for cracking, frequent cleaning of the retort and scrubbing of the gas, residual diesel oil (b.p. 300°-375°C.), a waste product from the Road Transport Department can be used as a substitute for kerosene oil in the Mansfield gas plant.

Heavy chemicals and fertilizers — A number of schemes have been undertaken for the industrial utilization of felspar found in the State. For the preparation of potassium bromide, calcium bromide prepared by treating iron bromide with slaked lime is heated with potassium liquor obtained from felspar. Potassium bromide formed is freed from the calcium sulphate and calcium hydroxide formed alongside by filtration. Sodium bromide (*c.* 7 per cent) is removed by fractional crystallization.

A method evolved for preparing potash alum and active silica from felspar consists in heating felspar with calcium carbonate at 900°C., treatment with sulphuric acid and recovering potash alum and sodium alum from the resulting solution.

Other projects undertaken include the production of sulphur and manganese sulphate from pyrites, sulphur dioxide and sodium carbonate from sodium sulphate, activated charcoal from groundnut hulls, fertilizer from rock phosphate and titanium from bauxite sludge.

Chemistry — A chloromenthol was obtained from carene, the hydrogenated product of Δ^3-carene. The toxaphene type of highly chlorinated turpentine (chlorine content over 60 per cent) was found to be highly toxic to pumpkin beetles and houseflies.

Investigations on the production of citric acid from molasses by fermentation showed that maximum yield of citric acid (30·8 per cent) was obtained in experiments where the initial sugar concentration was adjusted to 12 per cent, with small additions of ammonium nitrate (0·2 per cent), potassium dihydrogen phosphate (0·03 per cent) and magnesium sulphate (0·02 per cent). Good yield was obtained by keeping the initial *p*H at 6.

(*Continued on page* 604)

INDIAN PATENTS

[A few of the Patent Applications notified as accepted in the *Gazette of India*, Part III, Section 2, for October 1954, are listed below.]

Chemicals, plastics, rubber, paints and allied products

50271. Improvements in the manufacture of ammonium sulphate: *Circulating magma-containing ammonium sulphate crystals to provide a continual supply of such magma in the region of the saturator where super-saturation takes place* — GEORGE ROYSTON & SON LTD. & ROYSTON

50489. 2-Amino-5-nitrothiazole and 2-acyl-amino-5-nitrothiazole: *By distributing 2-amino-5-nitrothiazole and 2-acyl-amino-5-nitrothiazole in a therapeutic vehicle* — MERCK & CO. INC.

51782. Production of alkali metal hydroxides: *Causing the amalgam to flow vertically through a decomposition zone to which water is co-currently fed and thereafter causing the amalgam to flow through a horizontal decomposer in which it is counter-currently contacted withw ater* — RUMIANCA SOCIETA PER AZIONI

52009. Organic esters of 2-(2-diethylaminoethoxy)-ethanol and their process of preparation: *Esterifying 2-(2-diethylaminoethoxy)-ethanol with a derivative (corresponding to groups shown in figures 1-9 of drawings) of appropriate carboxylic acid* — MORREN

52027. Composition for preparing cylindrical rolls from washed safety base cinematographic films: *Composed of an active solvent consisting of dioxane, and a binder* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

52170. Method of stabilizing rubber and product thereof: *Comprising incorporating N-N′-dialkyl-p-phenylene diamine in which each of the alkyl groups contains at least 7 carbon atoms* — UNIVERSAL OIL PRODUCTS CO.

52240. Production of pseudo-sapogenin compounds: *Treating sapogenins or their esters at a temperature below 150°C. in a mixture of tertiary base and esterifying agent in presence of hydrogen halide* — ORGANON LABORATORIES LTD.

49187. Separation and/or recovery of fat and/or fat-like material from organic substances contained in cellular or similar systems: *Subjecting to intense impacts in presence of excess of liquid in which part of raw material is less soluble than in water* — BRITISH GLUES & CHEMICALS LTD.

50276. Purification of alcohol: *Replacing known methods of hydro-selection or purification by "super-purification" effected under vacuum and at low temperature* — SOCIETE DES ETABLISSEMENTS BARBET

51674. Improved potassium nitrate products and a method for their production: *Consisting of potassium nitrate crystals bearing on their surfaces a deposit comprising a salt soluble in a saturated potassium nitrate solution at 20°C. of a condensation product of 1 mol. of formaldehyde and 2 mol. of naphthalene monosulphonic acid* — I.C.I. LTD.

49309. Production of synthetic rubber products: *From an aqueous dispersion of a conjugated diene synthetic rubber containing a stabilizer which comprises gelling the dispersion in the presence of anacyclic polyalkylene polyamine* — DUNLOP RUBBER CO. LTD.

49310. Production of sponge rubber: *Gelling the frothed latex in the presence of an acyclic polyalkylene or a mixture thereof* — DUNLOP RUBBER CO. LTD.

49339. Manufacture of rubber products: *Compounding rubber dispersion with an organic thio-compound and an oxidizing agent, shaping the dispersion, gelling and then vulcanizing* — DUNLOP RUBBER CO. LTD.

49473. New pyrimidine derivatives: *Reacting a malondiamide derivative with formic acid or formamide* — I.C.I. LTD.

51807. Process for obtaining pure pre-polymerization products of 11-amino undecanoic acid: *Amino undecanoic acid is heated with water, water being removed from the amino undecanoic acid as it is separating during operation* — PERFOGIT SOCIETA PER AZIONI

51884. Process for fractionating starch into components with branched and linear chains: *Salt concentration of solution of starch in aqueous salt solution is increased after the separation of amylose until amylopectin precipitates without further cooling and separating amylopectin from the liquid* — CO-OPERATIVE VERKOOP — EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL EN DERIVATEN "AVEBE" G.A.

49188. Extraction of fatty material from raw materials: *Subjected to intense impacts in presence of excess of liquid having no deleterious effects and separating constituents by centrifuging* — BRITISH GLUES & CHEMICALS LTD.

49483. Amino acid compounds and methods for producing the same: *Reacting an acid addition salt of O-glycyl-(l)-serine or O-glycyl-(dl)-serine with a diazotizing agent to produce O-diazoacetyl-(l)-serine or O-diazoacetyl-(dl)-serine* — PARKE, DAVIS & CO.

50577. Production of a new hydroxymethyl amide and the alkyl ethers thereof: *Treating isonicotinic acid amide with formaldehyde in neutral or alkaline medium and, if desired, etherifying the product with alcohols containing not more than 12 carbon atoms* — CILAG LTD.

51152. Production of films of pre-determined shape: *Bringing surface of a former to a temperature higher than flocculation temperature of cellulose derivative and contacting the former at said temperature with solution of cellulose derivative* — MO OCH DOMSJÖ AKTIEBOLAG

51153. A process of preparing compositions comprising active material on a carrier consisting of a cellulose derivative: *Applying active material in form of solution, emulsion or dispersion in hot water to cellulose derivative carrier of the type soluble in cold water but insoluble in hot water* — MO OCH DOMSJÖ AKTIEBOLAG

51232. Polymerization of cyclic amides: *A lactone is used as a reaction initiator* — PERFOGIT SOCIETA PER AZIONI

Food and kindred products

51780. Agents for improving foodstuffs: *The agent consists of (a) one or more lactones of an aliphatic hydroxy carboxylic acid having a lactone ring of 4-6 carbon atoms incorporated in an ingredient of the foodstuff or (b) at least two such lactones without the ingredient* — ANGLO-SCOTTISH CREAMERIES LTD.

Drugs and pharmaceuticals

51677. Preparation of 5-n-heptyl-2-thiohydantoin: *Reacting 2-amino-nonanoic acid with water-soluble inorganic thiocyanate and lower alkanic acid, and deacylating the product* — STERLING DRUG INC.

49802. Process for the manufacture of compounds of the adreno-cortical hormone series: *By treating 16 unsaturated compounds of the pregnane series with agents capable of adding on to the 16:17-double bond a compound HO-R, R being hydrogen hydroxyl group, halogen or free or substituted alkyl radical* — CIBA LTD.

51006, 51007, 51008, 51009, 51010 and 51011. Amino acid compounds and methods for producing the same: *Cultivating a micro-organism called Streptomyces fragilis under aerobic conditions in an aqueous nutrient medium having a pH of 5-8·5 and containing sources of carbon, nitrogen and mineral salts so as to produce O-diazoacetyl-(l)-serine.*

Reacting an N-carbobenzoxy serine with a haloacetyl halide or haloacetic anhydride to produce O-haloacetyl-N-carbobenzoxy serine and reacting this latter compound with a metal azide to produce O-azidoacetyl-N-carbobenzoxy serine which is finally subjected to reduction in the presence of a mineral acid.

Reacting an N-carbobenzoxy serine with an azidoacetyl halide and subjecting the O-azidoacetyl-N-carbobenzoxy serine so obtained to reduction in the presence of a mineral acid.

Reacting N-carbobenzoxy serine with a mixed anhydride of carbobenzoxyglycine and subjecting the D-(N-carbobenzoxyglycyl)-N-carbobenzoxy serine so obtained to reduction in the presence of a mineral acid.

Reacting an N-carbobenzoxy derivative of serine with a glycyl halide or N-carboxyglycine anhydride and subjecting the O-glycyl-N-carbobenzoxy serine so obtained to reduction in the presence of one equivalent of a mineral acid.

Treating N-glycyl serine with a mineral acid under anhydrous conditions at 0°-100°C. so as to produce acid addition salts of O-glycyl serines — PARKE, DAVIS & CO.

52464. A process for preparing morphinane derivatives: *By heating (-)-3-hydroxy morphinane with a propergyl halide in an organic solvent in the presence of an acid-binding agent* — HOFFMANN-LA ROCHE & CO. AKTIENGESELLSCHAFT

Fuels and lubricants

49277. Briquetting of comminuted materials such as fuels, ores or the like: *Comprising mixing the base material with a binding agent and shaping the resulting mixture; the binding agent consists of a coal-tar pitch and an aromatic compound constituted by three rings* — GELSENKIRCHENER BERGWERKS AKTIENGESELLSCHAFT

Metals and metal products

51678. A method of separating silver and copper from coinage alloys: *Adding a halide to the electrolyte used for electrolysis of re-alloyed coinage* — DEMAG-ELEKTROMETALLURGIE G.M.B.H.

51206. Process for production of metallic iron concentrates and titanium dioxide concentrates from ores containing ilmenite: *Ore mixed with sodium compounds is heated in presence of solid carbonaceous reducing agent* — TITAN CO. A/S

51524. Electroplating of metals on aluminium or its alloys: *Aluminium or aluminium alloy is dipped in ferric chloride solution and then electroplating with nickel and/or chromium* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

51861. Method and apparatus for regulating the wall temperature in the melting zone of cupolas: *Forcing a cooling liquid through cooling elements in the melting zone of cupola and maintaining working pressure for cooling medium at constant level corresponding to the desired temperature* — STRIKFELDT & CO.

51873. Fusion joining of nickel alloys: *Consists of calcium fluoride with at least one alkali metal silicate* — THE INDIAN OXYGEN & ACETYLENE CO. LTD.

52080. Melting of high melting metals or alloys: *Comprising an arrangement of feed rolls and contact system consisting of a plurality of individually spring-loaded contact brushes arranged in one or more groups* — I.C.I. LTD.

52392. Process and apparatus for making additions to liquid metal: *Into molten metal is introduced addition agent in a pressure vessel by a plunger which passes through an inlet opening in the vessel and which in its innermost position closes the inlet opening* — THE MOND NICKEL CO. LTD.

49342. Manufacture of hollow metal bodies: *Coating heated metal blank with vitreous material and pressing it in a container closed at one end with ram* — COMPTOIR INDUSTRIAL D'ETIRAGE ET PROFILAGE DE METAUX

52184. Melting of high melting point metals or alloys: *Using a consumable electrode comprising a metal or alloy tube containing the metal or alloy to be melted in the form of powder, sponge* — I.C.I. LTD.

Glass and ceramics

52226. Methods of and apparatus for bending sheets of glass: *Applying the pressure of bending over the marginal areas only of the sheets* — PILKINGTON BROS. LTD.

Leather and leather products

49231. Surface treatment of leather cloth: *Applying to the surface of a leather cloth a gel comprising a polymer of vinyl chloride and a volatile ester of a lower fatty acid* — Dunlop Rubber Co. Ltd.

Building materials and methods

49787. Apparatus for handling cement: *The apparatus consists of a casing providing a chamber in which is rotatably mounted a disc, the chamber walls and the walls of the disc providing a passage for the adhesive, along a portion of the periphery of the disc connecting the inlet and outlet openings in the casing* — The British United Shoe Machinery Co. Ltd.

52283. Foaming composition for cellular concrete: *Comprising an aromatic sulphonic acid and a water-soluble cellulose compound* — I.C.I. Ltd.

49436. Manufacture of concrete articles: *Part newly removed from mould before hardening locally subjected to compressive stress to modify its shape; pressure maintained till part is sufficiently hard* — Compagnie Internationale Des Pieux Armes Franignoul, Societe Anonyme

51658. Process for improving the resistance to corrosion of concrete or other calcareous cementitious matter: *Treating concrete by successive applications of silico-fluoride, first by a weak solution of magnesium or zinc silico-fluoride and then by strong solution of aluminium silico-fluoride* — Rocla Pipes Ltd.

Miscellaneous

49202. Abrasive cloth and method of manufacturing: *Comprising a woven fabric containing a starch base filling material and a heat hardened synthetic resin filling material and having a layer of abrasive grains attached to the surface by a synthetic resin bond* — The Carborundum Co.

49239. Plant for the removal of furnace ash and dust by water sluicing: *In combination a sluice means, collecting means for ash, means for effecting periodical flow of ash at controlled rate, first and second pumping means for supplying water at low and high pressure, solids separating means for reception of water from the sluice means, dust delivery means* — Babcock & Wilcox Ltd.

51179. Artificial board: *Steps of dewatering the wet lap, applying a sheet of paper to the surface of the wet lap and consolidating the wet lap and sheet of paper under heat and pressure* — Abitibi Power & Paper Co. Ltd.

52111. Enamels for wire wound resistors: *Composed of (per cent)* PbO, 30-35; Al_2O_3, 10-12; B_2O_3, 12-15; SiO_2, 18-20; *colourants*, 0-3; *alkalies*, 18-22 *and fluorine*, 1-2 — Council of Scientific & Industrial Research

49370. Shearing machine for tea: *Tea is cut between a pair of toothed grooved rollers* — Eastwood

49383. Processes for stretching artificial filaments and fibres of proteins: *Artificial filaments of protein are subjected to slow progressive stretching over rollers in conjunction with treatments in aqueous saline baths* — American Patents Corp. & Ferretti

51337. An automatic tea sorting and upgrading machine: *Comprises a hopper with two adjustable blades attached to a crank and an adjustable handle, a set of hammers and cams mounted on respective shafts and a conveyer belt having a hairy cloth attached on it* — Bholanath Ghosh

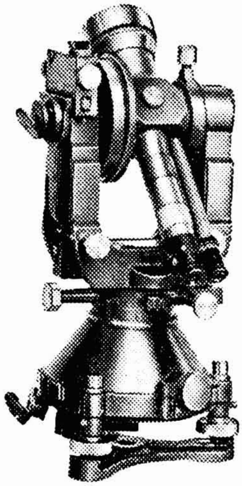
PROGRESS REPORTS — *Continued from page* 601

Experiments on the production of itaconic acid by the fermentation of sugars with *Aspergillus terrens* revealed that sucrose (and even molasses) gave as high yields as glucose. Properly clarified molasses gave up to 20 per cent itaconic acid.

A process has been worked out for the production of levulinic acid from bagasse. Bagasse is thoroughly washed in cold water, drained, dried in air and pulverized to 40-50 mesh powder. The pentosans are then hydrolysed by autoclaving the powder with 0·3 per cent sulphuric acid and the residual matter autoclaved with 8 per cent sulphuric acid to hydrolyse the cellulose. The reducing sugars obtained are then converted to levulinic acid. Pentosans and cellulose may also be hydrolysed together and the combined reducing sugars (pentoses and hexoses) used for preparing levulinic acid. In a typical experiment a yield of 4 g. pure levulinic acid from 50 g. bagasse was obtained.

Ceramics — Laboratory investigations for the development of a suitable engobe and glaze for Pachegaon clay bodies were completed. Pedestals for the P.C.E. furnaces and muffles for electric furnaces were made from indigenous clays, and their service life was comparable to imported materials. Successful compositions for fireclay crucibles capable of withstanding temperatures up to 1,500°C. for use in smelting and fritting have been evolved.

'WILD' HEERBRUGG (Switzerland)



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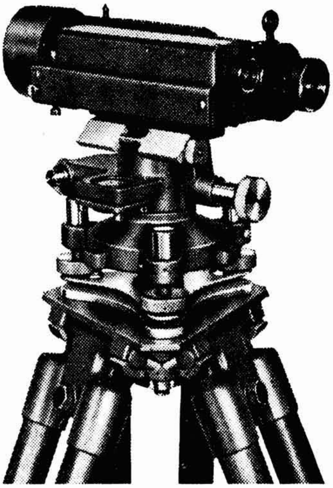

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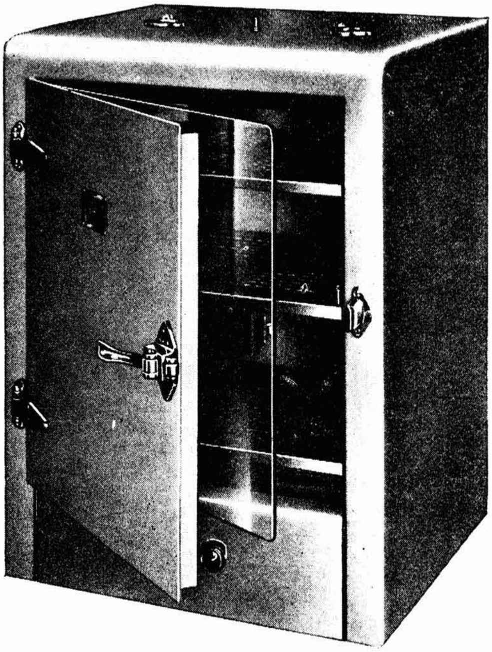

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Chance

'VERIDIA' PRECISION BORE GLASS TUBING

THE PROCESS

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The Veridia process is not limited to the production of tubing with a circular section. Tubes have been produced with square or hexagonal bores; contoured, taper and stepped bores can also be made. A recent development is capillary tubing down to 0·065 mm. diameter.

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Veridia tubes are being used for pump cylinders and hypodermic syringe barrels, and are extensively used in high grade viscometers and thermometers. There are a large number of applications in the field of graduated glass since Veridia tubing can be used without any need for individual calibration and the graduations are uniform. This is very useful where a separate non-calibrated scale must be employed and the dimensional tolerances make it quite possible to secure glass of NPL Grade A quality without trouble or special technique.

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Polymerization of Vinyl Monomers in Aqueous Solution by Radicals from Photo-excited Electron Transfer Reaction in the Ion-pair $Fe^{3+}OH^-$

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A photochemical method for the preparation of pure vinyl addition polymers is suggested. Polymerization kinetics of reaction of radicals from photo-excited ion-pair, $Fe^{3+}OH^-$, with vinyl monomers in aqueous solution are discussed.

FRANCK and Haber[1] were the first to postulate the formation of OH radicals in solution when the aqueous halide and sulphite ions were irradiated. Haber and Willstatter[2] have indicated that OH and HO_2 radicals are the chain carriers in the catalytic decomposition of hydrogen peroxide. This was followed by a study of the system ferrous or ferric ion-hydrogen peroxide and introduction of the theory of the formation of OH and HO_2 radicals into the field of reaction kinetics in solution by Haber and Weiss[3,4]. Baxendale, Evans and Park[5] have shown that free radicals produced in Haber and Weiss's reaction initiate polymerization of vinyl compounds. Rabinowitch and Stockmayer[6] interpreted the absorption spectra of ferric ion-pair complexes as electron transfer spectra, the primary photochemical process being $Fe^{3+}x^- \xrightarrow{h\nu} Fe^{2+} x$ where $x^- = OH^-$, halide, etc. Rabinowitch[7] predicted the occurrence of free radicals or atoms in irradiated ferric salt systems. Evans and Uri[8] showed that the free radicals produced photochemically from ferric ion-pair complexes lead to polymerization of vinyl compounds. Evans, Santappa and Uri[9] have reported on the polymerization of vinyl compounds in aqueous solution using $Fe^{3+}OH$, $Fe^{3+}Cl^-$, etc., as photo-sensitizers. Santappa[10] has reported the difference in behaviour between $Fe^{3+}OH^-$ or $Fe^{3+}Cl^-$ on the one hand and $Fe^{3+}N_3^-$ on the other as photo-sensitizers in the polymerization of vinyl compounds.

This paper presents a detailed kinetic study of the system $Fe^{3+}OH^-$ vinyl monomers, leading to polymerization of vinyl monomers in aqueous solution.

Experimental procedure

Optical arrangements — A light beam from a 250 watt high pressure mercury vapour lamp (B.T.H.) was rendered parallel by a quartz condenser lens and passed through filters for isolating the mercury lines[11]: (a) 313 mμ: 0·178 M $NiSO_4$ in a 5 cm. open quartz cell, Chance OX7; M/40 potassium biphthalate in 1 cm. open quartz cell; (b) 365 mμ: $CuSO_4$ in 1 cm. quartz cell; Chance OX1. Most of the experiments were carried out with 313 mμ filter. The light beam passed through an adjustable iris diaphragm into a thermostat and fell on the reaction cell which was mounted in the centre of a thermostat and maintained at a temperature $25° \pm 0{\cdot}1°C$. The diameter of the reaction cell was 5 cm., its optical depth 46 mm. and capacity 75 cc. A solution of ferric perchlorate, perchloric acid and vinyl monomer formed the system $Fe^{3+}OH^-$ vinyl monomer, for irradiation purposes. By adjusting the *p*H and ionic strength of the solution[6], the concentration of $Fe^{3+}OH^-$ could be controlled.

Reagents — Ferric perchlorate was prepared from precipitated brown ferric oxide and perchloric acid. Monomers, acrylonitrile, methyl methacrylate, methacrylic acid were freed from stabilizers and purified by repeated distillation under reduced pressure in an atmosphere of oxygen-free nitrogen.

Before irradiation, nitrogen purified in Fieser's solution[12] was bubbled through to displace air.

Estimations — The rate of ferrous ion production (dFe^{2+}/dt) was determined colorimetrically with *o*-phenanthroline. Concentrations of ferrous ion down to a minimum limit of 5×10^{-7}M could be determined. Monomer disappearance ($-dM/dt$) was followed by the weight of polymers purified after precipitation from acetone solution and dried at 100°C. to constant weight. Chain lengths of methyl methacrylate polymers (n) were determined by measuring the viscosities of the polymers in benzene solution and with the help of the factors given in Baxendale, Bywaters and Evans's[13] paper. Light absorption fraction (k_ϵ) by the ion-pair $Fe^{3+}OH^-$ was calculated[10] or measured spectrophotometrically, taking into account all the equilibria and species of ions present in the system. Light intensity or lamp output (I) was measured actinometrically[11] using uranium oxalate solution. Monomer concentration [M] for methyl methacrylate was measured by adding a known amount of bromine to the monomer solution and determining the excess of bromine by iodometry.

Results

(1) k_ϵ — It may be shown that in ferric perchlorate solutions the photochemically active species is the ion-pair complex $Fe^{3+}OH^-$. The concentration of $Fe^{3+}OH^-$ is dependent on the *p*H and ionic strength of the solution[6]. It is now well recognized that the purple colour of ferric perchlorate solutions or ferric nitrate solutions in both of which ferric ion does not complex with anion $(ClO_4)^-$ or $(NO_3)^-$ is due to absorption by hydrated ferric ion itself. Absorption by ferric ion moves to the far U.V. region in concentrated perchloric acid solutions and, therefore, the solution becomes colourless. But as the *p*H of the solution is increased the colour of the solution varies from faint yellow to yellow and deep yellow. This variation of colour is attributed to the presence of species like $Fe^{3+}OH^-$, $Fe^{3+}(OH)_2^{2-}$, $Fe^{+3}(OH)_3^{3-}$, etc. By controlling the acidity and ionic strength of the solution, the concentration of any one type of complex could be increased. At *p*H = 0, ferric perchlorate solutions are practically colourless showing the absence of $Fe^{3+}OH^-$. From the absorption spectra of $Fe^{3+}OH^-$ as well as Fe^{3+} (aq.) and also from the dependence of equilibrium constant (K_H) for $Fe^{3+}OH^- \rightleftharpoons Fe^{3+}+OH^-$ upon ionic strength of the solution (μ), the concentration of $Fe^{3+}OH^-$ as well as Fe^{3+}(aq.) could be calculated. When the system $Fe^{3+}OH^-$ methyl methacrylate or acrylonitrile is irradiated with a light beam of 313 or 365 mμ, there is in the primary photochemical process an electron transfer from the anion to the cation giving Fe^{2+} and OH. The OH radicals polymerize the vinyl monomer. It has been found that ferric salt solutions in the range 10^{-2} to 10^{-5}M and even at 10^{-6}M give rise to active ion-pair sensitizer $Fe^{3+}OH^-$. Tables 1 and 2 indicate the concentrations as well as dFe^{2+}/dt for $Fe^{3+}OH^-$ at various *p*H levels.

It was interesting to note that between *p*H 0·86 and 0·56 there was neither polymerization nor ferrous ion production when solution was irradiated for over 12 hr. Also, at a perchloric acid concentration of >>1N and [$Fe(ClO_4)_3$], as high as 10^{-2}M, ferrous ion formation and polymerization were practically negligible. Under the latter conditions the concentration of the species $Fe^{3+}OH^-$

TABLE 1 — INFLUENCE OF *p*H ON LIGHT ABSORPTION

([Fe^{3+}] = 10^{-2} and 10^{-4}M; [acrylonitrile] = 1·0M; intensity = 8·1 × 10^{-5} Nhν/hr.; μ = ionic strength)

[Fe^{3+}] (molar)	*p*H	μ	$k_H \times 10^3$	[Fe^{3+}] $\times 10^4$	[$Fe^{3+}OH$] $\times 10^4$	k_ϵ
10^{-2}	0·0	1·070	7·50	99	1·0	0·20
	0·6	0·345	3·28	96	4·0	0·80
	1·0	0·170	3·09	92	8·0	0·90
	1·3	0·120	3·16	88	12·0	0·94

TABLE 2 — INFLUENCE OF *p*H AND k_ϵ ON THE RATE OF FERROUS ION PRODUCTION

[Fe^{3+}]	*p*H	k_ϵ	dFe^{2+}/dt (moles/hr.) $\times 10^6$
10^{-4}	2·01	0·509	1·610
10^{-4}	1·73	0·356	1·190
10^{-4}	1·50M	0·265	0·631
10^{-4}	1·35	0·194	0·500
10^{-4}	1·04	0·085	0·314
10^{-4}	0·86 0·56	Not measurable	

would be minimal. These data show that $Fe^{3+}OH^{-}$ is the photochemically active species. It has also been shown[15] that the rate of monomer disappearance and the chain length (n) of the methyl methacrylate polymer are linear functions of k_{ϵ}.

(2) *Light intensity*—The results for dFe^{2+}/dt with variation of light intensity with $Fe^{3+}OH^{-}$ acrylonitrile monomer given in Fig. 1 and Table 3 respectively show that light intensity I is a better function of the expression

$$(dFe^{2+}/dt)\left(1+\frac{k_o[Fe^{2+}]}{k_i[M]}\right)$$

than I versus dFe^{2+}/dt alone. The significance of this is dealt with later. Further, the rate of monomer disappearance has already been shown[14] to be a linear function of square root of light intensity, and the chain length of methyl methacrylate polymer a linear function of reciprocal square root of light intensity.

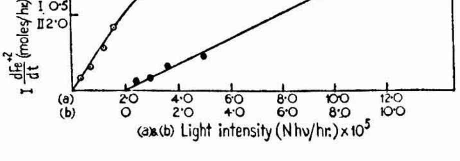

FIG. 1 — RATE OF FERROUS ION PRODUCTION WITH LIGHT INTENSITY [A — Non-linear variation of $\frac{dFe^{2+}}{dt}$ with light intensity for the system $Fe^{3+}OH^{-}$, acrylonitrile; $[Fe^{3+}] = 10^{-2}M$; $pH = 1{\cdot}0$. B — Linear variation of $\frac{dFe^{2+}}{dt}\left(1+\frac{k_o\,[Fe^{2+}]}{k_i\,[M]}\right)$ with light intensity under conditions as in A]

TABLE 3 — RATE OF FERROUS ION PRODUCTION WITH LIGHT INTENSITY

($[Fe^{3+}]=10^{-2}M$; [*acrylonitrile*] $=1{\cdot}2M$; $pH=1{\cdot}0$)

INTENSITY $Nh\nu/hr.$ 10^5	dFe^{2+}/dt (moles/hr.) $\times 10^6$	MEAN $(Fe^{2+})\times 10^5$ molar	$\frac{dFe^{2+}}{dt}\left(1+\frac{k_o[Fe^{2+}]}{k_i[M]}\right)$
8·00	0·970	6·94	1·496
6·80	0·800	5·72	1·150
5·40	0·690	4·93	0·956
3·30	0·450	3·22	0·564
2·04	0·300	2·15	0·350
1·23	0·200	1·43	0·230
0·63	0·155	1·11	0·170

(3) *Variation of monomer concentration* — An accurate investigation of the dependence of dFe^{2+}/dt on monomer concentration was rather difficult because, at very low concentrations of the monomer or even in the absence of monomer, the free radicals would be consumed, it is presumed, by the organic impurities in the distilled water used. The rate of ferrous ion production, therefore, with small concentration of monomer or even in the absence of any monomer was as high as in the presence of higher monomer concentrations. This aspect of impurities has been dealt with in greater detail elsewhere by the author[15]. The experimental results (TABLE 4) obtained with $Fe^{3+}OH^{-}$ show that the values of dFe^{2+}/dt are practically independent of the type and concentration of the monomer. The rate of monomer disappearance with methyl methacrylate was found[14] to be a linear function of first power of monomer concentration.

TABLE 4 — RATE OF FERROUS ION PRODUCTION WITH TYPE AND CONCENTRATION OF MONOMER

(*For* $[Fe^{3+}]=10^{-2}M$, $I=1{\cdot}32\times 10^{-4}$ $Nh\nu/hr.$; *and for* $[Fe^{3+}]=10^{-3}M$, $I=6{\cdot}9\times 10^{-5}$ $Nh\nu/hr.$)

$[Fe^{3+}]$ molar	MONOMER	[M] molar	dFe^{2+}/dt (moles/hr.) $\times 10^6$
10^{-2}	Acrylonitrile	1·00	6·3
10^{-2}	do	0·60	6·5
10^{-2}	do	0·30	6·2
10^{-2}	do	0·10	6·6
10^{-2}	do	0·01	6·8
10^{-2}	Methyl methacrylate	0·10	6·5
10^{-2}	nil	nil	6·0
10^{-3}	Acrylonitrile	0·10	3-4

(4) *The effect of ferrous ion* accumulating in the course of the reaction is similar to that of ferrous ion initially added. Because of secondary dark back reaction between Fe^{2+} and OH, it was observed (FIG. 2) that the rate of ferrous ion production decreased with increase in time or increase in mean ferrous ion concentration, i.e. ferrous ion initially added or present plus one-half of ferrous produced during the time interval. For the $Fe^{3+}OH^{-}$ sensitizer and in the presence of an initially added $[Fe^{2+}]$ as high as $10^{-4}M$, the total ferrous ion produced did not exceed $1{\cdot}3\times 10^{-4}M$ and, therefore, it was possible to measure ferrous ion produced during the time interval and subsequently compute mean ferrous ion concentration. The results in Table 5 indicate how dFe^{2+}/dt decreases as

mean [Fe^{2+}] increase or [$1/dFe^{2+}$]/dt increases with added ferrous ions. The mean ferrous ion concentration could also be computed at various intensities and the same uniform variation between mean [Fe^{2+}] and $1/\frac{dFe^{2+}}{dt}$ is observed (TABLE 6).

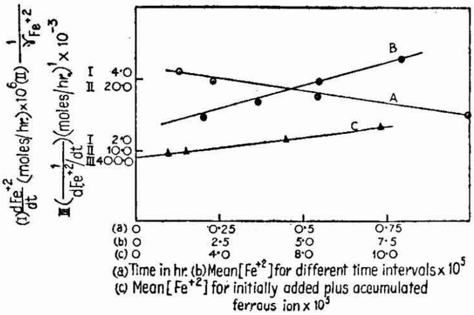

FIG. 2 — RATE OF FERROUS ION PRODUCTION WITH TIME AND MEAN FERROUS ION CONCENTRATION [A — Decrease of rate of ferrous ion production with time; [Fe^{3+}]=10^{-2}M, acrylonitrile; I=0·77 × 10^{-4}Nhν/hr. B — Increase of $\frac{1}{\gamma_{Fe^{2+}}}$ with mean ferrous ion concentration computed at different intervals. C — Increase of $1/\frac{dFe^{2+}}{dt}$ with mean ferrous ion concentration computed from initially added ferrous ion plus half ferrous ion produced during the time interval; [Fe^{3+}]=10^{-3}M; I=1·32 × 10^{-4} Nhν/hr.; pH=1·3]

TABLE 5 — EFFECT OF INITIALLY ADDED FERROUS ION UPON RATE OF FERROUS ION PRODUCTION

([$Fe^{3+}OH$]=10^{-3}M; pH=1·3; *intensity*=1·32 × 10^{-4} *Nhν/units/hr.; monomer, acrylonitrile*)

ADDED [Fe^{2+}] molar	TOTAL [Fe^{2+}] MEASURED MOLES × 10^5	[Fe^{2+}] PRODUCED molar × 10^5	MEAN [Fe^{2+}] molar × 10^5	dFe^{2+}/dt (moles/hr.) × 10^6	1/dFe^{2+}/dt (moles/hr.) × 10^5
nil	3·5	3·5	1·75	4·85	2·00
10^{-6}	3·5	3·4	1·80	4·75	2·10
10^{-5}	4·3	3·3	2·65	4·70	2·13
5 × 10^{-5}	8·1	3·2	6·60	4·54	2·20
10^{-4}	13·0	3·0	11·50	4·20	2·38

TABLE 6 — EFFECT OF MEAN FERROUS ION CONCENTRATION ON THE RATE OF FERROUS ION PRODUCTION

([Fe^{3+}]=10^{-2}M; [*acrylonitrile*]=1·2M; pH=1·0)

INTENSITY Nhν/hr. × 10^6	MEAN (Fe^{2+}) moles × 10^5	dFe^{2+}/dt (moles/hr.) × 10^5	RECIPROCAL QUANTUM YIELD
13·20	3·50	1·75	58·82
8·20	2·70	1·35	47·17
3·20	1·94	0·97	24·10
1·85	0·80	0·40	36·63
1·25	0·70	0·35	27·86
0·55	0·50	0·25	17·18
3·00	0·28	0·14	16·72

(5) *Quantum yields* — The quantum yields with respect to ferrous ion $\gamma_{Fe^{2+}}$ have been found to be dependent on (i) concentration of $Fe^{3+}OH^-$ and, therefore, upon pH of the system and (ii) wavelength. $\gamma_{Fe^{2+}}$ was practically equal at 313 and 365 mμ though it dropped steeply when the limit of the visible was reached. $\gamma_{Fe^{2+}}$ was found to be independent of (i) the intensity of light and (ii) type and concentration of monomer. The quantum yield with regard to monomer disappearance γ_M was found to be dependent on the concentration and type of the monomer used. A maximum value of ≈300 for γ_M for high light intensity and concentration of the monomer and a minimum value ≈5 to 10 for low light intensity were observed. The lower values of γ_M for higher intensities of the order of 1·3 to 1·5 × 10^{-4}Nhν/hr., [Fe^{3+}] = 10^{-2} to 10^{-3} and for [M] = 1·0 to 0·10 were occasionally observed. This must be attributed to the scattering of light by the polymer. The ideal conditions for minimizing the scattering of light were found for a light intensity 6 to 8 × 10^{-5}Nhν/hr. and for a [Fe^{3+}] = 4 × 10^{-5}M concentration were determined. The quantum yields for ferrous ion at various pH levels, ferric ion concentrations and light intensities are given in Table 7.

Discussion

The light absorption process is connected with the change $Fe^{3+}OH^- \xrightarrow{h\nu} Fe^{2+}OH$. The energetics of the system and the mechanism of how $Fe^{2+}OH$ dissociates into Fe^{2+} and OH because of non-equilibrium configuration of hydrated $Fe^{2+}OH$ have already been discussed[9,10]. The resulting OH free radicals initiate polymerization. The experimental results have been examined in the light of the following reaction mechanism to arrive at the actual mechanism of polymerization.

TABLE 7 — QUANTUM YIELDS FOR FERROUS ION AND MONOMER DISAPPEARANCE

pH	$\gamma_{Fe^{2+}}$ at Fe^{3+}			γ_M	
	10^{-2}M	10^{-3}M	10^{-4}M	At intensity 8·1 × 10^{-5} Nhν/hr.	At intensity 1·32 × 10^{-4} Nhν/hr.
2·00	0·060	—	0·040	0·06	0·06
1·70	0·055-0·06	—	0·040	—	—
1·50	0·050	—	0·032	0·05	0·05
1·30	0·050	—	0·032	—	—
1·00	0·050	0·050	0·030	0·03	0·05
0·83	0·050	0·042	0·005	—	—
0·54	0·039	—	—	—	0·04
0·34	0·017	—	—	0·03	—

(1) Light absorption process and primary dark back reaction: $Fe^{3+}OH^{-} \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} Fe^{2+}OH$.

(2) Initiation of polymerization by $Fe^{2+}OH$: $Fe^{2+}OH + M \xrightarrow{k_i'} Fe^{2+} + \dot{O}H-M$.

(3) Separation of the primary product: $Fe^{2+}OH - \xrightarrow{k_s} Fe^{2+} + OH$.

(4) Secondary dark back reaction: $Fe^{2+} + OH \xrightarrow{k_d} Fe^{3+} + OH^{-}$.

(5) Initiation of polymerization by OH radicals: $OH + M \xrightarrow{k_i} OH-M-$.

(6) Propagation:

$$OH-M- + M \xrightarrow{k_p} OH-M-M-.$$

(7) Termination by (a) recombination:

$$OH-(M)_{n-} + (M)_{n-}-OH \xrightarrow{k_t} OH-(M)_n-(M)_n-OH.$$

or (b) disproportionation by the radicals $Fe^{2+}OH$ or OH represented by the rate constants k_{t_1} and k_{t_2} respectively.

In the above scheme, the concentrations of the radicals OH, $Fe^{2+}OH$ or $OH-(M)_{n-}$ are assumed to be constant and stationary.

(i) If $Fe^{2+}OH$ radicals alone initiate polymerization and the radical chains terminate by disproportionation, then it is easy to show that

$$\frac{dFe^{2+}}{dt} = k_\varepsilon I \, k_i'[M]/k_d$$

$$\text{and } \frac{dM}{dt} = k_p k_i [M]^2/k_{t_1}$$

(ii) If $Fe^{2+}OH$ radicals initiate polymerization and termination is brought about by recombination of the radical chains, then dFe^{2+}/dt will be same as in (i);

$$\text{but } \frac{dM}{dt} = k_p[M]^{3/2}(k_i' k_\varepsilon I/k_t k_d)^{1/2}$$

(iii) On the other hand, if OH radicals alone initiate polymerization and the radical chains terminate by disproportionation, then

$$\text{(a) } dFe^{2+}/dt = \frac{k_s k_\varepsilon I}{k_d + k_s} \left(\frac{k_i[M]}{k_i[M] + k_o[Fe^{2+}]} \right)$$

and (b) $dM/dt = k_p k_i [M]^2/k_{t_2}$.

(iv) If OH radicals initiate the polymerization and termination of radical chains is by recombination of the radical chains, then dFe^{2+}/dt will be same as in (iii);

$$\text{but } dM/dt = k_p[M] \left\{ \frac{k_s k_\varepsilon I}{k_t(k_s + k_d)} \right\}$$

(v) If both $Fe^{2+}OH$ and OH radicals initiate polymerization and termination of the radical chains is by disproportionation as well as by recombination, then

$$dFe^{2+}/dt = \frac{k_s k_\varepsilon I}{k_d + k_s + k_i'[M]} \times \left\{ \frac{k_i'[M]}{k_s} + \frac{k_i[M]}{k_i[M] + k_o[Fe^{2+}]} \right\}$$

and for dM/dt expressions involving $[M^2]$ will be obtained for both types of terminations.

If polymerization is to be initiated by $Fe^{2+}OH$ radicals then according to (i) the quantum yield with regard to ferrous ion production must go on increasing as the monomer concentration is increased and not reach a constant value below unity. On the other hand, if OH radicals initiate, then according to (iii), production of ferrous ions must increase with monomer concentration and at high concentrations, i.e. when $k_i[M] >> k_o[Fe^{2+}]$ the quantum yield will be represented by $k_s/(k_s + k_d)$ which is a constant and which is also independent of monomer concentration. When $Fe^{2+}OH$ as well as OH radicals are assumed as initiators, then according to (v) the quantum yield cannot be represented by any constant quantity.

According to the experimental results presented in this paper, the quantum yield for ferrous ion attained a constant value of 0·05 (TABLE 7) both at lower as well as higher monomer concentrations and sometimes even in the absence of the monomer. This must be attributed to the reactions of free radicals with the organic impurities in the reaction system. Further, a plot of reciprocal ferrous ion production against mean ferrous ion (FIG. 2, graph C) gives the expected linearity. The slope of this graph gave $k_o/k_i \approx 4 \times 10^3$ for acrylonitrile and the intercept confirmed the quantum yield for ferrous ion to be $\approx 0·05$. The non-linearity of ferrous ion production with light intensity is attributed to the dark back reaction $Fe^{2+} + OH \xrightarrow{ko} Fe^{3+} + OH^{-}$. If this dark back reaction is considerable, the actual rate of ferrous ion production is then given by $(dFe^{2+}/dt)\left(1 + \frac{k_o[Fe^{2+}]}{k_i[M]}\right)$ and a plot of the latter quantity against light intensity must be linear. This has been found to be the case (FIG. 1).

It is also found that dFe^{2+}/dt is a linear function of k_{ϵ} as well as *p*H. These facts point to OH radicals being the initiators and, therefore, the correct expression for ferrous production would be represented by (iii).

In case of termination of the polymer chain by disproportionation by either $Fe^{2+}OH$ or OH radicals, the rate of monomer disappearance will be proportional to square of monomer concentration $[M]^2$. If $Fe^{2+}OH$ is the initiator and the chains are terminated by recombination, then dM/dt must vary linearly with [M]. On the other hand, if OH radicals initiate the reaction, then dM/dt must vary with [M] for termination by recombination. It has been found that dM/dt varies linearly with [M] proving thereby that the termination reaction is one of mutual recombination of active particles. Further details in support of the termination reaction for the sensitizer $Fe^{3+}Cl^-$ whose behaviour is similar to that of $Fe^{3+}OH^-$ are given elsewhere[14].

Summary

A method for photochemical initiation of polymerization of vinyl monomers in aqueous solution making use of the ion-pair complex $Fe^{3+}OH^-$ is described. The light absorption process by the ion-pair leads to an electron transfer causing the reduction of the cation and oxidation of OH^- to a free radical OH which initiates polymerization. Kinetics of the reaction between OH and vinyl monomer were studied from (a) the dependence of a rate of ferrous production; (b) overall rate of polymerization; and (c) chain length of polymethyl methacrylate (viscometric method) upon (i) light absorbed by the ion-pair; (ii) intensity of light; (iii) monomer concentration and (iv) accumulated or initially added ferrous ion. From the results obtained it is shown that polymerization reaction is initiated by OH radicals and termination of polymerization is by mutual recombination of the active radical chains.

Acknowledgement

I am greatly indebted to late Prof. M. G. Evans and Dr. N. Uri of the University of Manchester for their suggestions and advice during the course of this work.

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Anthraquinone & Anthrone Series: Part XVII—A Synthesis of 1:3:7-Trihydroxyanthraquinone & a New Synthesis of 1:3:8-Trihydroxyanthraquinone

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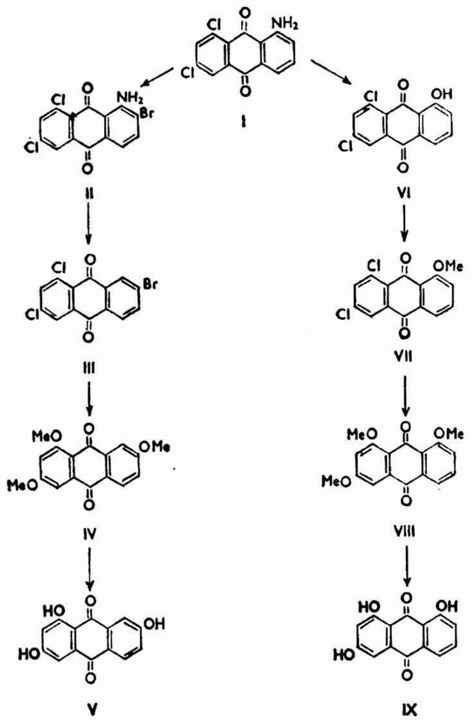
Bromination of 1 - amino - 6 : 8 - dichloroanthraquinone, followed by deamination, yielded 7-bromo-1:3-dichloroanthraquinone, which was converted into the corresponding trimethoxyanthraquinone. Demethylation to 1: 3: 7-trihydroxyanthraquinone was effected by aluminium bromide in boiling benzene. 1: 3-Dichloro-8-hydroxyanthraquinone, prepared from 1-amino-6: 8-dichloroanthraquinone, was converted to the corresponding trimethoxyanthraquinone. Demethylation yielded 1:3:8-trihydroxyanthraquinone, which is important because of its relation to *Frangula*-emodin, *Aloe*-emodin and other naturally occurring hydroxyanthraquinones. To complete the series of trichloroanthraquinones, 1: 3: 8-trichloroanthraquinone has been prepared from 1-amino-6: 8-dichloroanthraquinone by the Sandmeyer reaction.

IN an earlier communication we reported the synthesis of 1: 3: 5-trihydroxyanthraquinone, one of the four unknown trihydroxyanthraquinones[1]; the present work deals with the synthesis of 1: 3: 7-trihydroxyanthraquinone (V) and a new synthesis of 1: 3: 8-trihydroxyanthraquinone (IX).

During a discussion of the chromatographic behaviour of hydroxyanthraquinones on silica gel, Hoyer[2] has mentioned 1: 3: 7-trihydroxyanthraquinone (V), but the preparation and properties have not been described.

1: 3: 8-Trihydroxyanthraquinone (IX) has been prepared earlier by several methods, mainly from certain natural colouring matters. Anslow, Breen and Raistrick[3] obtained 1: 3: 8-trihydroxyanthraquinone (IX) by the decarboxylation of emodic acid (4: 5: 7-trihydroxyanthraquinone-2-carboxylic acid) by heating with copper chromite and quinoline. They drew attention to the fact that "1: 3: 8-trihydroxyanthraquinone has been described previously in a very imperfect fashion in spite of its importance in relation to *Frangula*-emodin and *Aloe*-emodin and the many naturally occurring hydroxyanthraquinones related to these substances". Rhein (4: 5-dihydroxyanthraquinone-2-carboxylic acid) was converted by Oesterle[4] into 2-amino-4: 5-dihydroxyanthraquinone via the acid chloride and amide; diazotization and hydrolysis of the amine gave a poor yield of (IX). Eder and Hauser[5] prepared (IX) from *Frangula*-emodin 7-methyl ether (physcion) through a series of reactions: oxidation to the carboxylic acid, conversion of the acid to the corresponding amine via the acid chloride and amide, reduction of the diazonium salt, and final demethylation. Anslow, Breen and Raistrick have also mentioned that no analyses of the supposed trihydroxyanthraquinone or its acetate were given either by Oesterle or by Eder and Hauser. By heating anthraquinone-1: 6-disulphonic acid with 40-60 per cent oleum at 160° and then heating the product with aqueous calcium hydroxide in an autoclave at 200°, Lauer[6] obtained (IX), together with 1: 2: 4: 5: 8-pentahydroxyanthraquinone and 1: 2: 4: 5: 7: 8-hexahydroxyanthraquinone. We have now synthesized 1: 3: 7- and 1: 3: 8-trihydroxyanthraquinones (V and IX) from 1-amino-6: 8-dichloroanthraquinone (I)[1] by the indicated series of reactions.

Bromination of (I) in glacial acetic acid gave the 2-bromo derivative (II), and deamination of (II) via the diazonium salt yielded 1: 3-dichloro-7-bromoanthraquinone (III). Conversion of (III) to the corres-



ponding trimethoxyanthraquinone (IV) was effected by heating with sodium methoxide and methanol in a sealed tube at 160°-70° for 8 hr. or by refluxing for 36 hr. The latter method gave a better yield of (IV). The orientation of the bromine atom in (II) was shown by the fact that the trimethoxyanthraquinone (IV), m.p. 203°, obtained from (III) is different from 1: 3: 5-trimethoxyanthraquinone[1], m.p. 226°. Demethylation of (IV) to 1: 3: 7-trihydroxyanthraquinone (V) was effected by the action of aluminium bromide in boiling benzene.

1:3-Dichloro-8-hydroxyanthraquinone (VI) was prepared from (I) via the diazonium sulphate. Methylation of (VI) gave 1: 3-dichloro-8-methoxyanthraquinone (VII), which was converted to the corresponding trimethoxyanthraquinone (VIII), m.p. 196°. The melting point and other properties of (VIII) are in agreement with those described by Anslow *et al.*[3]. Demethylation of (VIII) by aluminium bromide in boiling benzene led to 1: 3: 8-trihydroxyanthraquinone (IX), m.p. 287° (Anslow *et al.*[3], m.p. 287°-88°).

Of the 14 theoretically possible trichloroanthraquinones 13 are known, including 1: 3: 5-trichloroanthraquinone described by us in an earlier paper[1]; 1: 3: 8-trichloroanthraquinone has been prepared from 1-amino-6: 8-dichloroanthraquinone by the Sandmeyer reaction in the present work, thus completing the series of trichloroanthraquinones.

The main work on trichloroanthraquinones is due to Goldberg[7,8], whose method consisted essentially in sulphonating α-chloroanthraquinone or an appropriate dichloroanthraquinone, separating the isomeric chloroanthraquinone disulphonic acids and dichloroanthraquinone monosulphonic acids, and replacing the sulphonic groups by chlorine. Goldberg undertook the synthesis of the trichloroanthraquinones because they are readily crystallizable, they have sharp melting points, and the chlorine atoms can be replaced by hydroxyl, methoxyl and amino groups. They are consequently of value in determining the constitution of naturally occurring anthraquinone colouring matters.

TRICHLOROANTHRAQUINONES

No.	Trichloroanthraquinone	M.P. °C.	Reference
1	1: 2: 3-	194-95	7
2	1: 2: 4-	185·5	9, 10
3	1: 2: 5-	235-36	7
4	1: 2: 6-	222-23	7
5	1: 2: 7-	225-26	7
6	1: 2: 8-	190-92	8
7	1: 3: 5-	246-47	1
8	1: 3: 6-	212-13	7
9	1: 3: 7-	216-17	7
10	1: 3: 8-	220	—
11	1: 4: 5-	258	7, 11, 12, 13
12	1: 4: 6-	238	7, 14, 15
13	2: 3: 5-	227-28	8
14	2: 3: 6-	245	8

Goldberg prepared 1: 2: 8-trichloroanthraquinone by the α-sulphonation of 1: 7-dichloroanthraquinone in the presence of mercury and replacement of the sulphonic group by chlorine. Goldberg observed that the entry of the sulphonic group into the α-position *ortho* to the β-chlorine atom was highly probable, and the trichloro compound was, therefore, 1: 2: 8-trichloroanthraquinone; he added, however, that " this view must be accepted with reserve until substantiated by further evidence ". The three α-positions available for the entry of a sulphonic group in 1: 7-dichloroanthraquinone are 4, 5 and 8. Positions 4 and 5 are to be excluded as the trichloroanthraquinone is different from the known 1: 3: 5- and 1: 4: 6-trichloroanthraquinones[1,7,14,15].

Hence the sulphonation of 1:7-dichloroanthraquinone takes place in the 8-position, and Goldberg's 1:2:8-trichloroanthraquinone has the structure he assigned to it.

Experimental procedure

1 - *Amino* - 2 - *bromo* - 6: 8 - *dichloroanthraquinone* (II) — Finely powdered 1-amino-6:8-dichloroanthraquinone (I) (2·92 g.) was suspended in glacial acetic acid (70 cc.). Bromine (1·6 g.) in glacial acetic acid (25 cc.) was added at 40°-50° during 3 hr. with mechanical stirring. The temperature was raised to 100° and stirring continued for 2 hr. The mixture was cooled and the precipitate collected (3·4 g.). Crystallization from nitrobenzene gave red needles, m.p. 277° (found: C, 45·3; H, 1·7; N, 3·7; $C_{14}H_6O_2BrCl_2N$ requires: C, 45·3; H, 1·6; N, 3·8 per cent).

7-*Bromo*-1: 3-*dichloroanthraquinone* (III)— 1 - Amino - 2 - bromo - 6: 8 - dichloroanthraquinone (II) (3 g.) in concentrated sulphuric acid (40 cc.) was cooled to 5° and diazotized with a mixture of sodium nitrite (2 g.) and concentrated sulphuric acid (10 cc.). Glacial acetic acid (10 cc.) was added, followed after 1 hr. by crushed ice (100 g.) and alcohol (150 cc.). When the mixture was heated on a water bath for 1 hr., small orange-yellow needles separated, which were collected, washed and dried (2·5 g.). Crystallization from glacial acetic acid gave orange-yellow needles, m.p. 205° (found: C, 47·5; H, 1·5; $C_{14}H_5O_2BrCl_2$ requires: C, 47·1; H, 1·4 per cent).

1:3:7-*Trimethoxyanthraquinone* (IV) — (a) 7-Bromo-1:3-dichloroanthraquinone (III) (1 g.) was heated with a mixture of anhydrous methanol (20 cc.) and sodium (1 g.) in a sealed tube for 8 hr. at 160°-70°. On pouring the reaction mixture into water, the product was collected, washed free from alkali and dried (0·4 g.). Crystallization from xylene gave yellow needles, m.p. 226° (found: C, 68·9; H, 5·0; $C_{17}H_{14}O_5$ requires: C, 68·5; H, 4·8 per cent).

(b) A solution of sodium methoxide was prepared by adding as much sodium to anhydrous methanol (50 cc.) as dissolved in it at room temperature. The halide (III) (1 g.) was then introduced, and the mixture refluxed for 36 hr. After dilution with water the yellow precipitate was collected, washed and dried (0·7 g.). Crystallization from xylene gave yellow needles, m.p. 226°.

1 : 3 : 7-*Trihydroxyanthraquinone* (V) — 1:3:7-Trimethoxyanthraquinone (IV) (0·5 g.) was dissolved in dry benzene (300 cc.) and anhydrous aluminium bromide (1·5 g.) was added. A dark red complex separated. The mixture was refluxed on a water bath for 4 hr. and benzene distilled off. On cooling, the residue was treated with 2 per cent hydrochloric acid, when a yellow product (0·3 g.) separated. Crystallization from glacial acetic acid gave yellow microscopic needles. The substance darkened at about 330° and did not melt up to 360° (found: C, 65·6; H, 3·3; $C_{14}H_8O_5$ requires: C, 65·6; H, 3·1 per cent). The substance dissolves in concentrated sulphuric acid with a brownish red colour, in aqueous caustic soda with a reddish orange colour, and in 5 per cent sodium carbonate solution with a yellowish orange colour. An alcoholic solution gives with alcoholic ferric chloride a red colouration. The triacetate crystallized from alcohol in pale yellow needles, m.p. 175° (found: C, 63·3; H, 4·0; $C_{20}H_{14}O_8$ requires: C, 62·8; H, 3·7 per cent).

1 : 3-*Dichloro*-8-*hydroxyanthraquinone* (VI) — 1-Amino-6:8-dichloroanthraquinone (I) (5 g.) in concentrated sulphuric acid (100 cc.) was cooled to 5° and diazotized with a mixture of sodium nitrite (5 g.) and concentrated sulphuric acid (20 cc.). The diazonium solution was added to 50 per cent sulphuric acid (300 cc.) and the mixture heated at 140° for 1 hr., when a yellow product separated. After dilution, the precipitate was collected, washed and dried (4·75 g.), m.p. 224°-25°. Crystallization from glacial acetic acid gave golden yellow needles, m.p. 226° (found: C, 57·4; H, 2·4; Cl, 23·8; $C_{14}H_6O_3Cl_2$ requires: C, 57·0; H, 2·0; Cl, 24·2 per cent).

1 : 3-*Dichloro*-8-*acetoxyanthraquinone* — Acetylation of 1:3-dichloro-8-hydroxyanthraquinone (VI) (0·5 g.) with boiling pyridine (10 cc.) and acetic anhydride (1 cc.) during 30 min. and crystallization from acetic acid gave pale yellow needles, m.p. 190° (found: C, 57·1; H, 2·3; $C_{16}H_8O_4Cl_2$ requires: C, 57·3; H, 2·4 per cent).

1: 3-*Dichloro*-8-*methoxyanthraquinone* (VII) — Methylation of 1: 3-dichloro-8-hydroxyanthraquinone (VI) (1·0 g.) with anhydrous potassium carbonate (10 g.) and dimethyl sulphate (2 cc.) in boiling acetone (300 cc.) for 8 hr. gave the ether (VII) (1·02 g.), which crystallized from alcohol in shining lemon-yellow needles, m.p. 201° (found: C, 58·9; H, 2·6; $C_{15}H_8O_3Cl_2$ requires: C, 58·6; H, 2·6 per cent).

1: 3: 8-*Trimethoxyanthraquinone* (VIII) — 1: 3-Dichloro-8-methoxyanthraquinone (VII) (1·0 g.) was refluxed with a mixture of anhydrous methanol (50 cc.) and sodium (2·5 g.) for 20 hr. On dilution with water a yellow product separated. This was collected, washed and dried (0·8 g.). Crystallization from alcohol gave shining yellow plates, m.p. 196° (found: C, 68·8; H, 5·0; OMe, 31·9; calculated for $C_{17}H_{14}O_5$: C, 68·5; H, 4·8; OMe, 31·2 per cent). Anslow *et al.*[3] quote m.p. 195°-96°. The substance dissolves in concentrated sulphuric acid with a red colour, exhibiting a blue shade at the surface when the solution is shaken.

1: 3: 8-*Trihydroxyanthraquinone* (IX) — 1: 3: 8-Trimethoxyanthraquinone (VIII) (0·5 g.) was dissolved in dry benzene (200 cc.) and anhydrous aluminium bromide (1·5 g.) dissolved in benzene (20 cc.) was added, when a dark greenish complex separated. After refluxing on a water bath for 2 hr., benzene was distilled off, the complex broken with dilute hydrochloric acid, and the brown product (0·3 g.) crystallized from ethyl acetate. The brown elongated plates had m.p. 287° (found: C, 65·4; H, 3·3; calculated for $C_{14}H_8O_5$: C, 65·6; H, 3·1 per cent). Anslow *et al.*[3] cite the m.p. 287°-88°. The substance dissolves in concentrated sulphuric acid with a reddish orange colour and in aqueous sodium hydroxide and sodium carbonate with a red colour. These properties are in agreement with those described by Anslow *et al.*[3]. An alcoholic solution gives with alcoholic ferric chloride a cherry-red colouration.

1: 3: 8-*Trichloroanthraquinone* — Finely powdered 1-amino-6: 8-dichloroanthraquinone (I) (2·0 g.) was suspended in glacial acetic acid (40 cc.) and the mixture heated to boiling. Concentrated hydrochloric acid (10 cc.) was added, and after cooling to 0°, diazotization was effected with sodium nitrite (2 g.) in water (10 cc.). The diazonium solution was poured slowly into a freshly prepared and cooled solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (200 cc.) with continuous stirring. The mixture was allowed to warm up to room temperature and then heated on a water bath for 2 hr. A brownish yellow product separated. This was collected, washed and dried (1·75 g.). Crystallization from glacial acetic acid gave brownish yellow needles, m.p. 220° (found: C, 54·2; H, 2·0; $C_{14}H_5O_2Cl_3$ requires: C, 54·0; H, 1·6 per cent).

Acknowledgement

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Thiophenes & Thiapyrans: Part XIII—Syntheses of Benzodithiophenes & Benzodithionaphthenes

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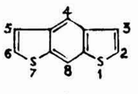
Syntheses of the hitherto unknown benzo-(1:2-b, 5:4-b′)-dithiophene (I), benzo-(1:2-b, 3:4-b′)-dithiophene (II) and benzo-(1:2-b, 3:4-b′)-dithionaphthene (IX) starting from benzene-*m*-dithiol, bromoacetaldehyde dimethyl acetal and 2-bromocyclohexanone are reported. The constitution of the products was proved by unambiguous synthesis of (II) and (IX) from 1-chloro-2:4-dimercaptobenzene. Oxidation of (IX) gave a colourless disulphone.

NONE of the five possible benzodithiophenes (I-IV and V; R = H) have so far been synthesized, although a few derivatives of (I), (III) and (V) (R = H) have been reported. Dihydroxybenzodithiophenes have been prepared by cyclization of phenylene-1:2-, 1:3- and 1:4-dithioglycollic acids[1]. Of these only phenylene-1:2-dithioglycollic acid would lead unambiguously to 3:6-dihydroxybenzo-(2:1-b, 3:4-b′)-dithiophene (V; R = OH), whereas each of the other two dithioglycollic acids may lead to two possible dihydroxybenzodithiophenes. The structures assigned earlier to these compounds[1] cannot, therefore, be regarded as proved. Oxidation of the above hydroxy derivatives leads to thioindigoid dyes which are of great interest on account of the fact that the parent dihydroxybenzodithiophenes are functionally capable of leading to a polymeric thioindigoid dye on oxidation. Buu Höi and Nguyen-Hoan prepared 2-methylbenzo-(1:2-b, 4:5-b′)-dithiophene by pyrolysis of 2:5-dimethyl-3-(2′-thenoyl)-thiophene, but they have described the product as of doubtful structure and purity[2]. Benzo-(1:2-b, 5:4-b′)-dithiophene (I) and benzo-(1:2-b, 3:4-b′)-dithiophene (II) have now been prepared starting from benzene-*m*-dithiol by the general method for the synthesis of thionaphthene and its derivatives[3].



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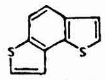

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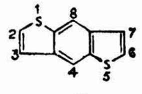

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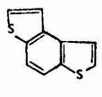

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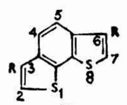
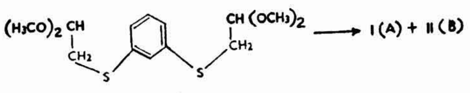


V

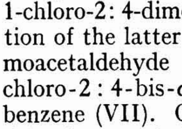
Condensation of benzene-*m*-dithiol with two molecules of bromoacetaldehyde dimethyl acetal gave 1:3-bis-ω-dimethoxyethylmercaptobenzene (VI).



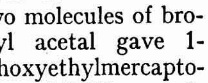
VI

Ring closure of (VI) gave two isomers: A, m.p. 184°, and B, m.p. 43°-44°. In view of the two alternative directions of cyclization of the side chains in (VI), A and B may be represented by either (I) or (II).

Benzo-(1:2-b, 3:4-b′)-dithiophene (II) was synthesized unambiguously starting from 1-chloro-2:4-dimercaptobenzene. Condensation of the latter with two molecules of bromoacetaldehyde dimethyl acetal gave 1-chloro-2:4-bis-ω-dimethoxyethylmercaptobenzene (VII). Cyclization of (VII) gave 8-chlorobenzo-(1:2-b, 3:4-b′)-dithiophene (VIII), which on subsequent dehalogenation gave (II).



VII



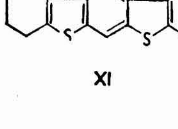
VIII

Product B obtained from (VI) proved to be identical with (II). Product A has, therefore, been assigned the structure benzo-

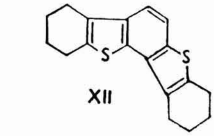
(1: 2-b, 5: 4-b′)-dithiophene (I). The yield of the mixture of A and B obtained from (VI) was 50 per cent, but the yield of the individual component in pure form was low. In order to determine the percentage composition of the above mixture, the absorption spectra of (I)A and (II)B and the cyclization product after one distillation were determined. On the basis of Friedel and Orchin spectrophotometric analysis[4], the mixture contained (I) and (II) in the proportion of 41 and 59 per cent respectively.

None of the five possible benzodithionaphthenes (dibenzo derivatives of I-V) have been prepared, although the 4: 8-quinones[5] and 4: 8-dimethyl derivatives[6] (*also* GHAISAS and TILAK, unpublished data) from the dibenzo derivatives from (I) and (III) have been reported. Benzo-(1: 2-b, 3: 4-b′)-dithionaphthene (IX) has now been prepared starting from benzene-*m*-dithiol by the general method for the synthesis of dibenzothiophenes described earlier by us[7].

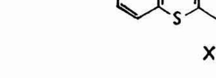
Condensation of benzene-*m*-dithiol with two molecules of 2-bromocyclohexanone gave *m*-di-(2-ketocyclohexyl)-mercaptobenzene (X). Ring closure of the latter gave C which may be assigned the structure (XI) or (XII). Dehydrogenation of C gave D which may be assigned the structure (IX) or benzo-(1: 2-b, 5: 4-b′)-dithionaphthene (XIII).



IX



X



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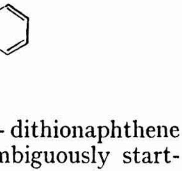
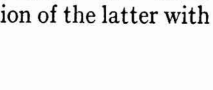


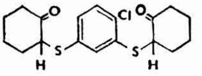
XII



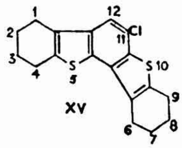
XIII

Benzo-(1: 2-b, 3: 4-b′)-dithionaphthene (IX) was synthesized unambiguously starting from 1-chloro-2: 4-dimercaptobenzene. Condensation of the latter with two molecules of 2-bromocyclohexanone gave 1-chloro-2: 4-di-(2-ketocyclohexylmercapto)-benzene (XIV) which on cyclization gave 11-chloro-1: 2: 3: 4: 6: 7: 8: 9-octahydrobenzo-(1: 2-b, 3: 4-b′)-dithionaphthene (XV). Dehalogenation of (XV) gave 1: 2: 3: 4: 6: 7: 8: 9-octahydrobenzo-(1: 2-b, 3: 4-b′)-dithionaphthene (XII) which was found to be identical with C. The latter has, therefore, been assigned the structure (XII). Dehydrogenation of (XII) gave (IX), a compound which was identical with D. The latter has, therefore, the structure (IX). Compound (XV) was also directly converted into (IX) in one step by heating with selenium.

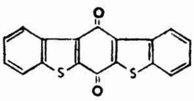
After the isolation of (XII)C from the crude product obtained by cyclization of (X), the remaining material was carefully worked up with a view to isolating (XI) which may be also formed along with (XII). These attempts, however, proved unsuccessful.



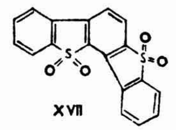
XIV



XV



XVI



XVII

The constitution of product D can be determined by studying its oxidation. If it had the linear structure (XIII), it would have led to the known 6: 12-diketobenzo-(1: 2-b, 5: 4-b′)-dithionaphthene (XVI)[5]. However, oxidation of D gave a colourless disulphone which, in view of the identity of D with (IX), is given the structure (XVII).

Methods described in literature for the preparation of benzene-*m*-dithiol and 1-chloro-2: 4-dimercaptobenzene are unsatisfactory. The dithiols have now been prepared by convenient laboratory methods starting from benzene, chlorobenzene and chlorosulphonic acid, through the *m*-disulphonyl chlorides. The overall yields of the dithiols on the basis of benzene and chlorobenzene used are 22-25 and 45 per cent respectively.

The absorption spectra of (I) and (II) have been compared with those of anthracene and phenanthrene (FIGS. 1 and 2). The similarities observed are in accord with our previous observations[6,8,9] and those of others[10] on similar compounds. The divergence in the spectra of (I) and anthracene after 260 mμ merits further investigation.

Experimental procedure

Benzene-m-dithiol — Chlorosulphonic acid (500 g.) was taken in a three-necked flask fitted with a stirrer, a water condenser, a calcium chloride tube and a dropping funnel. The acid was heated to 100°-120° and benzene (100 cc.) added dropwise in 1½ hr. The temperature was raised to 150°-60° and the mixture kept at this temperature for 3 hr. After cooling to room temperature, the mixture was poured over crushed ice with vigorous stirring. The precipitated disulphonyl chloride was used directly for reduction.

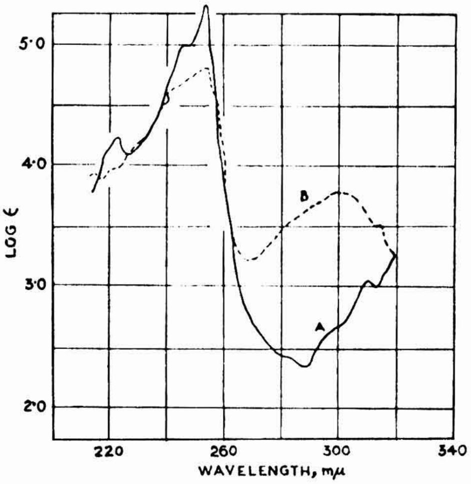


FIG. 1 — ABSORPTION SPECTRA OF ANTHRACENE (A) AND BENZO-(1 : 2-b, 5 : 4-b′)-DITHIOPHENE (B)

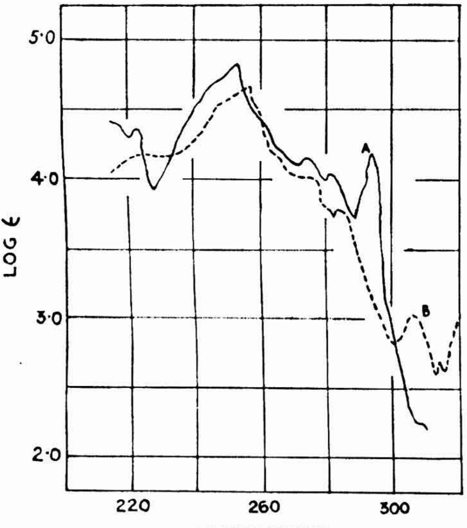


FIG. 2 — ABSORPTION SPECTRA OF PHENANTHRENE (A) AND BENZO-(1 : 2-b, 3 : 4-b′)-DITHIOPHENE (B)

Benzene-*m*-disulphonyl chloride, prepared above, was added to concentrated hydrochloric acid (800 cc.) kept in a 3-l. flask fitted with a stirrer and cooled externally with freezing mixture. After cooling the mixture to 0°-5°, zinc dust (250 g.) was added in 5 g. lots keeping the temperature below 25°-30°. The mixture was worked up in an ice bath for another 2 hr. and then left overnight at room temperature. Care was taken to see that an excess of zinc dust was present throughout the reduction. The dithiol was isolated from the reaction mixture by steam distillation, and ether extraction of the steam-distilled product. The crude product (33 g.) on distillation gave pure benzene-*m*-dithiol (31·41 g.; yield 22 per cent on the basis of benzene used), b.p. 90°-100° (bath temp.)/1·5 mm.; literature[11], b.p. 123°/17 mm.

1 : 3 - *Bis* - *ω* - *dimethoxyethylmercaptobenzene* (VI) — Benzene-*m*-dithiol (12·1 g.), sodium (4·0 g.), bromoacetaldehyde dimethyl acetal (32 g.) and absolute alcohol (200 cc.) were refluxed for 3 hr. After removal of the alcohol by distillation, the mixture was diluted with water and extracted with ether. The ether extract gave the sulphide (VI) (23 g.) which on distillation gave a pale yellow oil (18 g., yield 66 per cent), b.p. 175°-200° (bath temp.)/1·5 mm. All attempts to purify the sulphide by high vacuum distillation proved unsuccessful.

Ring closure of (VI) — Compound (VI) (9·5 g.), phosphorus pentoxide (40 g.) and benzene (100 cc.) were refluxed for 3 hr. The mixture was poured into crushed ice and the solution made just alkaline to phenolphthalein. The benzene layer was separated and the aqueous solution repeatedly extracted with more benzene. The benzene extracts were washed, dried (Na_2SO_4) and the solvent removed. The viscous liquid (4·0 g.) obtained gave, on distillation, a yellow oil (2·84 g., yield 50 per cent), b.p. 120°-250° (bath temp.)/3 mm. The product partly solidified on keeping. Treatment of the oil with hot alcohol and cooling gave product A (0·61 g.; m.p. 60°-85°). After three recrystallizations from alcohol, A gave m.p. 181°-83°. After further recrystallizations from petroleum ether (b.p. 60°-80°) it gave lustrous white plates, m.p. 184° (found: C, 63·3; H, 3·4; $C_{10}H_6S_2$ requires: C, 63·2; H, 3·2 per cent). The product did not give a monopicrate, but gave a dipicrate which crystallized from alcohol in orange-red needles, m.p. 136° (found: N, 13·4; $C_{22}H_{12}N_6O_{14}S_2$ requires: N, 13·0 per cent).

The mother liquor, after separation of A, was refluxed with a saturated alcoholic solution of picric acid (2 g.). The mixture on cooling gave orange needles of the picrate from product B. The picrate was sparingly soluble in alcohol from which it was recrystallized twice. The picrate, m.p. 145°-48°, (1·89 g.) obtained corresponds to 0·86 g. of the parent product B. The picrate was decomposed by 2 per cent aqueous ammonia solution and the precipitated product was extracted with ether. The ethereal layer was washed several times with ammonia solution to remove the residual picric acid and then dried over anhydrous sodium sulphate. The brown residue, left after the removal of ether, on distillation gave a pale yellow oil (0·51 g., yield 9 per cent), b.p. 120°-200° (bath temp.)/3 mm. The distilled product was crystallized twice from alcohol when lustrous white plates of B, m.p. 43°, were obtained (found: C, 63·8; H, 3·4; $C_{10}H_6S_2$ requires: C, 63·2; H, 3·2 per cent). The picrate gave orange needles from alcohol, m.p. 148°-49° (found: N, 9·7; $C_{16}H_9N_3O_7S_2$ requires: N, 10·0 per cent).

The melting points of product B and its picrate were not lowered when admixed with (II) and its picrate, showing thereby the identity of the two sets of compounds.

1-*Chloro*-2: 4-*dimercaptobenzene*—1-Chlorobenzene-2: 4-disulphonyl chloride was prepared by heating a mixture of chlorobenzene (110 g.) and chlorosulphonic acid (850 g.) at 150°-80° for 3 hr. The procedure followed was essentially the same as that described earlier for the preparation of benzene-*m*-disulphonyl chloride. The reaction mixture on pouring over crushed ice gave the disulphonyl chloride which was used for reduction.

The crude sulphonyl chloride was added to concentrated hydrochloric acid (1,000 cc.) under stirring at 0°-5°. Zinc dust (500 g.) was gradually added keeping temperature below 30°. Initially the reaction was vigorous and the addition of zinc dust had to be carefully controlled. The mixture was then stirred for 5 hr., meanwhile allowing the temperature of the mixture to rise to room temperature. After addition of concentrated hydrochloric acid (300 cc.) and a little zinc dust, the mixture was left overnight. More hydrochloric acid (300 cc.) was then added and the chlorodithiol isolated by steam distillation of the reaction mixture. The thiol was extracted with ether and purified by distillation (yield 80 g.; 45 per cent on the basis of chlorobenzene taken), b.p. 138°/8 mm.; literature[12], b.p. 145°-46°/13-14 mm.

1-*Chloro*-2: 4-*bis*-ω-*dimethoxyethylmercaptobenzene* (VII) — 1-Chloro-2: 4-dimercaptobenzene (10 g.), sodium (2·7 g.), bromoacetaldehyde dimethyl acetal (20 g.) and alcohol (125 cc.) were refluxed for 3 hr. The sulphide (16·5 g.), on distillation, gave a yellow oil (14·5 g., yield 72 per cent), b.p. 170°-200° (bath temp.)/1·75 mm. The product was redistilled five times and finally collected at 148°-52°, (bath temp.)/0·02 mm. (found: C, 48·2; H, 5·7; $C_{14}H_{21}ClO_4S_2$ requires: C, 47·7; H, 5·9 per cent).

8-*Chlorobenzo*-(1: 2-*b*, 3: 4-*b'*)-*dithiophene* (VIII) — The sulphide (VII) (14 g.), phosphorus pentoxide (80 g.) and benzene (150 cc.) were refluxed for 3 hr. The cyclization product (8·43 g.) on distillation gave a yellowish brown oil (3·99 g., yield 45 per cent), b.p. 160°-220° (bath temp.)/ 8-9 mm. The product, after separation from petroleum ether (b.p. 60°-80°) gave pale yellow needles (1·6 g.), m.p. 70°-74°. The product, after sublimation at 120°-30°, (bath temp.)/0·5 mm., was crystallized from petroleum ether when it gave needles, m.p. 74°-75°, raised to 76° by two more recrystallizations from the same solvent (found: C, 53·4; H, 2·3; Cl, 15·6; $C_{10}H_5ClS_2$ requires: C, 53·4; H, 2·2; Cl, 15·8 per cent). The picrate gave yellow needles from alcohol, m.p. 112°-13° (found: N, 9·2; $C_{16}H_8ClN_3O_7S_2$ requires: N, 9·3 per cent).

Benzo-(1: 2-*b*, 3: 4-*b'*)-*dithiophene* (II) — Chlorobenzodithiophene (VIII) was dehalogenated according to the method of Edwards and Stuart[13]. A mixture of (VIII) (0·67 g.), cuprous oxide (0·575 g.), acetic anhydride (0·43 g.) and pyridine (2 cc.) was heated at

150°-80° for 15 hr. The dehalogenated product (II) (0·56 g.) isolated by extraction with benzene gave on distillation a pale yellow oil (0·49 g., yield 86 per cent), b.p. 120°-40° (bath temp.)/1 mm., which soon solidified. On crystallization from alcohol, the product gave lustrous plates, m.p. 43°-44° (found: C, 63·7; H, 3·3; $C_{10}H_6S_2$ requires: C, 63·2; H, 3·2 per cent). The picrate gave orange needles from alcohol, m.p. 148°-49° (found: N, 9·8; $C_{16}H_9N_3O_7S_2$ requires: N, 10·0 per cent).

m-Di-(2-ketocyclohexyl)-mercaptobenzene (X) — Benzene-*m*-dithiol (10 g.) was dissolved in 10 per cent aqueous potassium hydroxide (8 g. in 80 cc. water). After cooling the solution to 20°-25°, 2-bromocyclohexanone (28 g.) was added dropwise in 15 min. under stirring and cooling. After stirring for 1 hr., the contents were diluted with water and extracted with ether. The product (19·6 g.), obtained after removal of ether, gave on distillation a pale yellow viscous oil (12·9 g., yield 55 per cent), b.p. 190°-220°/0·04 mm. It was distilled three times and finally collected at 200°-204°/0·04 mm. (found: C, 65·2; H, 6·8; $C_{18}H_{22}O_2S_2$ requires: C, 64·7; H, 6·6 per cent).

Cyclization of (X) *to* C — A mixture of (X) (12 g.), phosphorus pentoxide (80 g.) and benzene (150 cc.) was refluxed for 2½ hr. The cyclization product (9·97 g.) was dissolved in hot acetone (125 cc.), the solution decolourized with Norit and filtered. The cyclized product C separated on cooling and had a m.p. 123°-31°. The mother liquor was concentrated to 25 cc., treated with Norit, filtered and cooled when another crop of C, m.p. 120°-30° (0·87 g.) (total yield 5·97 g., 56 per cent), was obtained. Both the crops were mixed and recrystallized from acetone. The purified product (4·3 g.), m.p. 132°-37°, was recrystallized five times from benzene-petroleum ether (b.p. 60°-80°) mixture when C separated out as colourless needles, m.p. 136°-37° (found: C, 72·3; H, 6·0; $C_{18}H_{18}S_2$ requires: C, 72·5; H, 6·0 per cent). The sym-trinitrobenzene derivative gave orange-yellow needles, m.p. 200°-201°, from benzene-petroleum ether (b.p. 60°-80°) (found: N, 8·5; $C_{24}H_{21}N_3O_6S_2$ requires: N, 8·1 per cent).

Dehydrogenation of C *to* D — A mixture of C (1 g.) and selenium (1·5 g.) was heated at 300°-320° for 22 hr. The dehydrogenated product D (0·98 g.) isolated by extraction with benzene on crystallization from benzene-*n*-hexane gave needles, m.p. 166°-68° (0·45 g., yield 46 per cent), raised to 167°-68° after recrystallization from the same solvents (found: C, 74·4; H, 3·8; $C_{18}H_{10}S_2$ requires: C, 74·4; H, 3·4 per cent). The sym-trinitrobenzene derivative gave orange needles, m.p. 174°-75°, from a mixture of benzene and petroleum ether (found: N, 8·6; $C_{24}H_{13}N_3O_6S_2$ requires: N, 8·3 per cent).

The melting points of C and D and their sym-trinitrobenzene derivatives were not lowered on admixture with (XII) and (IX) and their respective sym-trinitrobenzene derivatives. Compounds C and D are, therefore, identical with (XII) and (IX) respectively.

1-Chloro-2:4-di-(2-ketocyclohexylmercapto)-benzene (XIV) — 1-Chloro-2:4-dimercaptobenzene (10 g.) was condensed with 2-bromocyclohexanone (20·5 g.) as in the synthesis of (X). The condensation product (20·1 g.) gave, on distillation, (XIV) as a viscous oil (11·4 g., yield 55 per cent), b.p. 200°-250° (bath temp.)/0·02 mm., which was used in the subsequent experiment without further purification.

11-*Chloro*-1:2:3:4:6:7:8:9-*octahydrobenzo-*(1:2-*b*, 3:4-*b′*)-*dithionaphthene* (XV) — A mixture of (XIV) (10 g.), phosphorus pentoxide (60 g.) and benzene (100 cc.) was refluxed for 3 hr. The cyclization product (9·42 g.) was dissolved in benzene and a saturated solution of picric acid in benzene was added and the mixture heated to boil. The clear solution on cooling gave a red-coloured picrate which was collected and decomposed with 2 per cent aqueous ammonia. The purified product (XV) (6·43 g.) on crystallization from benzene-petroleum ether (b.p. 60°-80°) gave needles, m.p. 137°-39° (4·19 g., yield 46 per cent), raised to 140° by three further recrystallizations from the same solvents (found: C, 64·9; H, 5·4; Cl, 11·0; $C_{18}H_{17}ClS_2$ requires: C, 65·0; H, 5·1; Cl, 10·7 per cent). The sym-trinitrobenzene derivative crystallized from benzene-petroleum ether (b.p. 60°-80°) in yellow needles, m.p. 200°-201° (found: N, 7·7; $C_{24}H_{20}ClN_3O_6S_2$ requires: N, 7·6 per cent).

1:2:3:4:6:7:8:9-*Octahydrobenzo-*(1:2-*b*, 3:4-*b′*)-*dithionaphthene* (XII) — A mixture of (XV) (3·1 g.), cuprous oxide (2·5 g.), acetic anhydride (1·55 g.) and pyridine (3 cc.) was heated at 150°-60° for 20 hr. The dehalogenation product (2·6 g.) isolated by extraction with benzene gave on crystallization from petroleum ether (b.p. 60°-80°) colourless needles (2·4 g., yield 86 per cent), m.p. 134°-36°, raised to 136°-37° by three further recrystallizations from benzene-petroleum ether (found: C, 72·5; H, 5·7; $C_{18}H_{18}S_2$ requires: C, 72·5; H, 6·0 per cent). The sym-trinitrobenzene derivative gave orange-yellow needles when crystallized from benzene-petroleum ether (b.p. 60°-80°), m.p. 200° (found: N, 8·3; $C_{24}H_{21}N_3O_6S_2$ requires: N, 8·1 per cent).

Benzo-(1:2-*b*, 3:4-*b'*)*-dithionaphthene* (IX): *Method A* — A mixture of (XV) (3·3 g.) and selenium (5 g.) was heated at 300°-350° for 48 hr. The product (2·8 g.), isolated by extraction with benzene and on crystallization from benzene-petroleum ether (b.p. 60°-80°), gave needles, m.p. 164°-66°, raised to 167°-68° by further recrystallization from ether (found: C, 74·2; H, 3·1; S, 22·8; $C_{18}H_{10}S_2$ requires: C, 74·4; H, 3·4; S, 22·0 per cent). The sym-trinitrodibenzene derivative crystallized from benzene-petroleum ether in orange-yellow needles, m.p. 174° (found: N, 7·9; $C_{24}H_{13}N_3O_6S_2$ requires: N, 8·3 per cent).

Method B — Compound (IX) was also prepared by the dehydrogenation of (XII). A mixture of (XII) (1·5 g.) and selenium (2 g.) was heated at 300°-350° for 24 hr. The product (1·39 g.) isolated as above crystallized from benzene-petroleum ether in colourless needles (0·98 g., yield 67 per cent). The latter after five recrystallizations from the same solvents gave needles melting at 167°-68°.

Sulphone (XVII) — A solution of chromium trioxide (0·34 g.) in acetic acid (3 cc.) and water (2 cc.) was added to a boiling solution of (IX) (0·170 g.) in acetic acid (15 cc.). The mixture was boiled under reflux for 2 hr. After cooling and dilution with water the mixture was filtered. The oxidation product crystallized from acetic acid in colourless needles which did not melt up to 360° (found: C, 61·5; H, 2·9; $C_{18}H_{10}O_4S_2$ requires: C, 61·0; H, 2·8 per cent).

Absorption spectra

Spectra of products (I) and (II) and the cyclization product [mixture of (I) and II)] obtained from (VI) were determined employing alcohol as solvent and a concentration of M/30,000. The log ϵ and mμ values are given below.

Compound (I) — $\lambda_{max.}$, 254, 302 mμ; log ϵ, 4·8, 3·7; $\lambda_{min.}$, 218, 270 mμ; log ϵ, 3·9, 3·2.

Compound (II) — $\lambda_{max.}$, 223, 254, 274, 284, 308 mμ; log ϵ, 4·2, 4·6, 4·0, 3·8, 3·1; $\lambda_{min.}$, 226, 280, 300, 312, 316 mμ; log ϵ, 4·1, 3·8, 2·8, 2·7, 2·6.

Mixture of (I) *and* (II) *obtained from* (VI) — $\lambda_{max.}$, 254, 274, 284, 306 mμ; log ϵ, 4·5, 3·9, 3·8, 3·5; $\lambda_{min.}$, 272, 280, 304, 318 mμ; log ϵ, 3·9, 3·8, 3·5, 3·3.

Acknowledgement

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Chemical Components of Commercial Woods & Related Plant Materials: Part II — The Heartwood of *Pinus excelsa* Wall.

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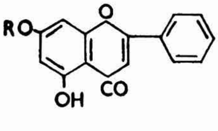
A study of the Himalayan (Simla) sample of *Pinus excelsa* has revealed the presence of the following compounds not reported earlier: galangin, izalpinin, pinobanksin-7-methyl ether, 2-hydroxy-4:6-dimethoxy chalkone, 4-hydroxy stilbene, 4-methoxy stilbene and pinosylvin dimethyl ether. The association of chalkone, flavanone, dihydroflavonol and flavonol is significant from the point of view of biogenesis. The occurrence of 4-methoxy and 4-hydroxy stilbene is also of considerable interest.

IN the course of a general investigation in this laboratory of Indian timber trees, *Pinus excelsa* of the Himalayas was also examined. We were originally under the impression (from literature available in abstracts[1]) that the earlier work of Lindstedt[2] related mainly to wood of Scandinavian origin. Recently, however, we obtained the original paper of Lindstedt which showed that his study related to the heartwood of Indian *Pinus excelsa*. As a result of the present study, some more compounds, not isolated by Lindstedt, have been obtained from the heartwood of this tree and characterized. These compounds give a further insight into the origin and evolution of heartwood components.

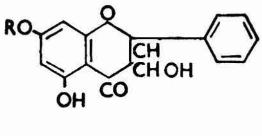
Pinus excelsa Wall. (syn. *Pinus wallichiana* Jacks; *Pinus griffithi* M'clelland) is a Haploxylon pine belonging to the group Strobi[3], growing on the slopes of the Himalayas at an altitude of 6,000-8,000 ft. above sea level. It is a conifer commonly known in India as *Kail*; its trade name is Blue Pine.

Lindstedt extracted the heartwood[2] in the cold with ether and subsequently with acetone. The first extract was then fractionated into portions soluble in petroleum ether, in aqueous sodium carbonate, and in 0·2 per cent and 4·0 per cent aqueous sodium hydroxide. The acetone extract was divided into fractions based on solubility in water and in different alkalies. The water soluble fraction was further fractioned with the help of phenyl hydrazine. The petroleum ether solution gave an oil and resin acids. From the other fractions he obtained the following



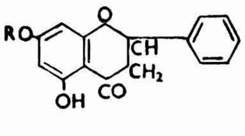
I R=H

II $R = CH_3$



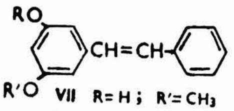
III R = H

IV $R = CH_3$



V R=H

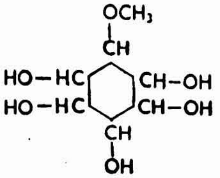
VI $R_1 = CH_3$



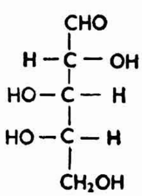
VII R=H ; $R' = CH_3$

VIII R= R'=H

IX $R = R' = CH_3$



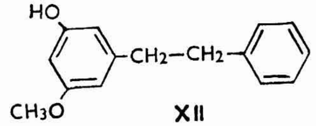
X



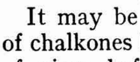
XI

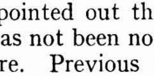
substances: chrysin (I), tectochrysin (II), pinobanksin (III), pinocembrin (V), pinosylvin monomethyl ether (VII), pinitol (X), and L-arabinose (XI).

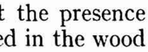
Subsequently, using paper chromatography[4], he detected the presence of pinosylvin (VIII), dihydro pinosylvin monomethyl ether (XII), pinostrobin (VI) and another phenolic component (R_f value 0·4), which could not be identified. His results also indicated that the Indian and British samples of *Pinus excelsa*[5] had the same chemical components.


XII

The method of extraction used in the present work is slightly different. It has been found more convenient to remove essential oils first by extraction with cold petroleum ether. This fraction yields a liquid giving triterpene reaction and a crystalline substance melting at 160° whose chemical nature is still under investigation. Subsequent extraction of the wood with cold ether and hot alcohol, and fractionation of these extracts with aqueous alkali have led to the isolation and characterization of the following compounds not detected before in *Pinus excelsa*: galangin (XIII), izalpinin (XIV), pinobanksin-7-methyl ether (IV), 2-hydroxy-4: 6-dimethoxy chalkone (XV), 4-hydroxy stilbene (XVI), 4-methoxy stilbene (XVII) and pinosylvin dimethyl ether (IX).


XIII R = H
XIV R = CH₃

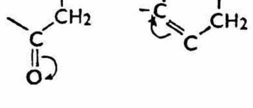

XV


XVI R = H
XVII R = CH₃

The scheme of extraction and the products isolated from different extracts are shown in the chart (FIG. 1).

It may be pointed out that the presence of chalkones has not been noted in the wood of pines before. Previous work indicated the common occurrence of dihydro flavonols; however, that the corresponding flavonols also accompany them in these woods is again a new observation. This association is known to occur elsewhere, e.g. fustin and fisetin in the wood of *Rhus succedanea*[6], and ampelopsin and myricetin in *Ampelopsis meliaefolia*[7] and is of value in the study of biogenesis. More interesting is the occurrence of the two stilbene derivatives, 4-hydroxy (XVI) and 4-methoxy stilbenes (XVII), not so far met with in natural products.

A highly significant observation is the simultaneous occurrence of closely related phloroglucinol derivatives: chalkone (XV), flavanone (V), hydroxy flavanone (III), flavone (I) and flavonol (XIII). All these have no substituent in the side phenyl nucleus. It could be suggested that the chalkone represents the earliest stage among them. As already established 2: 4: 6-trihydroxy chalkone (XVIII) would be unstable[8] and hence it would change into 5: 7-dihydroxy flavanone (V). The existence of the chalkone dimethyl ether (XV) is obviously due to prior methylation of the phenolic hydroxyl groups before the actual chalkone structure is produced and this stabilizes the chalkone. From flavanone (V) a stage of oxidation should be leading to the formation of 3-hydroxy flavanone (III). This stage involves hydroxylation of reactive CH_2 group of the flavanone (V). There is reason to believe that this can take place under biological conditions. It has been recently shown that N-bromo succinimide, which reacts by generation of bromine atoms, forms 3-bromo flavanones smoothly[9]. A close analogy is cholesterol which yields the 7-bromo compound with the above brominating agent and 7-hydroxy cholesterol by biological oxidation; the activity of the concerned CH_2 group is due to electromerism shown below; laboratory analogies in support of this suggestion are now available and will be described separately.



The subsequent changes which 3-hydroxy flavanone (III) undergoes have received considerable experimental support[10]. Earlier it was observed that under alkaline conditions in presence of air[11,12] or hydrogen peroxide[11,13], flavonols are formed. It has been

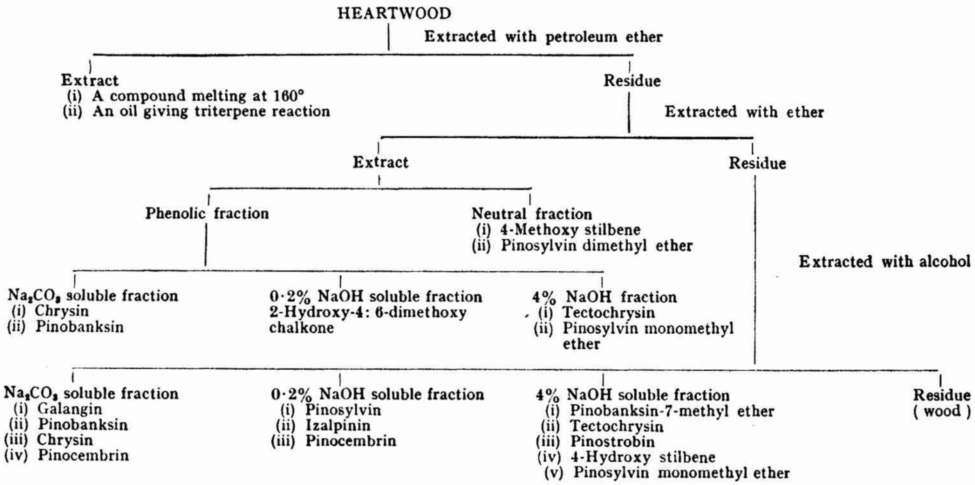
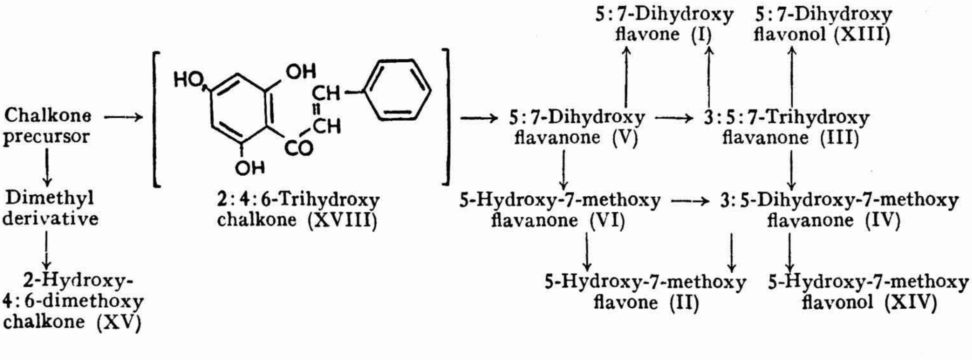


FIG. 1 — EXTRACTION OF HEARTWOOD OF *Pinus excelsa*

recently found that a very convenient method for this dehydrogenation is to use iodine in presence of sodium acetate (MAHESH and SESHADRI, unpublished work). The formation of the flavone (I) may take place in two ways: (1) dehydrogenation of the flavanone (V)[14,15] and (2) dehydration of the 3-hydroxy flavanone (III). Both have known laboratory anologies and are possible biologically. Even the action of selenium dioxide in converting flavanones into flavones may be considered to pass through an intermediate stage of 3-hydroxy flavanone which undergoes dehydration (BANERJEE and SESHADRI, unpublished work).

The following chart presents the tentative scheme of evolution and the interrelationship of the various flavonoids found in *Pinus excelsa*:

The occurrence of partial methyl ethers also deserves comment. It has been already mentioned that methylation prior to the formation of the chalkone structure gives rise to 2-hydroxy-4: 6-dimethoxy chalkone (XV). In all other cases only partial methylation has taken place in the 7-position, the resistant 5-hydroxyl being left out. Obviously these are products of methylation processes functioning after the flavanone structure is built up. It is significant that in 3-hydroxy-flavanones the alcoholic hydroxyl in the 3-position is again left out being more difficult to methylate. But even the flavonol hydroxyl in the 3-position which is reactive is left unmethylated. Obviously the methylating agent is available only in restricted amount and during a restricted period.



The yields of the various components obtained in this work are considerably lower than those recorded by Lindstedt. This and the occurrence of a bigger number of compounds may be due to difference in the habitat and age of the material.

Experimental procedure

Extraction — The dry heartwood of *Pinus excelsa* (6 kg.) was chipped and extracted thrice with cold petroleum ether, each extraction taking 24 hr. The yellow petroleum ether extract yielded on concentration a solid mixed with an oil (fraction A). The residual heartwood was air dried and next extracted thrice with cold ether, each extraction taking 24 hr. The ether extract was concentrated to *c.* 1,000 cc. and extracted with aqueous solutions of (saturated) sodium bicarbonate (no extraction), 20 per cent sodium carbonate (fraction B), 0·2 per cent sodium hydroxide (fraction C) and 4·0 per cent sodium hydroxide (fraction D). Complete evaporation of the remaining ether solution yielded a neutral fraction (E). The remaining wood chips after air drying were next extracted thrice with boiling alcohol, each extraction taking 6 hr. The alcohol extract was concentrated to *c.* 300 cc. and 1,000 cc. of ether added in order to precipitate more highly coloured impurities (4·0 g.). The ether-alcohol solution was fractionated as above with sodium bicarbonate (no extract), 20 per cent sodium carbonate (F), 0·2 per cent sodium hydroxide (G) and 4·0 per cent sodium hydroxide (H). No neutral fraction was present here.

Petroleum ether extract: Fraction A — The solid was filtered and it crystallized from a mixture of petroleum ether and acetone as pale brown rhombic prisms melting at 160°. It gave no colour with alcoholic ferric chloride, bis-diazotized benzidine reagent and magnesium and hydrochloric acid. It was insoluble in aqueous sodium hydroxide, but dissolved in sulphuric acid with a bright yellow colour and in nitric acid with a yellowish green colour. The substance did not answer tests for the carbonyl group, nor did it give triterpene colour reactions. Its molecular weight as determined by the macro-freezing point method is 368·5. Its probable molecular formula is $C_{24}H_{18}O_4$ (found: C, 77·8; H, 4·3; $C_{24}H_{18}O_4$ requires: C, 77·8; H, 4·8 per cent); yield 1·15 g.

The oil was insoluble in sodium hydroxide and gave no colour with alcoholic ferric chloride. It gave a bluish violet colour with acetic anhydride-sulphuric acid mixture which is characteristic of most of the triterpenes; yield 12 g.

Ether extract: Fraction B [chrysin (I) and pinobanksin (III)] — On acidification with hydrochloric acid this fraction yielded a brown solid. After drying it was dissolved in 100 cc. of ether and on keeping the solution in a refrigerator for 15 days a fraction separated out. It crystallized from alcohol as pale brown rectangular plates melting at 280°-81°. It gave a yellow colour with magnesium-hydrochloric acid and a bluish violet colour with ferric chloride. On refluxing with dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium it yielded a complete methyl ether which crystallized from alcohol as long rectangular rods and prisms melting at 75°-76°. With pyridine and acetic anhydride it yielded an acetate which crystallized from alcohol as colourless needles melting at 192°. The above properties agree with those of chrysin and a mixed melting point with an authentic sample was undepressed; yield 1·2 g.

The ether mother liquor was evaporated to dryness and the residue taken up in alcohol (2 cc.) and added to boiling water (400 cc.) and after the filtration of a small amount of resinous impurity, the aqueous solution was extracted with large quantities of ether. The substance thus obtained was crystallized twice from methanol and finally from benzene when it crystallized as pale yellow coloured needles melting at 177°-78°. It gave the following colour reactions: hot nitric acid, brownish violet; ferric chloride, reddish violet; diazotized benzidine, cherry red; magnesium-hydrochloric acid as well as zinc-hydrochloric acid, orange red. The above properties corresponded with those of pinobanksin. The identity was confirmed by its dehydrogenation to galangin by the use of sodium acetate and iodine (MAHESH and SESHADRI, unpublished work); yield 0·2 g.

Fraction C [2-hydroxy-4:6-dimethoxy chalkone (XV)] — On acidification with hydrochloric acid, a yellow solid was obtained which crystallized from alcohol as orange-yellow plates melting at 114°. It gave blood red colour with ferric chloride, no colour with magnesium-hydrochloric acid and a red colour when subjected to borocitric acid test. It agrees with 2-hydroxy-4: 6-dimethoxy chalkone and a mixed melting point with an authentic sample was undepressed; yield 1·5 g.

Fraction D [*tectochrysin* (II), *pinosylvin monomethyl ether* (VII)] — On standing for 24 hr., a yellow sodium salt separated (0·8 g.). It was decomposed with cold concentrated hydrochloric acid (5 cc.; 15 min.). The product crystallized from alcohol as cream-coloured rectangular rods melting at 163°-64°. It gave a greenish brown colour with ferric chloride and a yellow colour with magnesium-hydrochloric acid. The complete methyl ether crystallized from alcohol as colourless long rectangular rods and prisms melting at 75°-76° and agreed with chrysin dimethyl ether. The acetate crystallized from alcohol as long colourless needles melting at 140°. The above compound agreed with tectochrysin and a mixed melting point with an authentic sample was undepressed; yield 0·5 g.

The alkaline solution, on acidification, yielded a viscous liquid which distilled at 285°/5 mm. pressure. On stirring it solidified and then crystallized from methanol as colourless prisms melting at 118°-20°. It gave a brick-red colour with bis-diazotized benzidine reagent and no colour with ferric chloride and magnesium-hydrochloric acid. It readily added bromine and decolourized permanganate. On treatment with pyridine and benzoyl chloride it yielded a benzoate which crystallized from methanol as tiny colourless prisms melting at 85°-86°. This fraction thus agreed with pinosylvin monomethyl ether; yield 4·5 g.

Fraction E [*4-methoxy stilbene* (XVII), *pinosylvin dimethyl ether* (IX)] — The crude fraction (1·6 g.) was dissolved in boiling methanol (10 cc.). On rapid cooling a colourless substance was obtained which on a second crystallization from methanol separated as tiny colourless prisms melting at 136°-37°. It gave no colour with magnesium and hydrochloric acid and readily decolourized permanganate and bromine. It (0·5 g.) was suspended in 10 per cent aqueous sodium carbonate (15 cc.) and potassium permanganate solution (4 g. in 200 cc. water) was added gradually to the boiling suspension during 2 hr. After refluxing for another hour, 10 per cent sodium hydroxide (10 cc.) was added, the solution filtered hot, decolourized with sulphur dioxide and then strongly acidified with sulphuric acid. The oxidation products were extracted with ether, the solution dried over sodium sulphate and evaporated. The residue was then dissolved in benzene and fractionally precipitated with petroleum ether. The first fraction (100 mg.) crystallized from water as colourless long needles melting at 184° and agreed with anisic acid. The second fraction (100 mg.) crystallized from water as long colourless needles melting at 121° and agreed with benzoic acid. This indicated that the parent compound was 4-methoxy stilbene. A mixed melting point with a synthetic sample prepared by the method of Hewitt, Lewcock and Pope[16] was undepressed; yield 0·5 g.

The methanol mother liquor on evaporation gave a deeply coloured semi-solid which was dissolved in ethyl acetate and coloured impurities precipitated by petroleum ether. On evaporating the solution it was obtained as a pale yellow oil which gave no colour with magnesium and hydrochloric acid and readily decolourized permanganate and bromine indicating that it was a stilbene. The substance (200 mg.) was oxidized with alkaline permanganate as above and the oxidation products dissolved in boiling benzene. On cooling the sparingly soluble 3 : 5-dimethoxy benzoic acid (80 mg.) separated as long rectangular prisms melting at 182°-83°. Benzene was removed from the mother liquor and the residue crystallized from water when benzoic acid (80 mg.) separated as long colourless needles melting at 121°. The substance was, therefore, pinosylvin dimethyl ether; yield 0·25 g.

Alcohol extract: *Fraction F* [*galangin* (XIII), *chrysin* (I), *pinobanksin* (III), *pinocembrin* (V)] — On acidification a brown substance was obtained (8 g.). It was dissolved in 150 cc. ether and allowed to stand in a refrigerator for 10 days. A yellow solid separated which crystallized from alcohol as yellow prismatic rods melting at 214°-15°. It gave a bluish brown colour with ferric chloride, an orange colour with magnesium and hydrochloric acid and a pale yellow colour with zinc and hydrochloric acid. It yielded an acetate when refluxed with pyridine and acetic anhydride which crystallized as colourless thick rectangular plates from ethyl acetate and petroleum ether mixture melting at 142°-43°. The original compound (0·2 g.) was refluxed for 40 hr. with dimethyl sulphate (0·8 cc.) and potassium carbonate (2·0 g.) in dry acetone (50 cc.). A complete methyl ether was thus obtained which crystallized from alcohol as colourless rectangular rods and needles melting at 194°-95°. A mixed melting point with galangin trimethyl ether was undepressed; yield: galangin 0·5 g.

The ether solution was evaporated and the residue dissolved in alcohol (10 cc.) and added to boiling water (1,000 cc.). The solid product was filtered and again treated as before. The combined water extract was saturated with sodium chloride and extracted repeatedly with large quantitites of ether. The substance thus obtained was crystallized twice from methanol and subsequently from benzene when it separated out as pale yellow needles melting at 177°-78°. It was found to be identical with pinobanksin described earlier; yield 0·9 g.

The hot water insoluble residue (3 g.) was dissolved in alcohol (15 cc.) and allowed to cool slowly. A pale brown solid crystallized out, which on recrystallization from alcohol separated out as pale brown rectangular plates melting at 280°-81°. It agreed with chrysin described earlier; yield 1·2 g. The alcohol mother liquor was completely evaporated and the residue crystallized repeatedly from methanol when it separated out as colourless needles melting at 193°-94°. It gave no colour with magnesium and hydrochloric acid, a reddish blue colour with ferric chloride and a bluish brown colour with concentrated nitric acid. The compound corresponded to pinocembrin. This was confirmed by its oxidation to chrysin using iodine and sodium acetate (MAHESH and SESHADRI, unpublished work); yield 0·3 g.

Fraction G [*pinosylvin* (VIII), *izalpinin* (XIV), *pinocembrin* (V)] — The extract was acidified with hydrochloric acid and the precipitate thus obtained dried. The dry solid (2·5 g.) was treated with ether (100 cc.) and filtered. The small portion left undissolved crystallized from methanol as colourless tiny prisms melting at 153°-55°. It gave an acetate which crystallized from methanol as pale coloured tiny prisms melting at 100°-101°. With benzoyl chloride and pyridine a benzoate was obtained which crystallized from methanol as colourless tiny prisms melting at 150°-51°. The compound agreed with pinosylvin; yield 0·2 g.

The ether solution was evaporated and the residue (2 g.) was dissolved in boiling alcohol (8 cc.). On cooling rapidly a yellow substance separated out which on recrystallization yielded yellow prismatic needles melting at 192°-93°. It gave a bluish brown colour with ferric chloride, a pink colour with magnesium and hydrochloric acid and a yellow colour with zinc and hydrochloric acid. On methylation with methyl sulphate and potassium carbonate it gave rise to a complete methyl ether which crystallized from alcohol as colourless rectangular rods and needles melting at 194°-95°. Mixed melting point with the original compound was considerably depressed. The fully methylated product agreed with galangin trimethyl ether and mixed melting point was undepressed. The compound thus corresponded to izalpinin; yield 0·4 g. The original alcoholic mother liquor was evaporated to dryness and the residue subjected to repeated crystallizations from methanol when it separated out as colourless needles melting at 193°-94°. It agreed with pinocembrin described earlier; yield 1·0 g.

Fraction H [*pinobanksin-7-methyl ether* (IV), *pinostrobin* (VI), *4-hydroxy stilbene* (XVI), *tectochrysin* (II), *pinosylvin monomethyl ether* (VII)] — The sodium hydroxide solution on standing for 24 hr. gave a yellow sodium salt mixed with a jelly. The mixture was filtered and then treated with concentrated hydrochloric acid (15 cc.) for 15 min. The solid product thus obtained was treated with ether (200 cc.). A small fraction was left undissolved. It crystallized from benzene as pale yellow hairy needles melting at 180°-81°. It gave a reddish violet colour with ferric chloride, an orange-red colour with diazotized benzidine and on reduction with magnesium and hydrocloric acid, or zinc and hydrochloric acid gave an orange-red colour. It corresponded to pinobanksin-7-methyl ether. This was confirmed by oxidation to izalpinin using iodine and sodium acetate; yield 0·3 g.

The ether solution was evaporated to dryness and the residue (5·4 g.) fractionated from alcohol. The first fraction was recrystallized from alcohol when it separated out as cream-coloured rectangular rods melting at 163°-64° and agreed with tectochrysin described earlier; yield 1·8 g. The second fraction on repeated crystallization from methanol gave pale brown thick rectangular plates melting at 112°-13°. It gave no colour with magnesium and hydrochloric acid, a reddish brown colour with alcoholic ferric chloride and a brownish blue colour with concentrated nitric acid. It corresponded to pinostrobin. This was confirmed by iodine oxidation; yield 1·1 g. The third and the last fraction was crystallized from methanol in colourless tiny prisms melting at 186°-87°. It gave a faint red colour with ferric chloride, a red colour with diazotized benzidine and no colour with magnesium and hydrochloric acid. It readily decolourized bromine and permanganate. It gave an acetate which crystallized from alcohol as colourless needles melting at 134°-35°, and a methyl ether melting at 136°-37° and the mixed melting point with the synthetic 4-hydroxy stilbene[16] was undepressed; yield 1·2 g.

The remaining sodium hydroxide solution was acidified and on working it up in the same way as fraction D yielded pinosylvin monomethyl ether; yield 18·3 g.

Acknowledgement

Our thanks are due to the Council of Scientific & Industrial Research for a research grant and to Dr. S. K. Mukerjee for microanalyses.

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Metabolic Products of *Paecilomyces victoriae* V. Szilvinyi*

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Four metabolic products have been isolated from the culture filtrate of *P. victoriae* V. Szilvinyi. Of these, three have been shown to be ustic acid, dehydroustic acid and 4 : 6-dihydroxy-3-methoxy phthalic acid. The structure of the fourth compound has not been established but the presence of certain functional groups has been indicated.

THE mould *Paecilomyces victoriae* V. Szilvinyi belongs to the genus Paecilomyces, first established in 1907 by Bainer[1]. *Byssochlamys fulva*[2] is the only mould belonging to this genus which has been investigated in detail for its metabolic products.

P. victoriae, the mould under investigation, when grown on Raulin-Thom solution, gave bluish to intense bluish purple colour with aqueous ferric chloride. It was of further interest to note that similar colour reaction has been recorded for the metabolic solutions from *Penicillium breviocompactum*[3], *Aspergillus ustus*[4] and *Penicillium cyclopium* var. *album*[5].

Experimental procedure

The mould *P. victoriae* V. Szilvinyi (Pa 5) was obtained from the Central Bureau Voor Schimmelculture, Baarn, Holland.

A batch of 200 one-litre conical flasks each containing 350 ml. Raulin-Thom medium were sown with the spore suspension of the mould grown on wort-agar slants for 14 days. Table 1 gives the *p*H, residual glucose (polarimetrically) and bromine absorption value of the culture filtrate.

The bromine absorption values of the culture filtrates recorded in Table 1 indicate that up to 14 days the mould produced a metabolic product which did not absorb any bromine while at a later stage certain other products are produced which absorb bromine.

Isolation of the metabolic products — The culture filtrate from the 14 day old flask was made acid to Congo red paper, concentrated *in vacuo* to 100 ml. and extracted for 3 hr. with ether. The ether extract was dried and evaporated to dryness. The residue thus obtained was taken up in chloroform, concentrated to a small volume under vacuum and then allowed to evaporate gradually, when a crystalline gum was obtained from which a crystalline compound (A) (m.p. 169°-70°C. ; yield 0·05 g.) was isolated by treatment with ether.

Culture filtrate from 100 one-litre conical flasks harvested on the twenty-eighth day was concentrated *in vacuo* (at 35°C./17 mm.) to about 800 ml. This concentrated solution was allowed to stand at 0°C. for 48 hr. and filtered. The filtrate was extracted with ether at different *p*H levels (extract I at *p*H 7·0; extract II at *p*H 5·3; and extracts III and IV at *p*H 2·0).

Extract I did not yield any crystalline material.

Extract II on evaporation of ether yielded a gum from which on trituration with ether a crystalline compound (D) [m.p. 240°C. (decomp.) ; yield 0·15 g.] was isolated.

Extract III — The ether was removed under vacuum and the residue on standing

TABLE 1 — ANALYSIS OF CULTURE FILTRATE

No. of flasks	Period of incubation at 24°C. days	*p*H	Glucose % w/v	Bromine absorption value
1	14	3·0	0·63	—
10	21	4·2	0·18	5·6
10	26	5·2	0·09	6·4
5	27	5·5	0·09	6·4
174	28	5·3	0·08	6·4

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*Work reported here forms a part of the Ph.D. thesis submitted to the University of London in October 1951.

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crystallized. The crystalline material (B) (m.p. 120°-22°C.; yield 3·1 g.) was isolated by trituration with a little ether and filtration. On evaporation, the filtrate formed a gummy substance which was dissolved in ethanol (20·0 ml.) and treated with 5 per cent ethanolic solution of potassium acetate (100 ml.). The resulting flocculent precipitate was filtered after standing for 2 hr. and dissolved in water. The aqueous solution was acidified with hydrochloric acid and extracted with ether yielding a syrup which on standing gradually crystallized. The crystals were washed with a little ether and filtered and recrystallized from ethyl acetate-benzene (compound C: m.p. 193°-95°C.; yield 0·4 g.). The ethanolic mother liquor containing the soluble potassium salts was evaporated *in vacuo* and the residue dissolved in water. The aqueous solution was acidified and extracted with ether. From the ether extract a small quantity of compound B was isolated.

Extract IV — From this extract small amounts of compounds B and C were isolated.

Properties of isolated compounds

Compound A — From a comparison of the m.p. 169°-70°C., mixed m.p. and other properties the compound A was proved to be identical with ustic acid.

Compound B — The crude compound was purified by crystallization from water and finally recrystallized from chloroform. From its chemical properties, m.p. 121°-22°C. (decomp.) and mixed m.p. it was proved to be identical with dehydroustic acid (found: C, 48·7; H, 4·5; —OCH_3, 11·5; requires for $C_{11}H_{12}O_8$ or $C_{11}H_{10}O_7$, H_2O: C, 48·5; H, 4·4; 1—OCH_3, 11·4 per cent).

Compound C — This compound was purified by repeated crystallization from ethyl acetate: benzene mixture as small colourless prisms; m.p. 193°-94°C. (decomp.) (found: C, 47·2; H, 3·7; —OCH_3, 13·6; requires for $C_9H_8O_7$: C, 47·4; H, 3·5; 1—OCH_3, 13·6 per cent).

By a comparison of the chemical properties, melting point and mixed points, the compound was proved to be 4: 6-dihydroxy-3-methoxy phthalic acid.

Compound D — The compound was purified by crystallization from methanol: water (1: 5 vol.) mixture and subsequently by sublimation in a high vacuum at 160°-65°C. The cream-coloured prismatic crystals melted at 259°-60°C. with vigorous effervescence and reddening before melting (found: C, 54·5; H, 4·5; —OCH_3, nil; required for $C_9H_8O_5$: C, 55·1; H, 4·1 per cent).

Compound D was sparingly soluble in water and its aqueous solution was acid to Congo red. An ethanolic solution of the compound gave an intense ruby red colour which remained unchanged on dilution with water. The compound was readily soluble in 2N sodium hydroxide solution giving a yellow colour which became more intense on warming. The compound dissolved in concentrated ammonia (d, 0·88) to a yellow solution similar in intensity to its solution in 2N sodium hydroxide solution. This colour in a few minutes changed successively from orange red to pink red, red and finally to a deep ruby red colour. The compound reduced ammoniacal silver nitrate solution (containing a little 2N sodium hydroxide solution) on warming, but it did not reduce Fehling's solution.

Compound D dissolved in aqueous sodium bicarbonate solution with effervescence. It gave an orange colour with bleaching powder solution. When treated with 2:6-dichloroquinone chlorimide[6] the compound rapidly gave a stable deep blue colour.

It easily formed a D.N.P. which did not melt but decomposed above 310°C. An ethanolic solution of the D.N.P. gave a deep maroon colour with a drop of 2N sodium hydroxide solution (Neuberg reaction) (found: C, 47·4; H, 3·0; B, 14·9; requires for $C_{15}H_{12}O_8N_4$, i.e. the mono D.N.P. of $C_9H_8O_5$: C, 47·9; H, 3·2; N, 14·9 per cent).

Although it is not possible to assign a definite structural formula to compound D at present, it can be concluded that the compound is a meta-dihydroxy phenol with a carbonyl group (most probably —CHO[5]) which is in an ortho position to a —OH group; the compound possesses a —COOH group and one of the —OH groups is in a para position to a —COOH group or to a —OH the para position group is unsubstituted[6].

Discussion

The isolation of dehydroustic acid and 4: 6-dihydroxy-3-methoxy phthalic acid as metabolic products of *P. victoriae* during the later stages of its growth suggests that the mould synthesizes only ustic acid in the earlier period and that as soon as the sugar level goes down well below 1 per cent it begins to oxidize ustic acid to give dehydroustic acid and 4:6-dihydroxy-3-methoxy phthalic acid. Thus, it is of interest that a mould which has no close resemblance with *A. ustus* should synthesize the metabolic product of *A. ustus*, viz. ustic acid, as well as its degradation products which were not known in the past as mould metabolic products. At present it is not possible to explain the relationship that compound D may bear to ustic acid or its degradation products.

Acknowledgement

Thanks are due to Prof. H. Raistrick for his continued interest and guidance in this investigation. Thanks are also due to Dr. D. J. Ross for the methoxy determinations and technical help and to Dr. C. E. Stickings for repeating the work.

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Studies on the Enzyme Make-up of *Vibrio cholerae*: Part IV — Screening of Cholera & Other Vibrios for the Presence of Penicillinase

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The low susceptibility of *Vibrio cholerae* to penicillin led to a screening of several strains of this organism and other vibrios for the presence of penicillinase. A few strains of water and non-agglutinable vibrios only were found to elaborate this enzyme.

DURING our studies on the possible differences in susceptibility of various sub-types of cholera and other vibrios to penicillin, it was observed that a strain of water vibrio grew on a medium containing a fairly high concentration of penicillin. In order, therefore, to find out whether this penicillin resistance was due to the production of penicillinase, several strains of vibrios were examined for the production of this enzyme. The results of the investigations are presented in this communication.

Experimental procedure

The screening of *Vibrio cholerae* and other vibrios for penicillinase activity was carried out by Gots's method[1]. One cc. of penicillin G sodium (100 units/cc.) and 0·5 cc. of 24 hr. old broth culture of *Staph. aureus* (Oxford) were added to 100 cc. of papain-meat-agar at 42°-45°C., thoroughly mixed and dispensed into sterile petri dishes. Twenty-four hour old test organisms were streaked on such plates and incubated at 37°C. for 3 days. The appearance of *Staph. aureus* colonies around the streak was taken as an index of penicillinase production by the test organism.

For detailed studies, the Water Tank strain of water vibrio was used as the source of enzyme. Twenty-four hour growth of the organism on papain-meat-agar slopes (*p*H 8) was harvested with 0·85 per cent saline and centrifuged. The cells were then suspended in 0·85 per cent saline and the turbidity adjusted in Lumetron photoelectric colorimeter (red filter—650 mμ) to the desired percentage transmission and used for the determination of the optimum *p*H and other properties of the enzyme.

The optimum *p*H for penicillinase activity was determined by the cup-plate method[2] for the assay of penicillin, with *Staph. aureus* (Oxford) as the test organism. The reaction mixture consisted of 1 cc. M/15 phosphate buffer of appropriate *p*H, 3 cc. penicillin G sodium (50 units/3 cc.) and 1 cc. 0·85 per cent saline or cell suspension (70 per cent transmission). The mixture was incubated for 15 min. at 37°C., then cooled in an ice bath and diluted with an equal volume of distilled water. The residual penicillin was then assayed.

The properties of the enzyme were further studied by the manometric method of Henry and Housewright[3]. The main compartment of the Warburg flask contained 1 cc. each of 0·154M sodium bicarbonate solution, M/15 phosphate buffer and cell suspension (20 per cent transmission), while the side arm contained 0·5 cc. pure penicillin G sodium (8 mg./cc. unless otherwise stated). The final *p*H of the reaction mixture was 7·2 and the reaction was carried out at 39°C. in an atmosphere of air.

Results

Fifteen strains of Ogawa, 22 of Inaba, 4 of Rough vibrios, 3 each of El Tor and water vibrios and 9 non-agglutinable vibrios were screened for penicillinase activity. Two of water (Water Tank and Kimbu Ghat strains) and 2 non-agglutinable (NAG 2 and NAG 6 strains) vibrios were found positive, while the rest were negative. It was further noted that when the water vibrio was grown in broth, the penicillinase activity was present only in the cells and not in the culture centrifugate. This would indicate that the enzyme is endocellular.

The determination of the enzyme activity at different *p*H levels showed that the optimum lies between 7 and 8 (TABLE 1).

TABLE 1 — ACTIVITY OF PENICILLINASE AT DIFFERENT *p*H LEVELS

*p*H	DIAM. OF INHIBITION ZONE OF *S. aureus* GROWTH		
	Penicillin mm.	Penicillin + enzyme mm.	Net activity mm.
5·10	22	18	4
6·00	24	15	9
6·70	24	12	12
7·10	24	12	12
7·60	24	9	15
8·25	24	12	12

The effect of enzyme concentration was studied by using different dilutions of cell suspensions made from that with an opacity equivalent of 20 per cent transmission. Carbon dioxide evolution after 10, 20 and 30 min. was measured. The results are plotted in Fig. 1. It would be seen that there is a linear

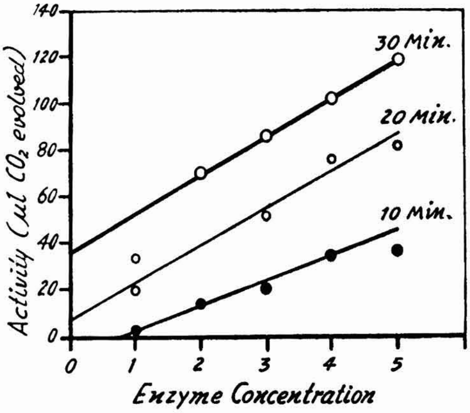

FIG. 1 — EFFECT OF ENZYME CONCENTRATION ON PENICILLIN-PENICILLINASE REACTION [The units of enzyme concentration 1, 2, 3, 4 and 5 respectively represent cell suspension (initial opacity equivalent of 20 per cent transmission in the Lumetron) diluted with saline in the following proportions: 1:4; 2:3; 3:2; 4:1 and 5:0]

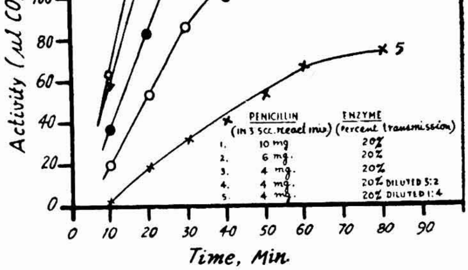

FIG. 2 — RATE OF PENICILLIN BREAKDOWN

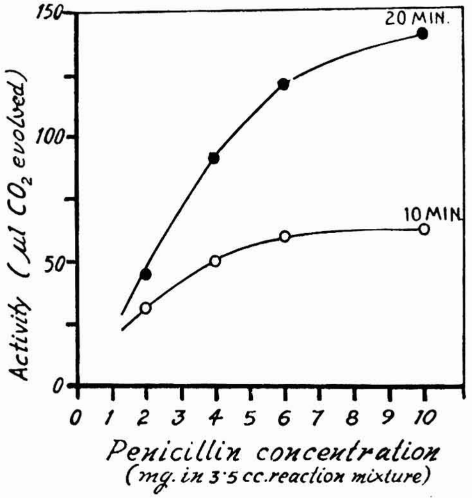

FIG. 3 — EFFECT OF PENICILLIN CONCENTRATION ON PENICILLIN-PENICILLINASE REACTION

increase in activity with increase in enzyme concentration.

The course of the penicillin-penicillinase reaction was followed for a period of 80 min. using different concentrations of the substrate and enzyme. The results presented in Fig. 2 show that there is an almost constant rate of evolution of carbon dioxide from 10 to nearly 30 min. of the reaction under the various conditions used, after which the reaction slows down, equilibrium being attained earlier at higher concentrations of the substrate and enzyme. Fig. 2 also shows that the rate of evolution of carbon dioxide is not constant during the first 10 min. of the reaction. A similar observation has been made in the case of the penicillinase of *B. cereus*[3]. The reaction appears to be of the zero order initially.

The effect of increasing concentrations of penicillin on the rate of reaction has been brought out in Fig. 3, which shows that the curves obtained are of the usual enzyme type.

To determine the heat stability of the enzyme, aliquots of cell suspension were heated for 15 min. at 25°, 40°, 50°, 60°, 80° and 100°C., cooled quickly in an ice bath and carbon dioxide evolution measured. It was found that there was no loss in activity at 25° and 40°C., while a complete inactivation occurred at 50°C. and higher temperatures. The cell suspension could be kept at 5°C. for 24 hr. without any appreciable loss in activity.

Discussion

In the present studies it has been found that the sub-types of *V. cholerae*, viz. Ogawa and Inaba, Rough and El Tor vibrios, do not exhibit any penicillinase activity. It would thus appear that the low susceptibility of some strains of *V. cholerae* to penicillin observed by the authors and also reported by Felsenfeld *et al.*[4] is not due to the elaboration of penicillinase by these organisms.

Of the non-agglutinable and water vibrios screened for the presence of penicillinase, only two of each were found positive. The enzyme is endocellular, like that of soil vibrios reported by Czekalowsky[5].

The penicillinase of water vibrio (Water Tank) has its optimum activity in the *p*H range 7-8 and very little activity at *p*H 5. Study of the rate of penicillin-penicillinase reaction at different concentrations of the substrate and enzyme indicates that initially the reaction is of the zero order. The enzyme is unstable at higher temperatures. The characteristics of the penicillinase reported herein appear to be similar to that of *B. cereus*[3], excepting that the enzyme studied is endocellular.

Summary

Of 56 strains of *Vibrio cholerae* and other vibrios, 2 water and 2 non-agglutinable vibrios have been observed to produce penicillinase.

The enzyme present in water vibrio is endocellular and is unstable at 50°C. and above.

Certain kinetic properties of the enzyme have been studied.

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Utilization of Amino Acids by *Streptomyces griseus* during the Production of Vitamin B_{12}

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Studies on the utilization of amino acids by *S. griseus* during fermentative production of vitamin B_{12} by the circular and two-dimensional chromatography have revealed preferential and progressive utilization of amino acids. Cystine, aspartic acid and arginine are utilized first followed by others.

The concentration of amino nitrogen in the medium falls during fermentation whereas the concentration of ammonia nitrogen increases. The nitrogen content of the cells increases during the first three days of fermentation after which it falls.

IN the course of an investigation by Ganguly *et al.*[1] of the factors affecting the optimal production of vitamin B_{12} by *Streptomyces griseus*, it became necessary to study the utilization of different amino acids by the micro-organism during its synthesis of the vitamin. The results of this study are reported in this paper.

Experimental procedure

The utilization of amino acids by *S. griseus* for the production of vitamin B_{12} was studied by subjecting the fermenting broth to the paper chromatographic analysis using both circular and two-dimensional methods. Fermentation was carried out by the submerged process described by Ganguly *et al.*[1] using a medium made up of casein hydrolysate (1·0 per cent) and beef extract (0·3 per cent). The *p*H of the medium was adjusted to 6·8-7·0. The composition of the broth with respect to different amino acids was determined at the end of the 3, 6, 12, 24, 48, 96 and 120-hr. fermentation. The production of vitamin B_{12} was maximum at 120 hr. after which it declined.

The technique employed for the circular paper chromatography was that of Giri and Rao[2]. Whatman No. 1 filter paper of 18·5 cm. diam. was used throughout the investigation. Broths were removed at different intervals, centrifuged to remove the cells and the solutions applied at the centre of the filter paper by means of a capillary tube. Multiple applications of the broth were found necessary to make the bands appear prominent and the spots were dried after each application. The method of development was the same as that of Giri and Rao[2]. Amino acids in the medium were identified by comparing their R_f values with those of known ones (TABLE 1) and also from chromatograms of known amino acids run side by side with the broths.

TABLE 1 — AMINO ACID UTILIZATION BY *S. GRISEUS*

AMINO ACIDS	INITIAL	3RD HR.	6TH HR.	12TH HR.	24TH HR.	48TH HR.	72ND HR.	96TH HR.	120TH HR.	R_f VALUE (CIRCULAR)
Leucine	+++	++	++	+	–	–	–	–	–	0·72
Valine	+++	+++	++	–	–	–	–	–	–	0·56
Proline	+++	+++	+++	++	++	+	+	–	–	0·45
Glutamic acid	+++	+++	+++	++	++	+	+	+	+	0·33
Serine	+++	+++	+++	+++	++	+	+	+	+	0·24
Lysine	+++	+++	+++	+++	++	+	+	+	+	0·22
Methionine	+++	+++	++	+	+	–	–	–	–	0·54
Alanine	+++	+++	+++	++	++	+	+	+	+	0·38
Glycine	+++	+++	++	++	+	+	+	+	+	0·31
Threonine	+++	+++	+++	++	+	+	+	+	+	0·32
Tryptophane	+++	++	–	–	–	–	–	–	–	0·53
Cystine	++	–	–	–	–	–	–	–	–	0·20
Aspartic acid	++	–	–	–	–	–	–	–	–	0·30
Arginine	++	–	–	–	–	–	–	–	–	0·21

+++, high concentration; ++, medium concentration; +, low concentration; and –, nil.

The results obtained with the circular chromatographic technique were confirmed by the two-dimensional descending paper chromatographic procedure (FIG. 1). The technique followed was that of Consden *et al.*[3] as modified by Dent[4] using phenol-water as the first solvent and benzyl alcohol-acetic acid-water as the second solvent (25:5:6·5) as suggested by Burma[5]. Phenol-water was allowed to run in a descending manner and the first run took about 14-15 hr. for travelling a distance of 45 cm. The papers were then taken out of the chamber and air-dried. The second solvent mixture, benzyl alcohol-acetic acid-water, was also allowed to run in the same way in another chamber at right angles to the phenol-water run. This run also took about 12-14 hr. for travelling a distance of 40 cm. On the usual treatment with ninhydrin, spots of amino acids appeared and were identified from the chromatograms of known acids.

The individual amino acids utilized by *S. griseus* during fermentation are given in Table 1.

The nitrogen balance of *S. griseus* during fermentation was determined from the total nitrogen, including amino nitrogen in the medium before fermentation and amino, ammonia and broth nitrogen in the media during successive periods of fermentation. The nitrogen gain by the mycelia was determined from the initial nitrogen and that left in the broth after removal of cells by centrifuging.

Total nitrogen was determined by the Kjeldahl method, amino nitrogen by the Sörensen's formol titration and ammonia nitrogen by the aeration method of Van Slyke. The results are given in Table 2. Vitamin B_{12} produced during fermentation was assayed by the paper disc assay method[6] with a mutant *Escherichia coli.*

TABLE 2 — NITROGEN BALANCE OF *S. GRISEUS* DURING VITAMIN B_{12} PRODUCTION

TIME hr.	TOTAL N IN BROTH mg./10 ml.	AMINO N IN BROTH mg./10 ml.	AMMONIA N IN BROTH mg./100 ml.	MYCELIA N mg./10 ml.	VITAMIN B_{12} γ/ml.
At start	11·19	5·05	—	—	—
22	10·25	3·88	5·66	0·94	—
45	9·01	2·72	6·88	2·08	—
70	8·70	1·94	7·90	2·49	0·28
94	9·19	1·55	8·11	2·00	0·52
120*	9·41	1·40	9·48	1·78	0·64

*After 120 hr. there was a sharp decline in the production of vitamin B_{12}.

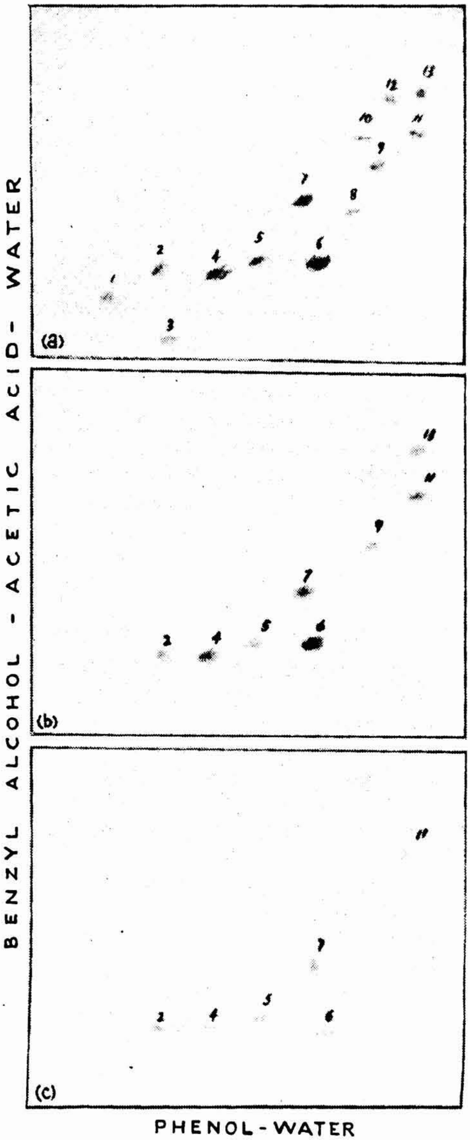

FIG. 1 — CHROMATOGRAMS OF FERMENTATION BROTH AT DIFFERENT STAGES OF FERMENTATION [(a), at start; (b) 18 hr.; (c) 48 hr.; (1) aspartic acid; (2) glutamic acid; (3) cystine; (4) serine; (5) glycine; (6) lysine; (7) alanine; (8) arginine; (9) methionine; (10) valine; (11) proline; (12) tryptophane; (13) leucine]

Discussion

It is seen from the results given in Table 1 that by the end of 3-hr. fermentation cystine, aspartic acid, arginine disappear from the medium and the concentrations of leucine, valine, methionine decrease, and by 12 hr. valine disappears completely and there is a further fall in the concentrations of leucine and methionine. By 24 hr. leucine and methionine disappear completely while concentrations of other amino acids fall at a comparatively higher rate up to 48 hr. and thereafter at a slower rate up to 120 hr. It, therefore, appears that some amino acids are preferentially utilized by the micro-organism for the synthesis of vitamin B_{12} and this is also highest during the initial stages of fermentation when the organism is at its lag phase of growth. Apparently the free amino acids seem to be utilized primarily for cell synthesis by the organism and might be indirectly related to the synthesis of B_{12}. The vitamin seems to be a product of intracellular synthesis, being liberated in the fermentation broth from the third day of fermentation during which the cells begin to undergo lysis spontaneously.

It is seen from the results in Table 2 that the concentration of amino nitrogen falls steadily during the fermentation (also supported by chromatographic analysis), while the concentration of the ammonia-nitrogen increases progressively with time. The nitrogen content of the cells increases during the first three days of fermentation, after which it begins to fall when the cells undergo lysis. The *p*H of the medium also changes from an initial value of 7·0-8·8 at the end of fermentation.

Acknowledgement

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Nutritive Value of Canned Foodstuffs: Part I—Effect of Canning Procedures on Vitamin Contents of Fruits & Vegetables

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The effect of various canning procedures on the retention of vitamins — carotene, ascorbic acid, thiamin, niacin and riboflavin — in fruits and vegetables has been investigated. Processed fruits retain more of the vitamins than processed vegetables. Of the vitamins, ascorbic acid is most affected by the processing treatments and carotene the least.

Blanching causes the maximum destruction and loss of ascorbic acid; steam blanching is better than hot water blanching.

IT has been found that food products undergo significant changes in their nutritive value as a result of processing them into canned products[1-4]. Very little data is, however, available regarding the effect of various canning procedures on the nutritive value of foodstuffs. The present study was, therefore, undertaken to assess the effect of various canning procedures on the nutritive value of fruits and vegetables with special reference to vitamin losses.

Materials and methods

The following fruits and vegetables were selected for the study:

Fruits — Mangoes, papayas, pineapples, guavas, peaches and tomatoes.

Vegetables — French beans, peas and potatoes.

Cans containing raw and processed fruits preserved in sugar syrup and vegetables were obtained from a local cannery.

Sampling — A representative sample for examination was obtained from 6 cans (irrespective of the size of the cans) selected at random. After noting the gross weight of each can, the contents of the cans were drained over a sieve placed in an inclined position for 15 min. and weighed separately. The solid and liquid portions in the fruit packs were blended separately and analysed in duplicates. In the vegetable packs the liquid and solid portions were blended together. The value for the vitamin content of the products recorded is the mean of four estimations.

Estimation of vitamins

Ascorbic acid was determined according to the xylene extraction method applying the formaldehyde correction for reductones as suggested by Robinson and Stotz[5].

Carotene was estimated spectroscopically according to the method of Moore and Ely[6].

Thiamine was estimated by the thiochrome method.

Riboflavin was estimated according to the fluorometric method of Scott *et al.*[7] with the modification that instead of acetone-hydrochloric acid reagent extract, enzyme-digested extracts were used.

Nicotinic acid was estimated according to the method of Sweeney[8].

Results and discussion

Mangoes, pineapples and papayas—Table 1 gives the effect of processing on the vitamin content of mangoes and papayas.

The results indicate that of the vitamins present in Bulsar mangoes, ascorbic acid is affected most during canning. Mango pulp, because of heating in open pans, retains a lower percentage of both ascorbic acid and thiamine.

Ratnagiri variety of Alfanso mangoes contained 23·88 mg. per cent of ascorbic acid. The percentage retention of the vitamin on blanching for 30 min. and processing for 15 min. at a pressure of 2 lb./sq. in. was 88·0 and 82·6 respectively.

In the case of pineapples (ascorbic acid content, 7·92 mg. per cent) the percentage retention of ascorbic acid on steam blanching for 30 min. and processing for 15 min. at a pressure of 5 lb./sq. in. was 93·8 and 92·7 per cent respectively.

Heating mango pulp in open pans before canning destroys a large percentage of vitamin C and riboflavin present in the pulp.

The destruction of vitamin C in unblanched papayas may be due to the activity of enzymes (oxidazes) in the fruit. The percentage destruction of vitamin C is higher in papayas than in mangoes which may be due to omitting the blanching operation while processing the fruit.

TABLE 1 — EFFECT OF PROCESSING ON THE RETENTION OF VITAMINS IN MANGOES AND PAPAYAS

(*Mangoes used were Bulsar Alfanso variety; mango slices and papaya cubes were packed in syrup*)

PRODUCT	PROCESSING CONDITIONS	VITAMIN C mg. %	CAROTENE mg. %	THIAMINE μg. %	RIBOFLAVIN μg. %	NIACIN mg. %
Mango slices	Raw	65·7	7·0	33·4	619·0	5·2
	Blanched for 30 sec. in steam and steam exhausted	55·9 (77·7)	7·1 (92·4)	36·4 (99·3)	585·0 (86·0)	5·0 (87·3)
	Processed for 20 min. at 2 lb./sq. in. pressure	58·6 (77·8)	7·1 (88·2)	37·7 (98·5)	598·0 (84·2)	5·0 (83·5)
Mango pulp	After pulping	40·0	3·1	24·0	469·0	4·7
	After open-air heating, filling and processing	33·1 (74·1)	3·3 (94·2)	23·8 (89·0)	518·5 (99·1)	5·2 (99·7)
Papaya cubes	Raw	31·9	0·4	8·0	273·0	—
	Steam blanched and steam exhausted	27·8 (83·0)	0·4 (93·1)	8·5 (100·0)	293·0 (101·0)	— —
	Processed for 20 min. at atm. pressure	24·7 (74·5)	0·4 (87·4)	8·1 (96·8)	274·0 (96·3)	— —

The figures given in parentheses refer to percentage retention of vitamin after processing.

TABLE 2 — EFFECT OF PROCESSING ON GUAVAS

CONDITION	VITAMIN C		RIBOFLAVIN	
	Total mg. %	% retention	Total μg. %	% retention
Fresh	213·6	—	446·0	—
Lye-peeled	147·0	68·8	444·0	99·6
Steam exhausted	146·0	68·4	440·0	99·5
Processed for 20 min. in open retorts	146·3	68·4	443·0	99·5

In the case of pineapples, the greater retention of ascorbic acid in unblanched fruit may be due to the absence of the enzymes ascorbase and phenolase.

Guavas — The fruit was peeled by boiling in 1 per cent alkali for 2 min. and then dipped successively in water, dilute citric acid solution and water to remove alkali adhering to the fruit. The peeled fruit was steam exhausted and finally processed for 20 min. in open vessels. The fruit was analysed for vitamin C and riboflavin at different stages and the results are recorded in Table 2. The results show that percentage retention of ascorbic acid in the fruit subjected to different processing treatments is the same, i.e. 68·4 per cent. Riboflavin is not much affected by the various treatments and as much as 99·5 per cent of the vitamin remains intact.

Tomato juice — The canning cycle in the case of tomato juice should be completed in as short an interval as possible to minimize the loss of vitamins. As the Indian canneries are not equipped with automatic filling and processing units, the juice is kept boiling for a considerable time in an open pan. If the juice is kept boiling for 45, 60 and 90 min., the loss in ascorbic acid is 38, 45 and 95 per cent respectively. The loss in ascorbic acid in cold-extracted tomato juice kept at room temperature for 30 and 60 min. is 5 and 84 per cent respectively, whereas if the juice is boiled immediately and cooled to room temperature, the loss of vitamin at the end of 90 min. is only 22 per cent.

There appears to be some difference of opinion[9-11] regarding the use of hot-break or cold-break method for extracting juice from tomatoes. Our studies show that tomato juice obtained by hot-break method retains 72·5 and 80·5 per cent respectively of ascorbic acid and thiamine originally present in it, whereas 63·0 per cent ascorbic acid and 65·2 per cent thiamine are retained in juice extracted by cold-break method.

The loss of vitamin C in juice extracted by cold-break method may be due to the destructive activity of enzymes (oxidazes) in the juice. If the canning cycle is completed within a short time, the cold-break extracted juice may retain more of the vitamin.

Peaches — Heavy loss of ascorbic acid (93·7 per cent) occurs as a result of lye-peeling of the fruit. Though steam peeling (2 min.) is definitely superior to other methods (as 95 per cent of the vitamin present in the fruit is retained after processing) it prolongs the canning cycle resulting ultimately in a greater loss of the vitamin. Further, the yield of processed material is not higher than that obtained by hot water blanching.

Peas — The effect of steam blanching and hot water blanching on the percentage retention of vitamins was studied under two sets of conditions: (1) blanching for 4 min. and processing for 25 min.; and (2) blanching for 2 min. and processing for 20 min.

Raw fresh peas contained moisture, 81·7; vitamin C, 16·6 mg.; carotene, 0·33 mg.; thiamine, 186·6 μg. and riboflavin, 444·7 μg. per cent. Both carotene and riboflavin remain intact (98-100 per cent retention) on blanching; when blanched for 4 min. in boiling the percentage of carotene and riboflavin in the vegetable was reduced to 94·7 and 81·7 per cent respectively.

The amount of ascorbic acid retained on blanching in steam and boiling water for 4 min. is 76·0 and 69·1 per cent respectively; further processing for 25 min. at 15 lb./sq. in. pressure reduces the overall retention of the vitamin to 69·1 and 57·1 per cent respectively.

The retention of vitamin C on reducing the blanching time to 2 min. and processing time to 20 min. was 97·5 and 91·7 per cent respectively; further processing for 20 min. at 15 lb./sq. in. brings down the amount of ascorbic acid retained to 79 and 70 per cent.

The thiamine content of samples blanched for 4 min. in steam and in boiling water was 96·4 and 86 per cent respectively of the original; the overall retention of the vitamin on further processing for 20 min. at 15 lb./sq. in. pressure was 79 and 70 per cent respectively. Blanching in steam for 2 min. does not reduce the vitamin content of the samples but it is reduced to 93 per cent by hot water blanching; further processing of the two samples brings down their vitamin content to 98·5 and 86·2 per cent respectively.

French beans and potatoes — The amount of ascorbic acid retained by French beans on blanching in steam and hot water was 35·2 and 47·1 per cent respectively. Steam exhausting causes a further loss of about 5 per cent but further processing does not result in any loss of the vitamin. Carotene was affected to a lesser degree under the same conditions; the amount of carotene retained after blanching in water and further processing was 85·7 and 77·5 per cent respectively. Steam-blanched samples retained all the carotene and the overall percentage retention of vitamin after processing was 93·6 per cent.

Potatoes (vitamin C content, 20·78 mg./100 g.) on blanching for 5 and 10 min. in hot water retained 95·3 and 88·6 per cent respectively of vitamin C present in them. The amount retained is 98·4 per cent when they are blanched for 8 min. in steam; further processing for 45 min. at 15 lb./sq. in. pressure has no effect.

The comparatively heavy loss of ascorbic acid in canning French beans may be due to stringing of the beans before blanching. This step involves cutting of the pod which not only exposes the surface to the action of enzymes but also facilitates the leaching out of the vitamin. In potatoes, the peel prevents the loss of vitamin.

The above studies show that of the vitamins present in fruits and vegetables, ascorbic acid is most affected by processing as it is both water soluble and heat labile, and gets oxidized easily on exposure to atmosphere. Carotene is least affected.

The results of studies on the processing of vegetables show that blanching operation causes maximum destruction of ascorbic acid; the loss is more in water blanching than in steam blanching.

Conclusions

1. Fruits which do not require a blanching treatment, when processed and canned retain more of the vitamins present than vegetables.
2. Heating mango pulp exposed to the atmosphere results in considerable loss of vitamin C.
3. " Hot-break " method of extracting tomato juice retains more of ascorbic acid in the juice than " cold-break " method.
4. The loss of vitamin C is more in lye-peeled peaches than in guavas.
5. Blanching in hot water causes a greater loss of vitamin C than steam blanching.

Acknowledgement

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Component Fatty Acids of the Oil from the Seeds of *Benincasa cerifera* Savi

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The seed kernels of *Benincasa cerifera* Savi (Petha) yield 44·3 per cent of a clear light yellow oil with the following characteristics: $n_D^{25°}$, 1·4739; $d^{30°}$, 0·9196; acid value, 3·4; sap. val., 189·1; iodine value, 125·0; unsaponifiable matter, 1·47 per cent. The fatty acids composition of the oil is: linolenic, 1·02; linoleic, 62·36; oleic, 20·03; palmitic, 10·56; stearic, 5·76; and arachidic, 0·27 per cent.

BENINCASA cerifera Savi (Hindi: Petha) belongs to the N.O. *Cucurbitaceae.* The plant is a native of Japan and Java, but is cultivated in India as a vegetable crop.

The seed oils from plants belonging to the family of *Cucurbitaceae* form an interesting subject of study on account of the diversity of the component fatty acids present in them. Whereas the oils from Telfairia and Trichosanthes species are characterized by the presence of fatty acids having conjugated double bonds, those from different varieties of cucumber and luffa are free from conjugated polyetheroid unsaturation.

This paper reports the results of investigations carried out on the fatty acids composition of oil from Agra variety of Petha*.

Experimental procedure

The kernels, which constitute 48 per cent of the seeds, yield 44·3 per cent of a clear and pale yellow oil on extraction with petroleum ether (60°-80°C.) with the following characteristics:

Sp. gr. at 30°/30°	0·9196
Refractive index at 25°C.	1·4739
Viscosity at 30°C. (c.s.)	46·67
Acid val.	3·4
Sap. val.	189·1
Sap. equiv.	296·6
Iodine val. (Wij's)	125·0
Acetyl val.	14·9
Thiocyanogen val.	87·2
Hexabromide val.	nil
Hehner val.	94·65
Soluble fatty acids, %	0·2
Saturated acids (modified Bertram method[2]), %	16·95
Unsaponifiable matter, %	1·47

The oil (200 g.) was saponified with alcoholic potash, alcohol distilled off and the residue dissolved in water. After the removal of unsaponifiable matter, the total fatty acids were isolated as usual. The neutralization equivalent and iodine value of total fatty acids were 281·3 and 137·4 respectively.

A portion of the acids was crystallized at –20°C. from acetone solution (10 per cent) and another portion was fractionated according to Twitchell's lead salt-alcohol method as modified by Hilditch[3]. The yield and characteristics of the liquid and solid fatty acids obtained in each case are given below:

	Low temperature crystallization		*Lead salt-alcohol method*	
	Liquid fraction	*Solid fraction*	*Liquid fraction*	*Solid fraction*
Yield, %	85·5	14·5	85·1	14·9
Iod. val.	143·5	34·36	152·2	3·39
Neutralization val.	201·4	203·6	199·8	205·4

As the lead salt method gave a better separation of liquid and solid acids than crystallization at low temperature, it was employed in the rest of the experiments.

Soluble lead salt fatty acids — The soluble lead salt fatty acids on oxidation with potassium permanganate (modified Bertram method[2]) gave 2 per cent saturated acid, which was characterized as palmitic acid.

The liquid acids were converted into methyl esters, 44·66 g. of which were fractionated under reduced pressure (at 0·2-0·3 mm. pressure). Seven fractions including

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*Since the completion of this work in January 1953 Chakravarty and Mukherji[1] have examined the seed oil from the Bengal variety of Petha and have reported the characteristics and the fatty acids composition of the oil.

the residue were collected between the temperatures 138° and 150°C. The loss in distillation (0·88 g.) was proportionately divided between each fraction. The first two fractions were found to contain methyl palmitate and the third and fourth contained methyl linolenate. The component unsaturated acids in each fraction were determined by ultraviolet absorption spectrophotometric method[4] and iodine value determinations. The final amounts of the different constituents were: methyl palmitate, 0·90; methyl linolenate, 0·54; methyl linoleate, 32·77 ; and methyl oleate, 10·45 g.

The acids from the third and the fifth fraction were oxidized with alkaline potassium permanganate[5] when tetrahydroxy stearic acid (m.p. 172°-73°C.) and dihydroxy stearic acid (m.p. 130°-31°C.) were obtained from both the fractions. The composition of the soluble lead salt fatty acids was found to be as follows:

	%
Palmitic acid	2·00
Linolenic acid	1·20
Linoleic acid	73·27
Oleic acid	23·53

Insoluble lead salt fatty acids — The insoluble lead salt fatty acids were similarly converted into methyl esters and fractionated (14·50 g.) into six fractions under reduced pressure (0·2-0·3 mm. pressure) between 134° and 145°C. The distillation losses (1·17 g.) were proportionately divided between each fraction. The amounts of various esters in the various fractions calculated according to the method of Jamieson and Baughmann[6] were: methyl palmitate, 8·53; methyl stearate, 5·51; methyl arachidate, 0·26; and unsaturated esters, 0·20 g.

The acids from the fifth fraction, on repeated crystallization from dilute alcohol and acetone, gave a product melting between 60° and 64°C. indicating it to be a mixture of palmitic (63°C.) and stearic acids (m.p. 69°C.).

The amounts of individual saturated components in the insoluble lead salt fatty acids were:

	%
Palmitic acid	59·50
Stearic acid	38·66
Arachidic acid	1·84

The fatty acid composition of the oil is thus as follows:

	%
Linolenic acid	1·02
Linoleic acid	62·36
Oleic acid	20·03
Palmitic acid	10·56
Stearic acid	5·76
Arachidic acid	0·27

Unsaponifiable matter — The unsaponifiable matter, on repeated crystallization from alcohol, gave a colourless product melting at 140°-41°C. and exhibiting well-defined Libermann Burchard colour test for sterols. It was identified as sitosterol (acetate, m.p. 130°C.).

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Determination of Small Amounts of Aluminium in Steel by a Spectrochemical Method

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A method is described for the spectrochemical determination of small amounts of aluminium in steels employing a medium quartz spectrograph and synthetic standards.

THE estimation of small amounts of aluminium in steel by chemical methods is extremely difficult and involves a lengthy procedure. Attempts have, therefore, been made to determine it by spectrochemical methods[1-6]. For the spectrochemical determinations, sufficient care has to be taken to prepare a homogeneous sample. Castro[2] recommended a solution method of analysis when there is an appreciable amount of alumina segregated in the steel sample. Schuissmann[3] and Spiers, Fisher and Proctor[5] determined the total aluminium in steel by the solution method. Majumder and Ghosh[6] determined small amounts of aluminium in ferrous alloys employing a medium quartz spectrograph, using the solution method.

In the present investigation, small amounts of dissolved aluminium (aluminium which can be dissolved by hydrochloric acid) in steels have been determined by taking the steel into solution.

Experimental procedure and results

The test samples contained: C, 0·4; Mn, 0·8; Si, 0·20; S, 0·05; and P, 0·05 per cent; and Al varying from 0·005 to 1·3 per cent; Fe, balance.

Standard solutions were prepared by dissolving separately spectroscopically pure iron, manganese and aluminium in extra pure hydrochloric acid. They were then mixed in such proportions that the aluminium content of the resulting solutions was 0·005, 0·01, 0·02, 0·03, 0·04, 0·05, 0·06, 0·08, 0·10, 0·12, 0·15 and 0·20 per cent; manganese, 0·8 per cent and the balance iron. Nitric acid was added to oxidize the ferrous iron to the ferric state. Drillings of the test samples containing varying amounts of aluminium were dissolved in hydrochloric acid and filtered. Nitric acid was added to oxidize the ferrous iron. Manganese, iron and acid content in both the standard and unknown sets of solutions were kept uniform and the volumes of all the solutions used were the same.

A Hilger medium quartz spectrograph (F_D 60 cm.) with a quartz spherical condenser placed at a distance of 2 cm. from the slit was used. The entire length of the slit was uniformly illuminated by radiation from whole of the light source. The source of excitation was a condensed spark with primary 240 V., secondary 8 kV., capacity 0·005 mF. and self-inductance 0·25 mH. The lower electrode was a graphite rod, 10 mm. diam. and 25 mm. long, suitably fitted to a brass holder and with a flat top. The upper electrode was a pointed carbon rod, 6 mm. in diameter. The flat top of the graphite electrode was sparked for about a minute to remove any impurities initially present.

Kodak B 20 plates (4 × 10 in.) were used for recording the spectra.

One to two drops of the solution were placed by means of a micropipette on the pre-sparked flat top of the graphite electrode and dried by slow heating. Heating was done by bringing a small flame about 1 in. below the bottom of the electrode. As soon as the drops dried, the spectrum was taken by passing the spark, the spark gap being 2 mm. and the time of exposure being 3 min. The slit was 2 mm. long and 0·02 mm. wide. To obtain a uniform radiation conditions 1 min. pre-sparking was given to the electrodes in each case. The conditions of exposure were kept as identical as possible in all cases.

Spectra of the standard and the unknown solutions were photographed on the same plate, care being taken to record the spectra of the unknown and the standard solution of nearest concentration side by side. Preliminary studies were carried out to get an idea of the concentration of the unknown solutions.

Photometric measurements were made with a Hilger non-recording photoelectric microphotometer. The aluminium analysis lines 3082·16, 3092·72 and 3961·5 and the corresponding iron reference lines 3077·17, 3098·19 and 3963·109 were used for photometric work. For lower concentrations of aluminium (0·005-0·06 per cent), the line 3961·5 was invariably used. Working curves were drawn by plotting log microphotometer deflection of aluminium line/log microphotometer deflection of iron line against the known percentage of aluminium in the standard solutions. The variable shunt of the galvanometer in the microphotometer was so adjusted that the clear plate deflection of the galvanometer was 40 cm. and the deflection of the analysis aluminium lines and reference iron lines were lying between 4 and 20 cm.

TABLE 1 — ANALYSIS OF STANDARD AND TEST SAMPLES

	DISSOLVED Al % (mean)	STANDARD DEVIATIONS $\sigma = \pm \sqrt{\frac{d^2}{n-1}}$ %
B	0·0075	± 0·00077 or ± 10·2
EAS1	0·0080	± 0·00084 or ± 10·5
C	0·0175	± 0·0013 or ± 7·4
A	0·0190	± 0·0014 or ± 7·3
Standard 0·02% Al	0·0215	± 0·00108 or ± 5·0
FNCR	0·0290	± 0·0018 or ± 6·0
ENCR2	0·0320	± 0·0022 or ± 7·1
EAS3	0·0400	± 0·00277 or ± 6·9
Standard 0·04% Al	0·0410	± 0·00216 or ± 5·3
Standard 0·12% Al	0·1225	± 0·00507 or ± 4·1
D	0·1610	± 0·00735 or ± 4·6
EAS4 (extrapolated)	0·2100	± 0·0091 or ± 4·3

The percentage of aluminium in the unknown solution was determined by interpolation of its log-galvanometer deflection ratio from the working curves. Fig. 1 represents the working curves of all the three pairs of lines. Table 1 gives the results of analysis of a few synthetic standards and test samples. The reproducibility that can be obtained is also indicated in Table 1 by standard deviations.

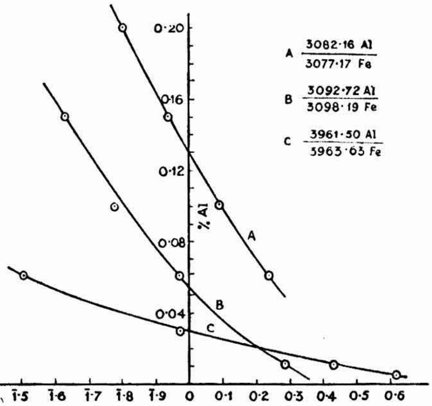

FIG. 1 — LOG DEFLECTION RATIO *vs.* PERCENTAGE OF ALUMINIUM

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Coal Systematics: Deductions from Proximate Analysis of Coal: Part I

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An attempt is made to correlate the different intrinsic properties of coal with its proximate analysis. For coals having volatiles above 35 per cent (unit coal), the amount of volatiles alone is not enough to fix the different properties of coal. Moisture, which is an intrinsic property of coal, can be co-ordinated with volatiles (unit coal) to serve as an index of their quality and heat value of coal, and can thus give an accurate assessment, even in high moisture coals, of calorific value, carbon (total), hydrogen and oxygen.

ONE of the earliest and still one of the most useful tests for the commercial evaluation and scientific classification of coals is the proximate analysis. Owing to its simplicity, it is often carried out to the exclusion of all other tests, and in the absence of other data we have to make the most of the information thus afforded. As a result of the classical work of Regnault[1], Johnson[2], Gruner[3], Frazer[4], and others, the significance of volatile matter (referred to hereafter as volatiles) in the broad classification of coals was realized and various attempts have been made to correlate the properties of a coal with the results of its proximate analysis. An important and vital deduction was made in 1902 by Goutal[5] who correlated calorific value with volatiles and fixed carbon. The relationship is given by the following equation:

$$Q = 82C + a.V., \text{ cal./g. (dry ash free)}$$

where Q, C and V denote calorific value in cal./g., fixed carbon and volatiles percentages respectively of the dry ash-free coal, and "a" is a varying factor depending on the dry ash-free volatiles. This is substantially the same as in the dry mineral matter free volatiles, when the ash is below 10 per cent, as in nearly all the coals chosen by Goutal.

Subsequently, various formulae[6] have been put forward from year to year, and among the latest* is that of Schuster[7] which states

$$Q = 8{,}000 + B(70 - 1{\cdot}65B)$$

where Q = gross calorific value, cal./g., on dry ash-free basis and B = per cent volatiles on dry ash-free basis. Several investigators have also noted a relationship between volatiles and total carbon and hydrogen of coals, one of the earliest being Diederichs[8] who correlated hydrogen (H) with volatiles (V) as follows:

$$H = V\left(\frac{7{\cdot}35}{V+10} - 0{\cdot}013\right)$$

Later, in 1907, Seyler[9] gave a logarithmic formula for hydrogen

$$H = 2{\cdot}80 \log V + 0{\cdot}95$$

The relationship of hydrogen with volatiles has been studied graphically by Fieldner and Selvig[10] and also more recently by Evans[11]. Korn[12] and Schuster[13] claimed a linear relationship between volatiles and total carbon, a conclusion disputed by Seyler, who in 1937 gave a quadratic equation[14] for the relation between carbon and hydrogen from volatiles:

$$H = 0{\cdot}1292V - 0{\cdot}00156V^2 + 2{\cdot}69$$
$$C = 0{\cdot}299V - 0{\cdot}01334V^2 + 90{\cdot}79$$

The formulae of Goutal, Schuster, and others for the calorific value, and those of Seyler and others for the elementary composition of coals deduced from the volatiles alone, suggest that coals having the same amount of volatiles have always the same calorific value and the same elementary composition. This, however, is only an approximation over a certain range, i.e. for coals having volatiles up to 35 per cent; even then, there are exceptions. When the

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*Attention of the author has been drawn to the recent work of C. Georgiadis [*J. Usin. Gaz.*, **76** (9) (1952), 314-16] correlating calorific value with volatiles and crucible index of coal. This will be dealt with in a subsequent communication.

volatiles exceed 35 per cent, we find, not infrequently, a wide variation in the calorific values and ultimate compositions (C, H and O) of coals having the same volatiles, especially if the coals are from different sources. Moreover, although Seyler's relationships are primarily intended for vitrains (brights) his equations often fail with coals having more than 35 per cent volatiles, *even if they are brights*. In Table 1, some Indian, British (predominantly brights), American and Canadian coals having approximately 40 per cent volatiles are presented along with their calorific values and ultimate compositions, all expressed on unit* coal basis. The wide variation in the properties of the coals having the same volatiles will at once be evident.

Irrespective of the rank of coal (at least, particularly for bituminous coals) the ultimate composition, and hence the heating value of the " fixed carbon " does not vary much but is almost constant. It has been established in these laboratories that a typical analysis of fixed carbon (dry ash-free) for Indian coals is approximately: Carbon, 97·0; hydrogen, 0·6; nitrogen, 1·4; sulphur, 0·5; and oxygen, 0·5 per cent. (The main Indian coals, i.e. coals from Bengal and Bihar, are low in sulphur—averaging 0·4 to 0·8 per cent.) The heating value of the " fixed carbon " appears to lie within the range of 14,300 ± 150 B.t.u./lb. The fixed carbon of lignites tends to have a heating value towards the lower limit, i.e. 14,150 B.t.u./lb., whereas that of low volatile coals approaches the upper limit, i.e. 14,450 B.t.u./lb. For bituminous coals the average figure is 14,400 B.t.u./lb. or 8,000 cal./g. The heating value of unit volatiles can then be calculated from the expression

$$\text{Heating value of volatiles in unit coal (B.t.u./lb.)} = \frac{\left\{\begin{matrix}\text{Cal. val. of unit}\\ \text{coal, B.t.u./lb.}\end{matrix}\right\} - \frac{1}{100}\left\{\begin{matrix}14{,}400 \times \text{fixed carbon \%}\\ \text{(in unit coal)}\end{matrix}\right\}}{\frac{1}{100} \times \text{volatiles \% (in unit coal)}}$$

The " calorific value of the volatiles " so defined will include heat of decomposition which, however, is small, especially for mature coals. The volatiles, however, do not include the water of hydration of the mineral matter and are thus referred to as " unit coal volatiles " — being the volatiles from unit coal. In Table 1, the heating values (in B.t.u./lb.) of unit coal volatiles have been calculated by the above formula. It is apparent that iso-vol. coals (i.e. coals of equal volatiles on unit coal basis) may have widely varying heating values for unit volatiles.

Table 1 shows that coals having the same volatiles (40 per cent) may have calorific values from 12,500 to 15,400 B.t.u./lb., carbon from 74 to 86 per cent, hydrogen from 4·8 to 6·0 per cent and oxygen from as low as 6·0 per cent to as high as 19·0 per cent or even more. Similar wide variations may also be shown to exist at any other range of volatiles beyond 35 per cent (unit coal). As will be seen from the results in Table 1, the calorific value of unit coal volatiles (B.t.u./lb.) of the iso-vol. coals appears to vary from 9,880 B.t.u./lb. to 16,820 B.t.u./lb. Clearly the amount of volatiles of a coal is, therefore, not an adequate or sufficient criterion for fixing the calorific value. In Figs. 1 and 2 the calorific values of the volatiles of the iso-vol. coals given in Table 1 have been plotted against (1) the carbon and (2) the oxygen contents of the coals.

It will be observed that the calorific value of the volatiles is linearly related to carbon and/or oxygen contents of the coals, either of which may, therefore, be a good measure of the composition or the *quality* of the volatiles.

The foregoing discussion emphasizes the need of an additional intrinsic factor or index to govern the quality of the volatiles for the precise evaluation of different properties of coal. Calorific value, oxygen and hydrogen are a few such factors which have been utilized in combination with volatiles by Calderwood[15], Seyler[16] and more recently by Spooner[17]. The relationships of Calderwood are rather complicated and except for carbon have been found to be much in error and have not been stated here. The formulae of Seyler and Spooner are:

Seyler :

$$C = (Q/100 - 1{\cdot}1\ V/3)\ 0{\cdot}59 + 43{\cdot}4$$

$$H = (Q/100 + V)\ 0{\cdot}069 - 2{\cdot}86$$

Spooner:

$$O = 63{\cdot}75 + 0{\cdot}1377V - 0{\cdot}007257Q$$

$$H = 0{\cdot}06624V + 0{\cdot}0006912Q - 2{\cdot}75$$

$$C = 39{\cdot}2 + 0{\cdot}006393Q - 0{\cdot}2205V$$

$$Q = 8781 + 19V - 144 \times O, \text{ cal./g.}$$

$$Q = 3787 - 100{\cdot}5V + 1506H, \text{ cal./g.}$$

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*Unit coal is the pure coal substance free from moisture and mineral matter. For most Indian coals it is given by the expression: 100 − (M + 1·1A), where M = per cent moisture, and A = per cent ash in the coal on "as received" basis. For high sulphur coals (S > 1 per cent) Parr's formula may be used, i.e. 100 − (M + 1·08A + 0·55S) where S = per cent total sulphur in the coal on " as received " basis.

TABLE 1 — ANALYSES AND HEATING VALUES OF UNIT VOLATILES OF ISO-VOLATILE COALS

(Results expressed on unit coal basis)

COAL No.	PARTICULARS OF SAMPLES	VOLATILES %	CAL. VAL. B.t.u./lb.	CARBON %	HYDROGEN %	OXYGEN %	CAL. VAL. OF UNIT VOLATILES B.t.u./lb. of volatiles	MOISTURE CONTENT OF AIR-DRIED OR AS RECEIVED COAL (MINERAL-FREE) %
India								
1	Raghunathbatti	40·5	15090	84·05	5·47	7·80	16100	4·0
2	Kasta	40·2	14890	84·53	5·45	7·88	15620	2·3
3	Poniati	39·7	14720	82·87	5·45	9·31	15210	6·2
4	Samla	40·0	14600	82·02	5·46	10·12	14900	7·5
5	Samla-Baidyanathpur	40·2	14020	80·58	5·19	11·84	13460	12·5
6	Nowrozabad	40·4	14010	81·06	5·10	12·21	13440	11·1
England								
7*	Belper Lawn (Notts)	40·3	15110	84·40	5·50	7·50	16160	3·4
8*	Alton (Notts)	40·4	15330	84·90	5·50	6·50	16700	2·8
9	Pemberton 5 ft. (Lancashire)	40·5	14950	83·00	5·73	9·70	15760	4·6
10	Leicester (E. Midlands)	40·2	13680	78·80	5·10	14·70	12610	14·2
11	Shropshire (Clod)	40·4	13800	78·90	5·40	14·20	12920	14·2
America								
12*	Chilton Bed Boone No. 2 Mine, Logan County, W.Va.	40·1	15270	85·40	5·70	7·20	16570	2·1†
13*	No. 2 Gas Bed, Point Lick, No. 4 Mine, W.Va.	40·2	15110	84·50	5·70	8·20	16170	2·4†
14*	Alma Bed, Spruce River No. 4 Mine, Boone County, W.Va.	40·9	15390	86·50	5·60	6·70	16820	0·8†
Canada								
15	Alberta	40·5	13330	77·00	5·10	16·20	11760	23·7‡
16	Alberta	40·5	12570	74·95	4·80	18·80	9880	30·8‡

*Data on coal Nos. 7, 8, 12, 13, 14 are on dry ash-free basis and the rest are on Parr basis. Coal Nos. 12, 13 and 14 are taken from " Relation of Microscopic Composition of Coal to Chemical, Coking and Byproduct Properties ", Sprunk and Thiessen, *Ind. Engng. Chem.*, **27** (1935), 446-51. Coal Nos. 15 and 16 are taken from " Studies on Some Properties of Alberta Coals, III ", Sherlock, E., *Fuel*, **30** (1951), 75. Data on English coals are collected from different published papers and books.

†Moisture percentages on " as received " basis.

‡These are " capacity " moisture percentages and are parts of moisture per 100 parts of dry mineral-free coal substance, which is *not* a percentage on the whole coal although approximating to it, more closely the less the moisture.

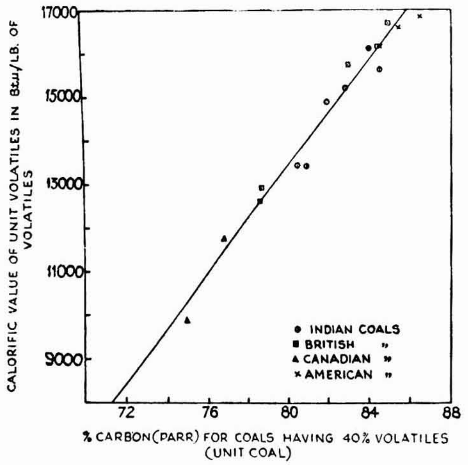

FIG. 1 — RELATION OF CARBON TO CALORIFIC VALUE OF UNIT VOLATILES

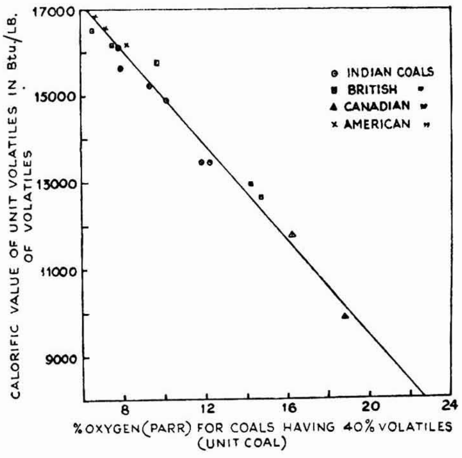

FIG. 2 — RELATION OF OXYGEN TO CALORIFIC VALUE OF UNIT VOLATILES

where C, H and O are carbon, hydrogen and oxygen percentages expressed on Parr's basis, and Q and V are gross calorific value (cal./g.) and per cent volatiles respectively on unit coal basis. (In Seyler's formulae C, H, Q and V are on dry ash-free basis.)

The above formulae are useful, but they necessitate a knowledge of calorific value (or of oxygen or of hydrogen) over and above the results of proximate analysis. A more readily available intrinsic index or property in the above formulae would make them more generally useful; and fortunately proximate analysis results have such a factor or index in the percentage moisture, which (in properly "conditioned" coal) may be used instead of calorific value or hydrogen or oxygen to "qualify" the volatiles.

The importance of moisture in coals as an index of the rank has long been recognized. It has also been shown graphically by Mott[18] (*see* Fig. 3 of his paper) that the natural moisture of coal and oxygen content (Parr basis) are linearly related. Again, as shown earlier (FIG. 2), oxygen can be used as a measure of the calorific value of the volatiles and is thus a good index of their composition or quality. In a word, moisture, which is more or less proportional to oxygen, may serve as an index of the quality of the volatiles. Further, such moisture for iso-vol. coals varies widely (TABLE 1) and is actually a measure of the calorific value of the volatiles (FIG. 3) and hence an index of the quality. Moisture, which is closely related to the physical and chemical properties of coal, in fact serves as a parameter for co-ordinating volatiles with the different properties of a coal.

These arguments have led to the following formulae (for unit coal) correlating calorific value, carbon, hydrogen and oxygen with volatiles and moisture.

1. $Q = 9170 - 16V - 60M_1\ (1 - 0{\cdot}001M_1)$, cal./g.
   $= 16510 - 29V - 108M_1\ (1 - 0{\cdot}001M_1)$, B.t.u./lb.
2. $C = 0{\cdot}97F + 0{\cdot}70V - M_1\ (0{\cdot}6 - 0{\cdot}01M_1)$
   $= 97 - 0{\cdot}27V - M_1\ (0{\cdot}6 - 0{\cdot}01M_1)$
3. $H = 3{\cdot}6 + 0{\cdot}05V - 0{\cdot}0035M_1^2 \times (1 - 0{\cdot}02M_1)$
4. $O = 0{\cdot}25V + 0{\cdot}4M_1 - 2{\cdot}80$

where Q = calorific value; C = per cent carbon; H = per cent hydrogen; O = per cent oxygen*; V = per cent volatiles; and F = per cent fixed carbon (all on dry mineral-free basis, i.e. unit coal); and M_1 = per cent air-dried equilibrium moisture [at 60 per cent relative humidity (R.H.)] expressed on mineral-free basis.

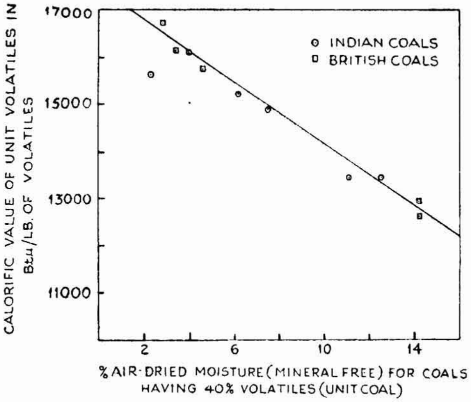

FIG. 3 — RELATION OF AIR-DRIED MOISTURE TO CALORIFIC VALUE OF UNIT VOLATILES

"Air-dried" moisture, though a characteristic property of coals, is, however, subject to wide variations when there are humidity fluctuations in the atmosphere. Hence a proper definition of air-dried moisture is essential. Here we define "air-dried equilibrium" moisture as that moisture which is retained by the coal (ground to pass 72 mesh B.S. sieve) after the coal attains equilibrium with an atmosphere of 60 per cent R.H. at 25° to 35°C. This atmosphere is easily obtained by keeping a solution of calcium chloride (sp. gr. 1·30) in a closed space. The "true" air-dried moisture is that moisture which the coal retains after coming to constant weight in such an atmosphere. The exact temperature in this range is not of importance.

The proposal to refer the moisture to 60 per cent R.H. is not without purpose. Systematic study of the reported air-dried moisture for hundreds of coal samples of different ranks (moisture 1 to 15 per cent) analysed at different seasons of the year has shown that most of the moisture figures refer to approximately 60 per cent R.H., although in India the R.H. may vary from 10 to 90

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*This oxygen includes organic sulphur. For high sulphur coals special treatment is necessary.

per cent during a year. These are, however, extreme limits of variation, and from our records the average R.H. in the laboratory appears to be in the region of 60 per cent. This assumption has been borne out by the studies on 146 widely different Indian coals. The volatiles in these coals ranged from 19 to 44 per cent (unit coal) and air-dried moisture (mineral-free) from 1 to 15 per cent. The applicability of the set of formulae has also been studied on 54 typical British coals (covering practically all the coalfields of Great Britain) having volatiles from 14 to 47 per cent and air-dried moisture from 0·6 to 16 per cent. The accuracy of the prediction of the calorific values and the ultimate analyses (C, H and O, all on unit coal basis) has been found to be satisfactory*. Although, the frequently correct predictions would point to the reported air-dried moisture for Indian and British coals to be (almost) in equilibrium with an atmosphere of 60-70 per cent R.H., it is not unusual to find wide variations of air-dried moisture of coal samples (especially high moisture) of a particular seam at different seasons of the year. For better evaluation of the intrinsic properties of coal (Q, C, H and O) from proximate analysis by means of these formulae, it is, therefore, desirable and indeed essential to determine the " air-dried equilibrium " moisture at 60 per cent R.H., as outlined above.

"Bed", "Seam", "Mine", "Capacity", or " Maximum Adsorbed Moisture (M.A.M.)[19] " (all of which are used in more or less the same sense) can be used, provided suitable modifications for moisture are made in the formulae. Studies on the variation of moisture with relative humidity have shown that bed moisture or capacity moisture (at 100 per cent R.H.) for most coals is approximately 40 per cent higher than the air-dried moisture at 60 per cent R.H. In the light of this study the air-dried moisture factors in the formulae have been converted to represent capacity moisture, other terms in the formulae remaining the same. The modified set of formulae, thus obtained, has been successfully applied for the calculations of unit coal calorific value, carbon, hydrogen and oxygen from proximate analyses in case of 100 Alberta coals whose capacity moisture varied from 1·4 to 60·0 per cent. (Capacity moisture used in the formulae is expressed as parts of moisture per 100 parts of dry mineral-free coal substance, *which is not the same as per cent moisture.*)

The following formulae have also been deduced for direct calculation of calorific value, carbon, hydrogen on "air-dried" basis from the proximate analysis reported on air-dried basis (i.e. at 60 per cent R.H.):

1. $Q_1 = 165F_1 + 136\ (V_1 - 0{\cdot}1A_1) - 108M_1\ (1 - 0{\cdot}001M_1)$
2. $C_1 = 0{\cdot}97F_1 + 0{\cdot}70\ (V_1 - 0{\cdot}1A_1) - M_1\ (0{\cdot}6 - 0{\cdot}01M_1)$
3. $H_1 = 0{\cdot}036F_1 + 0{\cdot}086\ (V_1 - 0{\cdot}1A_1) - 0{\cdot}0035M_1^2\ (1 - 0{\cdot}02M_1)$

where Q_1 = calorific value, B.t.u./lb.; C_1 = per cent carbon; H_1 = per cent hydrogen (corrected for moisture of coal and water of constitution of the shale in coal); F_1 = per cent fixed carbon; V_1 = per cent volatiles; A_1 = per cent ash; M = per cent moisture [all items on air-dried basis (60 per cent R.H.)]; and $(V_1 - 0{\cdot}1A_1)$ = per cent volatiles on air-dried basis after correcting for the shale moisture which has been taken as equal to one-tenth of the ash per cent. (Corrections of the volatiles for the carbon dioxide of carbonates and also for sulphur are advised if either the sulphur or carbon dioxide exceeds 1 per cent.)

These formulae have been found helpful in the checking of laboratory analyses: frequently, the calculated and the determined values are materially the same. For coals which are not highly "abnormal" (i.e. having very little or not more than 2 per cent " volatile displacement ") it is usual to find the predicted values of carbon and hydrogen on air-dried basis lying within ±0·50 and ±0·10 of the actual values respectively. For low moisture coals (moisture not exceeding 3-4 per cent) the predictions may be closer. Where there is great divergence, the coal has probably been weathered or is an outcrop coal or a highly abnormal coal.

Scope, accuracy, merits and limitations of the formulae

The details of development have been worked out for each of the formulae (corresponding regression formulae seem to be possible and have been evaluated) along

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*The average R.H. in England appears, however, to be somewhat higher than in India. Hence, the moisture factor in the set of formulae could be slightly adjusted to suit British conditions better.

with their range of application, the probable accuracy of the calculated values, the effect of variations in the petrological constituents on the results, as well as the significance of the ideas underlying the formulae in " coal systematics ". The following conclusions are tentatively drawn.

1. Unlike the formula of Goutal or Schuster (and other similar formulae for calorific value which are based on volatiles and fixed carbon only) the proposed formula takes into consideration the varying quality of the volatiles*, and hence does not give always the same calorific value for the same magnitude of volatiles. This point of contrast will be at once evident from an inspection of the formulae:

Goutal: $Q=82C+a.V.$, cal./g.

Schuster: $Q=8000+V\ (70-1{\cdot}65V)$, cal./g.

New formula (Mazumdar):

$$Q=9170-16V-60M_1\,(1-0{\cdot}001M_1),\ \text{cal./g.}$$

The new formula is applicable with good " fit " to all coals having more than 18 per cent volatiles (unit coal). The expected accuracy is within ±1 per cent, and only seldom will the error exceed ±1·7 per cent of the experimental values (unit coal). It is true even for coals having 15-16 per cent air-dried moisture. The real virtue of the new formula lies in its accuracy for both low and high moisture coals. The classical formula of Goutal, it should, however, be pointed out, is also accurate for coals up to about 35 per cent volatiles (pure coal); but above 35 per cent volatiles, errors are frequently high both for (1) low moisture and high volatile and (2) high moisture and high volatile coals. The reason for this is that in the high volatile coals especially it is not only the quantity but also the *quality* of volatiles that has to be taken into consideration to find the calorific value. The new formula assesses the quality of volatiles by means of the moisture factor. This is its important feature.

2. The formulae proposed for carbon and hydrogen (unit coal) embodying volatiles and moisture are as follows:

New formulae (Mazumdar):

$$\%\ C=97-0{\cdot}27V-M_1\ (0{\cdot}6-0{\cdot}01M_1)$$
$$\%\ H=3{\cdot}6+0{\cdot}05V-0{\cdot}0035M_1^2\,(1-0{\cdot}02M_1)$$

The formulae predict values as accurately as do Seyler's formulae involving volatiles alone — and often more accurately.

Seyler's formulae:

$$H=2{\cdot}80\log V+0{\cdot}95$$
$$H=0{\cdot}1292\ V-0{\cdot}00156\ V^2+2{\cdot}69$$
$$C=0{\cdot}299\ V-0{\cdot}01334\ V^2+90{\cdot}79$$

Seyler's relationships are for bright coals, but may also be used for other coals with some knowledge of their petrology, as pointed out by him. Even in bright coals, having more than 35 per cent volatiles, it is well known that for the same volatiles there is a wide scatter in the elementary composition (C, H and O), and it is in these coals especially that the new formulae will be found better. Furthermore, the new formulae have also been found to give comparable results as Seyler's later set of more exact formulae based on volatiles and calorific value. A comparative study of the application of the formulae to 18 typical British coals[20] (average vitrinite content above 80 per cent) having volatiles from 17 to 46·8 per cent (unit coal), and air-dried moisture (mineral-free) from 0·5 to 15·6 per cent gives the following results (TABLE 2).

The above accuracy has been obtained, in spite of the assumption that the reported air-dried per cent moistures relate to an equilibrium with 60 per cent R.H. Probably the results of the V and M formula would have been better had the coals been properly conditioned for the determination of the true air-dried moisture at 60 per cent R.H. The new formulae are, of course, based only on proximate analysis, and are thus more readily applicable to available analyses. An almost similar order of expected accuracy for the formulae for carbon and hydrogen has also been obtained for Indian coals. The Indian coals studied were not brights (volatile displacement usually about 2-3 per cent but in some cases more) and the average ash was considerably higher than 15 per cent. The accuracy obtained is, therefore, better than could be expected.

TABLE 2 — STANDARD DEVIATIONS OF SEYLER'S AND NEW FORMULAE

	SEYLER'S FORMULA (USING VOLATILES AND CAL. VAL.)	NEW FORMULA (USING VOLATILES AND MOISTURE)
Carbon (unit coal)	±0·56	±0·69
Hydrogen (unit coal)	±0·10	±0·09

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*Goutal or Schuster allows for this, but not for iso-vol. coals.

3. The proposed formula for oxygen (unit coal) is as follows:

New formula (Mazumdar):

$$\% \text{ oxygen} = 0{\cdot}25V + 0{\cdot}4M_1 - 2{\cdot}80$$

This formula for oxygen from proximate analysis alone compares not unfavourably with Spooner's which requires calorific value over and above the proximate analysis results. The expected accuracy of prediction of oxygen on the dry mineral basis [oxygen $= 100-(C+H+N)$]* works out to ±0·67 (68 per cent probability) in the case of 146 Indian coals (oxygen content varying from 2·5 to 15 per cent unit coal). The accuracy will probably improve with the proper conditioning of the coals for moisture, as recommended earlier.

4. The formulae have also been applied to sub-bituminous coals and lignites, where the capacity moisture may be high. It appears from a preliminary study that, even in these very low rank coals, the formulae are essentially sound. Excessive and irregular amounts of abnormal bodies, such as waxes and resins in these coals, however, in certain cases militate against the precision obtainable with true bituminous coals.

5. The correlating of volatiles and moisture (an index of quality) with the properties of a coal may be extended to other important properties, besides those considered here. The possibility that volatiles and *properly defined moisture*, along with a knowledge of the coal petrology, may be a most useful guide to other properties of coal (e.g. in combustion, carbonization, gasification) does not appear to be far-fetched.

Acknowledgement

Grateful acknowledgement is due to Dr. J. W. Whitaker, former Director, Fuel Research Institute, for offering many suggestions during the course of the work. The author's thanks are also due to the Officers-in-Charge of the Laboratories of the Indian Coal Survey Stations for generous co-operation, and particularly to Mr. S. Gupta of the Ranchi Coal Survey Station.

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*This is on Parr basis. Parr considers all the sulphur in coal as pyritic which is certainly not true for Indian coals, either from Assam or from Bengal and Bihar.

Histology of Red Hairy Sheep Skin

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The histology of red hairy sheep skin has been studied and compared with that of woolly sheep skin. Red hairy sheep skin is tougher than woolly sheep skin and possesses the basic characteristics required for the production of roller leather.

RED hairy sheep is found only in South India. Its skin is much prized in England and other European countries, and is used mostly for the manufacture of roller leather required in spinning mills. While considerable work on the histology of woolly sheep skin has been carried out, there has been practically no work on the histology of red hairy sheep skin. It has, therefore, not been possible to compare its basic qualities with woolly sheep skin and explain why red hairy sheep skins are best suited for roller leather.

This study was undertaken with a view to find out the structural features of the red hairy sheep skin which contribute to the special characteristics exhibited by roller leather. It is expected that this investigation would increase our knowledge of roller leather producing skins.

Materials and methods

The skins were obtained from freshly slaughtered animals for examination. Small pieces were cut off from different regions fixed in 10 per cent formol solution for histological work. The freezing method of sectioning was used. Sections *c.* 40 μ thick were obtained and stained with haematoxylin, eosin, gentian violet, scarlet red and Weigert's elastic tissue stain, depending on the structure to be examined. The thickness of the grain and corium of the skins were determined from the sections used for histological examinations. The histological technique followed was the same as that described in our earlier studies[1].

Microscopic characteristics

The general structure of fresh red hairy sheep skin and woolly sheep skin (FIGS. 1 and 2) show that they generally exhibit the same features. However, a characteristic difference which is readily observed is the thickness of the grain layer (corium minor). In red hairy sheep skin there is a much thicker grain layer and a relatively thinner corium. The thickness of the grain layer in the hairy sheep skin is 1·59 mm. whereas in the woolly sheep skin it is 1·10 mm. The total thickness of the grain plus corium layer in hairy and woolly sheep skins are 2·37 mm. and 2·00 mm. respectively.

The epidermis, the stratum corneum and stratum germinatum are quite distinct in red hairy sheep skin. The hair-pores in red hairy sheep skin are closer than in woolly sheep skin (FIG. 3). The hair follicles are more or less straight. They are longer and deeper than in woolly sheep skin. The erector pili muscles are large and well

FIG. 1 — VERTICAL SECTION OF RED HAIRY SHEEP SKIN (× 32)

developed and occupy the same relative position as in woolly sheep skin extending right up to the epidermis. The sebaceous and sudoriferous glands and their ducts are similar in both the skins. Fat cells and fat droplets are also observed in hairy sheep skin, but their number is smaller than that in woolly sheep skin.

Elastic tissue fibres in the hairy sheep skin are found mainly in the upper part of the grain layer and are arranged parallel to each other and to the surface. In sections cut horizontal to the skin surface and stained with a special stain, a network of elastic fibres is seen (FIG. 4). The hairy sheep skin contains more of this tissue than woolly sheep skin.

FIG. 2 — VERTICAL SECTION OF WOOLLY SHEEP SKIN (× 32)

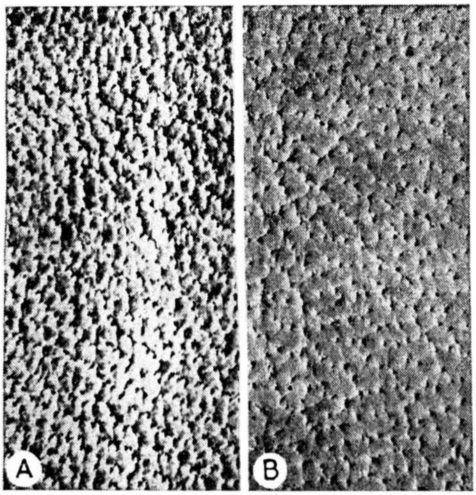

FIG. 3 — GRAIN SURFACE OF (A) RED HAIRY AND (B) WOOLLY SHEEP SKINS SHOWING ARRANGEMENT OF HAIR PORES (× 5)

FIG. 4 — HORIZONTAL SECTION OF RED HAIRY SHEEP SKIN (THROUGH GRAIN LAYER) SHOWING ELASTIN NETWORK OF THE GRAIN (× 98)

In the corium proper, the collagenous bundles are a little fuller in red hairy sheep skin than in woolly sheep skin. The fibre bundles are of low angle type in both the skins. The subcutaneous muscle is seen attached to the skin in both the skins. Reticular tissue which occurs in the hairy sheep skin in the form of a fibrous network is also found in woolly sheep skin.

Effect of liming

The effect of liming on the grain thickness, and the angulation of collagenous bundles of hairy and woolly sheep skins was studied. The liming operation consisted in soaking small pieces of skins separately in 10 per cent lime suspension liquor containing different proportions of sodium sulphide (0·25-1·0 per cent on the weight of skin) for 12 days. Sodium sulphide was added to the liming liquor to determine the extent of plumping of the skins.

The gain in thickness of the grain and angle of weave following liming are given in Table 1.

TABLE 1 — EFFECT OF LIMING

COMPOSITION OF LIME LIQUOR	RED HAIRY SHEEP SKIN		WOOLLY SHEEP SKIN	
	Grain thickness mm.	Angle of weave	Grain thickness mm.	Angle of weave
Lime, 10%	1·59	Less than medium	1·10	Medium
Lime, 10% + sodium sulphide, 0·25%	1·59	do	1·24	do
Lime, 10% + sodium sulphide, 0·50%	1·59	do	1·93	do
Lime, 10% + sodium sulphide, 0·75%	1·80	do	1·63	do
Lime, 10% + sodium sulphide, 1%	2·15	Low	1·20	Less than medium

From the results given in Table 1, it is evident that lime alone has practically no effect on the grain thickness of the skins. Sulphide liming appears to influence the plumping of red hairy sheep skin to a greater extent than of woolly sheep skin, and its effect on the angulation of the fibre bundles of red hairy sheep skin is negligible (FIG. 5). While there is a progressive increase in the thickness of the red hairy sheep skin when the amount of sulphide added to lime solution is increased from 0·75 to 1·0 per cent, an apparent decrease is noticed in the thickness of woolly sheep skin.

From a study of the microscopic characteristics of the skins, it appears that red hairy sheep skin is characterized by thick grain layer and relatively thin corium. This, together with closely located hair pores and well-developed elastin fibre of the grain, may account for the strong and smooth grain of the red hairy sheep skin.

The corium of red hairy sheep skin differs from that of woolly sheep skin in thickness and in the fullness of collagenous bundles. The fullness of the fibre bundles may account for the compactness of the red hairy sheep skin.

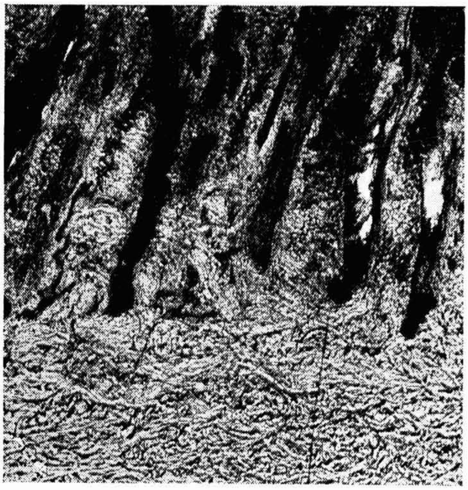

FIG. 5 — VERTICAL SECTION OF RED HAIRY SHEEP SKIN AFTER LIMING FOR 12 DAYS WITH 10 PER CENT LIME AND 1 PER CENT SODIUM SULPHIDE (× 23)

Red hairy sheep skin is thicker than woolly sheep skin and can apparently be plumped to a greater extent than woolly sheep skin without causing damage to its fibre structure. Sulphide liming increases the thickness of the grain layer but not the angulation of the fibre bundles of the red hairy sheep skin. This increase in grain thickness and low angulation of the fibre bundles may account for the firmness and good tensile strength of roller leathers made from hairy sheep skin.

This study indicates that red hairy sheep skin possesses the essential basic qualities required for the production of roller leathers, namely: (1) firmness and a smooth, strong grain, (2) low angulation of the fibre bundles with compact weave, and (3) full fibres with good tensile strength.

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A Survey of the Indigenous Tanning Materials of the Madras State: Part I — White-valem Bark (*Acacia leucophloea*)

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A systematic study has been made of white-valem (*Acacia leucophloea*) bark, one of the indigenous tanstuffs of Madras State, with a view to use it in place of imported wattle bark in the E.I. tannage of kips. Chemical examination of the bark and practical tanning trials have shown it to be a satisfactory substitute for wattle bark. Leathers produced by white-valem tannage compare favourably with those produced by wattle tannage. In admixture with avaram bark, white-valem bark gives a leather superior to that obtained with wattle tannage.

INDIA is not self-sufficient with respect to vegetable tanning materials and imports *c.* 30,000 tons of wattle bark and its extract (mimosa extract) annually to meet the requirements of the leather industry. It is essential, therefore, that suitable substitutes for imported wattle bark are developed from indigenous raw materials.

Edwards and co-workers[1] have examined a number of Indian plants for their suitability as tanning materials. The conclusions arrived at from these studies, according to the authors, were in many cases based on scanty data and fuller investigation of the plants was necessary to correct or confirm the findings reported by them[2]. The work on the tanstuffs investigated by these workers was mainly confined to the determination of the tannins and non-tannins by the official methods of analysis. Recent researches have shown that in addition to tannins and non-tannins in the tanstuff other constituents such as acids and salts in them have an important bearing on the tanning of leather. Published information on the acid and salt contents of indigenous tanstuffs is scanty and it is only recently that data on some important Indian tanstuffs were collected[3]. Similarly, information on the practical application of these vegetable tanstuffs and their performance in tanning of leather is meagre. It is possible to substitute imported wattle bark or its extract with suitable tanning materials, individually or in combination or by a judicious adjustment and modification of the chemical properties of tan liquors obtained from indigenous tanning materials. It was, therefore, considered desirable to carry out a systematic investigation of promising indigenous tanning materials which are in abundant supply. With the co-operation of the Forest Department of the Madras State, a systematic study of one such substitute, namely white-valem (*Acacia leucophloea*; *Hindi*: Kikard; *Telugu*: Tellatumma; *Tamil*: velvayalam) bark, has been carried out and the results are reported in this paper.

White-valem bark is similar to babul bark. The tree is a moderate sized one with a girth of 3 ft. and 8 ft. 10 in. bole. It is a thorny deciduous tree with a spreading crown and crooked trunk. The bark is light yellowish grey to nearly white, light red inside and smooth. This tree grows in plenty in the districts of Coimbatore, Vellore, Godavery in South India and on the plains of the Punjab and Uttar Pradesh. Though the exact quantity of the bark available is not known, it can be assumed that it will be available in plenty.

Experimental procedure

Chemical characteristics — The bark was obtained from the forest range, Santhavasal (Vellore East Division) and analysed for its chemical, physical and tanning characteristics. The total acid and salt contents of the bark were determined according to the method of O'Kell[4] and the amount of weak acids and their salts according to the method of Atkin and Burton[5]. The results

TABLE 1 — CHEMICAL ANALYSES OF TANNING MATERIALS

TANNING MATERIAL	TYPE OF TANNIN	TANNIN %	NON-TANNIN %	T/NT RATIO	TOTAL ACIDS†	TOTAL SALTS†	RATIO OF ACIDS TO SALTS	*p*H
White-valem*	Catechol	17·0	7·0	2·4	nil	156·0	—	5·9
Wattle	do	36·0	14·0	2·5	6·0	45·7	0·13	5·0
Babul	do	14·0	10·0	1·4	40·0	16·0	0·47	5·2
Avaram	do	17·0	10·0	1·7	12·6	121·0	0·10	5·2

*Insolubles, 66·0; ash, 1·2; sugars (glucose), 0·64; buffer index (cc. of N acid required to change the *p*H of 100 cc. of 20°Bk. liquor by one unit), 3·5.

†Total salts and acids expressed in mg. equiv./100 g. of total solubles in 1 l. of liquor.

of the chemical analysis of the bark are reported in Table 1. These results differ with those reported in literature. Fraymouth[6] reported an average tan content of 12 per cent and the T/NT ratio 1·6 as compared to 17·0 and 2·4 for this bark. The results of the chemical analyses of white-valem, wattle, babul and avaram barks are given in Table 1.

These results indicate that the white-valem bark is similar to wattle bark with regard to the T/NT ratio, total acids, and *p*H. The wattle and white-valem barks contain very little of acids and both are catechol types of tannins. The white-valem bark contains only 17 per cent of tannins as in babul or avaram bark, but it differs from them in respect of other properties. The results also indicate that white-valem bark alone can be used as a substitute for wattle bark.

Potentiometric titration studies — The tan liquor from the bark was titrated with standard alkali and acid according to the method of Atkin and Burton[5] and the weak acids and salts of weak acids determined. The results are given in Table 2 and plotted in Fig. 1. Similar data and titration curves for avaram, babul, konnan and wattle barks are included in Table 1 and Fig. 1 for comparison.

TABLE 2 — WEAK ACIDS AND SALTS OF WEAK ACIDS IN DIFFERENT TANNING MATERIALS

TANNING MATERIAL	WEAK ACIDS*	SALTS OF OF WEAK ACIDS*	RATIO OF ACIDS TO SALTS	BUFFER INDEX
Babul bark	37·5	242·0	0·15	1·86
Avaram bark	50·0	266·5	0·19	2·11
Konnan bark	32·5	366·5	0·09	2·66
Wattle bark	15·0	85·0	0·18	0·67
White-valem bark	nil	390·0	—	3·50

*Expressed in mg. equiv./100 g. of total solubles in 1 l. of 100°Bk. liquor.

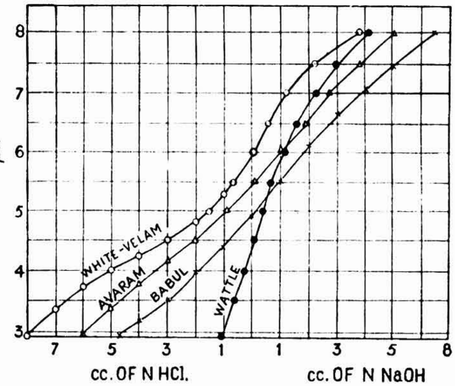

FIG. 1 — TITRATION CURVES OF TANNING MATERIALS

The data show that the white-valem bark contains a high amount of salts of weak acids as in avaram and konnan barks. White-valem bark liquor has a high buffer index, and contains negligible amount of weak acids as in wattle bark. From these studies it can be safely concluded that white-valem should prove to be a good tanning agent with properties similar to avaram, babul and wattle.

As the T/NT ratio in the white-valem bark is high (2·4), it is suitable for the preparation of tannin extract. The extracts were prepared by the following three methods: (i) successive leaching with water (six times)

TABLE 3 — ANALYSIS OF SOLID TANNIN EXTRACTS FROM WHITE-VALEM BARK

EXTRACTING LIQUID	TANNINS %	NON-TANNINS %	MOISTURE %	INSOLUBLES %	COLOUR		*p*H
					Yellow	Red	
Water	53·1	31·1	8·0	7·8	12	13	5·7
Water + 3% sod. sulphite	58·0	32·0	8·0	2·0	18	20	6·9
Water + 3% sod. hydrosulphite	52·0	31·0	8·2	8·8	14	15	6·3

TABLE 4 — CHEMICAL ANALYSES OF LEATHERS TANNED WITH WHITE-VALEM AND WATTLE BARK

	TRADITIONAL METHOD		MODIFIED METHOD				TANNING WITH BLENDS	
	White-valem tannage	Wattle tannage	Acetate pickle		Calgon pickle		White-valem and avaram tannage	Wattle tannage
			White-valem tannage	Wattle tannage	White-valem tannage	Wattle tannage		
Moisture, %	10·40	10·40	14·00	14·00	14·0	14·8	12·60	12·60
Hide substance, %	35·00	38·40	38·00	38·12	38·2	39·5	42·90	40·70
Water solubles, %	15·30	13·10	8·20	10·26	7·4	9·5	3·60	4·80
Total ash, %	1·35	1·35	0·58	2·58	0·8	3·0	0·73	0·60
Insoluble ash, %	0·10	0·10	0·10	0·64	0·4	1·5	0·12	0·10
Oils and fats, %	9·83	9·49	6·83	6·87	6·7	6·9	9·00	11·20
Fixed tannins, %	29·40	28·49	32·87	30·11	33·3	27·8	31·80	30·60
Degree of tannage, %	81·00	81·30	86·50	78·90	86·0	71·0	74·10	75·20
*p*H of water solubles	3·70	3·70	3·60	3·70	3·6	3·7	3·50	3·60

TABLE 5 — MICROSCOPIC CHARACTERISTICS OF LEATHER

TANNING PROCESS ADOPTED	TANNING MATERIAL	MICROSCOPICAL APPEARANCE	REF. TO PHOTOMICROGRAPH
Traditional E.I. tanning process	White-valem	Fairly bold fibre bundles; fairly compact and regular weave pattern; low angle of weave; large amount of splitting with a little resticking; fibre bundles show large curve with slightly fuzzy outline	1050
do	Wattle	Slightly ill-defined fibre bundles with fairly compact and slightly irregular weave pattern and low angle of weave. Large amount of splitting. Fibre bundles show medium curve with slightly fuzzy outline	1051
Modified E.I. tanning process — acetate pickle	White-valem	Ill-defined fibre bundles with loose and slightly irregular weave pattern, and very low angle of weave. Very large amount of splitting; fibre bundles show small and medium curves with fuzzy outline	1052
do	Wattle	Fairly bold fibre bundles with compact and regular weave pattern, and medium angle of weave; medium amount of splitting; fibre bundles show small and medium curve	1053
Modified E.I. tanning process — Calgon pickle	White-valem	Ill-defined fibre bundles with slightly loose and irregular weave pattern, and angle of weave less than medium. Large amount of splitting with a little resticking; fibre bundles show medium curve with slightly fuzzy outline	1054
do	Wattle	Fairly bold and ill-defined fibre bundles with compact and fairly regular weave pattern, and less than medium angle of weave; large amount of splitting; fibre bundles show small and medium curve with slightly fuzzy outline	1055
Traditional E.I. tanning process using blends	White-valem +avaram	Fairly bold and ill-defined fibre bundles with fairly compact and fairly regular weave pattern, and medium angle of weave; large amount of splitting; fibre bundles show large curve with slightly fuzzy outline	1056
do	Wattle	Fairly bold fibre bundles with fairly compact and fairly regular weave pattern, and high angle of weave; medium amount of splitting; fibre bundles show large and medium curve with slightly fuzzy outline	1057

(ii) successive leaching with water containing 3 per cent (on the weight of the bark) sodium sulphite (six times); and (iii) successive leaching with water containing 3 per cent (on the weight of the bark) sodium hydrosulphite (six times).

The leached liquors were concentrated and evaporated under vacuum and the solid extracts (>50 per cent tannin) analysed. The results are tabulated in Table 3.

The addition of sodium sulphite to the extracting liquid increases the tannin content of the leach liquors and more of the insolubles go into solution. The addition of sodium hydrosulphite, however, does not improve the extraction of tannin from the bark. The addition of sodium sulphite to the leaching vats is beneficial and extracts of high tannin content and good colour can be prepared.

Practical tanning trials

Preliminary laboratory tanning trials showed that white-valem bark gives a leather

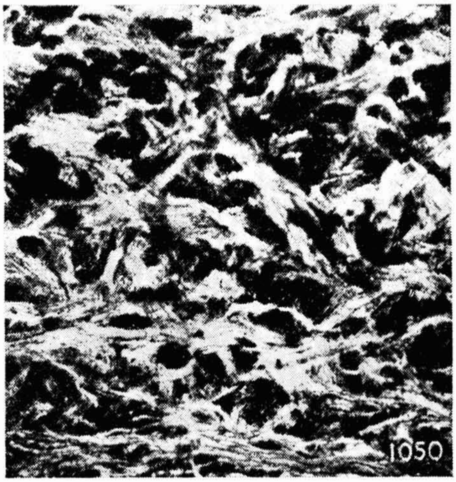

FIG. 2 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO TRADITIONAL E.I. TANNING PROCESS WITH WHITE-VALEM (×34) [Sample from butt region; thickness of section, 40 μ]

FIG. 3 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO TRADITIONAL E.I. TANNING PROCESS WITH WATTLE (×34) [Sample from butt region; thickness of section, 40 μ]

of good strength, colour and weight. To confirm these results, trials were carried out on a larger scale in the tannery. Parallel experiments were conducted with wattle bark for comparison. The trials were carried out according to the traditional E.I. tanning process. Wet-salted cow hides were soaked in water, limed for a period of 6 days and delimed in the usual way. The pelt was then tanned by the traditional method by placing it in between layers of tanning bark and the material tanned according to the two-pit system for 18 days. An amount of bark equivalent to the expected yield of the leather (on the basis of 16 per cent tan on the weight of pelt) was used for tanning. The delimed pelt was cut into sides and the " lefts " were tanned with wattle bark and the " rights " with white-valem bark. After tanning, the leathers were finished as in the traditional E.I. tannage of kips. The yields of leather using white-valem and wattle tannages were 40 and 42 per cent respectively.

The chemical analyses of the leathers are given in Table 4. Except for higher water solubles content, white-valem tanned leathers resemble closely those tanned with wattle bark. The leathers also resemble each other in their physical characteristics. They possess a good general appearance and colour, are strong, firm, tight and full, and do not exhibit any crackiness on folding (single or double-fold). The white-valem tanned leathers are lighter in colour but less firm than those obtained by wattle tannage.

The microscopic characteristics of the leathers[8] are also similar (TABLE 5 and FIGS. 2-3).

Modified E.I. tanning method

The method worked out in this Institute[9] to reduce the duration of tanning and the amount of the tanning material used in the traditional E.I. tanning process was employed in the tanning of E.I. kips using white-valem bark. The modified method consisted of pre-treatment of the delimed pelt with Calgon and sulphuric acid or acetate and sulphuric acid followed by thorough washing and tanning with the vegetable tan liquors.

The tanning was conducted according to the traditional two-pit system using the bark and placing the pelt in between the layers of the bark. The only difference between this experiment and the experiments carried out earlier in the traditional process was the pre-treatment of the pelt. Parallel experiments were conducted as reported earlier with both white-valem and wattle barks. In the case of wattle tanning, it was observed that the tanning was complete on the eighth day in the first pit itself, thereby reducing the time of tanning from 18 days to 8 days as compared to the traditional process. But this period could further be reduced to 3 days if leached liquors were used in the place of the bark[10]. It was further noted that, in tanning with white-valem bark, the penetration of tannin was slow and the tanning was complete only on the sixteenth day. This showed that the leaching of tannin from this bark was rather slow whereas in the case of wattle, the tannin was leached out much quicker. The pre-treated pelt readily

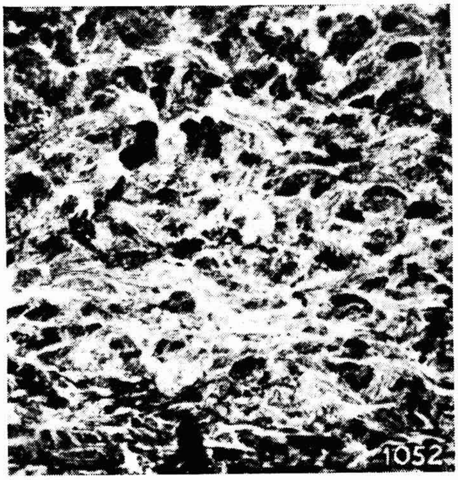

FIG. 4 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO MODIFIED E.I. TANNING PROCESS WITH WHITE-VALEM AFTER ACETATE PICKLE (×34) [Sample from butt region; thickness of section, 40 μ]

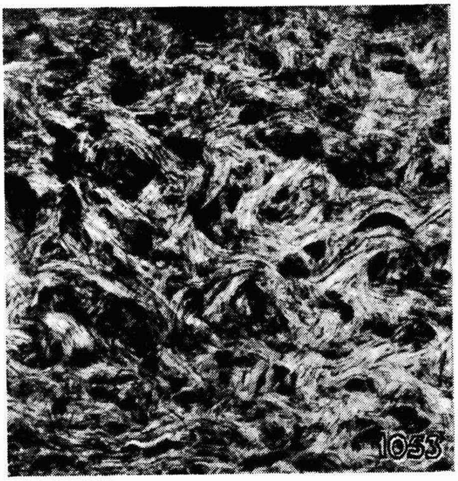

FIG. 5 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO MODIFIED E.I. TANNING PROCESS WITH WATTLE AFTER ACETATE PICKLE (×34) [Sample from butt region; thickness of section,40 μ]

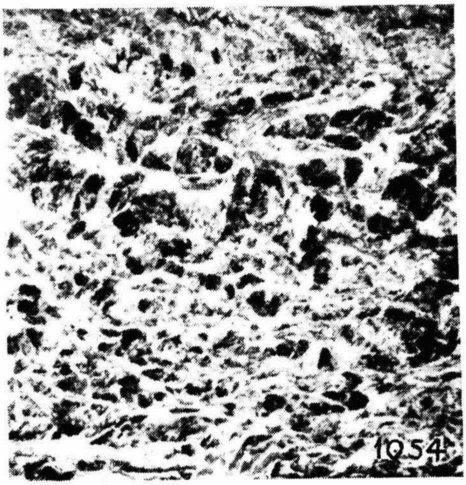

FIG. 6 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO MODIFIED E.I. TANNING PROCESS WITH WHITE-VALEM AFTER CALGON PICKLE (×34) [Sample from butt region; thickness of section, 40 μ]

FIG. 7 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO MODIFIED E.I. TANNING PROCESS WITH WATTLE AFTER CALGON PICKLE (×34) [Sample from butt region; thickness of section, 40 μ]

absorbs the tannin leached out from the material and, therefore, the period of tanning is reduced. But in the case of white-valem bark, this pre-treatment is not effective unless leach liquors are used or necessary arrangements made for proper and quick leaching of the bark. The addition of sodium sulphite or sodium bisulphite to the leach pits or tanning pits hastens the leaching and tanning processes. The leathers produced according to the modified process were tested for their chemical, physical and microscopic characteristics. The yields of leather obtained from Calgon and acetate pickled pelts with white-valem and wattle tannages were 38 and 40, and 40 and 42 per cent respectively.

The chemical analyses of the leathers are given in Table 4 and the microscopic characteristics are described in Table 5. The photomicrographs are shown in Figs. 4-7.

The leathers obtained by white-valem tannage compare favourably with those tanned by wattle bark. The water solubles content of white-valem tanned leather is lower than that of wattle tanned leather but the percentage of fixed tannins and the degree of tannage are higher. The colour of leather subjected to Calgon pickle and tanned by white-valem bark was lighter than that of leather obtained by acetate pickle; both were lighter than wattle tanned leather. The Calgon pickled leather exhibited slight cracking (double-fold), otherwise it was similar to acetate pickled leather and wattle tanned leather.

Tanning trials with white-valem and avaram blend — In the traditional E.I. tanning process avaram bark is mixed with wattle bark or mimosa extract and used for tanning leather. Experiments were planned to find out if a similar admixture of avaram and white-valem would prove to be better than using white-valem alone or wattle-avaram mixture. Delimed pelt was tanned with a blend of avaram and white-valem in the proportion of 1 : 3 and an amount of the blend equivalent to the expected yield of leather (on the basis of 16 per cent tan on the weight of pelt). Tanning was carried out as in the traditional method in a two-pit system for 18 days. The leathers were finished as usual and tested for their chemical, physical and microscopic characteristics. The results of chemical and microscopic examination are recorded in Tables 4 and 5 respectively. Photomicrographs of the leathers are given in Figs. 8-9. The yields of leather were 35·0 and 36·3 per cent for white-valem-avaram blend and wattle bark tannages respectively.

The results show that leathers tanned with white-valem-avaram blend are superior to

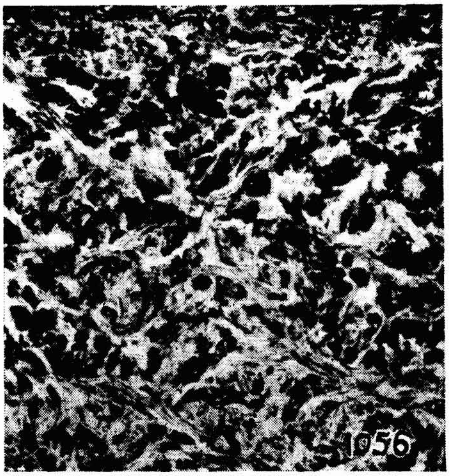

FIG. 8 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO TRADITIONAL E.I. TANNING PROCESS WITH WHITE-VALEM-AVARAM BLEND (×34) [Sample from butt region; thickness of section, 40 μ]

FIG. 9 — PHOTOMICROGRAPH OF LEATHER TANNED ACCORDING TO TRADITIONAL E.I. TANNING PROCESS WITH WATTLE (×34) [Sample from butt region; thickness of section, 40 μ]

those obtained by wattle tannage. White-valem-avaram tanned leathers are lighter in colour and stronger than wattle tanned leathers. They show no crackiness on folding (double-fold) whereas wattle tanned leathers exhibited slight crackiness.

Conclusions

1. The chemical composition of white-valem bark and tanning trials with it indicate it to be a promising substitute for wattle bark in E.I. tanning of skins.
2. As the T/NT ratio in the bark is high, it is suitable for the preparation of concentrated extracts.
3. Addition of sodium sulphite (3 per cent) to leach water improves the efficiency of leaching of white-valem bark. A concentrated extract containing 58 per cent tannin can be obtained by evaporating the leach liquor under vacuum.
4. Leathers tanned with white-valem bark as in the traditional E.I. tanning process possess good colour and strength. They compare favourably with leathers produced with wattle bark.
5. The amount of tanning material consumed and the duration of tanning can be reduced by subjecting the pelts to acetate or Calgon pickle prior to tanning. The tanning is complete in 16 days (8 days for wattle bark) when white-valem bark is used as such. Addition of sodium sulphite to leach water or use of leach liquors in place of bark reduces the duration of tanning further.
6. Leathers tanned with a mixture of white-valem bark and avaram bark (3:1) are superior to those obtained by wattle tannage in respect of general appearance, colour, feel and strength.

Acknowledgement

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Production of Fructose Syrup from *Agave vera cruz* Mill*

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The stem of *Agave vera cruz*, a rich source of polyfructosans, has been utilized for the preparation of an edible and wholesome fructose syrup. Production on a semi-pilot plant scale is described.

IT was previously reported from these laboratories that the stem of *Agave vera cruz* is a rich source of polyfructosans[1-3]. Of the total reducing sugars obtained by hydrolysing the stem juice, fructose amounted sometimes to as high as 94·6 per cent. This discovery of the agave stem as a cheap and rich source of polyfructosans deserves attention in future schemes for the manufacture of fructose. The basis for such a scheme is discussed in this paper.

Fructose is produced, to a limited extent, mainly from the tubers of Jerusalem artichoke[4-11]. Alternative natural sources which have been considered are dahlia[12], chicory[6,13-16] and also sucrose[17]. The stem of *Furcroea gigantea*[18] also contains fructosans as the major carbohydrate, while Sanchez-Morroquin and Hope[19] have recently reported from Mexico that at least eight species of agave examined are rich in fructosans, described by them as inulin. Additional considerations favouring the use of agave for the production of fructose are: (i) its worldwide distribution[20,21], (ii) easy propagation[21] at little cost[22], (iii) no exacting cultural conditions[21], (iv) its hardiness[20], and (v) freedom from serious pests[23] and resistance to fires[22]. About 1,300 plants can be reared on an acre of land[20,24]. Of the 114 plants examined by us, all well developed, but of unknown age (not one of them had poled), the average stem weight was 60 lb., though some stems weighed as much as 112 lb. *Agave vera cruz*, which along with a few others among the 275 species in this genus[25], occurs in India[25,26], matures (poles) in about 6 years under Indian conditions[25]. As the plant ceases to put forth leaves after poling, the stem after this stage becomes a waste material. No systematic industrial use of the stem has been recorded in the literature for the agave stem, excepting a suggestion that it could be used for making paper pulp[27] and its use for the production of alcohol or of fermented beverages[19,26].

Production of fructose syrup

In main, the procedure involves the acid hydrolysis of polyfructosans in the agave stem to fructose. A typical experiment is as described below.

In one instance, the tuber less the leaf attachments and other rejections had a weight of 56 lb. The dressed material, cut into small cubes, was transferred to glass containers (4 l. flasks) and steeped in acid water (hydrochloric acid; 0·5 per cent v/v). The containers were heated on a water bath. When the solids content in the steep liquor had become fairly constant (usually in about 16 hr.), as determined by the refractometer, this solution containing the hydrolysed material was decanted off, a fresh charge of acid put in and the material subjected to further hydrolysis as before. After the second treatment, the cubes had very little sweetness left in them. The two combined extracts were concentrated, without neutralization, in porcelain basins on a water bath. Concentration without neutralization had the additional advantage of completing

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*Covered by Indian Patent No. 48719; a second patent, Indian Patent No. 51575, has been filed.

the hydrolysis of polyfructosans to fructose. Thus, a syrup was obtained equivalent to 7·6 lb. of fructose, corresponding to an yield of 13·6 per cent on the fresh weight (56 lb.) of the tuber taken for hydrolysis.

Properties of the syrup: (i) *General* — The syrup was golden yellow in colour, and, as judged by a panel of judges, was sweet and pleasantly tart to taste. It analysed as follows, per cent (w/v): fructose, 63·0; glucose, 6·6; N, 0·26; ash, 1·52 (Ca, 0·41; Mg, 0·14; Cl, 0·21 per cent). It gave a positive ninhydrin reaction and a negative test for alkaloids.

(ii) *Nutritive value* — Thirty litter-mate weanling rats were distributed into three groups comparable with regard to litter, sex and body weight. The three groups were fed on diets of the composition described in Table 1. All the diets contained 10 per cent cane sugar, 2 per cent salt mixture and 1 per cent vitaminized starch which furnished adequate amounts of all the B vitamins. Adexolin, suitably diluted with refined groundnut oil, was administered daily to provide the requirements of vitamins A and D.

TABLE 1 — COMPOSITION OF THE DIETS

All diets contained 10% cane sugar, 2% salt mixture and 1% vitaminized starch)

DIET	COMPOSITION			
	Protein* %	Fat† %	Carbohydrate	
			Starch %	Fructose‡ %
I Control	10	10	67	—
II (25% of starch replaced by fructose from agave syrup)	10	10	50·3	16·7
III (50% of starch replaced by fructose from agave syrup)	10	10	33·5	33·5

*Fat and vitamin-free casein.

†Refined groundnut oil.

‡Requisite amounts of 70 per cent fructose syrup were added to the diets.

Daily food intake and weekly increase in growth were recorded individually over an experimental period of 8 weeks. The data obtained were subjected to statistical analysis. The results are recorded in Table 2.

The gains in weight were found to vary linearly with food intake and were, therefore, adjusted to the mean food intake of 53·58 g. by the method of co-variance. The adjusted gains in weight are indicated in the last column in Table 2. The difference in the growth rates between animals receiving diet I on the one hand and diet II or III on the other is statistically significant, but rather small (less than 10 per cent) and does not appear to be important, particularly because the gains in weight of the animals in the last two groups are identical in spite of the fact that one diet (III) contains twice as much syrup as the other (II). Thus, the growth data show that the fructose in the syrup is fully available for energy purposes in young growing animals and, in accord with theoretical expectations, is comparable to corn starch in calorific value.

(iii) *Freedom from deleterious substances* — The animals on diet III were dissected at the end of 16 weeks and their internal organs, especially the gastro-intestinal tract, the liver, the spleen and the kidney, were examined and found to be normal.

Also, tested at various dilutions with sheep blood corpuscles, the syrup even at a dilution of 1:1 did not show any haemolytic effect, unlike the raw agave juice. These observations indicate that the syrup is free from any deleterious constituents and is innocuous when ingested even at high levels in the diet.

Pilot plant scale trials

For putting through large-scale trials with the equipment and facilities available, hydrolysis of the water-extract of the agave stem was found to be an easier and a more efficient method than subjecting the sliced stem as

TABLE 2 — GROWTH RATE OF EXPERIMENTAL ANIMALS

DIET No.	No. OF ANIMALS	BODY WEIGHT		FOOD INTAKE g./week/rat	GROWTH RATE g./week/rat	ADJUSTED GROWTH RATE
		Initial g.	Final g.			
I	10	41·6	117·0	56·11 ±1·148 (18 d.f.)	9·50 ±0·226 (18 d.f.)	9·10
II	10	41·5	108·4	52·33	8·36	8·56
III	10	41·8	108·4	52·29	8·30	8·56

TABLE 3 — HYDROLYSIS OF THE JUICE CONCENTRATE WITH H_2SO_4

(*Temperature of hydrolysis*, 85°; *solids content of juice*, 46-50%)

FINAL NORMALITY OF H_2SO_4 IN THE MIXTURE	TIME min.	HYDROLYSIS %
0·21	30	50
do	60	65
do	90	84
do	120	85
0·36	30	96
do	60	100

such to hydrolysis. Preliminary experiments had shown that by extracting the sliced material thrice with water, most of the carbohydrates was recovered in solution. The combined extract thus obtained, containing 10-12 per cent solids, could be concentrated about four-fold, without loss of carbohydrates, in steam-jacketed open pans, though the concentrate was somewhat discoloured and had also become slightly sweetish. The optimal acid (sulphuric) concentration, time and temperature required for effecting complete hydrolysis of juice concentrate, as determined, are given in Table 3.

The conditions of hydrolysis finally adopted for large-scale trials were: to a concentrated extract containing about 40 per cent solids enough sulphuric acid was added so that the mixture had a final acidity of 0·36N. The mixture was then heated to and maintained at 85°C. for 1 hr.

Out of 60 lb. average gross weight per stem, the material after dressing to make it fit for processing was about 50 lb. Thus, the net weight of raw material available for fructose production works out, approximately, to 35 tons per acre of 1,300 plants. Even at the lowest computation of 10 per cent for the net yield of fructose on the fresh weight of agave, at least 3·5 tons of fructose (in the form of syrup) is the potential of an acre of land under agave. This is a favourable figure, especially as the experimental material is the stem, which is little prized because hitherto it has not been put to much other use.

Demand for fructose — Because of its sweetness (1·73 times sweeter than cane sugar[28]), and its high solubility, the use of fructose, in place of sucrose, in jams, jellies, marmalades and ice-cream should improve their quality in that such preparations would be free from the defects of granulation and sandiness, common to preparations with sucrose[29]. Further, fructose syrup would be an efficient source of carbohydrate for the production of food yeast and of citric acid by fermentation. The syrup is also the starting material for the production of fructose powder and for further refinements for special use as in intravenous alimentation[30].

A NOTE ON THE SEMI-PILOT PLANT SCALE PRODUCTION OF FRUCTOSE SYRUP FROM *AGAVE* STEM

B. H. KRISHNA & S. K. LAKSHMINARAYANA

Scope for manufacture — Fructose is not manufactured in India and only to a limited extent elsewhere. Until such time that fructose industry is well established and can stand on its own, it would be economically more feasible to associate the production of fructose from agave with a pharmaceutical or a fine chemical concern, where equipment of the type required for the production of fructose syrup is normally available. However, in the estimates given, provision has been made for the simplest types of equipment consistent with obtaining a good grade product and with minimum capital outlay for a prospective unit of production, where all plant facilities except the usually available services like steam, water and power, have to be provided afresh. The equipment suggested is only representative, for, the operations, being all comparatively simple, permit of a good deal of flexibility in selecting the type of equipment and of its choice being made from what is often available in a good pharmaceutical concern.

In India, the collection of agave plants presents difficulties as the plants occur in scattered areas. Until such time when agave farms and fructose factories co-exist, it would help to acquire the raw material in the dried condition. Procurement of raw material in this condition would effect a great saving in freight charges and help storage and handling on " as required " basis. However, our estimates are based on the provision of weekly supplies of the raw material in fresh condition to the manufactory from areas within a radius of about 10 miles.

Description of the process — Stems obtained from the fields are dressed to remove the outer skin and certain other parts of the plant. It is advisable to provide workmen with hand-gloves during dressing and slicing of agave. The sliced material is extracted with hot water (batchwise countercurrent extraction) to extract all the soluble solids, the extract concentrated and the matter coagulating filtered off. The clear, filtered concentrate is hydrolysed with sulphuric acid. The acid is then neutralized with lime and the filtrate is treated with decolourizing carbon, refiltered, and concentrated at reduced pressure, to 80 per cent solids (w/w). Concentration to about 45-50 per cent and a second treatment with decolourizing carbon before finally concentrating to 80 per cent yields a finer grade product.

Economics of the process

Basis of production — 1 cwt. per day of 80 per cent syrup or 25 cwt. per month of 25 working days

	Rs.	a.	p.
(A) *Equipment cost*			
(1) Wooden tubs, 3 @ Rs. 200 each	600	0	0
(2) Evaporating pan, 1 (wooden) @ Rs. 250	250	0	0
(3) Filter press (gun metal), 1 —12×12×1 in., 11 plates	5,000	0	0
(4) Wooden vat (50 gal.), 1	200	0	0
(5) Wooden vats, 50 gal. capacity with propeller agitator, 1	700	0	0
(6) Evaporator or vacuum still, 1	12,000	0	0
(B) *Building and services*	5,750	0	0
TOTAL	25,000	0	0

	Rs.	a.	p.
(C) *Processing cost*			
(1) (a) Raw material — 150 cwt. of dressed material equivalent to 180 cwt. of raw material = 9 tons per month. This on the average gross weight of stem at 60 lb. would be 336 stems at @ as. 8 per stem	168	0	0
(b) Transport charge at Re. 1 per ton-mile assuming a radius of 10 miles for collection	90	0	0
(c) Acid, lime, decolouring carbon, filter aids, etc.	232	0	0
TOTAL	500	0	0
(2) Labour			
(a) Skilled, 1 @ Rs. 120	120	0	0
(b) Semi-skilled, 2 @ Rs. 60 each	120	0	0
(c) Unskilled, 2 @ Rs. 50 each	100	0	0
(3) Services			
(a) Steam 250 cwt. @ Rs. 10 per ton	125	0	0
(b) Water (filtered) for processing, 500 gal. per day @ Re. 1 per 1,000 gal.	15	0	0
(c) Water for condensers (assumed available at cost of pumping), 3,000 gal. per day @ as. 6 per 1,000 gal.	28	0	0
(d) Electricity 4 kW. per day of 8 hr. = 32 kWh. @ one anna	50	0	0
(4) Maintenance	50	0	0
(5) Depreciation and interest @ 10 and 5 per cent respectively on Rs. 25,000, Rs. $\frac{3,750}{12}$ = Rs. 312-8			
or say	315	0	0
(6) Overheads @ $33\frac{1}{3}$ per cent	475	0	0
Yield, 2,800 lb. of syrup, valued at	1,900	0	0
Price (loose), approximately, per lb.	0	11	0
Price (packed in 28 lb. tins), per lb.	0	12	0

Summary

1. The stem of *Agave vera cruz* (or other species of agave), being a rich and a fairly pure source of polyfructosans, is a suitable raw material for the production of fructose.

2. Further favourable factors for such production are the cheapness of agave, its easy cultural conditions and the availability of stems in bulk either as such or arising as a waste material from the agave fibre industry.

3. The broad details of the process are described.

4. Analysis of the syrup and results of animal feeding experiments proving its wholesomeness are given.

5. Salient features of semi-pilot plant scale trials together with the approximate cost of production of syrup are presented.

Acknowledgement

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Letters to the Editor

VIBRATIONAL TEMPERATURES IN C_2 (SWAN) SYSTEM IN RARE GASES & RAMSAUER EFFECT

INVESTIGATIONS INTO THE EFFICIENCY OF THE development of C_2 (Swan) bands in various rare gases have been made by quantitative intensity study of the system. The bands were observed in a discharge tube fitted with carbon electrodes and filled with rare gases helium, neon, argon, krypton and xenon at pressures ranging from a few mm. to about 30 mm.

Computation of temperature from the observations on the basis of Maxwell-Boltzmann distribution of vibrational energy has yielded values which are shown in Fig. 1.

Similar type of curves (FIG. 2) were obtained in the case of these rare gases with the weight (Σ^{I/v^1}) of any v^1 level of the system as a function of pressure. In helium development of the system was rather sketchy and partial and hence curves of the above type could not be prepared for it.

The evident conclusions from these observations are: (i) The temperatures derived are in the order of the atomic number of rare gases at any one pressure; (ii) the magnitude of temperature change with pressure is also in the same order within the observed ranges of pressures; and (iii) there is certain pressure (P_{max}) at which the overall intensity of the system is maximum and this pressure (P_{max}) varies from gas to gas in a systematic manner.

The explanation of the above observations can be sought on the basis of electronic excitation of dicarbon (C_2) gas formed in traces by some mechanism in the discharge column. The cause of the relatively increased populations of the upper levels, indicated by the higher temperatures and the sensitiveness of these populations to small changes in pressure indicated by relatively increasing magnitude of temperature changes with increasing atomic number of gases, is to be traced to the dependence on the electron energy of the probability of collision between electrons and rare gas atoms. Within a small range of 2 to 3 V., between which the excitation energy (2·4 V.) for different levels of C_2 (Swan) bands lies, the collision probability-electron energy curves show a precipitous but graded rise, such that there is a large change in probability with small variation in electron energy (Ramsauer effect). The slope increases in the order of the gases Ne, Ar, Kr, and Xe (LOEB)[1]. In neon, the curve is almost flat. This means that the buffer action of the rare gas atoms will be relatively greater for faster electrons in the range of 2 to 3 V. It will increase relatively the probability of C_2 getting excited in the upper levels as compared to the lower ones and hence the existence of increasing temperature values as one goes from Ne to gases higher up in the periodic table. For the same reason, we should expect increasing magnitude of temperature changes for a given pressure change as one goes from neon to xenon.

The excitation of C_2 is supposed to be caused by slow electrons resulting from the buffer action of rare gas atoms. This buffer

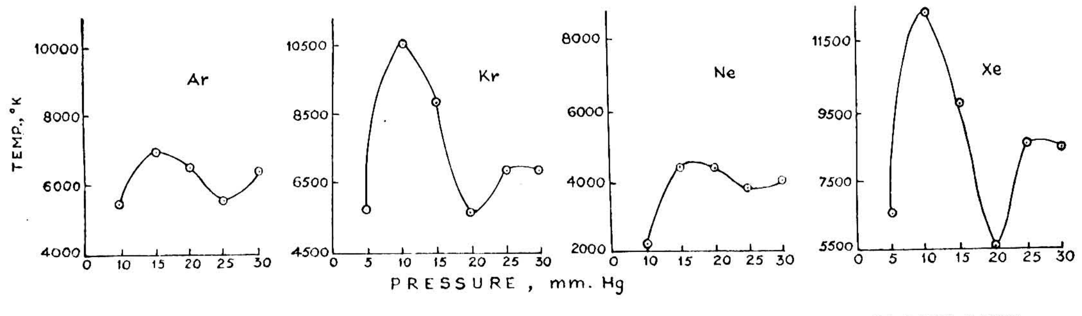

FIG. 1 — EFFECTIVE VIBRATIONAL TEMPERATURE AS FUNCTION OF PRESSURE OF RARE GASES

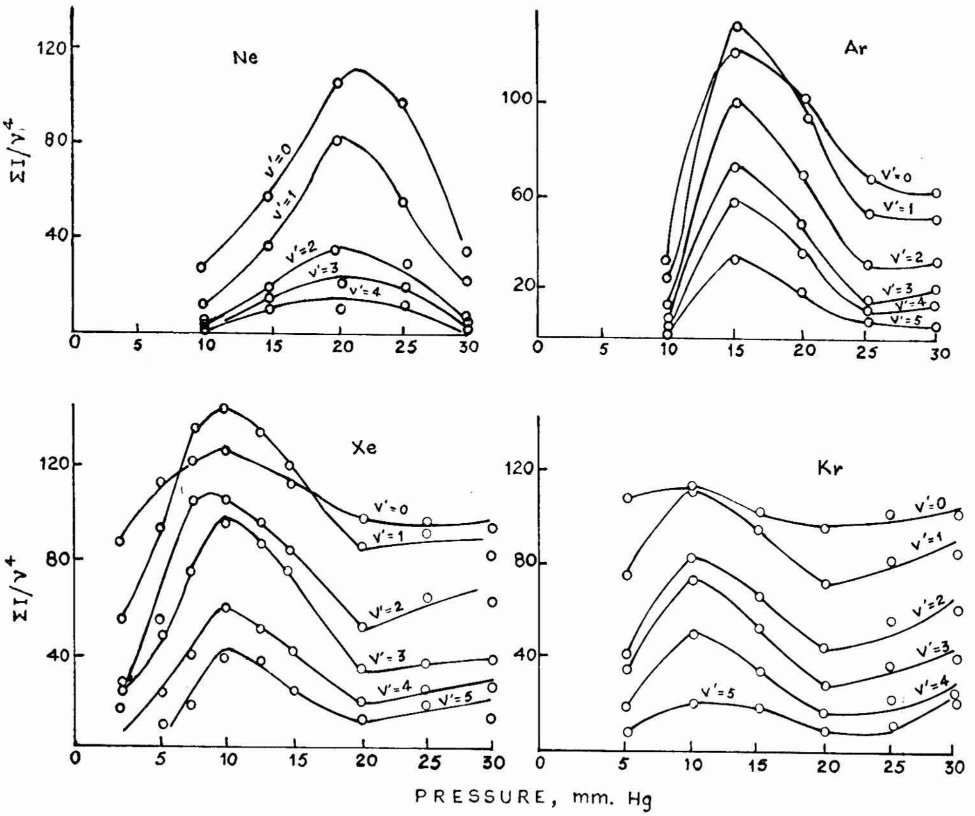

FIG. 2 — VARIATION OF Σ^{I}/ν^4 WITH PRESSURE OF RARE GASES

action is affected mainly by pressure and to some extent by the value of mean electron energy. It will be controlled, therefore, by the effective cross-section of the atom with slow electrons depending upon Ramsauer free paths. These are different for different rare gases according to their position in the periodic table and hence the systematic change in P_{max} value at which the bands develop with high efficiency. On this basis the Swan bands come out best in xenon, i.e. with a small trace of the gas in the discharge tube having carbon as impurity as found in these experiments and a pressure of the order of even 2 mm. So far the development of these bands in rare gases was being carried out using mainly argon gas at high pressure. The nebulous development of bands of helium even with relatively high pressures of the order of 10 mm. and above follows as a natural consequence of the considerations advanced above.

The details of the investigation are being reported elsewhere.

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VARIATION OF THE ANGLE OF ARRIVAL OF THE DOWN-COMING RADIO WAVES FROM THE IONOSPHERE WITH THE APPEARANCE OF SCATTERED SIGNALS

WHEN THE ELECTRONIC DENSITY IN THE ionosphere gradually decreases, the ordinary ray disappears and the reception of the signal is accomplished by the extraordinary ray alone. If the electronic density further decreases, the extraordinary ray also vanishes and communication is generally found to fail. But under suitable conditions of the ionosphere[1] reception may be maintained due to the scattered signals, presumably from the ground, which are usually very weak and the intensity of which varies rapidly in a random manner. The scattering centres on such occasions observed in the evening hours, when the electronic density in the ionosphere increases from east to west, necessarily lie on the side of the transmitter away from the receiver[2,3] when it is situated to the east of the transmitter. The angle of arrival of the down-coming waves will in such cases be less than the normal angle which is observed during reception due to the extraordinary ray alone. If the electronic density, however, happens to decrease still further, the sources of scattering will move away from the transmitter and the angle of arrival of the wave will be found to diminish accordingly. It may be mentioned that in the forenoon hours, the scattering centres will lie on the other side of the receiver away from the transmitter and there should be a horizontal gradient of ionization in the ionosphere for the occurrence of such scattered signals. Typical observations on the variation of angle of arrival of the down-coming radio waves from the F_2 region of the ionosphere as observed in the afternoon hours, before and after the appearance of scattered signals, are recorded in the present communication.

The angle of arrival of the down-coming radio waves for transmissions on 31 metre band from the All India Radio, Delhi, at a distance of about 680 km. from Banaras, was determined from the phase difference in the e.m.f.s induced by these waves into two horizontal dipole aerials according to the method used originally by Friis[4] and later modified by Wilkins[5]. In the present arrangement, however, the dipoles were vertically spaced instead of horizontally as used by the above investigators. The separation between the aerials was kept below half a wavelength for the highest frequency used for reception, so that the effect of the ground wave was almost similar in the two aerials and the aerial system was reasonably in a homogeneous field. The phase difference between the two e.m.f.s in the present system will then be given by the relation

$$\phi = \frac{2 \pi d}{\lambda} \sin \theta$$

where ϕ is the phase angle, d the separation between the dipoles, λ the wavelength used, and θ the angle of arrival of the down-coming waves measured with respect to the ground.

Two matched feeder lines from the dipoles were connected to two identical superheterodyne receivers fed by a common oscillator. The outputs of the receivers were connected to the two opposite pairs of the deflecting plates of a cathode-ray oscillograph. The small difference in the intensity of the received signal in the two receivers due to the vertical separation between the two horizontal dipoles was compensated by the amplifier gain in the cathode-ray oscillograph unit. After careful adjustment of the two receivers the phase angle was calculated from the ratio between the minor and major axes of the ellipses obtained on the oscillographic screen[6]. Before the disappearance of the ordinary ray there is a rapid and anomalous variation in the angle of arrival of the down-coming waves due to magneto-ionic interference as observed on previous occasions[7], then the pattern becomes suddenly steady when the ordinary ray disappears and the communication is maintained by the extraordinary ray only. After some time, however, when the extraordinary ray also disappears, the signal continues with less intensity and the ellipse becomes narrower showing that the angle of arrival is reduced. As the electronic density decreases with time the ellipse is almost reduced to a straight line and the intensity of the scattered signal becomes very feeble.

Fig. 1 shows the type of variation of the elliptic patterns which are obtained just before and after the appearance of the scattered signal. Fig. 1a shows the normal pattern which is obtained when the reception is due to the extraordinary ray alone, the presence of which is verified by simultaneous record made with the fading recorder

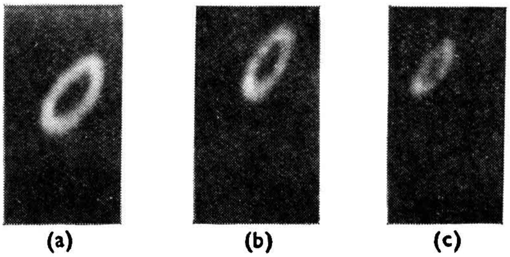

FIG. 1 — TYPE OF VARIATION OF THE ELLIPTIC PATTERNS OBTAINED BEFORE AND AFTER THE APPEARANCE OF THE SCATTERED SIGNAL [Reception due to: (a) extraordinary ray alone; angle of arrival 42°; (b) scattered signals from short distance; angle of arrival 36°; and (c) scattered signals from long distance; angle of arrival 16°]

developed in this laboratory[8]. The angle of arrival obtained during this period is almost constant and is found to lie around 42° at 20.00 hr. I.S.T. on 15 June 1954, which corresponds to single reflection between Delhi and Banaras for the observed heights of the F_2 layer at these two places. This is followed by the weak scattered signals, the intensity of which shows quick and random variations and the angle of arrival is found to decrease to 36° at 20.15 hr. I.S.T., corresponding to the ellipse shown in Fig. 1b. Later on, as the scattering centres move away from the transmitter due to the lowering of the electronic density, the minor axis of the ellipse is considerably reduced as shown in Fig. 1c, which corresponds to the down-coming angle of 16° as observed at 20.30 hr. I.S.T. The calculated distances of the scattering centres for the angles measured in the above two cases, shown in Figs. 1b and 1c, are found to be 850 and 2,180 km. respectively from the receiver, and the scattering centres should lie to the west.

Similar observations in the early morning hours, when the gradient of ionization is in the east to west direction, show that the scattering centres lie at fairly long distances from the receiver on the eastern side, but the intensity of the scattered signals is generally higher than that in the evening hours. The above results indicate that in the evening when the gradient of ionization is in the west to east direction the scattering centres for signals from the Delhi station will be always on the west of Banaras and may lie somewhere near the Hindukush mountains. In the morning, however, the direction of the ionization gradient is reversed, and so the scattering centres will lie on the eastern side of Banaras and may be extended to the Bay of Bengal. The greater intensity of the scattered signals in the morning hours may thus be due to the higher reflecting coefficient of sea water[9].

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DIFFERENTIAL THERMAL ANALYSIS OF CATALYST POWDERS: PART V — FERRIC OXIDE GEL

WEISER AND MILLIGAN[1] HAVE CONCLUDED FROM X-ray diffraction studies of hydrous ferric oxides that while the freshly precipitated gels are amorphous in structure, on aging the structure of the gels changes and they exhibit feeble lines in the pattern after aging them for five months. In every case, it has been reported that the amorphous form changes directly to α-Fe_2O_3 on aging. Kulp and Trites[2] from their studies of ferric oxide gels have also arrived at the conclusion that the direct neutralization of ferric ion solutions results in hydrous ferric oxide which, on aging, transforms to haematite rather than to goethite (α-Fe_2O_3, H_2O) or lepidocrocite (γ-Fe_2O_3, H_2O). Gheith[3] has, however, reported the possibility of the presence of goethite in aged gels. The reports, thus, seem to be rather conflicting.

Ferric oxide, dehydrated at a temperature of *c*. 350°C., has been reported to be an active catalyst for the dehydration of alcohol. Since the activity of the catalyst depends on the temperature of activation and the method of its preparation, there might be some relationship between the activity of the catalyst and its structure. In order to throw more light on the structural changes which develop during heating and/or aging, differential thermal analysis (D.T.A.) of the hydrous ferric oxide, freshly precipitated and on aging for different periods was studied.

The experimental technique was similar to that reported earlier[4]. The rate of heating of the sample was kept at (10° ± 1°C./min.). The deflection in the galvanometer, which is a measure of the differential temperature, is plotted such that the endothermal peaks are shown downwards, and the exothermic peaks upwards with respect to the base line representing the temperature of the sample block.

Ferric oxide gel was prepared by adding ammonium hydroxide or sodium hydroxide (M/2) to a solution of ferric nitrate (0·5M with respect to Fe_2O_3) and the resulting gel washed once with water to avoid aging. The remaining gel was washed well and aged under water for 7, 17 and 90 days respectively, air dried, ground to 100 mesh size, well packed in the sample and subjected to analysis.

The results are graphically represented in Figs. 1 and 2. The ferric oxide gel prepared by ammonium hydroxide as the precipitant and washed once with water exhibits an endothermal peak of large magnitude at 180°C. (range 100°-212°C.) which may be due to the removal of adsorbed water from the gel. The exothermal change at 380°C. (range 276°-438°C.) is due to the amorphous gel transforming to haematite (α-Fe_2O_3). As the aging of the gel is increased the exothermal peak due to the formation of haematite decreases. The gel aged for 90 days fails to show the exothermal effect but an additional endothermic peak appears at a temperature of 260°C. (range 222°-285°C.). This may be due to the dehydration of goethite which is formed as a result of aging.

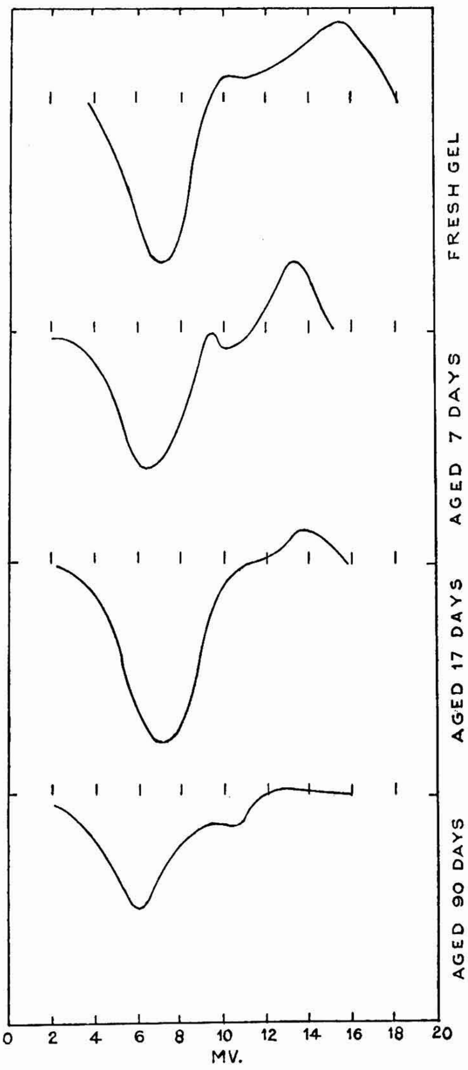

FIG. 1 — DIFFERENTIAL THERMAL ANALYSIS OF AGED FERRIC OXIDE GELS PRECIPITATED FROM AMMONIUM HYDROXIDE

Fig. 2, curve 1, represents the thermal behaviour of the gel precipitated from sodium hydroxide and washed once with water. It exhibits an endothermic peak at 186°C. (range 92°-305°C.) due to the loss of adsorbed water and an exothermic peak at 443°C. (range 368°-486°C.) due to the formation of α-Fe_2O_3. As the aging increased the endothermal peak due to the dehydration of goethite appears and the exothermal peak due to the formation of haematite disappears. In both cases (FIGS. 1 and 2) the dehydration peak of goethite occurs below 280°C. Welo and Bandisch[5] have observed that the water of crystallization of well-crystallized goethite is lost below 270°C.

The above results also indicate that the aged gel, precipitated from sodium hydroxide, transforms to the crystalline form more rapidly than that precipitated from ammonium hydroxide.

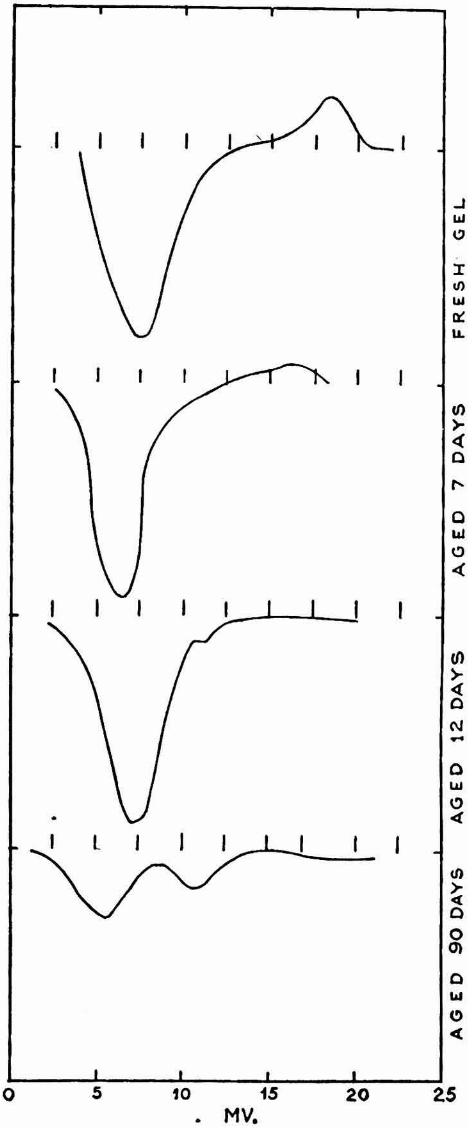

FIG. 2 — DIFFERENTIAL THERMAL ANALYSIS OF AGED FERRIC OXIDE GELS PRECIPITATED FROM SODIUM HYDROXIDE

The D.T.A. of a pure unaged sample of hydrous ferric oxide prepared from ferric nitrate and ammonium hydroxide and washed free of nitrate by centrifuging was also studied. It exhibits an endothermal change at a lower temperature and an exothermal effect at 360°C. (range 310°-400°C.) due to the formation of α-Fe_2O_3. Sabatier[6] has found that for dehydration of alcohols, the ferric oxide catalyst dehydrated below 350°C. has much higher activity than that dehydrated at higher temperatures. In light of above discussion it may be concluded that the hydrous ferric oxide in an amorphous state is the real catalyst for the reaction and it loses its activity with the formation of α-Fe_2O_3.

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A NEW SYNTHESIS OF TELOSCHISTIN

THE CONSTITUTION OF TELOSCHISTIN, OBtained from the Indian lichen *Teloschistes flavicans*, was proposed as 2-hydroxymethyl-4: 5-dihydroxy-7-methoxy anthraquinone[1], and this was confirmed by (i) its conversion via emodin into physcion and (ii) the partial methylation of ω-hydroxy emodin to teloschistin[2,3]. A third transformation which will be similarly useful and which will also emphasize the natural relationship between physcion and teloschistin occurring together in the same lichen would be the conversion of the former into the latter. This has now been done using the reactivity of the $-CH_3$ group which is comparable with that present in 2-methyl chromones, isoflavones and 4-methyl coumarins whose conversion into the corresponding hydroxymethyl derivatives has been effected in these laboratories[4-7] by means of N-bromosuccinimide.

Physcion diacetate (m.p. 186°-87°) is converted into the ω-bromo derivative using N-bromosuccinimide and benzoyl peroxide in carbon tetrachloride solution. Treatment of the bromo compound with silver acetate and acetic anhydride gives in good yield the known triacetate (m.p. 192°-93°) which could be hydrolysed to teloschistin (m.p. 245°-47°) identical with a natural sample.

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PREPARATION OF 17, 18-OCTADECENOIC ACID

17, 18-OCTADECENOIC ACID HAS BEEN SYNthesized by Kapp and Knoll[1] from 10,11-undecenoic acid through a number of stages but the yield of the final compound is low. It is a higher homologue of 10, 11-undecenoic acid and may be useful in the manufacture of plastics. Its oxidation product (1, 15-pentadecane dicarboxylic acid) is the starting material for the synthesis of dihydrocivetone. An easy method giving a higher yield of 17, 18-octadecenoic acid has been developed from ω-hydroxy stearic acid[2] which is obtained from kamala seed oil.

ω-Hydroxy stearic acid (10 g.) and thionyl chloride (20 cc.) were refluxed for 3 hr. on the water bath. Excess of thionyl chloride was distilled off and the residue was poured over crushed ice. The solid product was separated, washed with water and crystallized (white needles) from petroleum ether; m.p. 74°-74·5°C.; yield 6·5 g. (found: Cl, 11·3; $C_{18}H_{35}O_2Cl$ requires: Cl, 11·1 per cent).

The corresponding bromo derivative has been prepared by the action of phosphorus pentabromine on ω-hydroxy stearic acid in benzene solution which on crystallization from petroleum ether (b.p. 40°-60°C.) melted at 76·5°-77·0°C.

ω-Chloro octadecenoic acid (5 g.) was heated on a steam bath with 50 cc. of 20 per cent alcoholic potash solution for 2 hr. Excess of alcohol was distilled off and the free acid was liberated from the residue by the addition of dilute hydrochloric acid in the cold. The solid acid was extracted with ether and crystallized from dilute methyl alcohol when 17, 18-octadecenoic acid was obtained as a white crystalline mass; m.p. 55·0°-55·5°C.; yield 3·5 g. (found: C, 76·54; H, 12·00; $C_{18}H_{34}O_2$ requires: C, 76·53; H, 12·05 per cent).

This product on hydrogenation in alcoholic solution with platinum catalyst gave stearic acid (m.p. 68°-69°C.).

The oxidation of the acid with potassium permanganate in acetone solution gave 1, 15-pentadecane dicarboxylic acid, which on crystallization from ethylene dichloride melted at 117°-17·5°C.

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PHYTOCHEMICAL STUDY OF THE GLYCOSIDE FROM *SAPINDUS TRIFOLIATUS* LINN.

WORK ON THE NON-CARBOHYDRATE PART OF the saponins from various species of *Sapindaceae* plants has been reported by various workers[1] and in all cases the aglycone was found to be identical with hederagenin. But work on the sugar part of these saponins is limited. Recently Mateu Amengual[2] reported the presence of arabinose, rhamnose, glucose and lactose by paper chromatography after mild acid hydrolysis of the saponins from *Sapindus saponaria*.

Two species of soapnut tree, namely *Sapindus mukorossi* Gaertn. and *Sapindus trifoliatus* Linn., are indigenous to India. No systematic investigation appears to have been made on the qualitative characterization of the sugars obtained by the hydrolysis of the saponins from the above species of soapnut. The saponins isolated by different workers have also not been properly characterized. The present communication deals with the isolation of the glycoside in a pure form from *Sapindus trifoliatus* by a simple process and characterization of the sugar constituents by paper-partition chromatography according to Partridge[3]. This work was undertaken as a part of a systematic study of the composition of the saponin glycosides present in common saponin-bearing plants in India[4,5].

The saponin was isolated from the pericarp of *Sapindus trifoliatus* (identified and obtained through the kind courtesy of Dr. K. Biswas, Director, Botanical Gardens, Calcutta) by 50 per cent alcohol and purified by removing pectin and inorganic materials by repeated precipitation with alcohol according to the procedure followed earlier[5]. Finally, the glycoside was obtained as a white hygroscopic powder by treating the alcoholic solution with excess of ether. The aqueous solution of the saponin exhibits intense foaming properties. The saponin is easily soluble in water and methyl alcohol, fairly in ethyl alcohol, insoluble in acetone, chloroform and ether. It has an ash content of 0·27 per cent, *p*H (aqueous solution; C, 2·9) 4·5; $[\alpha]_D = -22{\cdot}4^\circ$ (C, 2·9, water); [found: C, 47·8; H, 7·7; $(C_7H_{14}O_5)_n$ requires: C, 47·2; H, 7·8 per cent].

Paper chromatography of the saponin hydrolysate showed the presence of glucose, xylose, arabinose and rhamnose. The sugars were present in almost in equal proportions (by visual comparison of the intensity of colour in the chromatogram). It is interesting to note that the same sugars[4] were found to be present in the case of *Bassia latifolia* saponin hydrolysate, the proportions of sugars being different.

The qualitative characterization of the sugars was performed on Whatman No. 1 filter paper by the descending method[3], through the parallel spotting of the known pure sugars and not through the absolute R_f values. The systems (a) *n*-butanol-acetic acid-water (4: 1: 5) for 48 hr. and (b) phenol-water for 24 hr. were made use of. Sugars were detected on the chromatograms with aniline oxalate and benzidine.

The presence of trace of free sugar as glucose in the saponin itself was indicated in the paper chromatogram. The absence of galacturonic acid[6] in the chromatogram showed the saponin to be free from pectin.

Further work is in progress and the details will be published later. My grateful thanks are due to Dr. S. C. Bhattacharyya and Prof. R. C. Shah for their kind interest in the work.

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COLOURING MATTER OF PONDEROSA PINE BARK

KURTH AND HUBBARD[1] REPORTED THE ISOlation of a pentahydroxy flavone from Ponderosa pine bark and proposed for it the structure of 3: 5: 8: 3′: 4′-pentahydroxy flavone. The flavone of this constitution was independently synthesized by Ahluwalia and Seshadri[2] and Ramanathan and Venkataraman[3] by two independent methods, and they came to the same conclusion that the naturally occurring flavone did not have the structure assigned to it. The subject has, therefore, been re-examined.

The flavonoid material obtained by extracting the pine bark with ether, and further recrystallization with alcohol and having the properties described by Kurth and Hubbard[1] was subjected to complete methylation using dimethyl sulphate and potassium carbonate in anhydrous acetone solution, and refluxing till the product gave no ferric chloride colour (30 hr.). The total product was directly subjected to fission with alcoholic potash. The ketonic fission product was obtained in good yield, was readily purified from ether-petroleum ether mixture and appeared to be a single entity; the m.p. and mixed m.p. were 102°-3° showing that it was ω-4: 6-trimethoxy-2-hydroxy acetophenone; whereas the acid product was a mixture giving two rings (Rf_1, 0·40; Rf_2, 0·50) in circular paper chromatography using butanol saturated with ammonia. The mixture of acids could be separated by fractional crystallization, using initially ether and petroleum ether and subsequently water; the major component was identified as veratric acid by m.p. and mixed m.p. 180°-81° and Rf, 0·40; the second component (minor) was trimethyl gallic acid, m.p. and mixed m.p. 165°-66° and circular Rf, 0·50. This method seems to be quite useful for the study of mixtures and in the present case indicated that a mixture of quercetin and myricetin was involved. This was confirmed by the following study.

The crystallized sample of the bark flavonoid yielded two prominent yellow rings (Rf_1, 0·42; Rf_2, 0·60) in paper chromatography. These corresponded to myricetin and quercetin. The colour reactions of the sample also agreed with the behaviour of a mixture of these two substances. Particular mention should be made of the action by sodium carbonate solution in which the display of colours is characteristic. By fractional crystallizations using alcohol or ethyl acetate, quercetin could be isolated as the major component and characterized by melting point, acetate, Rf value and colour reactions. Myricetin could not be obtained pure by this process. However, after acetylation, the acetate mixture can be more successfully separated by fractional crystallization from ethyl acetate and petroleum ether mixture, yielding quercetin acetate as the major fraction and myricetin acetate as the minor fraction.

The air-dried bark was also examined in detail. It was subjected to extraction successively with cold petroleum ether and ether and with hot alcohol. The petroleum ether extract contained only fatty and waxy matter and gave no test for anthoxanthins. The ether extract gave three rings in circular paper chromatography; two of these appeared before spraying (Rf_1, 0·42· Rf_2, 0·60) corresponding to myricetin and quercetin and the third one appeared faintly after spraying with aqueous ammonia, Rf_3, 0·70. It may be mentioned here that the first ring turned red after spraying, again confirming its identification as due to myricetin. The third ring could be attributed to the presence of dihydroquercetin and this was confirmed by comparison with the ring produced by an authentic sample. In order to concentrate and isolate dihydroquercetin, the crude ether-extracted product was crystallized from ethyl acetate-petroleum ether mixture; the dihydroquercetin was thus concentrated in the mother liquor. The residue obtained from it was dissolved in alcohol and poured into hot water with shaking. The semi-solid mass which separated out was filtered off and was tested by chromatography (Rf_1, 0·42; Rf_2, 0·60) which indicated the presence of myricetin and quercetin in this fraction. The aqueous solution was repeatedly extracted with ether, the extract evaporated and the residue tested by chromatography when three rings (Rf_1, 0·42; Rf_2, 0·60; Rf_3, 0·70) corresponding to myricetin, quercetin and dihydroquercetin (prominent) respectively were obtained. An alcoholic solution of the above residue when reduced with zinc and hydrochloric acid gave a purple red colour, characteristic of 3-hydroxy flavanones. Hence, the presence of a small amount of dihydroquercetin in the ether extract of the bark was established.

The final alcoholic extract of the bark was concentrated under reduced pressure to a small bulk. The concentrate was refluxed with aqueous sulphuric acid (7 per cent) for 3 hr. and the mixture extracted with ether. After the ether extract was evaporated, the residue dissolved in a small volume of alcohol. The alcoholic solution was poured into excess of boiling water with vigorous stirring. The dark brown semi-solid that separated out was filtered off. By paper chromatography it was found to contain myricetin, quercetin and dihydroquercetin. The aqueous solution was then extracted repeatedly with ether and the ether extract evaporated. The residue crystallized from ether-petroleum ether mixture yielding very pale yellow needles melting at 240°-42° (d). The mixed melting point with an authentic sample of dihydroquercetin was undepressed. The colour reactions and Rf value also agreed. Thus, it was clear that the major portion of dihydroquercetin was contained in the alcohol soluble fraction. It was probably present as a glycoside.

Ponderosa pine bark, therefore, contains quercetin and myricetin along with dihydroquercetin. The crystalline flavonoid obtained from the ether extract by crystallization proved to be a mixture of quercetin and myricetin.

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OESTROGENIC ACTIVITY OF BIOCHANIN-A*

Bradbury and White[1] isolated two isoflavones, genistein and formononetin, from subterranean clover (*Trifolium subterraneum* L.). The plant, which is oestrogenically active, is extensively cultivated in Western Australia for sheep pasturage and is considered to be responsible for certain reproductive disorders in ewes fed on it. Genistein which is present to the extent of 0·0006 per cent in the plant is regarded as the principal oestrogenic substance.

Biochanin-A, which is 4′-methyl ether of genistein[2] occurs along with formononetin[3] in the fresh germ of chana (*Cicer arietinum* L.) to the extent of 0·005-0·01 per cent depending on the variety of chana. In view of the importance of chana as a major foodgrain in India, work on the biological evaluation of oestrogenic activity of biochanin-A and some of its derivatives and reduction products was undertaken in this laboratory.

Recently, Pope *et al.*[4] have found the British pasture plant, red clover (*Trifolium pratense* L.), to be also oestrogenic. The substance responsible for the activity has been isolated and found to be identical with biochanin-A. Its activity as determined by the mouse-uterine weight method has been reported to be about equal to that of genistein (10^{-5} of oestrone). No details of the results, however, are yet available.

The present note records the results of biological evaluation of oestrogenic activity of biochanin-A (from fresh chana germ) by the vaginal cornification method (Allen-Doisy procedure) using spayed albino rats[5]. Adult female rats showing normal oestrus were ovariectomized and tested for two weeks for anoestrus and then primed with injections of 2 μg. of aqueous oestrone. Smears were taken by introducing a little normal saline by means of a pipette, sucking back and forth a few times, and then were stained with 1 per cent solution of methylene blue. Predominance of cornified epithelial cells in the smears was regarded as positive indication of oestrus. Rats showing positive smears were divided into groups of ten. After a preliminary estimate of the dosage of biochanin-A to be employed in the assay, one group of rats was given subcutaneous injections of a dose of biochanin-A in maize oil in two equal portions at an interval of 6 hr., a control group being given a corresponding dose of oestrone in maize oil. Smears were examined 48, 52, 56 and 72 hr. after the first injection and positive responses recorded. The other doses were administered at intervals of one week each, the control group getting the corresponding doses of oestrone. Solutions of biochanin-A and the standard contained 5 per cent alcohol in all cases.

Table 1 gives the results of the assay of biochanin-A carried out in 3 dosage levels and statistically analysed by the Probit method[6]. The minimum effective dose of biochanin-A for a 50 per cent response in rats is about 4·2 mg. which is approximately 238 rat-units/g.

The total alcohol-soluble crystalline product from the fresh chana germ consisting mainly of biochanin-A and formononetin

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*After this note was communicated for publication, we came across a note entitled " Oestrogenic isoflavones in red clover and subterranean clover " by Pepe and Wright [*Chem. & Ind.*, (1954), 1019] in which the activity of biochanin-A (from red clover) has been reported to be *c.* 0·63 of the activity of genistein, which has approximately 10^{-5} of the activity of oestradiol-17β. The presence of biochanin-A in subterranean clover has also been established.

TABLE 1 — STATISTICAL ANALYSIS OF THE RESULTS OF ASSAY OF BIOCHANIN-A FOR ITS OESTROGENIC ACTIVITY

DOSE	LOG DOSE (x)	RESPONSE %	PROBIT (y)	WT. (W) = n × WEIGHTING COEFFICIENT OF PROBIT, WHERE n IS NUMBER OF ANIMALS IN EACH GROUP
Oestrone (mg. × 10^{-4})				
3	0·477	20	4·16	4·901
6	0·778	60	5·25	6·217
12	1·079	90	6·28	3·428
Biochanin-A (mg.)				
3	0·477	30	4·48	5·764
6	0·778	70	5·52	5·764
10	1·000	90	6·28	3·428

	OESTRONE	BIOCHANIN-A
Σw	14·546	14·956
Σwx	10·874	10·661
$\bar{x} = \Sigma wx/\Sigma w$	0·7476	0·7127
Σwy	74·560	79·160
$\bar{y} = \Sigma wy/\Sigma w$	5·126	5·291
Σwx^2	8·870	8·228
Σwxy	58·370	58·590
$[wx^2] = \Sigma wx^2 - \bar{x}\Sigma wx$	0·738	0·630
$[wxy^2] = \Sigma wxy - \bar{y}\Sigma wx$	2·610	2·180

Combining oestrone and biochanin-A

$$\Sigma[wx^2] = 1{\cdot}368$$

$$\Sigma[wxy] = 4{\cdot}790$$

$$bc = \frac{\Sigma[wxy]}{\Sigma[wx^2]} = 3{\cdot}497$$

$$M = \bar{x}_{\text{oestrone}} - \bar{x}_{\text{biochanin-A}} - \frac{1}{bc}\left(\bar{y}_{\text{oestrone}} - \bar{y}_{\text{biochanin-A}}\right) = 0{\cdot}8021$$

Potency = antilog (2 + M) = 120·8

Standard error of potency = 2·3026x σ_M × potency = ±29·5

∴ the potency of biochanin-A is equal to (1·21 ± 0·3) × 10^{-4} of oestrone.

was also examined and its activity found to be proportional to its biochanin-A content. Further work is in progress.

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STUDIES IN THE CONSTITUTION OF KAMLOLENIC ACID BY OZONIZATION

THE CONSTITUTION OF KAMLOLENIC ACID obtained from the seed oil of *Mallotus philippinensis* Muell. Arg. (kamala) as determined through the acetylation and oxidation products of the acid and its ultraviolet absorption spectra has been reported to be ω-hydroxy, 9, 11, 13-octadecatrienoic acid[1,2] (I). An alternative constitution, ω-hydroxy, 5, 7, 9-octadecatrienoic acid (II), was, however, not accepted[1] only on the analogy that in the naturally occurring unsaturated acids of the C_{18} series, $(CH_2)_7$ carbon atom chain is generally attached to the carboxyl group. The recent work on the isolation and characterization of azelaic half-aldehyde obtained from the products of ozonization of this acid has confirmed the structure (I) for kamlolenic acid.

Kamlolenic acid was dissolved in chloroform (5 per cent) and ozonized oxygen was passed through the solution immersed in ice bath. After the completion of the reaction, chloroform was removed and the residue was decomposed with moist ether. A 10 per cent solution of potassium bicarbonate was added and the azelaic half-aldehyde was isolated from the aqueous solution. It was identified through its semi-carbazone (m.p. 162·0°-62·5°C.) and further confirmed by its oxidation to azelaic acid.

δ-Hydroxy valeraldehyde, as indicated by its boiling point (62°-63°C. at 10 mm.) and $n_D^{24°} = 1{\cdot}4509$, was also obtained from the products of ozonization showing thereby that the third double bond in kamlolenic acid is present between 13 and 14 carbon atoms. The complete details will be published elsewhere.

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HIGH PRESSURE HYDROGENATION OF SOME INEDIBLE OILS & FATS

HIGH YIELDS OF FATTY ALCOHOLS HAVE BEEN reported[1] in the high pressure hydrogenation of coconut oil and its esters and of lauric, stearic and oleic acids. In the present work, unrefined karanja (*Pongamia glabra*) and neem (*Azadirachta indica*) oils and unrefined kokum (*Garcinia indica*), mowrah (*Modhuca latifolia*), dhupa (*Vateria indica*) and pisa (*Actinodaphne hookeri*) fats were hydrogenated under the following conditions: temperature, 325°F.; catalyst, cobalt-stabilized copper chromite, 5 per cent; pressure of hydrogenation at room temperature, 2,500 lb./sq. in.; excess of hydrogen at the beginning, 175 per cent; period of hydrogenation, 2 hr.

Kokum, mowrah, dhupa and pisa fats were found to have been converted into fatty alcohols to the extent of 45-70 per cent, the conversion of karanja oil was not more than 15 per cent and neem oil was not hydrogenated at all. Coconut oil, under the same conditions, was hydrogenated to more than 70 per cent. Since the inedible oils and fats are characterized by high contents of unsaponifiable matter (2-5 per cent), it is likely that the copper chromite catalyst is poisoned to different degrees by the different unsaponifiable constituents.

Refining of inedible oils and fats by ethyl alcohol extraction followed by alkali refining brought down the unsaponifiable matter content considerably and improved the conversion of kokum, mowrah, dhupa and pisa fats. Refined karanja and neem oils, however, did not show any improvement. Methyl esters of the two oils were then prepared and, after their purification by distillation, were hydrogenated as before. The karanja oil methyl esters were converted to the extent of 76 per cent, but neem oil esters showed no conversion at all.

The poisoning effect of neem oil was shown by the fact that a mixture of 90 per cent coconut oil and 10 per cent neem oil was hydrogenated to the extent of 20 per cent only.

The conversion of castor oil into fatty alcohols under the same conditions of hydrogenation was *c.* 72 per cent. It was observed that fatty alcohol formation in this case was accompanied by dehydroxylation (removal of OH group in the ricinoleic acid chain) which amounted to nearly 76 per cent when the time of reaction was increased to 4 hr.

The products of hydrogenation of the oils and fats were found to have low iodine values (2-10) thus showing the non-selective nature of the catalyst.

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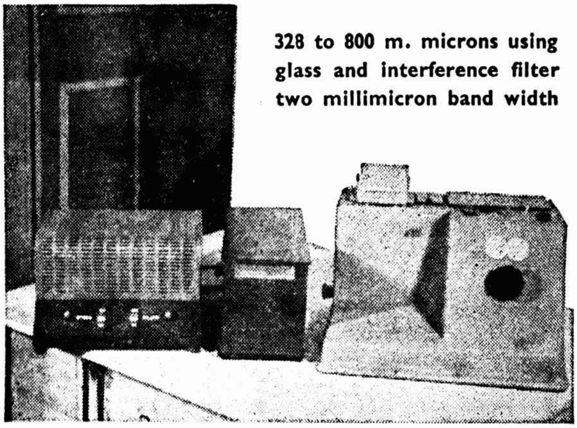

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