Journal of Scientific & Industrial Research

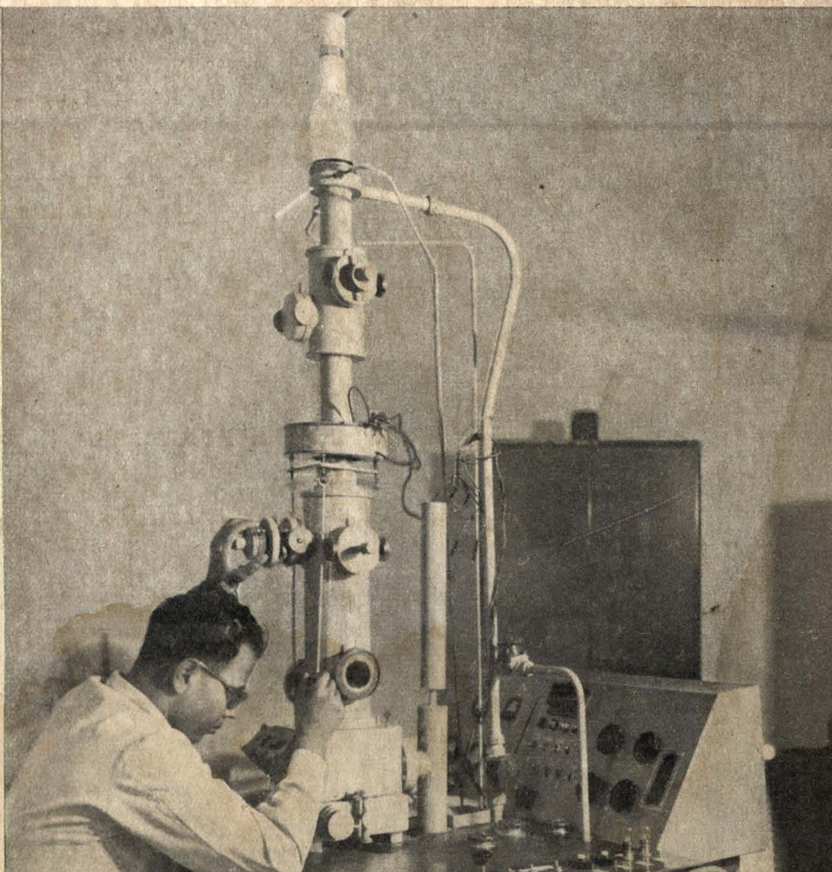
✓Vol. 13, No. 3, MARCH 1954

IN THIS ISSUE

- Plant viruses and virus diseases
- Biosynthesis of mould products
- Preparation of diiodotyrosine
- Determination of carbon and hydrogen by calorimeter bomb
- Mixed fertilizer and light magnesia from sea bitterns
- Carbonization of South Arcot lignite

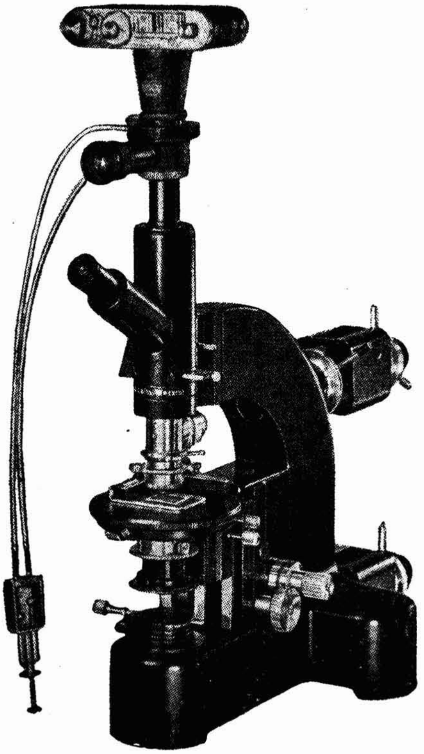
SECTION A : GENERAL
For Contents see page A3

SECTION B : RESEARCH PAPERS
For Contents see page A31



PUBLISHED BY THE COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, INDIA
NEW DELHI

J. sci. industr. Res., Vol. 13A, No. 3, Pp. 101-156; & Vol. 13B, No. 3, Pp. 151-224. March 1954



Journal of Scientific & Industrial Research

Vol. 13A, No. 3, MARCH 1954

CONTENTS

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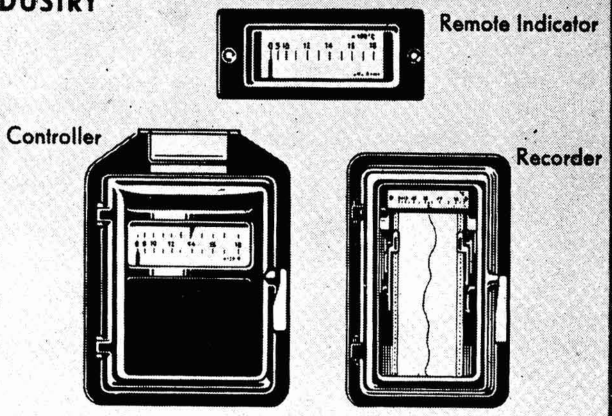
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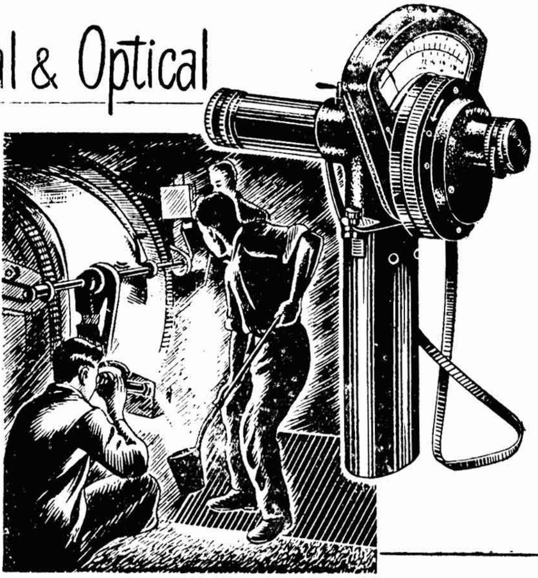

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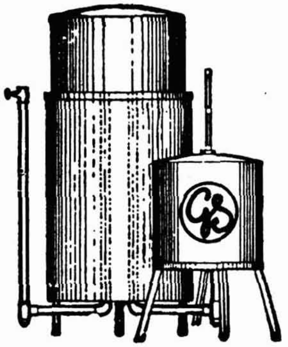

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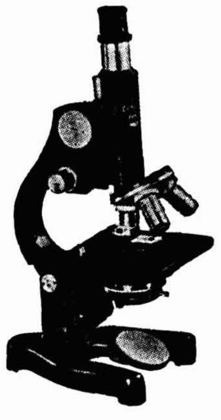

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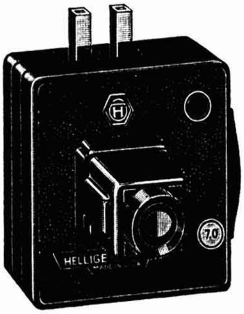
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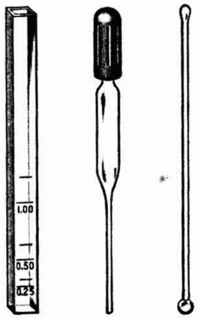
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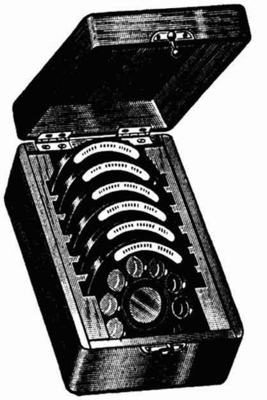

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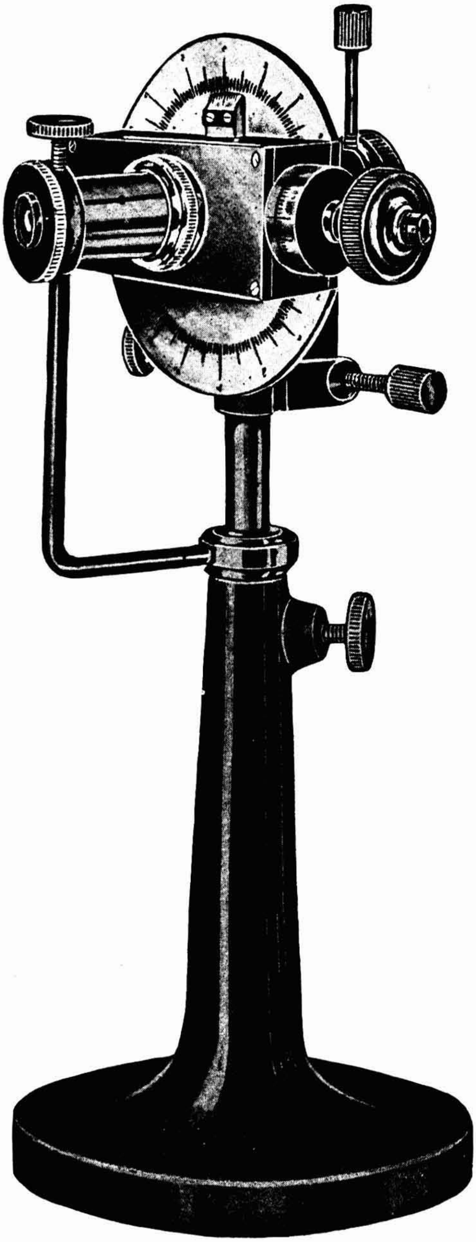

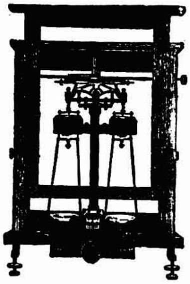

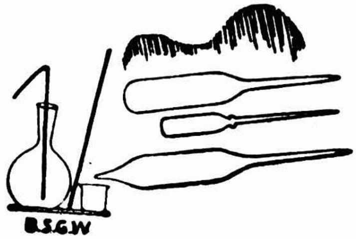
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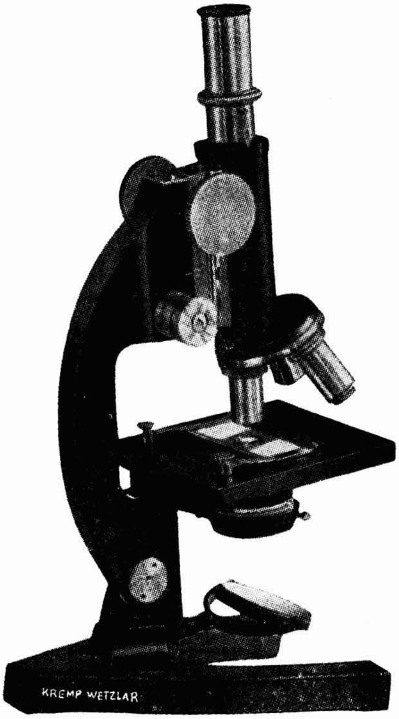
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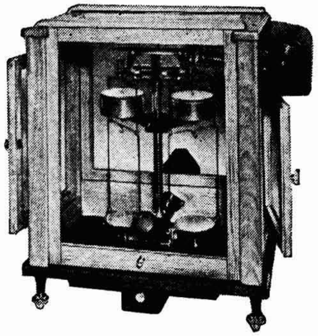

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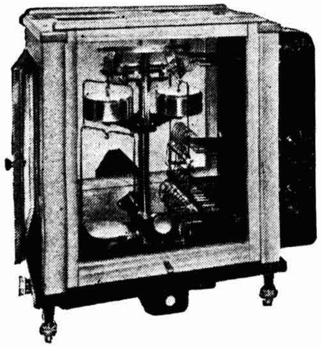

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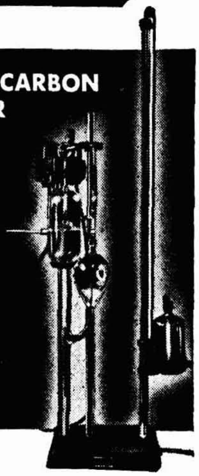


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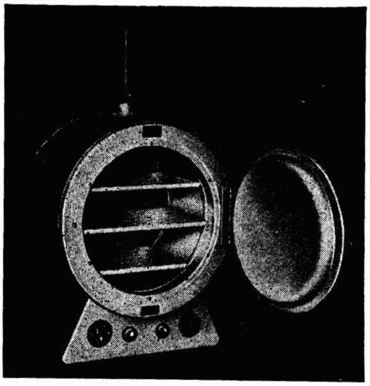

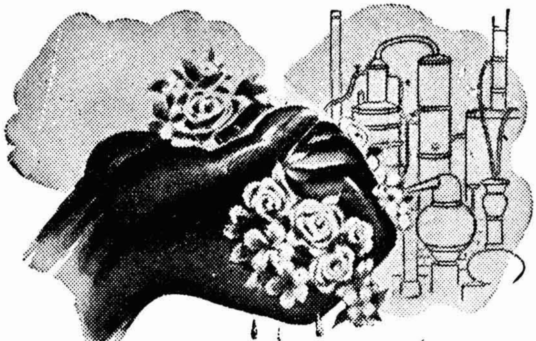


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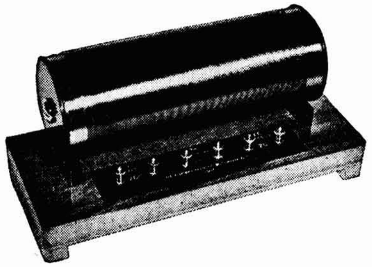

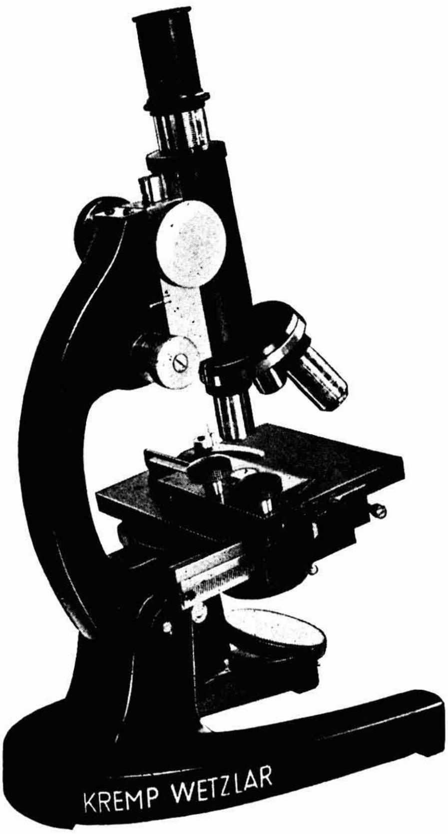

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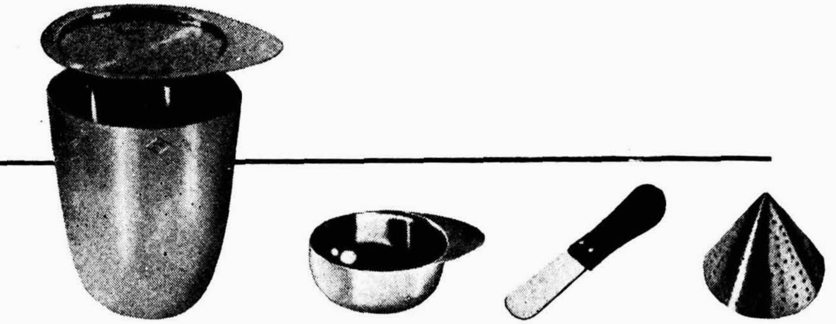

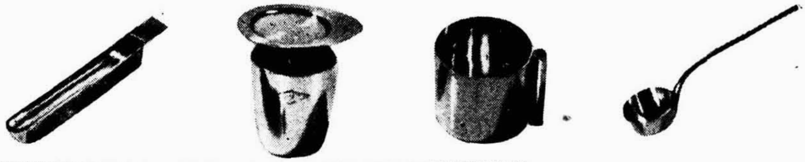

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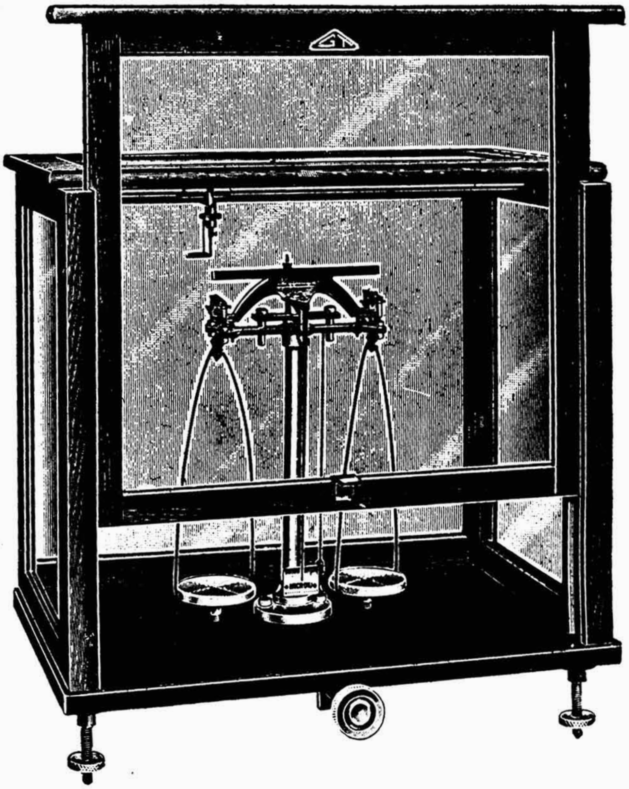

Non-ferrous Metal Industry in India

A THREE-DAY symposium on *Non-ferrous Metal Industry in India* was organized by the National Metallurgical Laboratory, Jamshedpur, on 1-3 Feb. 1954, at which research workers and representatives of industry and Government departments discussed problems relating to the conservation and planned utilization of India's non-ferrous mineral resources. The importance of the discussions and the need for taking positive measures to make the best use of our resources will be clear when it is remembered that with the continuous increase in the world consumption of metals and consequent depletion of mineral resources, every country has begun to direct attention to the conservation of metals and, wherever possible, to find substitutes. India's resources of non-ferrous minerals are by no means abundant (TABLE 1). Excepting the rich deposits of bauxite, ilmenite, beryl and manganese ores, deposits of other non-ferrous minerals are poor.

The non-ferrous metal industry in India is of recent origin. The Indian Copper Corporation Ltd., Ghatsila, was the first to exploit copper deposits on modern metallurgical lines. The Indian Smelting & Refining Co., Bombay, recovers copper from scrap besides making other non-ferrous alloys. Two plants are now extracting commercial aluminium from bauxite. A plant near Dhanbad is extracting lead. Antimony is recovered in a plant established near Bombay. There are scattered over the country small units for remelting scrap, making brass utensils and decorative articles. Indian non-ferrous metal production in 1952 was: copper, 6,079 tons; aluminium, 3,565 tons; lead, 1,124 tons; antimony, 172 tons; gold, 226,357 oz.; and silver, 14,612 oz.

TABLE 1 — INDIAN NON-FERROUS MINERAL PRODUCTION IN 1952*

	1951 tons	1952 tons	ESTIMATED RESERVE tons
Copper ore	369,057	324,636	3,000,000 (short tons)
Lead-zinc ore	—	5,823 (concentrates)	700,000
Ilmenite	219,568	224,895	250 million
Manganese ore	1,283,929	1,374,012	—
Bauxite	67,047	62,812	25 million
Magnesite	117,071	88,821	80 million
Chromite	15,802	26,000	0·2 million

*India is the principal source of high grade manganese ore which is a valuable dollar earner. There are rich deposits in Travancore beach sands of ilmenite required for the production of the modern wonder metal, titanium. India has rich deposits of beryl.

India requires annually about 50,000 tons of copper, 18,000 tons of lead, 12,000 to 16,000 tons of aluminium and 4,000 tons of tin. With plentiful deposits of high grade bauxite and the projected development of hydro-electric power, aluminium industry can be developed to produce about 20,000 tons per annum as envisaged in the programme of industrial development under the First Five-Year Plan.

The progress of non-ferrous metal industry to-date has been slow. At present the production of non-ferrous metals falls short ot the requirements, with the result that 75 per cent of the latter are met by imports. The value of imports was Rs. 18·70 crores during 1952. Our deficiency in winning non-ferrous metals constitutes a serious handicap to the development of ancillary engineering industries.

The National Metallurgical Laboratory has rendered a great service to non-ferrous producing and consuming industries by bringing together representatives of the Indian non-ferrous industrial and engineering organizations and technologists to exchange views for stimulating the growth of indigenous industry to meet present and future requirements.

Dr. S. S. Bhatnagar Felicitated

FELICITATIONS ON THE OCCASION OF HIS sixtieth birthday were conveyed to Dr. S. S. Bhatnagar, Director, Scientific & Industrial Research, by the Prime Minister and distinguished foreign and Indian scientists at a function organized at the National Physical Laboratory, New Delhi, on Sunday, 21 February 1954, by the Council of Scientific & Industrial Research.

The Prime Minister, who presided over the function, said it had been an exciting experience in his life to work with Dr. Bhatnagar in building up science in the country. Though there were several aspects of scientific development which had to be taken up, the Prime Minister said, we had substantial achievements to our credit and Dr. Bhatnagar had undoubtedly the chief credit for this record. He referred to Dr. Bhatnagar's rare capacity for " getting things done ", a quality not frequently met with, and expressed the hope that he would still have long and hard years of work before him.

Sir Charles Darwin, the British scientist, congratulated Dr. Bhatnagar on bringing about " a tremendous development in science in a surprisingly short time ".

Sir Alfred Egerton referred to the great role science was playing today in advancing material progress and affording opportunities for creative work and paid a tribute to Dr. Bhatnagar's contribution to the development of science in India.

Among the other speakers were Dr. K. S. Krishnan, Prof. Gaston Dupouy, Director of National Centre of Scientific Research, Paris, Shri Sri Ram, Dr. H. J. Bhabha, Chairman of the Atomic Energy Commission, Dr. Vikram Sarabhai, Shri R. P. Bahadur, Dr. Ernst Zipkes, Dr. V. Subramanian, Dr. Mata Prasad and Shri D. Padmanabham. Messages from national laboratories, research institutions, learned societies and industrialists were read out by Dr. K. S. Krishnan. Dr. S. Radhakrishnan sent a message congratulating Dr. Bhatnagar on his " monumental work ".

Earlier, a portrait of Dr. S. S. Bhatnagar, executed by the well-known artist Shri Gopal Deuskar, was unveiled by Sir Alfred Egerton.

Ionospheric Data—December 1953

CHARACTERISTICS OF THE IONOSPHERE OVER CALCUTTA

S. S. Baral, R. K. Mitra, A. K. Saha,
B. Chatterjee & M. R. Kundu

Ionosphere Laboratory, Institute of Radio Physics & Electronics, University College of Science, Calcutta

FIG. 1 shows the monthly average diurnal variations of the ordinary ray critical frequencies of regions E and F_2 ($f°E$ and $f°F_2$) and also similar variations of the heights of maximum ionization (hpF_2) and the bottom ($h'F_2$) of the F_2 layer during December 1953. The $f°F_2$ 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 the limiting frequencies, 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. 3 gives the mean M.U.F.

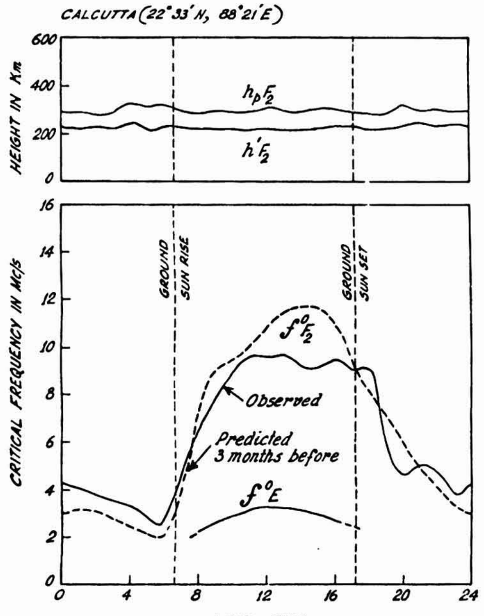

FIG. 1 — MONTHLY MEAN IONOSPHERIC CHARACTERISTICS FOR DECEMBER 1953

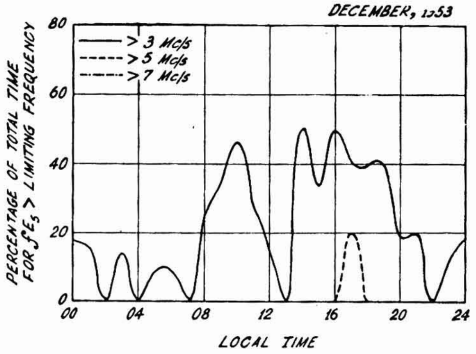

FIG. 2 — PERCENTAGES OF TOTAL NUMBER OF OCCASIONS WHEN fE_s WAS GREATER THAN 3, 5 AND 7 MC./S. DURING DECEMBER 1953

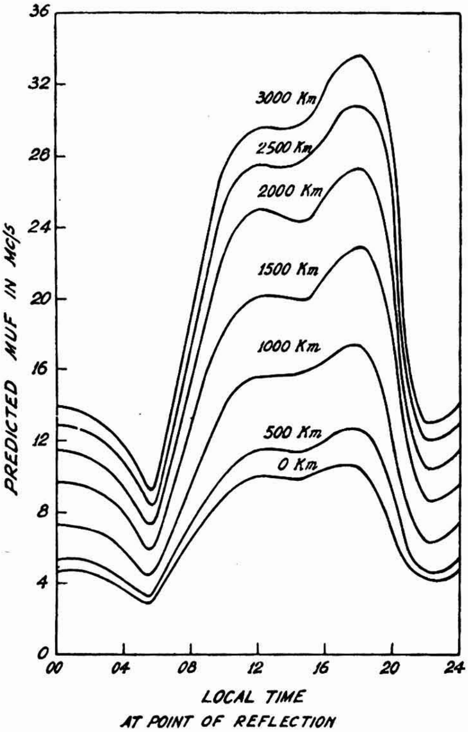

FIG. 3 — PREDICTED M.U.F. VIA F_2 LAYER OVER CALCUTTA DURING MARCH 1953

TABLE 1 — MONTHLY MEDIAN VALUES

(*December* 1953)

TIME*	f°F_2 Mc./s.	hpF_2 km.	h'F_2 km.	f°E Mc./s.	fE_S Mc./s.	(M3000)F_2
00	4·60	270	210			3·30
01	4·20	300	210			
02	4·10	300	240			
03	3·60	285	225			3·20
04	3·25	300	240			
05	2·55	285	210			
06	3·15	330	210			3·05
07	4·85	300	218			
08	6·55	300	210	2·40		
09	7·75	300	210	2·70		3·05
10	8·75	300	210	2·95		
11	10·00	285	210	3·20		
12	9·60	300	210	3·10		3·05
13	9·45	300	210	3·15		
14	9·60	300	210	3·05	(3·25)	
15	9·60	300	233	3·00		3·00
16	9·00	300	240	2·70	(3·10)	
17	8·85	300	240			
18	9·60	270	210			3·25
19	5·20	270	210			
20	4·60	300	210			
21	4·60	300	240			3·10
22	4·10	300	210			
23	4·00	300	210			

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

predictions for transmission to different distances via F_2 region over Calcutta during March 1954.

The sporadic E layer was of very infrequent occurrence during December 1953. The f°F_2 values during daytime were found to be unusually low on most of the days.

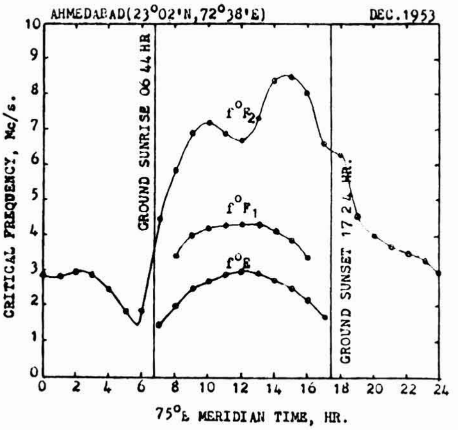

FIG. 1 — DIURNAL VARIATION OF CRITICAL FREQUENCIES OF ORDINARY WAVES REFLECTED FROM E, F_1 AND F_2 REGIONS

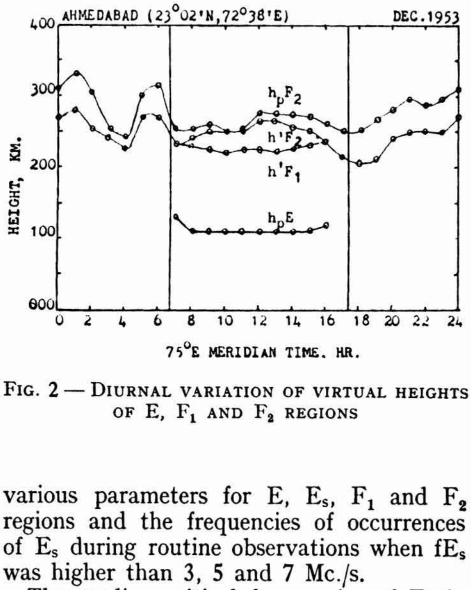

FIG. 2 — DIURNAL VARIATION OF VIRTUAL HEIGHTS OF E, F_1 AND F_2 REGIONS

CHARACTERISTICS OF THE IONOSPHERE OVER AHMEDABAD

K. M. KOTADIA & R. G. RASTOGI

Ionospheric Research Station, Physical Research Laboratory, Ahmedabad

FIG. 1 shows the variations of the critical frequencies of the ordinary waves reflected from E, F_1 and F_2; Fig. 2 shows the variations of the height of maximum electron density and of the minimum virtual height 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 occurrences of E_s during routine observations when fE_s was higher than 3, 5 and 7 Mc./s.

The median critical frequencies of F_2 in this month were lower than in the previous month practically for all the hours; a pronounced fall during noon-time was observed. The F_2 echo totally disappeared on five days from 05 to 06 hr. The frequency and intensity of E_s occurrences showed a sharp rise over that in the previous month for all the hours. The overall percentage of E_s occurrences was almost equal to that for summer solstice.

TABLE 1 — IONOSPHERIC DATA — AHMEDABAD, DECEMBER 1953

(Tabulated hours 75° E. Meridian Time)

TIME hr.	MEDIAN VALUES								NO. OF OCCURRENCES OF SPORADIC E WITH			TOTAL NO. OF DAYS FOR WHICH E_s DATA ARE AVAILABLE
	$f^\circ F_2$ Mc./s.	h_pF_2 km.	$h'F_2$ km.	$f^\circ F_1$ Mc./s.	$h'F_1$ km.	$f^\circ E$ Mc./s.	h_pE km.	fE_s Mc./s.	$fE_s >$ 3 Mc./s.	$fE_s >$ 5 Mc./s.	$fE_s >$ 7 Mc./s.	
0	2·9	310	270	—	—	—	—	3·6	13	2	—	27
1	2·9	330	280	—	—	—	—	3·4	12	1	—	27
2	3·0	305	253	—	—	—	—	3·6	16	2	—	26
3	2·9	253	240	—	—	—	—	4·0	15	1	—	28
4	2·5	240	225	—	—	—	—	3·7	14	1	—	27
5	1·9	300	270	—	—	—	—	4·0	23	7	1	27
6	1·9	315	270	—	—	—	—	5·0	25	11	1	27
7	4·5	250	230	1·95*	230*	1·4	130	3·7	23	1	—	27
8	5·8	252	240	3·40	230	2·0	110	5·1	18	9	1	25
9	6·9	260	250	4·00	225	2·5	110	4·1	17	6	—	27
10	7·2	250	250	4·20	220	2·7	110	4·2	16	7	2	28
11	6·9	253	250	4·30	225	2·9	110	5·3	12	8	1	27
12	6·7	275	265	4·30	225	3·0	110	4·2	14	7	1	26
13	7·3	275	265	4·30	220	2·9	110	5·3	13	9	2	25
14	8·4	272	255	4·10	225	2·7	110	5·0	20	9	1	27
15	8·5	270	250	3·90	230	2·5	110	5·0	17	8	1	26
16	8·1	260	235	3·40	235	2·2	120	4·0	19	6	1	27
17	6·6	250	215	—	—	1·7*	125*	4·1	25	6	3	29
18	6·3	250	206	—	—	—	—	4·3	21	8	1	28
19	4·6	268	210	—	—	—	—	3·4	17	3	—	28
20	4·0	280	240	—	—	—	—	3·2	15	2	—	28
21	3·7	295	247	—	—	—	—	3·3	14	—	—	28
22	3·5	285	250	—	—	—	—	3·6	14	—	—	28
23	3·3	295	247	—	—	—	—	3·3	14	—	—	28

*Observations less than ten.

Indian National Commission for Unesco — First Conference, 9-11 January 1954

THE FIRST CONFERENCE OF THE INDIAN National Commission for Co-operation with Unesco was inaugurated in New Delhi on 9 January 1954 by the Prime Minister. Fraternal delegates from eight Asian and African countries attended the Conference. Among the distinguished guests present were Mrs. Vijayalakshmi Pandit, President of the U.N. General Assembly; Dr. Luther Evans, Director-General of Unesco; Prof. Julian Huxley, former Director-General, Unesco; and Sir Ronald Adam, Chairman of the Executive Board.

The Indian National Commission was set up in July 1952 in pursuance of Article VII of the final Act of the United Nations Conference. According to this Article, member States should associate national bodies interested in educational, scientific and cultural matters with the work of the Unesco, preferably by the formation of a representative National Commission.

The Indian National Commission has three sub-commissions, one each for education, science and culture. The Education Sub-commission consists of nominees of the Central Advisory Board of Education, the Inter-University Board, the All-India Federation of Educational Associations, the All-India Council for Technical Education, and representatives of such bodies as the Indian

(*Continued on page* 124)

The Development of Knowledge on Plant Viruses & Virus Diseases*

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THE idea of a contagion that can spread from one individual to another is thousands of years old, but only during the last hundred years or so have the varied causes of infectious diseases gradually been uncovered. Belief in the spontaneous generation of one kind of organism from another so dominated men's thinking that, although fungi and bacteria were for long known to be associated with certain diseases, they were unquestioningly regarded as products of the diseased organisms. During the first half of the nineteenth century, some botanists were suggesting that fungi caused such diseases as potato blight, but the germ theory of disease did not become generally accepted until the second half, when Pasteur successfully exposed the fallacies of spontaneous generation. There followed what can be described as the golden age of bacteriology and mycology, when it was confidently thought that a specific bacterium or fungus would be identified as the cause of every disease. But this was not to be. Not all diseases are infectious; some are caused by an inadequate diet or an unfavourable environment. And not all infectious diseases are caused by bacteria or fungi; some have no visible causes, and these are what today we label virus diseases. The causes of many of these still remain obscure, but at least we are now beginning to understand some.

The study of virus diseases is usually considered to have started with Iwanowski's demonstration in 1892 that the cause of tobacco mosaic, a disease that occurs wherever tobacco or tomato crops are grown, will pass through filters that retain bacteria. Several other plant diseases now recognized as caused by viruses had been described before this, and some had been transmitted by grafting or by injecting healthy plants with juice from diseased ones. Probably a more appropriate starting date would be 1896, when not only was an important animal disease, foot-and-mouth of cattle, also shown to be caused by a " filter-passer ", but Beijerinck, in confirming Iwanowski's results, suggested that the cause of tobacco mosaic differed fundamentally from even the smallest organisms. He labelled it a *contagium vivum fluidum*, an infectious living fluid, and thereby started controversies on the nature of viruses that have continued ever since.

Viruses at first got scant attention compared with bacteria and fungi, but as an increasing number of important diseases, affecting man, all kinds of animals, higher plants and bacteria, came gradually to be recognized as virus diseases, research developed at an increasingly rapid rate, until now it ranks as one of the major branches of pathology. Indeed, its relative importance becomes increasingly great, since cures and preventives have been found for more and more of the diseases caused by bacteria and fungi, whereas the virus diseases in the main still remain intractable. Modern conditions of life and agriculture favour their spread, and new virus diseases of plants are now being described with an alarming frequency. They are responsible for many crop failures that pass undiagnosed and for the miserably small yields that are only too common with many perennial crops or crops that are propagated vegetatively. If yields are to be increased, much more work will be needed on virus diseases, particularly ecological work, to find where the viruses are coming from, how they are being transmitted, and how they can be combated.

For the first 40 years after their discovery, nothing definite was known about the nature of viruses. Many new virus diseases were described; also, much was learnt about the kinds of symptoms viruses cause, their host ranges, their ability to vary, the methods whereby they are transmitted, and preventive

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*Address delivered at the forty-first session of the Indian Science Congress, Hyderabad, 6 January 1954.

measures were designed against some. Their study was largely left in the hands of bacteriologists and mycologists, for it was generally assumed that viruses are the smallest kinds of organisms and differ chiefly from bacteria in being inconveniently small. There was little to conflict with this idea, for their behaviour in susceptible organisms in many ways resembles that of pathogenic bacteria. Viruses clearly possess the two qualities normally considered characteristic of organisms: they obviously multiply, because they can be transmitted in series through susceptible hosts; also they can vary or mutate, for although the progeny usually resembles the parent type, clinically distinct variants sometimes occur. The failure to culture any virus on artificial medium was no serious obstacle to the idea that they were organisms, because there are examples of obligately parasitic bacteria and fungi to provide convenient analogies.

The customary cultural and staining techniques of bacteriologists and mycologists, however, were singularly ill adapted for the study of agents whose prime features are invisibility and inability to multiply *in vitro*, and it is not surprising that the nature of viruses remained for long a matter of speculation rather than fact. Not until new techniques were introduced was any substantial progress made; those that proved most valuable were modifications of methods by which enzymes and certain other proteins had been purified. Early attempts to purify tobacco mosaic virus led to claims that it had been obtained in the form of various kinds of substances, but the first claim that has stood the test of time was made in 1936, when juice from infected plants was shown to contain a specific nucleoprotein. Since then the juice from plants infected with a dozen or so other viruses has also been found to contain specific nucleoproteins which, there is every reason to assume, are the viruses themselves. Some of these resemble tobacco mosaic virus in having rod-shaped particles of variable lengths, and because of this their purified preparations have some unusual physical properties. Dilute solutions strongly show the phenomenon of anisotropy of flow and concentrated solutions are liquid crystalline. Other plant viruses that have been purified have spherical or near-spherical particles, and most of them crystallize in characteristic forms when precipitated in appropriate conditions.

The different viruses occur in extracts from infected plants in widely differing amounts; they also have different constitutions, but all seem to contain only two components, protein and nucleic acid. The nucleic acid so far identified in plant viruses has always been of the ribose type, but this is not common to all viruses; some bacteriophages and animal viruses have been found with deoxynucleic acid. The constitution of several strains of tobacco mosaic virus has now been fully determined; no differences have been found between the nucleic acid fractions from different strains, but strains that have different antigenic constitutions also differ in the amounts of some individual amino acids they contain. Unrelated viruses differ not only in the proportion of nucleic acid to protein they contain, but also in the relative proportions in which different purines and pyrimidines occur in their nucleic acid.

The isolation of viruses as crystals and liquid crystals made it possible to study them by X-ray diffraction. This not only gave the first accurate measurements of the sizes of virus particles, but it also showed that internally the individual virus particles have a fixed and regular structure that conflicts strikingly with the variability in constitution that characterizes cells. The viruses much more closely resemble single components from cells than whole cells themselves. This resemblance, too, is shown by their relative chemical simplicity; the smallest bacterium contains, in addition to nucleoproteins, many other substances, other proteins, lipoids and carbohydrates, to mention only a few, whereas the plant viruses so far studied seem to be simply nucleoprotein. How far this applies to all viruses, or even to all plant viruses, is still uncertain, for nothing is known about the chemical constitution of most. No animal or bacterial virus has yet been obtained in crystalline or liquid crystalline forms, but this may mean only that they have not been sufficiently purified or that they lack the geometrical regularity necessary to form crystals. Some bacterial viruses are morphologically more complex than the small plant viruses; shaped like tadpoles they also seem to consist only of nucleic acid and protein, with the nucleic acid carried in the centre of the head and surrounded by a protein coat. Electron microscopy is now providing evidence on the size and shapes of plant viruses that have not been rigorously purified. The results suggest that some, potato yellow dwarf, for instance, are much larger than tobacco mosaic and other viruses that have been identified as nucleoproteins, and so there is the obvious possibility that they are also chemically more complex. It will be a long time before the chemical nature of most plant viruses will become known. Many of them occur at such high dilutions, and are so unstable, or so closely resemble other components of plant extracts, that current techniques are unlikely to be successful in isolating them pure enough, or in quantity enough, for chemical analyses to have any significance. The dozen or so that have been identified as nucleoproteins cover a range of types, differing in stability and in the ways in which they are transmitted, and so it is safe to assume that many others are also nucleoproteins. Perhaps the simplest way to summarize the present position is to say that, from now on, the identification of a plant virus as a nucleoprotein will simply add another to a growing list, whereas the identification of one as anything else will be a major event.

Purified preparations of some plant viruses, particularly of some spherical particles, show no signs of heterogeneity when subjected to the usual physico-chemical tests such as ultra-centrifugation or electrophoresis. This led some workers to call virus particles molecules, a word implying an exact duplication of structure that fits ill with the observed mutability of viruses. Its use has become increasingly inappropriate as the anomalous nucleoproteins present in extracts from infected plants have been studied in greater detail, for it becomes increasingly obvious that the first appearance of homogeneity was partly illusory. Virus multiplication seems not to lead to a single end product that exactly resembles the original infecting particles, but rather to a range of related though not identical products. The nucleoprotein that is serologically related to tobacco mosaic virus, for example, can be separated by differential centrifugation into fractions that contain particles of the same width but greatly different average lengths and that have different infectivities. The shortest particles have little or no ability to initiate infections in healthy plants, and the infectivity per unit weight of protein increases as the average length of the particles in the fraction increases up to about 300 mμ. Various treatments *in vitro* make the small particles aggregate end to end to give long rods indistinguishable morphologically from those characteristic of infective preparations, but this increase in length does not increase their ability to infect healthy plants. Sap from plants infected with the Rothamsted culture of tobacco necrosis contains specific particles of two different sizes, and much of the protein that is serologically related to infective virus seems to be non-infective. Similarly, sap from plants infected with turnip yellow mosaic virus regularly contains two distinguishable specific proteins. Both have spherical particles of the same size, and both seem to be antigenically identical, but they have different weights and one contains nucleic acid while the other does not. Only the particles that contain nucleic acid infect healthy plants, and there is good presumptive evidence that the nucleic acid occurs in these as a central core surrounded by a hollow sphere of protein. Recently, evidence has also been advanced that some of the small non-infective particles that occur in sap from plants infected with tobacco mosaic virus may also lack nucleic acid and constitute only the protein part of the virus particles.

The significance that should be given to these various particles possessing the serological specificity of the viruses, and their exact relationships to one another, still remain to be determined. There is no definite evidence to show whether the non-infective particles represent partial products formed as stages in the synthesis of infective particles, whether they are produced by the disruption of infective particles, or whether they are necessary adjuncts to virus multiplication. It is perhaps worth the comment that, although they seem unable to initiate infection in healthy plants, this does not necessarily mean they had no biological activity in the cells from which they came. On present knowledge it seems less reasonable to regard plant virus diseases as being analogous to the result of one organism parasitizing another than to regard them as derangements of the protein metabolism of the host. Viruses seem not to depend on their hosts simply for a supply of metabolites, but also for the synthetic mechanisms whereby they are made. Infection is most plausibly regarded as adding a new organizer to the mechanism that determines the general direction of metabolism, so that the infected cell synthesizes a new range of proteins, either in addition to or instead of those it previously produced. Some of these proteins resemble the infecting particles in themselves being infective, but not all are.

The close dependence of infection and virus synthesis on the physiological condition of the host plants has been amply demonstrated by many workers who have studied infected plants grown in widely different environments. It is clear, too, that conditions that make healthy plants more likely to contract infection are not also those that necessarily favour virus multiplication. There is more than a suggestion from recent work that susceptibility to infection is increased by subjecting plants to conditions that encourage protein breakdown. The multiplication of viruses in infected plants, however, seems to be increased by conditions that favour protein synthesis. However, the multiplication of too few viruses has yet been studied for any generalizations to be possible. There are certainly great individual differences in the extent to which viruses occur in infected tissues, and the severity of symptoms shown by infected plants is no guide to the amount of virus they contain. Mosaic of tobacco and tomato is a relatively mild disease, but this virus occurs in hundreds or thousands of times the amount of other viruses that cause crippling or lethal diseases. Indeed, tobacco mosaic virus can become the predominant protein of infected plants; when infected plants are nitrogen-deficient, it may amount to two-thirds of the total leaf protein. If the plants are given abundant nitrogen, the amount of virus per unit weight of leaf will increase, so that a kilogram of fresh leaf may contain 10 g. of virus, but in these conditions it may represent only a fifth of the total protein, for the normal proteins will be increased proportionately more than the virus. Virus and other leaf proteins are both synthesized from the same basic units, and when these are limited, the synthesis of virus takes precedence over that of many of the normal proteins. However, the lack of correlation between the amount of virus produced and the severity of the disease suffered by infected plants shows that symptoms result from something more subtle than the total amount of amino acids and purines and pyrimidines that are sequestrated during the formation of virus. Much more work will be needed before we understand the manner in which different viruses and different strains of one virus cause their different effects, but some of the normal proteins may be more readily dispensed with than others, and severity of symptoms may reflect the relative importance of the proteins whose synthesis is most affected by virus formation.

Although studies on the nature of viruses and on the mechanism of virus multiplication produce some fascinating results and are full of potential discoveries for the future, they do not immediately promise to help in controlling plant virus diseases. For this another kind of work is needed. An ecological or epidemiological study must be made of each disease; the sources of infection must be found, also how the virus spreads from plant to plant and the factors that encourage or limit spread, for only from such knowledge can conditions be determined for keeping plants healthy. There is abundant evidence that such work repays handsome dividends in increased yields. It is no mere coincidence that yields of crops are highest in countries where plant diseases, including virus diseases, have been most studied. One example will suffice. Twenty or so years ago the potato stocks in the United Kingdom were heavily infected with virus diseases, the aphid-transmitted leaf roll and severe mosaic, and mild mosaic, which is not aphid transmitted. Now these diseases are becoming rarities. They have been overcome by raising special seed stocks in the north and west of the British Isles, where aphids are relatively few and inactive, and removing from these crops all plants that show any symptoms. The cost of these diseases is still high to the potato grower in the south and east of England, for to avoid them he has continually to replace his stocks of potato with new ones, but the cost is now the cost of a successful control measure and not to be reckoned in so many tons of potatoes lost to the acre. Similar schemes for producing virus-free stocks of many other vegetatively propagated plants are also now operated in the United Kingdom, and there is probably no single measure of disease control that, could it be applied the world over to all such crops, would produce such immediate increases in yield. In East Africa, for instance, virus-free clones of cassava were found to yield seven times as much as the infected ones being locally cultivated.

Although an increasing number of viruses are now being found to be soil-borne, the usual place to seek a source of infection is a living plant. Viruses appear to be obligate parasites and only the most stable ones, such as tobacco mosaic virus, can persist for long outside living cells. And the most common source of infection will be a perennial plant or one that is vegetatively propagated. There is a simple reason for this. Once a virus enters a plant, it usually permeates all the leaves, stems and roots, and it remains in these vegetative parts as long as they remain alive. By contrast, viruses rarely enter into true (sexually produced) seeds, and crops grown annually from seed, with few exceptions such as lettuce and some leguminous crops, can usually be relied on to start life free from virus diseases. This explains the need for ensuring that, when crops are propagated vegetatively, by tubers, cuttings, runners, bulbs or the like, the parent plants are healthy, for any viruses they have will be passed on to the progeny. This explains, too, the old belief that reproduction by seed invigorates a stock, whereas vegetative reproduction debilitates it, for a clone continually kept in cultivation will become infected with more and more viruses and become increasingly debilitated, whereas seedlings from it will be virus-free and strong. The modern tendency to seek uniform crops of high quality is leading to the increased use of vegetative propagation, and unless care is taken to ensure that the lines in cultivation are healthy, this otherwise desirable practice will certainly result in the increased spread of virus diseases. Although curative measures can be applied to some infected plants, these have only limited applications. Normally there is no chance that virus-infected plants will recover, and they should be destroyed. While alive, not only do they usually yield poorly themselves, but they are a menace to other nearby plants. And they may be menaces not only to related species, but to wholly unrelated ones, for some, but fortunately by no means all, plant viruses can infect many species in widely differing families. Detecting sources of infection is relatively simple when the infected plants show clear symptoms, but viruses do not always obviously cause diseases in all their host plants. The carrier, the virus-infected but seemingly healthy plant, is a common phenomenon, which greatly complicates disease control and whose detection and destruction calls for much shrewd judgement and keen observation. As viruses are obligately parasites, their future is uncertain in plants they affect too severely. It can be taken as axiomatic that a virus found causing a lethal disease in one kind of plant will infect others in which it causes only a mild disease or is carried.

In seeking the method whereby a virus spreads, all past work shows that it is reasonable first to suspect some insect, for there is no doubt that most common viruses are insect-transmitted. Transmission, however, is usually a specific thing and not something that any insect can do. The search for the vector of a given virus may be easy if the species concerned is a pest of the crop in which the disease occurs, but this is not always so. Viruses can be spread widely by insects that are never sufficiently abundant on a crop to be obvious pests, and even by insects that do not breed on the crop at all. The search then may be long and tedious, particularly as there are many groups of insects in which vectors are known to occur. Most of these are insects that feed by sucking juice from plants, and they include aphids, leaf-hoppers, mealy-bugs, white-fly and thrips, but the biting insects such as beetles and grasshoppers cannot be wholly neglected for they do transmit some viruses. Indeed, their role as vectors has possibly been underestimated in the past, though it is unlikely that they will prove to be as important as the sucking insects, for many of them feed too voraciously and damage leaves too much to be successful vectors of viruses.

Although much of the mechanism underlying the transmission of plant viruses by insects remains to be unravelled, already enough has been done to show a bewildering variety of behaviour. Some viruses can be transmitted by aphids immediately after they have fed for only a few minutes or even seconds on an infected plant. Such viruses are often transmitted more readily by aphids that have been starved for a time immediately before they feed on an infected plant than by aphids that have been feeding continuously. More of the previously starved aphids transmit when they feed for only a short period on an infected plant than when they feed for an hour or longer. This seemingly paradoxical behaviour, for it would seem only rational to expect that the longer the insects imbibe juice from infected plants, the more virus they would be likely to acquire, cannot be explained with certainty, but present evidence suggests that viruses transmitted in this odd manner occur predominantly in the epidermal cells of infected plants. It seems that aphids that have been prevented from feeding for some time are more prone to imbibe juice from the epidermis than are aphids that have been feeding continuously; as their stay on an infected plant is prolonged, so the previously fasted aphids feed from deeper tissues that contain less virus. Only the amount of virus that is retained in the aphid stylets seems to be transmissible to healthy plants, which may explain why aphids cease to be able to transmit this kind of virus within a short period, often an hour or less, of leaving an infected plant. It is a fortunate dispensation that viruses which insects can acquire so readily are also almost equally rapidly lost by them.

At the opposite extreme from this type of rapid acquisition and rapid loss of infectivity by insect vectors is the behaviour of some leaf-hopper-transmitted viruses. Many of these seem to occur predominantly in the phloem of infected plants and, fortunately, at relatively low concentrations. To become infective, vectors need to feed for a considerable time on infected plants, and even after they have acquired virus there is still a prolonged incubation period before they can transmit the virus to healthy plants on which they feed. There is now unequivocal evidence with some of these viruses that this period is occupied by the viruses multiplying in their insects. Indeed, it is a matter of speculation as to whether these viruses are primarily to be considered as plant or animal viruses. They appear not to harm their insect vectors, evidence perhaps that they have been associated with them for longer than with the plants they are known to injure. Certainly some seem to multiply more freely in their insect hosts than they do in their plant hosts. Once insects have become able to transmit this type of virus, they retain their ability to infect healthy plants for as long as the insects remain alive. Indeed, some do even better than this, for they pass their viruses through their eggs, so that their youngs are born infective. However, this is exceptional; most plant viruses do not pass from parent insects to their offspring, which, if they are to become infective, must themselves feed on infected plants.

Between the two extremes, on the one hand, of viruses that can be rapidly acquired and almost equally rapidly lost by insects, and on the other, those that are acquired slowly but then maintain themselves indefinitely in their vectors, there are viruses that show almost every intermediate type of behaviour. These differences seem to be determined by the identity of the virus rather than that of the insect vector, for one species of aphis, such as the peach-potato aphid, *Myzus persicae*, can transmit many different viruses, and with some, for instance, potato virus Y, it is a transient vector, whereas with others, for instance, potato leaf roll, it can remain infective for long periods. Knowledge of the behaviour of the insect vector in transmitting a virus is not only of academic interest, for the type of behaviour is also of great practical importance in determining the extent to which viruses spread and what kind of control measure is likely to be valuable.

As there are now insecticides that effectively deal with all kinds of insects known to transmit plant virus diseases, it is reasonable to ask why these diseases are still troublesome, for at first sight all that is needed to control them is to control the insect vectors. Controlling insect pests, however, is a different problem from controlling virus diseases. All that an insecticide needs to do to be valuable against a pest is to keep its numbers below the level at which they do appreciable damage to a crop, but this may have no effect in decreasing the spread of virus diseases. The spread of a virus cannot be computed simply from the numbers of potential vector insects that are produced in a crop. Viruses are spread only when vectors move from one plant to another; stationary insects may do great damage by feeding on plants, but they are not spreading viruses, which they do only when their feeding behaviour first allows them to become infective and they then move. The greater mobility of leaf-hoppers compared with aphids makes them more dangerous vectors of viruses; and of the vast populations of aphids that often develop on crops, most are wingless and, although important as pests, are usually unimportant as vectors of viruses compared with the relatively few winged forms.

In many experiments during the 1940's to try and control potato virus diseases by such treatments as fumigating crops with nicotine, we not only found no beneficial effect but often we had increased the spread of virus diseases. And this happened even though the treatment was very effective in getting rid of heavy aphis infestations. We could only attribute this result to the fact that the insecticide, while killing the vast majority of the wingless aphis, did not kill them all immediately, and some that would otherwise have stayed on the plants where they were bred became irritated by the treatment and moved to nearby plants which they infected. Within the last few years rather more promising results have been obtained with some of the new persistent insecticides, but even these can sometimes increase the spread of viruses. In the U.S.A., where DDT is widely used on potato crops, treated crops have often been found to have more plants with leaf roll than untreated ones. There the explanation seems to be different from ours. The use of DDT so prolongs the life of potatoes, by killing off many damaging insect pests, that sprayed crops remain alive much longer than unsprayed ones. Hence, when unsprayed crops die, the aphids migrate to the still green sprayed ones, and take their viruses with them. Spraying all the potato crops in a district would, no doubt, be generally beneficial, but spraying isolated ones is not. Indeed it is often apparent that a healthy crop would be better safeguarded, not by being sprayed itself, but by spraying the infected plants that provide both the sources of infection and insect vectors for it. The same safeguard, however, could better be provided and be more lasting by destroying the infected crops and replacing them with healthy ones.

The number of virus-infected plants in a crop increases in two ways: (1) by plants that become infected as a result of infective insects coming into it from outside, and (2) by spread from infected to healthy plants within a crop. As yet there is little evidence that even the most effective of the new persistent insecticides greatly affect the number of plants that become infected by incoming insects. Some insecticides, however, do decrease the extent to which insects spread viruses from infected to healthy plants within a crop. Particularly is this so with viruses whose vectors acquire infectivity only slowly, for even if they feed on infected plants, the insects are killed before they can transmit to healthy ones. To prevent the spread of viruses whose vectors become infective within a few minutes, substances will be needed that kill insects immediately they alight on plants, or, better still, substances that act as deterrents to the vectors and prevent them from even attempting to feed on the plants.

The spread of virus diseases can sometimes be checked by much cheaper methods than spraying with insecticides, but to develop such methods calls for a detailed knowledge of all factors that affect the spread of the specific virus. Virus diseases are individual things and no generalizations are possible. Control, too, is something that demands local knowledge, and methods that are useful in one country, or part of a country, may be useless elsewhere. As an example I may say that, whereas in the south and east of the British Isles, removing plants with leaf roll and severe mosaic from potato crops will not maintain the health of the crops and is little more than waste of effort, the same thing in the north and west will not only maintain but will actually improve the standard of health. When the sources of infection are known, the vector or vectors identified, and their habits understood, a modification of ordinary agricultural practice can sometimes be devised that will produce beneficial results. But the knowledge and benefits do not come easily. They demand intensive study by trained workers, primarily biologists who appreciate that the really important problems are to be found in the crops themselves rather than in the laboratory.

Much more work of all kinds is needed on viruses and virus diseases, in the laboratory no less than in the field, but where workers are few and virus diseases are causing large losses, field work is the more likely to return practical results. Laboratory work has the attraction of producing results more quickly and with a certainty that is rare with field experiments, but work on such problems as the nature of viruses and virus multiplication can be done anywhere and the results will apply everywhere. Work on the control of virus diseases, however, must be done locally and must be done everywhere the diseases occur. The results will be no less interesting, or of less scientific value, because they can be got without expensive apparatus.

Our knowledge of viruses and virus diseases has increased remarkably in recent years, but even so we are obviously only now beginning to appreciate rather than to solve the variety of complex problems they set. The worker on virus diseases of men and animals can always work in the expectation of producing a vaccine, either an inactivated virus or an avirulent strain, that will stimulate antibody production and confer immunity from serious virus diseases. The worker on plant virus diseases is given no such simple approach to a control measure. This is not because viruses that attack plants necessarily differ fundamentally from those that attack animals, but because plants seem unable to produce antibodies. It is true that avirulent strains of some viruses will protect plants from the effects of virulent strains, but this merely simulates the appearance of vaccination in animals without duplicating it. It provides no practical control measure, and could indeed be dangerous, for the " protected " plants are continually infected with a virus that might cause serious diseases in other plants. The aim of the plant pathologist must always be to decrease the number of infected plants, and his task in identifying already existing sources of diseases is already difficult enough without increasing them by deliberately infecting plants. In his difficult task, too, he is usually likely to be less well supported financially than his medical colleagues. It is natural enough that man should regard his own infectious diseases as more important than those of his crops, but in a world with an expanding population and limited amounts of land suitable for agriculture, the health of crops will become an increasingly vital matter. The future depends mainly on increasing yields per acre, rather than on increasing acres under cultivation. Only this way, too, can the cultivator get an adequate return for his labour. Yields can, no doubt, be increased in various ways, by breeding higher-yielding varieties, by better manuring and by irrigation, but prime among the causes of current low yields are the losses caused by pests and diseases. Of these, virus diseases may not yet be the most important, but as general standards of cultivation increase they will become so, unless research is increased so that we know how they can be combated.

A Theory of Biosynthesis of Some Mould Products

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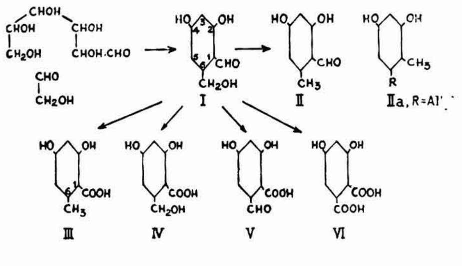
IN an earlier publication[1] a theory of biogenesis of lichen depsides and depsidones was discussed. The most important feature of the theory was the recognition of the C_8 unit (I) (orsellinic unit) as the invariable component of these two groups of lichen acids. It was considered to arise from a molecule of hexose and a molecule of biose by condensation of the aldol type. Subsequent modifications are due to oxidation and reduction of the side chains leading to all the known variations (II to VI). Out of these orsellinic acid unit (III) is the most important in depsides and depsidones. The possibility of a carbinol, aldehyde or a carboxyl taking the place of the 6-methyl group in (III) is also known to exist in special cases. Till recently there seemed to be no variation in the carboxyl group as found in orsellinic acid (1-position). The discovery of pannarin[2], a depsidone involving an orsellin aldehyde unit (II) would indicate possible variations, though to a small extent, in the nature of the group in the 1-position also. A similar unit as shown in (IIa) is found in mould products. These add further validity to the proposed C_8 unit (I) as representing the fundamental stage in evolution since it allows of these variations also. The degree of coincidence is remarkable and all the compounds (depsides and depsidones) of established constitution are built up following the normal rules of organic chemistry in regard to all later modifications involving nuclear methylation, nuclear oxidation and depside and depsidone formation.



Lichen compounds found in moulds

A large number of products found in lichens are also found to occur in moulds as the select examples given in Table 1 will show.

Further, there is close structural similarity between a number of mould products and lichen substances. Sparassol occurring in the mould *Sparassis ramosa*[19] is clearly a derivative of orsellinic acid. Chlorine-containing metabolic products are found both in moulds and lichens and they also seem to have some structural similarity. Examples of such chlorine-containing compounds in lichens are diploicin[20], gangaleoidin[21] and pannarin[2] while ustin and nidulin[22] are from moulds. Consequently the common features in the structural make-up of lichen and mould products may be found to be more general than has been realized so far. Since the C_8 unit is so widely prevalent in lichen acids it may be expected to be largely present in mould products also. The difference may probably be that in the lichen acids its presence is

TABLE 1 — COMPOUNDS OCCURRING IN LICHENS AND FUNGI

COMPOUND	LICHEN	FUNGUS
Erythritol	*Roccella montagnei*[3]	*Penicillium cyclopium* and *P. brevi-compactum*[4]
β-Carotene	*Roccella montagnei*[5]	*Phycomyces blakesleeanus*[6]
Ergosterol	*Cladonia rangiferina* and *Peltigera canina*[7,8]	*Penicillium carmino-violaceum*[9]
Polyporic acid	*Sticta* species[10]	*Polyporus nidulans* [11,12]
Physcion	*Xanthoria* and *Placodium* species[13]	*Aspergillus glaucus* series[14]
Endocrocin	*Nephromopsis endocroceae*[15]	*A. amstelodami*[16]
Thelephoric acid	*Lobaria* species[17]	*Thelephora palmata*[18]

obvious whereas in mould products it may have to be looked for. An examination of the structures of compounds belonging to various categories, keeping this point in mind, has given interesting results and has revealed a wide occurrence of the C_8 unit having undergone various transformations. One particular reaction which is not commonly met with in lichens is nuclear reduction. Decarboxylation may come next as being rare though not altogether absent. These two processes are used more frequently in the evolution of mould products. The existence of nuclear reduction involving removal of a phenolic hydroxyl group in particular locations is supported by the study of the evolution of anthoxanthins[23].

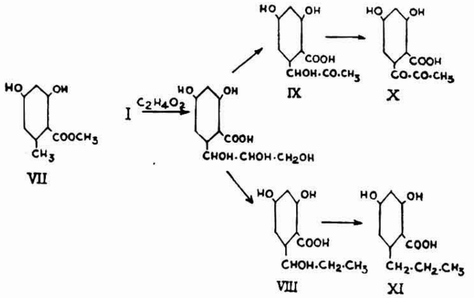
In his Bakerian lecture delivered before the Royal Society, Raistrick[24] has divided mould metabolic products into a large number of classes and traced the interrelationships in chemical structure. The biogenesis of only a few groups of these products relevant to the present theme is discussed in the present communication and, wherever necessary, analogies have been drawn from members of the lichen acid series.

Benzene derivatives

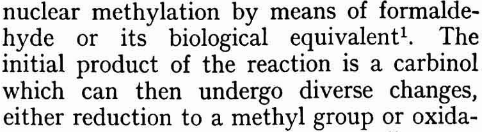
More than 20 mould products fall under this category. In a large number of them the existence of the C_8 unit having the familiar modifications known to occur in lichen acids is very clear.

Sparassol (VII) obtained from *Sparassis ramosa*[19] and 3:5-dihydroxy phthalic acid (VI) (DHP) isolated from a species of *Penicillium brevi-compactum*[25] are the most obvious examples. The former is a simple methylation product of orsellinic acid. The latter is a derived C_8 unit obtained by the side chain oxidation of the fundamental C_8 unit as already indicated. DHP and its derivatives seem to play a very important part in the evolution of more complex compounds produced by lichens as well as by moulds though its presence may not be so obvious.

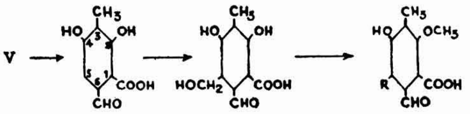
Along with DHP three related acids are found to occur in the mould *P. brevi-compactum*[25]. For convenience of discussion they have now been named compactone A (VIII), compactone B (IX) and compactone C (X). Just as in divarinol carboxylic acid (divarinic acid)[26] (XI) in the lichen series, these ketones also involve chain lengthening of the alkyl group in the 6-position. But the side chain exists in them in different states of oxidation. The earlier suggestion regarding the mode of this chain lengthening involving condensation with a biose seems to be quite appropriate for these mould products also.



It was suggested in the earlier publication[1] that 5-hydroxy orsellinic acid (XII) occurring in the lichen depsides arises from orsellinic acid (III) by a stage of para nuclear oxidation and this has recently been confirmed by laboratory experiments in which good yields are obtained[27]. An analogous case is found in ustic acid (XIII) which is produced by *Aspergillus ustus*[28]. It could be considered to be formed from compactone B by para nuclear oxidation and subsequent partial methylation. The last reaction should naturally involve the preliminary protection of the reactive 4-hydroxy group.

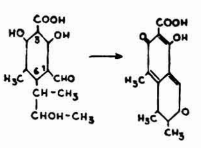


In the case of lichen acids, β-orcinol derivatives were considered to be formed from orsellinic acid units by a stage involving nuclear methylation by means of formaldehyde or its biological equivalent[1]. The initial product of the reaction is a carbinol which can then undergo diverse changes, either reduction to a methyl group or oxidation to an aldehyde and eventually to a carboxyl. In laboratory experiments[29] an aldehyde group can be introduced in position 3 easily and this group has also been reduced to a methyl[30]. Repeating the same procedure it is possible to introduce another alkyl group in the 5-position also[30]. Representative units with both these positions alkylated are not found in lichen acids. They seem to be well represented in the mould products. Cyclopolic acid (XIVa) and cyclopaldic acid (XIVb) occurring together in *Penicillium cyclopium*[31] are examples of this type and their possible evolution is indicated below. Here too the partial methylation would involve earlier protection of a more reactive hydroxyl group.

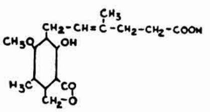


XIVa, $R = CH_2OH$
b, $R = CHO$

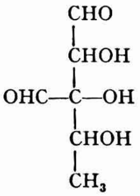
There is a novel feature in regard to chain lengthening in the mould products series. Whereas in lichen depsides and depsidones, chain lengthening occurs only in the 6-alkyl group of C_8 unit and has not been noticed in the newly coming alkyl group in the 3-position, in the mould products it is noticed both in the 6 and 3-positions. Further, these chains are frequently branched and do not necessarily consist of odd number of carbon atoms. As examples could be mentioned citrinin (XV), metabolic product of *A. terreus*[32,33] and mycophenolic acid (XVI) found in a species of *P. brevi-compactum*[34]. In citrinin the alkyl group in the 6-position is branched (C-methylation of a reactive methylene group) and the one in the 3-position is oxidized to a carboxyl. It has already been pointed out that the 1-position need not always carry a carboxy group; in citrinin it is an aldehyde. The nature of the side chain in the 3-position of the second compound is explicable on the basis that a branched chain hexose is involved in the chain lengthening. This type of sugars seem to be not uncommon in mould products, cf. the sugar (XVII) present in streptomycin and also cardycepose (XVIII) found in *Cordyceps militaris*[35].



Citrinin precursor XV

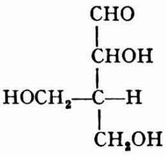


XVI



$$OHC-\overset{\overset{\overset{CHO}{|}}{CHOH}}{\underset{\underset{\underset{CH_3}{|}}{CHOH}}{\overset{|}{\underset{|}{C}}}}-OH$$

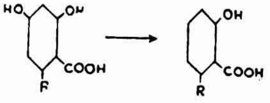
XVII



$$HOCH_2-\overset{\overset{CHO}{|}}{\overset{CHOH}{|}}\!\!\!\underset{\underset{CH_2OH}{|}}{C}-H$$

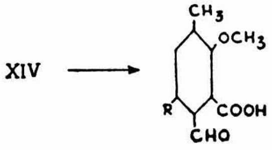
XVIII

As already mentioned nuclear reduction is not commonly met with in depsides and depsidones, but seems to be of frequent occurrence in moulds. 6-Methyl salicylic acid (XIXa), a metabolic product of a number of species of *Penicillium* moulds[36], and mellein (XIXb), the metabolic product of *Aspergillus melleus*[37], would constitute the simplest examples, the former being derived from orsellinic acid and the latter from compactone B by a stage of nuclear reduction. The preferential removal of the 4-hydroxy group can be carried out fairly easily in the laboratory and thus orsellinic acid forms 6-methyl salicylic acid in satisfactory yield[38]. An analogous preferential reduction would be the conversion of phloroglucinol carboxylic acid into γ-resorcylic acid (XIXc)[39].



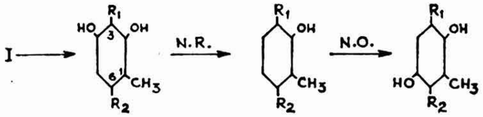
XIX a, $R = CH_3$
b, $R = CHOH{\cdot}CH_2{\cdot}CH_3$
c, $R = OH$
d, $R = CH_2OH$

Similar derivation involving nuclear reduction could be given for gladiolic acid (XXa) and dihydrogladiolic acid (XXb) found in *P. gladioli*[40]. They are obviously related to cyclopaldic acid (XIVa) and cyclopolic acid (XIVb) and involve one more stage (nuclear reduction) in evolution.



XX a, $R = CHO$
b, $R = CH_2OH$

Flavoglaucin (XXIa) and auroglaucin (XXIb) are two related toluquinols occurring in moulds of *Aspergillus glaucus* series[42,43]. The corresponding quinones have not been so far isolated. They are clearly deivatives of the C_8 unit having undergone, among other changes, chain lengthening in the 3 and 6-positions, nuclear oxidation and nuclear reduction. The aldehyde group of the original precursor (I) instead of undergoing oxidation to the carboxyl (IV) has undergone reduction to a methyl (unit IIa) and the new side chain in the 3-position is branched just as in the case of mycophenolic acid.



XXI

$R_1 = CO-CH=C(CH_3)_2$

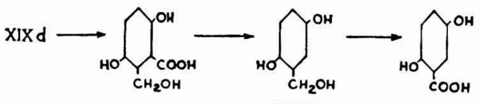
a, $R_2 = C_7H_{15}$

b, $R_2 = -(CH=CH)_3-CH_3$

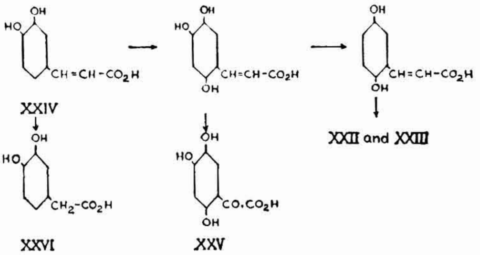
The incidence of nuclear reduction was postulated earlier in the evolution of anthoxanthins[23]. For example, primuletin (5-hydroxy flavone) and gardenin were considered to involve a stage of reduction of the 7-hydroxy group and reso-compounds of the type of robinetin and fisetin, a stage of reduction of the 5-hydroxy group. The laboratory analogy of this reaction would be the reduction of the appropriate tosyl ester by hydrogen in the presence of a catalyst (Raney nickel)[44]. Similar appropriate ester formation and reduction in the presence of an enzyme catalyst could be visualized as producing these changes in the mould systems.

The origin of gentisyl alcohol (XXII) and gentisic acid (XXIII) metabolic products of *Penicillium patulum*[45] and *P. griseo-fulvum*[46] respectively could also be traced to the C_8 unit. The occurrence of 6-methyl salicylic acid has already been discussed. Though the 6-hydroxy-methyl compound (XIXd) has not so far been isolated from moulds, its formation could be taken as being quite in accordance with the postulates of the theory. From this acid, a stage of para nuclear oxidation and decarboxylation leads to gentisyl alcohol and its side chain oxidation to gentisic acid.

The above derivation may not be unique for these two simple substances. But there is good support for it as the stages in the evolution could be traced among compounds occurring in moulds. The alternative course would involve caffeic acid (XXIV) (C_9 system) undergoing transformations as indicated in the following formulae. This is probably the preferred process for the production of trihydroxy phenyl glyoxalic acid (XXV) and homoprotocatechuic acid (XXVI) occurring in *Polyporus tumulosus*[47].



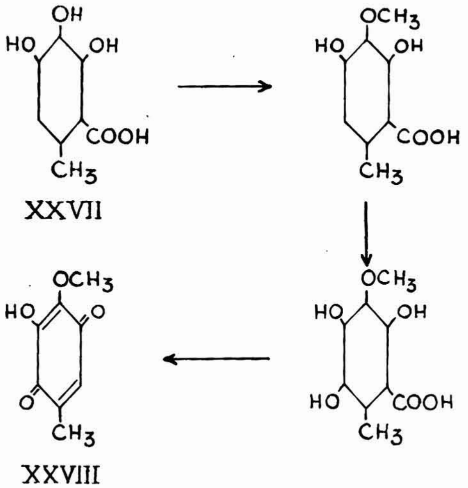
XXII XXIII

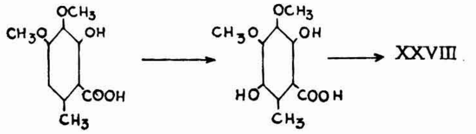


Toluquinone derivatives

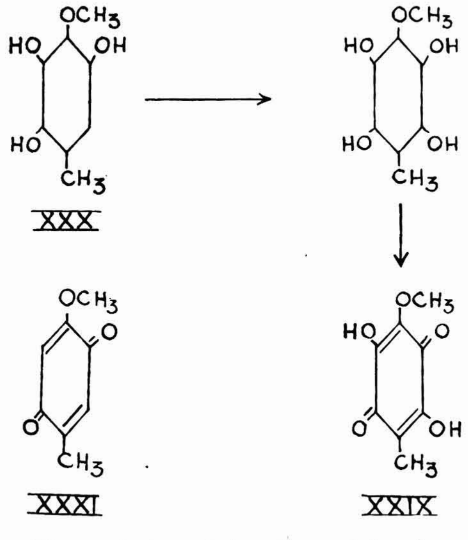
Among mould products quinones occur usually in association with quinols and obviously constitute oxidation-reduction systems. Many of them contain C-methyl groups and seem to be capable of derivation from the C_8 unit. As important intermediates may be mentioned 3-hydroxy orsellinic acid (XXVII) and 5-hydroxy orsellinic acid (XII) whose evolution by nuclear oxidation has already been discussed[23]. The formation of fumigatin (XXVIII), a metabolic product of *Aspergillus fumigatus*[48], could be developed from 3-hydroxy orsellinic acid through stages involving methylation, oxidation and decarboxylation.

The partial methylation of the 3-position may require explanation. It may involve preliminary protection of the more reactive 4-hydroxy group. It is also possible to visualize a different course in which the dimethyl ether is involved. During the final stage of oxidation to form the quinone, demethylation of the neighbouring methoxyl can occur. This is known to be a facile process in the laboratory and takes place very readily in the presence of mild alkali or acid[49,50].



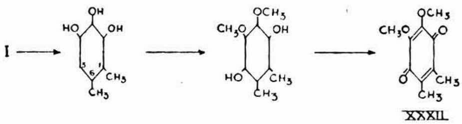


From fumigatin to spinulosin (XXIX), a product occurring in another species of *A. fumigatus*[51], is an easy stage of para nuclear oxidation; probably the quinol of fumigatin (XXX) is involved in this process.

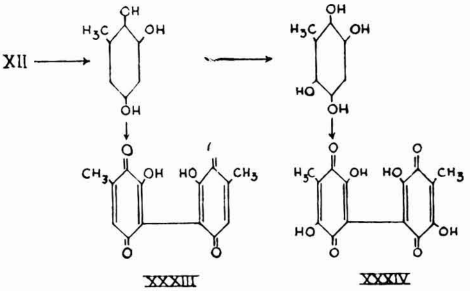


The evolution of 4-methoxy toluquinone (XXXI) a metabolic product of *Coprinus similis* and *Lentinus degner*[52] becomes clear when its structure is compared with that of fumigatin. It would involve an extra stage of nuclear reduction.

Aurantiogliocladin (XXXII), a quinone which has been recently discovered in a species of *Gliocladium*[53,54], can also be derived from the C_8 unit by a series of changes analogous to the route mentioned for the biogenesis of fumigatin. The only difference is that the aldehyde group of the original precursor (I), instead of undergoing oxidation to the carboxyl and getting eventually eliminated, suffers reduction to a methyl (unit IIa), as indicated earlier, which persists to the end of the evolution. 4-Methoxy toluquinone (XXXI) represents a type derived from 3:5-dihydroxy orsellinic acid.

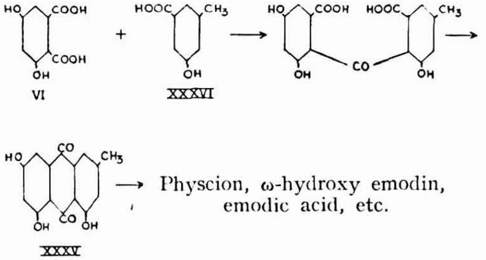


As compounds derived from 5-hydroxy orsellinic acid (XII) may be mentioned phoenicin (XXXIII)[55,56] found in *Penicillium phoeniceum* and öosporein (XXXIV) found in *Öospora colorans*[57]. In these compounds the simple quinone units have further undergone coupling by dehydrogenation.

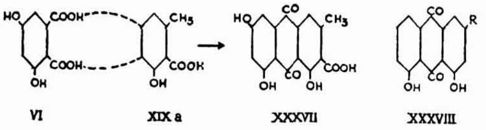


Anthraquinone derivatives

Among mould products, the anthraquinone derivatives occupy a special place. They seem to be very readily formed from glucose in very high yields and some moulds contain them in very high concentration, for example, helminthosporin (LIII) and catenarin (XLIX), occurring together in the fungus *Helminthosporium gramineum*[58] constitute about 30 per cent of its dry weight. These compounds have also been considered by Raistrick to be involved in oxidation-reduction mechanisms since the corresponding anthranols accompany them. Some attention has been given earlier to the possible biogenesis of a few of these compounds. In his tentative scheme for the evolution of physcion (XLVI), frangula emodin (XXXV) and its derivatives, Tatum[59] utilized DHP (VI) as one intermediate which was considered to condense with another intermediate 3-methyl-5-hydroxy benzoic acid (XXXVI). The former was known to occur in mould products, whereas the latter was hypothetical.



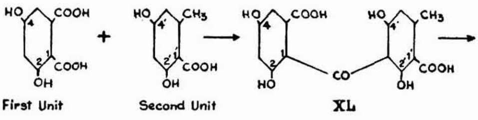
The above idea was adopted by Raistrick[60] who substituted 6-methyl salicylic acid (XIXa) for the second intermediate in order to work out the possible evolution of endocrocin (XXXVII).

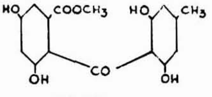


Since chrysophanol (XXXVIII, $R = CH_3$) happens to have the simplest structure, the suggestion has been made[61,62] that it should be considered to be the parent substance of this group of compounds and the others should be evolved from it. But no scheme has been worked out in support.

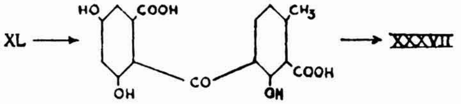
It may be mentioned at this stage that the anthraquinone molecule has been known to be highly stable and unreactive under mild conditions, particularly for electrophilic reagents. Nuclear oxidation with alkaline persulphate does not take place to any appreciable extent with hydroxy anthraquinones[63]. It is true that because of the high stability of the structure drastic methods could be adopted successfully. But these vigorous reactions do not provide correct laboratory models for biosynthesis. However, nuclear reduction seems to be comparatively more easy[44]. Hence in the following discussion nuclear oxidation will not be suggested after the anthraquinone skeleton has been built up whereas no such limitation will be placed for nuclear reduction.

A survey of lichen and mould anthraquinones leaves no doubt about their evolution from two C_8 units. The validity of the DHP unit (VI) as one of them follows from the fact that it is a derived C_8 unit and its status should be as important as that of orsellinic acid since it occurs free in mould products. It seems to constitute an important part of anthraquinone structures. The second C_8 unit seems to undergo greater modifications as will be indicated in the sequel. Sulochrin (XXXIX) occurring in the mycelium of *P. brevi-compactum*[64] may be considered to be related to the mould anthraquinones and it probably represents an earlier stage in evolution. The first step would be the linking up of the DHP unit with an orsellinic acid unit in position 3 of the latter, a position that is known to be highly reactive, to form the intermediate (XL). Subsequent decarboxylation would yield sulochrin. The carboxyl group that persists, probably owes this survival to an earlier esterification.



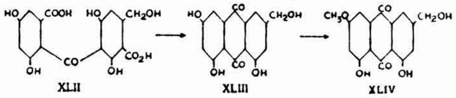

XXXIX

(a) *Frangula emodin derivatives* — Endocrocin (XXXVII) would represent a simple type since its construction follows readily from the above intermediate (XL). It would further involve only nuclear reduction of the 4′-hydroxy group of the right half to give (XLI) and subsequent ring closure. Such reactions have already been shown to occur in benzene derivatives. Whereas in sulochrin the second C_8 unit has suffered earlier decarboxylation, in endocrocin there is nuclear reduction and anthraquinone ring closure.

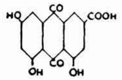


XLI

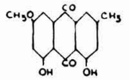
The two related anthraquinones frangula emodin (XXXV) and physcion (XLVI) follow endocrocin, the former involving a further stage of decarboxylation and the latter both decarboxylation and partial methylation of the reactive 7-hydroxy group. ω-Hydroxy emodin (XLIII) and teloschistin (XLIV) are closely related substances having a primary alcoholic group in the 2-position instead of a methyl group and are evolved from the intermediate (XLII). It seems to be reasonable to suggest that they represent an earlier stage in evolution as compared with emodin and physcion which should involve an extra stage of side chain reduction. It may be that this reduction took place earlier in the independent C_8 unit or later in the anthraquinone stage. In nature these ω-hydroxy derivatives accompany the corresponding reduction products, cf. the occurrence of teloschistin and physcion in the lichen *Teloschistes flavicans*[65]. This suggestion that hydroxy-methyl compounds represent an earlier stage should be acceptable because it follows from the theory of the evolution of the C_8 units and further on this basis the evolution of emodic acid (XLV) would only involve a stage of easy oxidation. An example where these related compounds having the alcohol, methyl and carboxyl groups occur together is provided by aloe emodin (XXXVIII, $R = CH_2OH$), rhein (XXXVIII, $R = COOH$) and chrysophanol (XXXVIII, $R = CH_3$)[66].



XLII XLIII XLIV

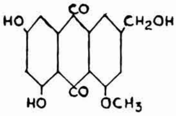


XLV

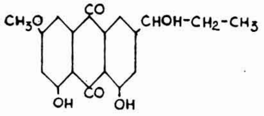


XLVI

Carviolin (XLVII) as a methyl ether of ω-hydroxy emodin requires some comment. The methylation has taken place in the less reactive hydroxy group. Obviously the 7-position has received earlier protection by some method. This point has been noted in connection with benzene derivatives also. Nalgiovensin (XLVIII) is closely related to teloschistin with the side chain lengthening according to processes already discussed in connection with lichen acids and the compactones.

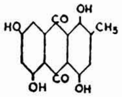


XLVII

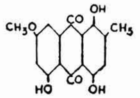


XLVIII

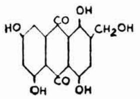
Other emodin derivatives like catenarin (XLIX), erythroglaucin (L) and tritisporin (LI) are obtained as the result of additional stages of nuclear oxidation in the 1-position. The first of these is related to emodin (XXXV), the second to physcion (XLVI) and the third to ω-hydroxy emodin (XLII). These reactions should be considered to take place conveniently in the pre-anthraquinone stages.



XLIX

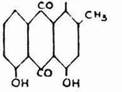


L

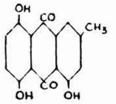


LI

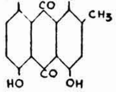
Whereas frangula emodin derivatives needed for their formation nuclear reduction in the 4′-position of the second C_8 unit, chrysophanol derivatives result from a further nuclear reduction in the corresponding position of the DHP unit. Chrysophanol itself is related to emodin (XXXV); islandicin (LII) is similarly related to catenarin (XLIX). As compared with these two, helminthosporin (LIII) and cynodontin (LIV) involve additional nuclear oxidation of position 5 in the DHP unit.



LII

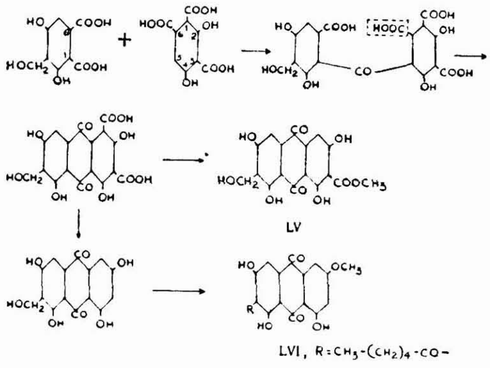


LIII

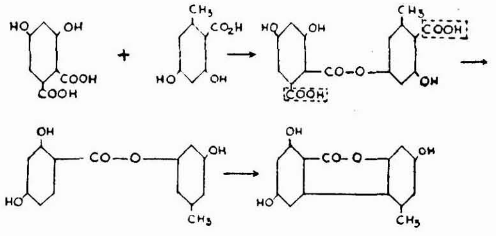


LIV

(b) *β-Orsellinic derivatives* — All the anthraquinones already mentioned are derived from DHP and orsellinic acid and have no further nuclear alkyl groups. Rhodocladonic acid (LV) and solorinic acid (LVI), on the other hand, are comparable to the β-orcinol derivatives occurring in depsides and depsidones. Actually these two compounds are found to occur in lichens[67] and have not so far been detected in mould products. The difference between them is small and is confined to minor details. According to the constitutions suggested for them they seem to result from a different sequence of reactions as compared with other anthraquinones mentioned above. The anthraquinone ring closure itself seems to have involved two derived DHP units. Since the 3-position in the second unit has been occupied by a substituent (carboxyl in this case probably resulted by the oxidation of CH_2OH), the linking is initiated by an attack on the 5-position. Subsequently instead of obtaining the required vacant nuclear position by the removal of the hydroxyl in the 4-position (nuclear reduction) this seems to be secured by a ready decarboxylation in the 6-position. The relevant steps in the evolution of the two anthraquinones are represented below.



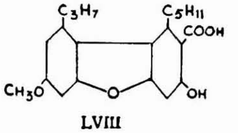
In this connection may be mentioned the interesting case of alternariol (LVII)[68] which is described as a dibenzo-α-pyrone and which can also be considered to be a diphenyl derivative. Its evolution from two C$_8$ units seems to be quite possible, the important modifications involved being decarboxylation in the appropriate positions and subsequent diphenyl formation by dehydrogenation. Obviously the initial stage is depside formation between a DHP unit and an orsellinic acid unit. Somewhat similar reactions are met with in the case of diphenyl ethers whose consideration follows.



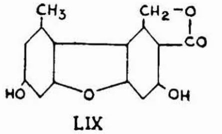
LVII

Dibenzofurans

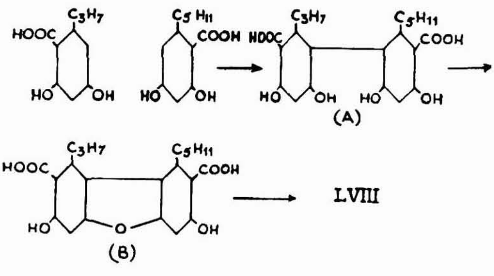
The anthraquinones represent compounds in which two C$_8$ units have condensed together. A simpler combination of two such units would be depsides and depsidones. A third variation is represented by the dibenzofuran derivatives, viz. didymic acid (LVIII)[69] and strepsilin (LIX)[70]. These are found in the lichens. The formation of dibenzofurans is somewhat analogous to the formation of ellagic acid from gallic acid, the diphenyl link (A) being formed between two C$_8$ units by dehydrogenation in the reactive 5-positions. Subsequent elimination of water from the two hydroxyl groups in (A) would lead to the formation of the dibenzofuran system (B). Decarboxylation and methylation of the unprotected (unchelated) hydroxy group would then yield didymic acid. The evolution of strepsilin could also be understood on the same basis except for the difference that the second C$_8$ unit has a hydroxy-methyl group in the 6-position instead of a methyl group and this leads to the lactone formation.



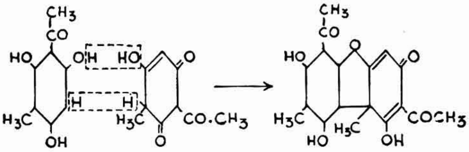
LVIII



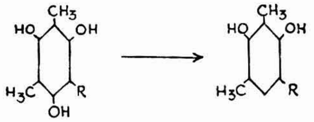
LIX



Usnic acid (LX), an important lichen acid, could be taken to be another dibenzofuran derivative. But it does not contain C_8 units. It is derived from two C-methyl phloroacetophenone units (LXI)[71]. Incidentally it may be mentioned that such nuclear methylated resacetophenone derivatives as clavatol (LXIIa) occurring in *Aspergillus clavatus*[72] and sorbicillin (LXIIb) occurring in *Penicillium notatum*[73] could be considered to be derived from the related phloroacetophenones (LXIII) by a process of nuclear reduction.



LXI LX



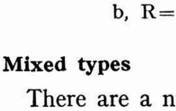
LXIII LXII

a, $R{=}CO{\cdot}CH_3$

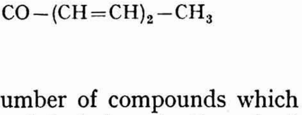
b, $R{=}CO{-}(CH{=}CH)_2{-}CH_3$

Mixed types

There are a number of compounds which could be considered to belong to the mixed type in which a C_8 unit has undergone condensation with a phloroglucinol unit. A simple example of this category is lichexanthone (LXIV)[74,75] in which (A) is an orsellinic acid unit and (B) is a phloroglucinol unit. Ravenellin (LXV)[76] contains a modification of the two units. The phloroglucinol part (B) has undergone a nuclear reduction to resorcinol; the other unit (A) is a derived orsellinic acid in which there is a carboxyl group in the 3-position which is used for the xanthone condensation. Nuclear oxidation in the 5-position and decarboxylation of the original carboxyl group in the 1-position are other modifications in the C_8 unit.

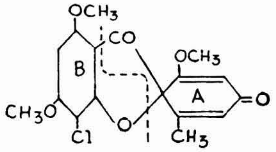


LXIV



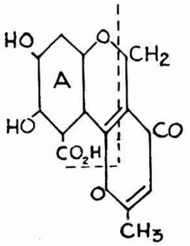
LXV

Under this category may also be mentioned griseofulvin (LXVI), a substance of extraordinary structure occurring in *P. griseofulvum*[77]. The existence of the C_8 unit (A) and the phloroglucinol unit (chlorinated) (B) are indicated in the structure.

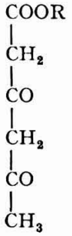


LXVI

Another compound is citromycetin (LXVII) occurring in *P. frequentans*[78] and having rings of various types. The C_8 unit (A) is an oxidized one (para nuclear oxidation) and has undergone condensation with a 6-carbon system having an acetyl-acetoacetic ester framework.



LXVII



$COOR{-}CH_2{-}CO{-}CH_2{-}CO{-}CH_3$

Thus a large number of compounds belonging to the category of lichen and mould products fall into one scheme based on the orsellinic (C_8) unit. Further additions may be made to this list in future. There may be a number of others which do not fall into this scheme and are obviously derived from other well-known units. However, there seems to be little doubt that just like the C_5, C_6 and C_9 units, this new orsellinic unit (C_8) plays an important role in the biosynthesis of a large group of compounds. From the enumerations given in this paper, the evolution of remote types can be followed stage by stage from the fundamental unit, and the transformations involved have well-known laboratory analogies. The application of these ideas may be expected not only to systematize existing knowledge making the chemistry of these substances easy to follow, but may also help future study of new compounds and lead to more easy synthesis of these substances.

Summary

Like lichen depsides and depsidones, a large number of mould products also fall into the scheme of biosynthesis based on the orsellinic unit (C_8 unit). Benzene derivatives and toluquinones contain one C_8 unit each whereas anthraquinones and others are made up of two such units. Mixed types are combinations of this unit with others. The evolution of remote types can be followed stage by stage from the fundamental unit.

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INDIAN NATIONAL COMMISSION FOR UNESCO — FIRST CONFERENCE, 9-11 JANUARY 1954 — *Continued from page* 105

Philosophical Congress, the Indian History Congress, etc. The Science Sub-commission consists of nominees of the Council of Scientific & Industrial Research, the National Institute of Sciences of India, the All-India Council for Technical Education and the Inter-University Board. The Sub-commission for Culture consists of nominees of the Inter-University Board, the Sangeet Natak Akadamy and the Academy of Letters and the Academy of Fine Arts (when they are formed).

The three Sub-commissions, which met on 10 January, held preliminary discussions on various measures which could be recommended to the Unesco. The Sub-commission on Science was of the opinion that in order to develop the scientific attitude among the people of the east, study of science and scientific principles should be integrated with basic and fundamental educational programmes and popular science should be given weight in this integration.

It was felt that the introduction of suitable new crops in the arid, semi-arid and humid zone research programmes, already being undertaken by the Unesco, would help in the solution of the food problem.

The meeting also discussed the case for establishing a centre for studies in environment physiology, a central astronomical observatory in India for co-operating in international astronomical programmes and a high-pressure technology laboratory.

The establishment of a centre for the development of mechanical appliances to help cottage and small-scale industries was also considered.

The Commission emphasized the desirability of having two types of science museums, the bigger ones for the bigger cities and smaller ones to be attached to the 30 universities of India.

The meeting recommended the establishment of an Electronic Computation Centre in India or in some other country in this region.

Kaka Saheb Kalelkar, Prof. A. R. Wadia and Prof. Mohd. Mujeeb were elected as Chairman, Vice-Chairman and Rapporteur respectively of the Education Sub-commission. The members elected for the other two Sub-commissions are Prof. S. N. Bose, Dr. D. S. Kothari and Dr. B. Mukerji for Science and Mr. R. P. Masani, Mrs. Kamaladevi Chattopadhyay and Dr. V. Narayana Menon for Culture.

Radiation Patterns of Small Pyramidal Horn at 3·3 cm.

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THE transmitting patterns of small horn radiators are of considerable practical importance because they are often used as primary feeds for composite directional aerials. The problem of predicting field patterns due to horn radiators is similar to the calculation of the diffraction field produced by a rectangular aperture in an infinite screen when illuminated by a point source. The problem was solved by Kirchoff on the optical theory and later Stratton and Chu[1] and Schelkunoff[2] gave another solution for sectoral horns after considering the defects of Kirchoff's solution. The experimental verification of these formulae was taken up by Woonton and co-workers[3-5] for horns of slant lengths 25, 50 and 100 cm., and an aperture of 10 wavelengths square. It is clear from their graphs that the formulae derived from physical optics can predict E plane graph with good accuracy and H plane pattern with a fair accuracy for the horn sizes taken by them. The observations reported in the present communication were taken to determine the situation with regard to very short horn radiators. The horn used by us had an aperture of 4λ × 3λ with a slant height of 6λ only.

Apparatus and measurement technique

The technique used in the measurements is similar in principle to that described by Silver[6] and used by Woonton[4] for near pattern measurements. A schematic arrangement of the apparatus is shown in Fig. 1. The horn radiator is fed by a microwave line including a matching section, a frequency meter and an attenuator. The microwave energy is supplied by a square-wave modulated reflex Klystron 2K39. The radiation pattern is drawn by picking up microwave energy in various directions at a constant distance from the centre of the horn aperture. The energy is picked up by a crystal detector mounted in a short piece of X-band wave guide moving on a thin rod which is graduated and bent in the form of an arc centred on the midpoint of the horn aperture. The modulation output of the crystal detector is amplified by a low-noise, high-gain tuned amplifier and recorded by an a.c. voltmeter. Due to the short aperture of the horn, the Fresnel zone is limited to a short distance and so the radiation pattern could be observed inside the laboratory hall. The horn radiator and the pick-up were kept 5 ft. above the ground and mounted well away from the walls. No trouble due to reflections was experienced after removing all the large reflecting objects from the neighbourhood.

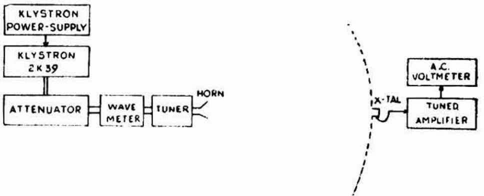

FIG. 1 — SET-UP FOR RADIATION PATTERN MEASUREMENTS

Results and discussion

The patterns in the E and H planes taken at two distances are shown in Figs. 2-5 while Fig. 6 shows the axial pattern. The slight asymmetry in the patterns is due to slight imperfections in the construction of the horn. The solid line graphs shown in Figs. 2 and 4 are calculated by the Kirchoff's formula[3,7]

$$|E| = \frac{ab\lambda}{2(a+b)}\left[\left\{\int_{-v_1}^{+v_2} \cos\frac{\pi v^2}{2}\,dv\right\}^2 + \left\{\int_{-v_1}^{+v_2} \sin\frac{\pi v^2}{2}\,dv\right\}^2\right]$$

where E = the absolute value of the electric field strength; a = slant length of the horn from mouth to vertex; b = the distance of the receiver from the horn aperture; and λ = the wavelength of radiation.

$$V_1=\sqrt{\frac{2a}{\lambda}}\left(\frac{W}{2a}+\phi\right) \text{ and } V_2=\sqrt{\frac{2a}{\lambda}}\left(\frac{W}{2a}-\phi\right)$$

where ϕ is the angle in radians and W is the width of the horn mouth.

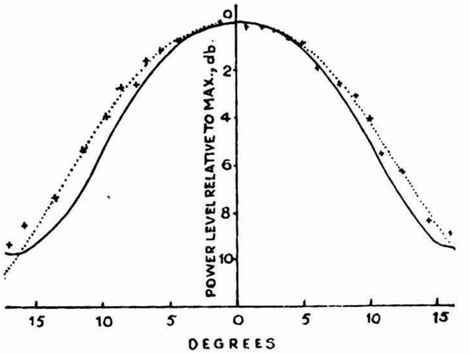

FIG. 2 — RADIATION PATTERN IN E PLANE AT 250 CM. [(×—×), experimental; (———), theoretical (optical slit); and (.........), theoretical (sectoral horn)]

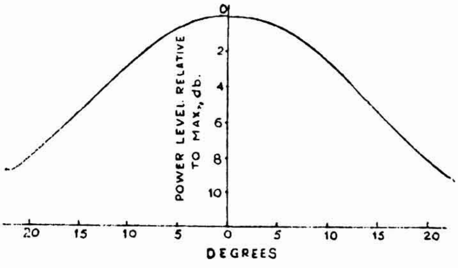

FIG. 3 — RADIATION PATTERN OF HORN IN H PLANE AT 250 CM. (EXPERIMENTAL)

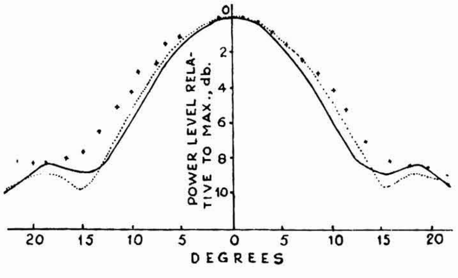

FIG. 4 — RADIATION PATTERN OF HORN IN E PLANE AT 1 METRE [(×—×), experimental; (———), optical pattern; and (.........), sectoral horn pattern]

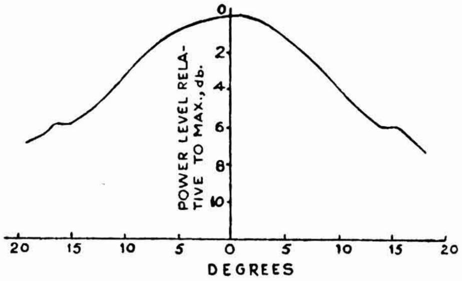

FIG. 5 — RADIATION PATTERN OF HORN IN H PLANE AT 1 METRE (EXPERIMENTAL)

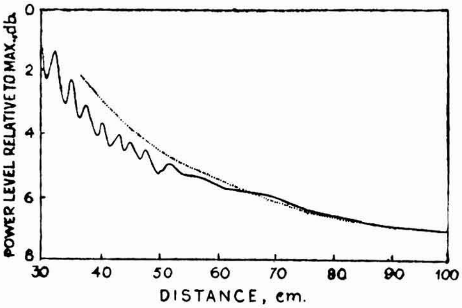

FIG. 6 — AXIAL FIELD PATTERN OF THE MICROWAVE HORN AT 3·3 CM. WAVELENGTH [(———), experimental; and (.........), theoretical]

The values of the Fresnel integrals are calculated with the help of the Cornu's spiral. It is seen that there is good agreement between the observed and theoretical graphs for small angles only, whereas for larger angles, the experimental values are about 2 db. more than the calculated values. The values for the dotted curve have been calculated by the sectoral horn formula[8]

$$\left|E_{\xi,\eta}\right| = \left|\frac{E_o}{2\lambda R}\right| \left| e^{j\frac{\pi}{2}\cdot\frac{B^2}{4A}} \int_{-a/2}^{+a/2} \exp.\left[-j\frac{\pi}{2}\left(\sqrt{A}y-\frac{B}{2\sqrt{A}}\right)^2\right]dy + e^{j\frac{\pi}{2}\cdot\frac{C^2}{4A}} \int_{-a/2}^{a/2} \exp.\left[-j\frac{\pi}{2}\left(\sqrt{A}y-\frac{C}{2\sqrt{A}}\right)^2\right]dy \right|$$

$$\times \left| e^{j\frac{\pi}{2}\cdot\frac{F^2}{4D}} \int_{-b/2}^{+b/2} \exp.\left[-j\frac{\pi}{2}\left(\sqrt{D}x-\frac{F}{2\sqrt{D}}\right)^2\right]dx \right|$$

where (ξ,η) = the co-ordinates of the receiver;

E_0=field at the aperture; λ=the wavelength of radiation; a=length of the horn aperture; and b=breadth of the horn aperture.

$$A=\frac{2}{\lambda}\left(\frac{1}{l_H}+\frac{1}{R}\right),\ B=2\left(\frac{2\eta}{\lambda R}+\frac{1}{a}\right),\ C=2\left(\frac{2\eta}{\lambda R}-\frac{1}{a}\right),$$

$$D=\frac{2}{\lambda}\left(\frac{1}{l_E}+\frac{1}{R}\right) \text{ and } F=\frac{4\xi}{\lambda R}$$

where R is the distance of the receiver from the horn aperture and l_E and l_H are the E and H plane slant heights respectively of the horn.

It is seen that there is good agreement between the observed values and those calculated by the electromagnetic sectoral horn theory over an angle of ±15°. This agreement is much better than that observed for large horns by other workers[4]. It seems, therefore, that the sectoral horn theory can predict E plane radiation pattern for small horns well over a limited angle.

Fig. 6 shows the observed axial field pattern as well as the theoretical pattern calculated on sectoral horn theory. It is observed that the Fresnel zone is limited to about half a metre beyond which (in the Fraunhofer region) there is close agreement between the two curves.

Acknowledgement

Thanks are due to the Chairman, Radio Research Committee, Council of Scientific & Industrial Research, for permission to undertake and to publish this work.

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Indian Coal-tars: Part I

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IN India, coal-tar is mainly produced in coke ovens operating primarily for the production of coke (the tar being considered of minor importance). Most of the coal-tar produced in India is used for making road tar and as a furnace fuel. Some of the plants, however, recover naphthalene, solvent naphtha, etc.

The average production of coal-tar in India is 81,000 tons per annum, most of which comes from the Tata Iron & Steel Co. Ltd., Jamshedpur, and from the Indian Iron & Steel Co. Ltd., Burnpur. The yield of tar per ton of coal carbonized in India is nearly half of the yield obtained in U.K. and U.S.A. The yield of tar at gas works is about 10 gal. per ton of coal; from the coke ovens it is 4-5 gal. per ton.

The quantity of benzene, toluene and xylene obtained from Indian tars is reported to be negligible and the yields of light oil and middle oil are also low. Naphthalene, however, is reported to be present in fair amounts in some coke oven tars. The percentage of tar acids present in Indian tars is also low.

In view of the low yields and the inferior quality of tars from Indian coal, a subcommittee was appointed by the Council of Scientific & Industrial Research in 1949 to go into the question and it was decided that the Fuel Research Institute should undertake investigations on the following problems: (1) properties of various types of products produced at the byproduct ovens and correlate them with the operating conditions of

TABLE 1 — PARTICULARS OF THE COKE OVENS

NAME OF FIRM	DESIGN OF OVEN	WIDTH in.	LENGTH ft.	HEIGHT ft.	LOADING LENGTH ft.	LOADING WEIGHT tons	TYPE (REGENERATIVE OR WASTE HEAT)	CONDITION OF OVEN WALLS	OUTPUT PER RETORT tons	TOTAL OUTPUT tons
Bhowra Coke Co. Ltd., Bhowra	Vertical	20·0	33·0	8·3	31·0	9·0	Waste heat	Leakage	6·7	3300/month
Lodna Coke Co. Ltd., Lodna	do	19·5	35·0	8·0	34·0	8·5	do	Battery No. 1, no leakage; battery No. 2, slight leakage	6·4	87661/year
Loyabad Coke Co. Ltd., Loyabad	Koppers vertical flue transverse	19·5	34·0	7·5	6·5	8·0	Regenerative	Leakage	Varies from 4·0 to 6·5	73522/year
Bararee Coke Co. Ltd., Kusunda	Vertical with horizontal flues	17·3-18·5	37·4	8·3	36·0	10·0	Waste heat	do	7·0	210/day
Giridih Coke Plant, Giridih	Vertical fluid (Simon-Carves)	20·0	33·0	8·0	32·0	10·0 (approx.)	Regenerative	Condition bad (24 years old)	7·3	132/day
Tata Iron & Steel Co. Ltd., Jamshedpur	(a) Simon-Carves	17·8	44·5	14·5	41·5	19·0	do	Normal	15 ton/pushing or 17·0 ton/24 hr./oven	2790/24 hr.
	(b) W.C. ovens (horizontal)	17·7	39·4	10·5	38·0	11·5	Regenerative, rich gas fired	do	9 ton/pushing or 9·1 ton/24 hr./oven	459/24 hr.
Indian Iron & Steel Co. Ltd., Burnpur (battery Nos. 5 and 6)	Vertical	15-17 taper	37·4	10·6	35·0	10·4	Regenerative	Leakage	14·4/day	1100/day
Indian Iron & Steel Co. Ltd., Burnpur (battery No. 7)	do	17-19 taper	45·0	15·0	43·4	20·0	do	No leakage	22·2/day	1600/day
Bombay Gas Corporation Ltd., Bombay	Horizontal	24	20·0	16·5	17·0	13·5 cwt.	do	Slight leakage	—	—

the ovens; (2) fundamental investigations on the nature of tar from various Indian coals and their relation to petrographic constituents of coal; and (3) installation of pilot plant high temperature narrow ovens for carrying out carbonization of weakly and medium coking coals and for obtaining increased yields of tar and byproducts from such ovens. Investigations were accordingly initiated at the Fuel Research Institute and this paper reports the results of investigations on the quality of coal-tars from several coke plants in the country.

Many of the coke ovens now in use in India are old (20 years or more) and some are in a very bad condition. The data concerning the type, capacity, etc., of the existing coke ovens and the operating conditions are summarized in Table 1. A comparative statement on the dimensions of coke ovens employed in Great Britain and India is given in Table 2. The types of coal used in the different coke plants together with the yield of tar are given in Table 3.

Materials and methods — Samples of tar in 5 gal. lots were received from the following firms: (1) Tata Iron & Steel Co. Ltd., Jamshedpur; (2) Indian Iron & Steel Co. Ltd., Burnpur; (3) Bararee Coke Co. Ltd., Kusunda; (4) Lodna Coke Co. Ltd., Lodna; (5) Loyabad Coke Co. Ltd., Loyabad; (6) Bhowra Coke Co. Ltd., Bhowra; (7) Giridih Coke Plant, Giridih; (8) Oriental Gas Co. Ltd., Calcutta; and (9) Bombay Gas Corporation Ltd., Bombay.

The tar samples were examined for the following: distillation cuts, water content, tar acids, " ash-free " free carbon, crude naphthalene, crude anthracene, etc. The yields of distillates and tar acids are recorded in Tables 4 and 5 respectively. The analyses of the coke oven gases from different sources are given in Table 6.

TABLE 2 — DIMENSIONS AND PERFORMANCE OF COKE OVENS IN U.K. AND INDIA

PARTICULARS		U.K.		INDIA
		Pre-war	Modern	
Oven dimensions	Length, ft.	30-33	40-45	33-45
	Height, ft.	5·75-7·50	12-20	7·5-15·0
	Width, in.	17-22	14-20	15-20
Charge, tons		8-12	15-25	8-20
Coking time, hr.		28-36	12-22	20
Throughput per day per oven, tons		6-8	25-30	4-22

TABLE 3 — COALS USED IN COKE OVENS*

NAME OF FIRM	TYPE OF COAL CARBONIZED	VOLATILE MATTER IN DRY COAL %	ASH IN DRY COAL %	TAR YIELD (GALLON) PER TON OF COAL
Bhowra Coke Co. Ltd., Bhowra (metallurgical)	Bituminous from Jharia and Katras fields, 11, 12, 14, 15 and 16 seams	22·88	15·34	5·8
Lodna Coke Co. Ltd., Lodna	12, 13, 14 and 15 seams	23·00-24·00	16·22	4·6
Loyabad Coke Co. Ltd., Loyabad	Jharia coalfields, Barakar measures, 14 and 15 seams	26·00	15·70	4-5
Bararee Coke Co. Ltd., Kusunda	Jharia, Sel. grade, mostly 14 and 15 seams	27·60	12·68	5·0
Giridih Coke Plant, Giridih (metallurgical)	Coking, Khuhurbaree seam	22·00-24·00	13·00-15·00	6·0 approx.
Tata Iron & Steel Co. Ltd., Jamshedpur (metallurgical)	Coking, bituminous	25·60	16·00	5·1
Indian Iron & Steel Co. Ltd., Burnpur (No. 7 battery, metallurgical)	Meta-bituminous	25·00-26·00	16·00-17·00	5·3
Indian Iron & Steel Co. Ltd., Burnpur (No. 7 battery, metallurgical)	do	25·00-26·00	16·00-17·00	5·5

*Data supplied by the respective coke-oven plants.

TABLE 4 — TAR DISTILLATION TESTS

SOURCE OF TAR	WATER %	OILS — " AS RECEIVED BASIS ", %						TOTAL OIL UP TO 360°C. %	PITCH %	LOSS %
		Up to 210°C.	210°-30°C.	230°-70°C.	270°-300°C.	300°-330°C.	330°-60°C.			
Bhowra Coke Co. Ltd., Bhowra	1·21	2·76	6·84	11·30	4·25	9·85	9·84	44·84	52·77	1·18
Lodna Coke Co. Ltd., Lodna	3·70	0·80	2·10	6·30	3·00	6·40	10·00	32·30	62·44	1·56
Loyabad Coke Co. Ltd., Loyabad	0·91	1·61	2·62	11·45	4·73	2·93	10·72	34·06	64·70	0·33
Bararee Coke Co. Ltd., Kusunda	1·73	1·20	2·70	8·30	5·90	10·80	11·20	40·10	58·00	0·17
Tata Iron & Steel Co. Ltd., Jamshedpur	3·17	1·26	3·23	11·37	1·90	4·80	8·29	30·85	64·97	1·00
Indian Iron & Steel Co. Ltd., Burnpur (battery No. 7, I sample)	3·60	1·18	4·71	7·78	5·34	4·24	8·64	31·89	62·88	1·63
Indian Iron & Steel Co. Ltd., Burnpur (battery No. 7, II sample)	4·61	1·50	1·70	5·61	6·24	6·51	8·16	29·72	63·78	1·89
Bombay Gas Corporation Ltd., Bombay	2·08	4·60	7·32	13·23	7·76	7·50	10·02	50·43	46·49	1·00
Oriental Gas Co. Ltd., Calcutta	2·68	8·30	10·10	7·70	8·90	5·20	10·60	50·80	45·60	0·92
Giridih Coke Plant, Giridih	0·85	2·83	5·40	9·59	6·36	6·74	12·43	43·35	54·93	0·87

TABLE 5 — ANALYTICAL AND OTHER TESTS

SOURCE OF TAR	TAR ACIDS %	FREE CARBON (ASH-FREE) %	CRUDE NAPHTHALENE %	CRUDE ANTHRACENE %
Bhowra Coke Co. Ltd., Bhowra	6·48	1·60	Negligible	2·61
Lodna Coke Co. Ltd., Lodna	0·50	17·08	3·66	3·55
Loyabad Coke Co. Ltd., Loyabad	1·09	11·40	8·00	4·90
Bararee Coke Co. Ltd., Kusunda	2·92	4·08	1·03	4·64
Tata Iron & Steel Co. Ltd., Jamshedpur	0·34	14·31	9·43	4·94
Indian Iron & Steel Co. Ltd., Burnpur (battery No. 7, sample II)	0·33	14·31	6·34	3·00
Indian Iron & Steel Co. Ltd., Burnpur (battery No. 7, sample I)	0·55	10·11	7·53	3·72
Bombay Gas Co.	13·47	9·23	Negligible	3·09
Oriental Gas Co., Calcutta	11·05	4·55	do	1·55
Giridih Coke Plant, Giridih	5·11	2·90	3·39	0·97

TABLE 6 — ANALYSIS OF COKE-OVEN GAS

SOURCE OF GAS	CO_2 %	UNSATURATED HYDROCARBONS %	OXYGEN %	CARBON MONOXIDE %	HYDROCARBONS (AS METHANE) %	HYDROGEN %	NITROGEN %
Bhowra Coke Co. Ltd., Bhowra	4·70	2·60	0·30	5·71	26·81	57·48	2·40
Bararee Coke Co. Ltd., Kusunda	4·40	2·50	0·80	6·50	22·90	55·80	7·10
Lodna Coke Co. Ltd., Lodna	3·90	2·40	0·90	8·50	26·80	55·20	2·30
Loyabad Coke Co. Ltd., Loyabad	5·90	2·95	1·31	6·23	18·56	57·23	7·82
Tata Iron & Steel Co. Ltd., Jamshedpur	3·60	2·70	0·90	9·30	22·50	50·20	10·80
Indian Iron & Steel Co. Ltd., Burnpur	3·90	2·20	0·30	7·10	23·70	52·20	10·60
Giridih Coke Plant, Giridih	4·95	3·30	1·32	4·95	29·12	42·74	13·62

Discussion

It will be seen from Tables 4 and 5 that the percentage of total distillable oils are higher in the tar samples from coke ovens at Bhowra, Bararee and Giridih, and the pitch content is 52-58 per cent as against 60 per cent in the samples from other plants. On the basis of tar acids, free carbon, naphthalene and anthracene content (TABLE 5), the tar samples can be grouped into the following categories: (i) Bhowra, Bararee and Giridih; (ii) TISCO, IISCO, Lodna and Loyabad; and (iii) gas works tars from the Bombay Gas Works and the Oriental Gas Works, Calcutta.

Tars from the first group contain appreciably higher percentages of tar acids but less naphthalene and free carbon compared to tars of the second group. There is apparently less cracking of the products during carbonization suggesting lower operating temperatures in the three plants of group 1. Although no reliable data regarding the oven operating temperatures were available, the data given in Table 5 show the relative degree of cracking in the ovens. It has been found in our experiments on the pyrolysis of phenol that the chief products of pyrolysis are aromatic hydrocarbons of the naphthalene type and carbon. This explains the higher percentages of free carbon and naphthalene and low yield of tar acids in highly cracked samples of tar in group 2. Table 3 gives the details of the types of coal generally used in coke ovens. Bituminous coals from the Jharia field having volatile matter of 22-28 per cent (30-35 per cent on unit coal) and containing 13-17 per cent ash are generally used for carbonization. Data from U.K. and U.S.A. indicate that the volatile matter of the coal used is usually above 30 per cent (32-35 per cent on unit coal) and the ash percentage is about 5. But the disparity in tar yields from the British coals and Indian coals cannot be explained on the basis of a higher percentage of foreign matter and the *pro rata* fall in amount of tar on unit coal basis. The calorific value of the volatile matter of coals used for carbonization is uniform indicating fair constancy of composition of volatile matter of different coals. Low tar yields in coke ovens in India are perhaps mainly due to the cracking of the tarry vapours due to longer period of contact with the " hot top " of the ovens.

The role of the finely disseminated shaly matter, common in Indian coals, in the cracking of tar has also been investigated, and the results of these studies are reported in the next part of this series.

The dimensions of the coke ovens used in India and the U.K. are given in Table 2. It is sometimes stated that the coke ovens now in use in India are of old design and need replacement by modern ones in order to increase the yield of tar. This is not entirely true and in any case the new ovens at the TISCO and the IISCO do not give greater yields of tar nor is the quality any better. The Beimann main (battery No. 7) installed by the IISCO at the Hirapur Works was expected to lessen the cracking and produce more tar, but the data (TABLE 4) show that there has been no such improvement. The yield of tar acids is remarkably low and percentage of free carbon high.

A higher yield of tar containing about 10 per cent of tar acids is obtained in gas works. Although the production of gas tar is not large, the high percentage of tar acids points to the desirability of tapping this tar as a potential source of such acids. Contamination of gas with air is noted in certain cases, particularly with Giridih, apparently due to leakages.

Nature of the tar acids — Tar acids from Bhowra and TISCO tars were extracted in bulk by conventional alkali treatment, and subjected to fractional distillation. These two tars were selected as they form the two extreme types of coke-oven tars of the first two groups.

Bhowra tar acids — 420 g. of tar acids extracted from about 16 lb. of tar were distilled under atmospheric pressure up to 250°C. The residue left over which constituted the high boiling fractions was distilled under 5-10 mm. pressure. The yield of fractions collected and their percentages with respect to total tar acids and tar are given in Tables 7 and 8.

TISCO tar acids — Tar acids (61 g.) recovered by bulk distillation of about 40 lb. of the tar were distilled at atmospheric pressure and the results are given in Table 9.

The residue was small and could not be distilled further like the other sample.

The fractionation of the two samples of tar acids shows that the Bhowra tar acids contain a considerable amount of high boiling tar acids, whereas the TISCO sample contains only about 13 per cent acids boiling

TABLE 7 — FRACTIONAL DISTILLATION OF TAR ACIDS

(*Quantity of tar acids distilled*, 420 *g.; distillation carried out a atm. pressure*)

BOILING RANGE °C.	WT. OF FRACTION g.	% FRACTION WITH RESPECT TO TOTAL TAR ACIDS	% FRACTION WITH RESPECT TO TAR
Below 175	2·34	0·56	0·03
175-85	1·34	0·32	0·02
185-95	11·22	2·67	0·16
195-205	120·21	28·60	1·66
205-15	86·23	20·60	1·19
215-25	29·81	7·10	0·41
225-35	13·42	3·20	0·19
235-50	8·02	1·19	0·11

TABLE 8 — DISTILLATION OF TAR ACIDS RESIDUE

(*Pressure*, 5-10 *mm. Hg*)

BOILING RANGE °C.	WT. OF FRACTION g.	% OF FRACTION WITH RESPECT TO TAR ACIDS	% OF FRACTION WITH RESPECT TO TAR
Up to 160	7·36	1·75	0·10
160-80	7·86	1·87	0·11
180-90	12·21	2·92	0·17
190-200	10·30	2·42	0·14
200-20	14·28	3·40	0·20
220-40	15·33	3·65	0·21
240-60	14·11	3·36	0·21
260-70	14·98	3·56	0·21
Residue (diff.)	51·18	12·11	0·71

TABLE 9 — DISTILLATION OF TISCO TAR ACIDS

(*Atmospheric pressure*)

BOILING RANGE °C.	WT. OF FRACTION g.	% FRACTION WITH RESPECT TO TOTAL TAR ACIDS	% FRACTION WITH RESPECT TO TAR
Up to 197	21·53	35·20	0·120
197-205	15·27	25·00	0·080
205-12	3·07	5·03	0·002
212-20	2·30	3·77	0·001
220-42	5·91	9·68	0·003
Residue (diff.)	12·92	21·32	0·070

above 242°C. Due to higher operating temperature in the TISCO ovens, the higher tar acids decompose giving low boiling fractions. The lower operating temperature of Bhowra Coke Co. ovens gives rise to less cracking resulting in more of high boiling fractions. The high percentages of naphthalene and anthracene in the TISCO tar probably result from the decomposition of the tar acids. With both the tars, however, phenol, cresols and xylenols form the major constituents of the tar acids.

Acknowledgement

Our thanks are due to Dr. J. W. Whitaker, the Director, for his kind suggestion of undertaking the work and for the valuable and helpful criticisms. Thanks are also due to Dr. A. Lahiri, the Deputy Director, for constant guidance and direction during the course of the investigation.

Model IV Fluid Catalytic Cracking Unit*

THE fluid catalytic cracking unit, which is being installed by the Standard-Vacuum Refining Co. of India Ltd. as a part of their new refinery at Bombay, incorporates one of the recent advances in fluid catalytic cracking. The unit is named Model IV because it represents the fourth development in applying the fluidized solids principle to the catalytic cracking of gas oil. The petroleum intermediate produced by this unit may comprise all or part of the fractions ranging from gasoline to asphalt. In some cases it may represent as much as 70 per cent of the crude oil but it does not contain any gasoline. The objective of catalytic cracking is to obtain the highest economical yield of high octane gasoline from the gas oil.

In catalytic cracking, a specific kind of catalyst, at a temperature of 1,100°F., is brought into contact with the hydrocarbon in such ratio of catalyst to oil that the final temperature of the mixture approximates to 900°F. The oil is cracked in the presence of the catalyst, and while the exact mechanism of the reaction is not clearly known, the result in terms of higher yields of higher octane products has been definitely established.

One of the basic problems in all catalytic cracking, however, is that of catalyst

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*Contributed by the Standard-Vacuum Refining Company of India Ltd., Bombay.

regeneration. After about 10 min. in the reaction phase of catalytic cracking, the catalyst receives a heavy coating of carbon. To burn off this carbon, the catalyst must be removed from the reactor to a second vessel, called the regenerator, where the carbon is burnt off the catalyst in the presence of air. It was in the method of catalyst transfer from reactor to regenerator and back again that the Standard Oil Development Co.'s " fluid " catalytic cracking units made such notable advances.

Over three years of research and development went into the creation of the first fluid catalytic cracking process by the Standard Oil Development Co. The original concept of mixing a highly heated catalyst with a hydrocarbon is still the basic cracking mechanism in use today. All fluid catalytic cracking units, whether they be models II, III or IV, are but design improvements on the fluid principle, and all the improvements gained as a result of research, development, pilot plants and operation of commercial size units since the first fluid catalytic cracking unit went into operation in 1942 are embodied in the new unit at Edmonton refinery of the Imperial Oil Ltd., Canada. Imperial is an affiliate of the Standard Oil Co.

The Model IV fluid catalytic cracking unit embodies an entirely new catalyst transfer system which eliminates the use of throttling slide valves for controlling the rate of catalyst transfer between vessels. The catalyst transfer between reactor and generator is controlled by altering the rate of air flow to the spent catalyst line. The tangential feed of both oil and air reduces erosion to the absolute minimum. In its construction, the Model IV requires 30 per cent less steel than the previous fluid units. Lower overall height, simplified vessel design, and simple reactor and regenerator internals have combined to produce a saving in terms of steel needed. Further, with all controls grouped at a single level, a smaller operating crew can run the unit and no elevator system is required.

The Model IV is more stable in operation and chances of reverse flow are minimized. A serious pressure differential between reactor and regenerator — a situation conducive to reverse flow — causes the catalyst to defluidize or form a temporary dense phase in the catalyst transfer line. As soon as the vessels are in balance again, the catalyst refluidizes and normal circulation is restored.

The design capacity of the Edmonton Model IV fluid catalytic cracking unit is 11,000 barrels per day, of which 8,510 barrels per day are fresh gas-oil feed (average API gravity, 25·7) and 2,490 barrels per day of recycle oil (API gravity, 11·8). From this combined stock the conversion to products boiling below 430°F. is 60 per cent. A CFFR clear octane of 96 is obtained. The design capacity of the Bombay Model IV fluid catalytic cracking unit is 7,570 barrels per day of combined fresh and recycle stocks. This unit has only 70 per cent of the rated capacity of the unit which recently went into operation at the Alberta refinery of the Imperial Oil Ltd., Canada.

The following account gives a brief description of the unit under construction and of the processing of oil with special reference to the hot catalyst process.

Vacuum flash unit — This unit is designed to produce 6,800 barrels per day of catalytic cracking feed stock from 9,360 barrels per day of a 40·5 per cent reduced Redwater crude. The unit consists of a vacuum tower, direct fired heater, vacuum producing equipment and the necessary auxiliaries such as heat exchangers, coolers, pumps, etc. The design of the vacuum tower, which is 68 ft. high and 20 ft. in diameter, also provides for the future installation of 23 trays for the production of 4 lubricating oil side streams. In the present operation for catalytic cracking stock only 11 trays are required. Adequate space has also been provided for the future addition of a stripping tower and the necessary exchangers and coolers for the lubricating oil operation.

Light ends recovery unit — This unit processes the overhead stream from the main fractionater of the fluid catalytic cracking unit. It comprises an absorber, 3 ft. 6 in. in diameter and 48 ft. high, a stabilizer, 4 ft. 6 in. in diameter and 66 ft. high, and a debutanizer, 4 ft. in diameter and 70 ft. high. These three towers plus the necessary auxiliaries such as drums, pumps, compressors, coolers and exchangers will separate the combined gas and gasoline from the fluid catalytic cracking unit into three main streams, viz. a dry gas mainly comprising propane and lighter, a butane-butylene fraction, and a debutanized gasoline.

Flow description — The reduced Redwater crude, either from storage or from the atmospheric pipe still, is pumped into the reduced crude surge drum. From this drum the main charging pump for the vacuum flash unit moves the oil through the first exchanger where its temperature is raised by heat exchange with the heavy gas oil as it passes through a reflux pump-around system. The reduced crude then moves to another exchanger where it picks up more heat from the asphalt bottoms being pumped from the bottom of the vacuum tower. The preheated crude then enters the direct fired tubular heater where its temperature is raised to achieve the maximum vaporization. Superheated steam also produced in the convection section of the direct fired heater is injected into the outlet tubes of the heater and into the transfer line to assist vaporization. This mixture of steam, oil vapour and heavy unvaporized residual passes into the vacuum flash tower where it is separated as follows: the heavy residue falls to the stripping section of the vacuum flash tower and is stripped to flash specifications and is then pumped through the heat exchanger where it gives up its heat to the entering charging stock; it is then blended with gas oil to specification viscosity, cooled, and sent to storage as bunker C fuel, or further processed to asphalt.

Two cuts are removed from the vacuum flash tower: heavy gas oil, which is also utilized in a pump-around system to exchange heat with the incoming feed, and a light gas oil, which is also used to reflux the tower after passing through a cooler. Steam, a small amount of uncondensed oil vapour, and inert gases flow from the top of the tower into a condenser where the steam and oil vapour are condensed and separated in a separating drum. The uncondensed steam and the inert gases are drawn through the steam ejector vacuum system so that the maximum vacuum may be maintained on the entire system for the purpose of effecting the maximum vaporization of the reduced crude. Another circulating stream is removed from one of the lower plates in the column and returned higher up the column for the purpose of maintaining an adequate liquid status on the lower plates so as to prevent entrainment of asphaltic particles which would contaminate the charging stock for the catalytic cracking unit. To assist further vaporization, and to reduce the viscosity in the direct fired heater, a small portion of the circulating stream is also pumped to the inlet of the heater, and mixed with the preheated reduced crude.

The light and heavy gas oil products from the vacuum flash unit flow to a surge drum from which the combined gas oil is pumped to the catalytic cracking system by way of heat exchanger with the circulating stream of the bottoms from the main fractionator. The stock, preheated to a temperature of *c.* 445°F., enters directly into the transfer line carrying regenerated catalyst from the regenerator to the reactor, where it mixes with the hot regenerated catalyst and is instantly vaporized. The mixture of oil vapours and powdered catalyst flow up into the reactor, where cracking takes place. The spent catalyst in the reactor, made inactive by coke deposition, flows down into the stripper section at the bottom of the reactor, and is thoroughly stripped by steam to remove heavy hydrocarbons. It then returns to the regenerator by way of the other transfer line. Air is injected into this line to control the rate of flow of spent catalyst up into the regenerator. The bulk of air for regeneration enters the bottom of regenerator and moves upward through the grid into the catalyst bed, where most of the coke is burnt off. The regenerated catalyst spills into the overflow and flows through the transfer line carrying regenerated catalyst, joins the charging stock, and the catalyst-oil cycle is completed.

The gases of combustion from the regeneration of the catalyst pass into a two-stage cyclone separator in which the greatest part of any entrained catalyst is removed. The gases then pass through a control valve and stack to the atmosphere. This valve maintains a pressure of 16·5 lb./sq. in. on the regenerator and is so controlled as to achieve a balanced pressure differential between the regenerator and the reactor for the purpose of controlling the flow of catalyst.

The products of reaction in the reactor also pass through a two-stage cyclone separator inside the reactor where practically all of the entrained catalyst in the vapour is removed. The vapours then pass directly into the bottom of the main fractionator, where they are separated into gas and gasoline as a top-of-column product, light gas oil, heavy gas oil, and bottoms. The light gas oil leaves the column and enters the side stream stripper to be stripped to flash specifications. It is then cooled and pumped to storage. Part of this stream leaving the column is pumped directly through a cooler to the absorber tower of the light end vapour recovery unit, where it functions as a lean absorption medium. Leaving the bottom of the absorber, it returns to the main fractionator, where it is separated into light gasoline fractions and light gas oil. The heavy gas oil fraction is removed from the column near the middle point and enters the lower section of the stripper, where it is stripped to flash specifications. The major part of this stream is the recycle stock which is pumped back to the cracking section for further conversion to gasoline. A relatively small portion of this stream moves to storage after cooling. Another portion is pumped to the reboiler of the stabilizer in the vapour recovery unit to provide heat for the fractionation required in the stabilization of the lighter products. The heavy gas oil fraction passes through a cooler and re-enters the main fractionator. The bottoms from the main fractionator are first pumped through a heat exchanger where they preheat the incoming charging stock to the cracking unit. The bottoms enter a steam generator, which provides substantial quantities of high pressure steam for use in the refinery. Feed water to this steam generator is also preheated by exchange with the light gas oil as it is being pumped from the stripper. A portion of the bottoms stream also returns to the reactor for further cracking.

The combined gas and gasoline vapour from the fractionator, removed as the overhead, pass through a cooler-condenser, where most of the liquefiable constituents are condensed. The mixture of liquid and gas enters the first separating drum, and water is removed at this point. The gas from this drum is compressed and sent to a second separating drum, where it is combined with the liquid pumped to this drum. The gas from this higher pressure separation flows directly to the absorber. Any condensable light fractions are absorbed by the light gas oil absorption medium and are recycled back to the main fractionator. Gas not condensed in the absorber goes to the plant fuel system.

The liquid leaving the second separating drum is pumped, after heat exchange, into the stabilizer with the stabilized gasoline leaving the bottom of the stabilizer. Gases lighter than butanes are removed and enter the plant fuel system, or are segregated as such. A portion of the overhead stream is condensed and returned to the column as reflux. The heavier stabilized gasoline fraction, containing mainly butanes, flows from the bottom of the stabilizer to the debutanizer after heat exchange with the feed. Here separation is effected between the butane fractions, butane-butylene fraction, and a debutanized gasoline fraction. The butane-butylene fraction is removed as a top-of-column product and part of this stream is also returned to the column to act as reflux. The debutanizer is equipped with a steam reboiler for providing the necessary heat for debutanization. The product leaving the column is cooled and moved to storage as debutanized gasoline.

REVIEWS

TELEVISION, by F. Kerkhof & W. Werner (Published by the Philips Technical Library, Eindhoven and distributed by Cleaver-Hume Press Ltd., London), 1952, pp. xv + 434 + 28 pages of appendix. Price Rs. 55

Messrs Kerkhof and Werner are the Principals of the Television Development Laboratory of Philips Industries, Eindhoven (Holland).

Vast amount of information has been published on the development of television during the past two decades and much of it is found scattered over many periodicals and publications from many countries. The biggest hurdle before a study of television can be undertaken is to know where to locate the information. The authors have done a very good job in putting together all the extensive and varied information on television in one book. This book deals very thoroughly with the British and Continental systems, as well as the American system. Such treatment is rarely available in U.S. publications which mostly concentrate on the U.S. standards.

The reader is expected to be a graduate with radio engineering as his special subject to make the best use of the book. Initial knowledge of calculus, differential equations, transmission lines and wave filters would be helpful. However, there is no reason why an intelligent reader of lesser qualifications should not derive much benefit from this book even if he has to omit the intricate mathematical portions.

This book uses the MKS system of units for calculations and even for ordinary measurements French system is commonly employed. For example, the 17 or 21 in. tube is referred to as 45 or 55 cm. tube.

The introductory chapter gives the special physical properties of the human eye and the composition of the TV picture, the relation between the band width and the quality of the picture reproduced, and block diagrams of the transmitting and the receiving chains. The propagation properties at the TV carrier frequencies have also been briefly discussed.

In chapter 2, starting with a full mathematical treatment of the motion of electrons in electrostatic and electromagnetic fields, the authors have given a good treatment of electron optics. The gun, focusing and deflection are other topics discussed.

Chapter 3 deals descriptively with Farnsworth image dissector, the iconoscope, the orthicon and image-orthicon pick-up tubes. The receiving picture tube is described at the end. This, perhaps, could have been the starting point.

Chapter 4 deals with various standards for television signals, and the basic informations, i.e. the horizontal and vertical sync, the picture information and sound that this signal must carry in order to reproduce the original picture. The difference between the British and U.S. systems and the CCIR standards have been very well discussed. The different methods of d.c. restoration under various systems are given. Methods of sync separation for the negative and positive modulations are also discussed.

Chapter 5 deals with pulse generators and multivibrators. Methods of locking the picture to the mains frequency and derivation of vertical and horizontal sync pulses have been discussed.

Chapter 6 discusses the electrostatic and electromagnetic deflection and time-base generators. The discussion on electrostatic deflection is very short and some discussion on the latest large screen tubes with electrostatic deflection would have been desirable. The electromagnetic deflection is well covered with good mathematical treatment.

Chapter 7 discusses the generation of extra-high voltages required for the picture tube. The flyback circuit, the high frequency generator and the pulse generator type have been covered. The first is commonly used in receivers but greater detail is also given of the other two types which are required in projection tubes.

A certain amount of diligent reading is necessary in the case of chapter 8. The authors have discussed the amplifying stages in television work (the RF, the IF, and the Video) exhaustively and this chapter covers almost a third of the book. Band width versus amplification, phase transmission characteristics and wave forms as also various peaking circuits of the Video amplifier have been discussed in detail with a good bit of mathematical treatment. A discussion of wave filters of constants "K" and "M" derived follows this treatment. The application of negative feedback has been covered. The discussion on automatic gain control is rather inadequate. The considerations involved in the selection of IF and the problem of rejection of the adjacent sound and Video carriers have been very well discussed.

Chapter 9 deals with properties of transmission lines. A good mathematical treatment of voltage current distribution and of standing waves is given. Also, the use of line as a transformer and as high "Q" tank circuit has been brought out.

The chapter 10 on aerials is very short and only a few receiving and transmitting aerials have been discussed. The latest superturnstyle antenna has been mentioned.

Chapter 11 deals with problems involved in projection of television picture. A short chapter 12 at the end gives the recent developments in colour television.

Finally, two complete circuit diagrams of different types of receivers have been explained and a set of photographs showing the effects on the television picture of various misadjustments in the receiver are appended.

This book covers a very wide field and the authors have dealt with almost all phases of television technology. The first one-third of the book gives the reader an impression that the book is interestingly descriptive, but the middle one-third becomes rather dull though it is mathematically quite exhaustive. The last portion is hurried and gives rather inadequate coverage to many subjects. In the chapter on wide band amplifiers, the authors could have discussed a little more about the automatic gain control and particularly about the latest keyed A.G.C. and the inversed keyed A.G.C. circuits. Similarly, more details on transmission lines could have been given in chapter 9. The introduction to Smith chart would not have been out of place. In the next chapter on the TV aerials, a discussion, or at least a mention, of the slot antennas is expected. In the chapter on colour television, a discussion on the latest standards evolved on compatible colour TV signals in the United States (N.T.S.C.) and the evolution of mixed-highs, dot interlace and colour sub-carrier should have been included.

Among the diagrams included in the book, two important and interesting phenomena of folded over pictures have been omitted. One is due to fall of the plate current of a over-driven horizontal oscillator and other is due to limitation of the plate current of the vertical oscillator. The book has made little reference to the transmitting circuits except in the fifth chapter where pulse mixing circuits have been discussed.

Apart from these minor omissions, the authors must be commended for producing a book covering so thoroughly the many subjects that come under the TV technique. To all radio engineers, who would like to do advance reading on television, this book is highly recommended.

N. D. MATANGE (SIGMA XI)

SCINTILLATION COUNTERS, by J. B. Birks (McGraw-Hill Book Co. Inc., New York & Pergamon Press Ltd., London), 1953, pp. viii + 148. Price $ 4.50

This is a timely publication in the Pergamon Science Series of monographs entitled " Electronics and Waves " under the editorship of D. W. Fry. It refers to a very important field of technique that is finding increasing application in many branches of science, particularly nuclear physics.

The author has developed the subject of scintillation counter from its classical concepts as a visual device to its present-day form as a more versatile instrument, having time resolving power of a high order of magnitude. This transformation has been traced to the development of the photomultiplier tube and naturally one finds in this work a good deal of attention devoted to the treatment of the photomultiplier from fundamental principles to the discussion of the characteristics and performance of the commercial RCA and EMI types of tubes.

A clear analysis of the two major properties of photomultiplier tubes, viz. the pulse height and the time resolution, has been given, and this has been illustrated by the limits attained in recent studies. The author has, however, dwelt on the satellite after-pulses in a sketchy manner. Considering this effect to be an inherent property of photomultiplier tubes, it ought to have received more adequate attention in a book devoted to the subject of scintillation counters, its technique and applications.

The later and the major part of the book contains the study of the characteristic scintillation properties of phosphors, both organic and inorganic, in which the different photo-luminescence processes are discussed; the main emphasis is on the author's own photon exchange theory. Copious references are given to recent work, which is confined mostly to the years from 1947 onwards.

The most informative part of the book is the last chapter in which varied applications of scintillation counters are described. This will be of absorbing interest, particularly to nuclear and cosmic ray physicists, from the point of view of modern experimental technique.

A special feature of the monograph is the author's critical digest of important research papers on the subject and this makes the volume a useful and indispensable guide to an experimental worker in the various fields in which the technique of scintillation counters finds application. It is needless to say that the growing applications of the counter device will require subsequent editions of the book to appear at comparatively quicker intervals.

N. R. TAWDE

THE ECONOMICS OF CHEMICAL PRODUCTION, by A. K. Madan (A. MacRae & Co. Ltd., Bombay), 1953, pp. 130. Price Rs. 10

The author of this publication has published another book entitled *The Economic Prospects of Chemical Industries in India.* In the publication under review the author has also confined his survey to the economic factors affecting chemical production in India. The author does not discuss the world chemical industry in general, but restricts his survey to India. To this extent, the title of the publication under review is somewhat misleading. In nine chapters, each reflecting painstaking study, he discusses the problems of finance and capital investments, location of industry, conditions of transport, labour, standardization of products and organization of marketing, controls, the economic and tariff policy of the Government and the role of the Government at the present time in influencing and directing developments.

The conditions under which industry began to develop in India under the British rule did not only not favour the development of chemical industry but also seriously limited its scope. However, the pattern of development resembled the British, who for a long time — till the end of the World War I — concentrated their attention mainly on heavy chemicals alone. This, important by itself, has affected the development of other lines of chemical industries.

Fine chemicals, in some form or other, are essential in every industry and their importance to industry and to the health of a nation is so vital that their manufacture has rightly been regarded as a key industry in Britain and in other industrially advanced countries.

If we should define the term " Economics " in a wide sense to describe statistically the part which the industry plays in the life of the nation, the importance of this branch of chemical industry, which is of particular importance to us, has not been adequately recognized and the existing conditions, it would appear, are not favourable for its development. The author has certainly brought out the factors that contributed to this unbalanced development. One of them was that the heavy chemicals attracted more attention from the Indian capitalists who found in this line resemblance to other lines with which he was familiar, namely textile, sugar, steel and cement. He calculated on getting a " turn key " plant and equipment from outside. He could hire cheap technical labour and, while getting best out of them, never made any attempt to build on the experience of the technologist new plants to serve the industry or to develop new processes more suited to local conditions. Attention was concentrated on getting over economic hurdles and fighting competition in the local market. The success of the enterprise depended entirely upon the exploitation of every favourable local condition and of labour, both technical and manual. Thus a few lines of heavy chemicals that were started in this country just appeared to suit the temper of the capitalist and his outlook trained and influenced by foreign domination.

This outlook would not help development of fine chemical industries where processes, plant and equipment change rapidly and also called for a degree of attention to details and of ability to invest large sums which under the then existing conditions in our country were considered far too much commensurate with the overall value of production. However, in no other line could research find so ready an application as in the development of fine chemicals. In its absence chemical research itself could not but be entirely unrelated to the economy of our country.

However, there has been profound change in governmental outlook and policy since attaining our independence though one still fails to notice adequate recognition of the requirements of chemical industries or the pursuit of a consistent policy favouring its development.

In addition to these considerations, the social aspects of recent developments in other established industries in India have profound effect on the economics of chemical production in our country. If we should agree that the pattern of development in each country should meet the special requirements of that country, though influenced by developments elsewhere, chemical industry should have received greater consideration at the hands of the Government than it has obtained so far. The author has rightly observed that some of the influences which stifled chemical industries before independence are still at work and a large part of this industry relegated to the private sector in the First Five-Year Plan has thus little chance of achieving any worth while results.

In his preface to this volume, the author says: " I have tried to make a direct approach to specify that the technological and the economic issues are inextricably intertwined ". It would appear that he has not adequately considered the profound influence of our existing social conditions on both these aspects. A welfare state, as we would like to develop, will have to consider the development of each industry in the light of its influence on the amelioration of the condition of our people. Our ideas of technological efficiency or productivity or economics, as influenced by the conditions in industrially advanced countries, will have to be profoundly modified to meet the challenging conditions existing in our still underdeveloped country. After all, chemical production, like any other line of production, is not an end in itself. Its importance should be recognized to the extent that it contributes to the overall well-being of the community. The prospects of development of chemical industries in the context of the present situation do not present a rosy picture. Perhaps that is because we are trying to judge the feasibility of development of chemical lines in India according to the system of economics with which we are familiar for long, while at the same time trying to meet the demands of social forces which do not permit a young industry like chemical industry to come to the standards of achievement or the power to compete with similar industries without a large measure of encouragement and assistance from the Government — very much more so than what appears to be obtainable through the Tariff Commission, however sympathetic in its attitude.

This book presents a carefully compiled outline of the complex problems facing new and existing chemical production in our country. The author deserves to be congratulated on bringing out a valuable compendium of useful information which should find a place in the bookshelf of every one interested in the development of chemical industry in India now.

B. H. KRISHNA

GEOLOGICAL MAPS, by G. W. Chiplonkar (Dastane Brothers' Home Service Ltd., Poona), 1952, pp. iv + 92. Price Rs. 7/8

This is a book on structural geology containing material found in most text-books, but the arrangement and exposition of the subject-matter indicate the years of experience on the part of the author as a teacher of standing on the subject.

The book is divided into the following eleven chapter headings: introduction; topography — its representation and interpretation; dip and strike of stratified rocks; thickness of strata; outcrops of strata; folds; unconformity; faults; outliers and inliers; igneous rocks; and interpretation of geological maps. Besides, it carries a selected bibliography and four appendices. The appendix on the use of the rectangular protractor is especially useful to the students. In the introductory chapter, the author has dealt with in a brief manner the three main rock types, igneous, sedimentary and metamorphic, and has also added a stratigraphical table of Indian rock formations after Dr. M. S. Krishnan, which is an useful aspect, particularly to the field geologists. Particularly interesting are the chapters on outcrops of strata, folds, unconformity and faults wherein the author has dealt with in a clear and easily understandable manner the various aspects of these structural features and their relationships with one another in the field. The book also contains practical hints on geological maps and drawing geological sections. It is well written and adequately illustrated with maps, sections and line drawings, and the subject is presented in a manner to stimulate the interest of the student. Very rightly the author has emphasized the need for visualizing the structural features in a three-dimensional aspect and has accordingly given block diagrams, wherever necessary, to illustrate the particular points. Among the highlights of the book may be mentioned the inclusion of the geological maps of the Geological Survey of India of certain well-known classical areas in Indian geology, as for example, the Jubbulpore Cantt. area, the Jharia and Raniganj coalfields, etc., as examples of the different features explained in the text. The last chapter on the " interpretation of geological maps ", where the author explains in great detail how to interpret a given geological map and draw sections and also how to make out a geological map of an area from a given geological section, is a useful addition and is more than what is to be found in a conventional text-book.

Perhaps a mild protest is in order at the author's adoption of *horizontal section* as the generic term for the more commonly used and easily understood term *geological section*. A horizontal section generally conveys to a beginner the sense that it is parallel to the horizontal plane. The term had been adopted by some earlier writers, but there is no justification in retaining it now.

The value of the book for students could have been well enhanced had there been an additional chapter on geological field work and also a folio containing few simple worked out maps and structural problems. A short description of the different methods of projecting varying dips of the beds, as seen on the surface, underground in geolgical sections, like the " method of tangents ", " method of arc ", etc., may be usefully incorporated in the second edition.

Several years ago, the senior reviewer (NLS) had written a pamphlet *Notes on Geological Maps & Sections* (Calcutta Geographical Society), and he was feeling the need of a more explanatory and illustrated book on the subject by an Indian author. We are glad to find that Dr. Chiplonkar's book fulfils this need. The author is to be congratulated for bringing out a book which will be welcomed by both students and teachers of geology. The get-up of the book is good except the stitching which could have been more durable.

N. L. SHARMA & T. NARASIMHAN

PUBLICATIONS RECEIVED

AN ATLAS OF END-GRAIN PHOTOMICROGRAPHS FOR THE IDENTIFICATION OF HARDWOODS — D.S.I.R. Forest Products Research Bulletin No. 26 (Her Majesty's Stationery Office, London), 1953, iv + 87, price 12*s*. 6*d*.

THE STRENGTH PROPERTIES OF TIMBER — D.S.I.R. Forest Products Research Bulletin No. 28 (Her Majesty's Stationery Office, London), 1953, v + 41, price 2*s*.

THE CHARNOCKITE PROBLEM, by C. S. Pichamuthu (Mysore Geologists' Association, Bangalore), 1953, pp. 178, price Rs. 5

RADIO RECEIVER DESIGN, by K. R. Sturley (Chapman & Hall Ltd., London), 1953, pp. xx + 667, price 56*s*.

EXPERIMENTAL INORGANIC CHEMISTRY, by R. E. Dodd & P. L. Robinson (Elsevier Publishing Co. Ltd., London), 1954, pp. xii + 424, price 42*s*.

HIGHER TRANSCENDENTAL FUNCTIONS, Vol. II, Editor, A. Erdelyi (McGraw-Hill International Corporation, New York), 1953, pp. xvii + 396, price $ 7.50

INDUSTRIAL ELECTRONICS, by R. Kretzmann (Philips' Technical Library, N. V. Philips' Gloeilampenfabrieken, Eindhoven), 1953, pp. 236, price Rs. 14

LOW FREQUENCY AMPLIFICATION, by N. A. J. Voorhoeve (Philips' Technical Library, N .V. Philips' Gloeilampenfabrieken, Eindhoven), 1953, pp. xv + 495, price Rs. 24/4

Indian Science Congress—Science Exhibition: New Instruments & Appliances

ANDHRA SCIENTIFIC CO. LTD., MASULIPATAM

ASCO Constant Deviation Spectroscope — The spectroscope is mounted on a heavy cast-iron bed with angle iron supports for the collimator and telescope. A constant deviation Pellin and Broca type prism of dense flint glass is provided which gives a deviation of 90° for all wavelengths and facilitates observation, focussing, etc.

The wavelength of spectral lines can be read directly from a graduated drum. A camera attachment is provided.

The prism is 25 mm. high with the emergent face 30 mm. in length. The collimating lens is 30 mm. in diam. and 250 mm. in focal length. The telescope lens is 30 mm. in diam. and 400 mm. in focal length.

The slit is of the micrometer type with its width measurable to an accuracy of 0·01 mm. The length of the slit can be varied by a wedge diaphragm which is also provided with a set of Hartmann diaphragms. A right-angled prism is attached for comparison of spectra.

The eyepiece is of the shutter type, having a pointer and illuminating mirror with Ramsden combination of lenses.

ASCO Analytical Balance — Rapid weighing is made possible with the aid of a detachable air damping device. The beam is short armed with inner edges lacquered. The fixed rider scale is divided into fifty divisions from the centre. The maximum load permissible is 200 g. and weighings correct to 0·1 mg. are obtainable.

ASCO Rocking Microtome (FIG. 1) — Specimens from 2 to 24 microns in thickness are obtainable with the instrument which is suitable for use with objects embedded in a paraffin block of 12 × 15 mm. cross-section. The total excursion is 10 mm.

Other items manufactured by the firm and presented for display were spectrometers for teaching and research, petrological microscope, babinet compensator, photo-measuring micrometer, Michelson's interferometer, refractometer, etc.

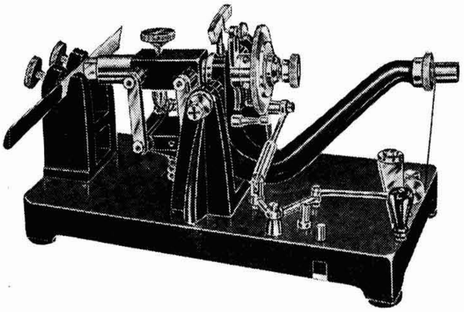

FIG. 1 — ASCO ROCKING MICROTOME

ASSOCIATED INSTRUMENT MANUFACTURERS (INDIA) LTD., INDIA HOUSE, FORT STREET, BOMBAY 1

New Spekker Fluorimeter — The instrument is an improved model of the original Spekker fluorimeter and is stated to be 100 times more sensitive than the original model. The reflecting galvanometer provided in the original is replaced by the space-saving Cambridge spot galvanometer and Spekker absorptiometer H 760. A photomultiplier (operated directly from a.c. mains) to receive the fluorescent light is employed instead of rectifier cells. Besides, the special features of the earlier types of the instrument — self-compensation of light source variation, mechanical-optical system of measurement by a permanently calibrated open scale, stable null-point measuring system, etc.— are all retained in the present model.

The new Hilger Biochem, Ehrenberg and Spear microfocus X-ray tube and the Hilger Abbe refractometer were among the other instruments on show.

CRAFTSMAN ELECTRONIC CORPN. LTD., NESBIT ROAD, BOMBAY 10

Craftsman Incubator — The incubator comprises a chamber, 20 × 20 × 26 in. of copper, lined inside with a wooden frame and with asbestos cement panels on the outside. The temperature control of equipment consists of a Sunvic thermo-regulator which ensures temperature control within ±0·25°C.

Craftsman Photoelectric Colorimeter-Fluorimeter (FIG. 2) — The instrument has a balanced cell circuit with provision to interchange the tungsten filament lamp with mercury vapour lamp or hydrogen lamp for ultraviolet analysis. Compensatory circuits to adjust the external impedance of each photocell and for suppression of the blank are provided to spread the dial readings on the 24-in. scale marked to read optical density as well as percentage transmission. A full-length potentiometer is suitably located behind the scale and can be adjusted to one-twentieth of 1 per cent transmission scale.

A fluorescence pick-up unit (similar to Lumetron Model 402 EF), a multi-reflection galvanometer having a total sensitivity of *c.* 0·00088 microamp./mm. and a quartz optical system with 100 watt intensity lamps permit the use of the narrow band monochromatic filters. A monochromator of the single or double prism type can be employed for spectrophotometric measurement. Sintered glass and quartz cells employed permit a wide variety of applications from estimation of vitamins, hormones, turbidity estimations to metallurgical analysis.

Craftsman Oven — The oven is a double-walled glass wool insulated thermostatically controlled chamber for operating up to 180°C. for baking, drying, conditioning, preheating, etc. A hydraulic

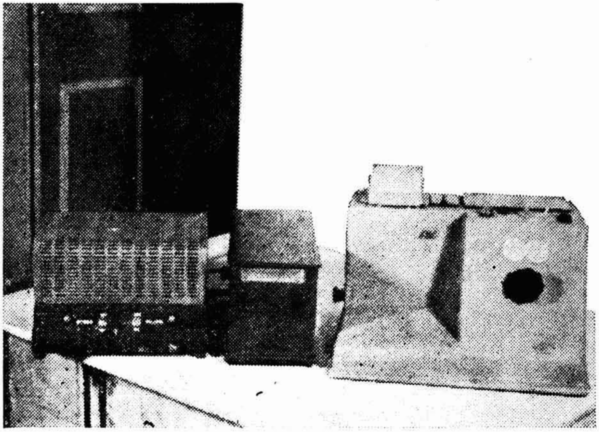

FIG. 2 — CRAFTSMAN PHOTOELECTRIC COLORIMETER-FLUORIMETER

thermostat controls temperature within ±1°C. The heating cell consists of nickel-chromium wires. The oven operates on 220 V., 50 cycles, single phase a.c. consuming approximately 800 watts.

Craftsman Sinter Meter — The meter is a small resistance furnace which attains temperatures of the order of 1,900°C. quickly with small loading of the mains. It measures sintering point of refractories, " burning on " point of foundry clays, moulding sands, core sands, " facing " materials, ceramics, cement, and can be used for testing optical and radiation pyrometers by comparing melting points of various materials.

The heating element is the platinum-rhodium ribbon. Temperatures are recorded with a radiation or optical pyrometer. A variac transformer is provided for the controls. Current consumption is *c.* 2·75 amp.

Cambridge Bench Pattern pH Meter — The instrument is a compact and convenient laboratory unit reading directly to 0·02 *p*H over a range 0-14·2 *p*H. It is provided with a temperature compensator and a millivolt scale readable to 2 millivolts against a self-contained Weston standard cell. The instrument can be employed with glass, hydrogen or metal electrodes of usual type.

Cambridge Conductivity Bridge — The instrument is designed for measuring the conductivity or resistance of electrolytes and covers the entire range from distilled water to strong salt solutions. It is simple to operate and readings within 0·5 per cent can be obtained rapidly. Power is supplied to the bridge at a frequency of 1,000 c./s. from a self-contained oscillator.

Pye's " Scalamp " Galvanometer — The two new features of the present model are: (1) a slow-motion zero control and (2) an automatic short-circuiting switch. The latter device operates whenever the instrument is lifted from the bench and ensures that the coil is electrically clamped during transit, thus preventing damage to the suspension. The instrument consists of a self-contained taut suspension reflecting galvanometer incorporating a constant current, constant damping shunt which provides a range of four sensitivities. All components are mounted within a functional moulded case; anti-vibration feet are fitted to allow the instrument to be used on an ordinary bench or table. The range has been extended to provide a 0·1 second period instrument.

Other exhibits displayed were: *Craftsman* — Anhydrous titration equipment, bimetallic thermometer, portable colorimeter and Kahn shaker. *Cambridge* — Portable *p*H meter, polarograph, indicators and fluxmeters.

W. G. Pye — Kelvin bridge, electromagnet, universal *p*H meter and potentiometer.

GANSONS LTD., 6 WEST VIEW, DADAR, BOMBAY

The firm specializes in various types of burners, stands, clamps, tongs and other appliances used in routine laboratory work. A number of improved and easy-to-handle types recently designed were displayed.

The GS gas plant (household model) suitable for small laboratories using about 10 Bunsen burners was a notable exhibit.

Among the imported items (Japanese make) on show were a variety of microscopes, micro-camera attachments and accessories.

HARGOLAL & SONS, AMBALA CANTT.

A large variety of instruments and appliances for advanced research and equipment for teaching manufactured by the firm was displayed. These included the following:

Physics — Cathetometer, vernier microscope, micrometer, viscometer, colorimeter, Stephen's radiation constant apparatus, spectrometer rheostats, tangent galvanometer, Wheatstone bridge, potentiometer.

Chemistry — Electric ovens and compaction apparatus (for soil and cement test).

Biology — Micro-projector, microtome, life-history models, etc.

The imported items displayed included a variety of equipment manufactured by W. G. Pye & Co. Ltd., Cambridge; Cambridge Instrument Co. Ltd., London; J. W. Towers, Widnes (U.K.); George Kremp, Wetzlar, Fritz Hellige, Feiburg im Breisgav; Paul Bunge, Hamburg, and Jena Glaswerk, Stutzerbach.

K. ROY CHOWDHURY, 32 LATAFAT HUSAIN LANE, CALCUTTA 10

A wide range of laboratory balances manufactured by the firm for routine analysis and high precision work was exhibited. A semi-micro balance with a 3 in. bronze alloy beam of bridge type construction with notched graduations (0 to 100) and agate knife edges and planes is shown in Fig. 3. It has a sensitivity of 1/50 of a mg. and a capacity of 20 g. Combination lenses are provided for reading the scale.

MARTIN & HARRIS LTD., SCIENCE DEPARTMENT, SAVOY CHAMBERS, WALLACE STREET, BOMBAY 1

Sunvic Bimetal Thermostats — The thermostats designed by Sunvic Controls Ltd., London, for

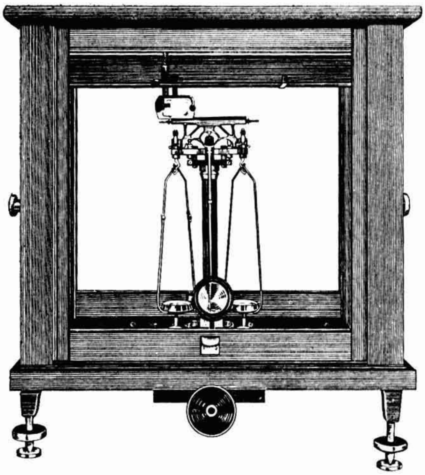

FIG. 3 — KEROY SEMI-MICRO BALANCE

controlling temperatures up to 300°C. with a sensitivity of ±0·1°C. have a variety of applications in research and industry, such as control of laboratory ovens, incubators, water baths, moulding platens, refrigerators, etc. Their operation is based on the deflection of a bimetal element.

Sunvic Hot-wire Vacuum Switch — This is a non-arcing electric relay capable of controlling up to 10 kW. at 440 V. The operating current is exceedingly small, being 25 to 80 milliamps. The switches are, therefore, particularly suitable for use with sensitive thermostats.

Sunvic Electronic Relay — The relay is designed to allow light contact instruments such as toluene regulators or contact thermometers to achieve, in service, precise control. It is operated by a few microwatts to control loads up to 2 kW. at 200/250 V. a.c. or d.c. The unit is self-contained and consists of a mains transformer, gas-filled relay and Sunvic hot-wire vacuum switch mounted on a base plate and enclosed in a steel case.

Gallenkamp Combustion Furnace — The furnace is made for combustions in accordance with BSS No. 1016. It is used for the determination of carbon and hydrogen in organic substances. There are three movable sections, 9·5, 18·5 and 8·5 in. long respectively. Each section is controlled by a regulator and is fitted with a double-bore refractory tube combined with a pocket for inserting a thermocouple.

Gallenkamp Bomb Calorimeter (FIG. 4) — This instrument is Berthelot-Mahler bomb type with stainless steel bomb tested to 80 atmospheres. It is suitable for determining the calorific value of fuels according to standard specifications BS 1016, I.P.-12/45 and ASTM D. 240-39 (modified).

Bausch & Lomb Improved Monochromatic Colorimeter — This is a single cell direct reading photoelectric colorimeter. The improved performance of this model is primarily due to the use of Bausch & Lomb transmission type interference filters. These filters are characterized by narrow pass bands, and consequently transmit light of high spectral purity. Especially designed for colorimetry, these optical elements also possess a high degree of transmission.

**PHILIPS ELECTRICAL CO. (INDIA) LTD.,
PHILIPS HOUSE, 7 JUSTICE CHANDRA
MADHAB ROAD, CALCUTTA 20**

Fast Time Base Oscilloscope GM 5660 (FIG. 5) — The oscilloscope is specially designed for pulse technique and radar work. The special features of the instrument are built-in pulse generator with repetition frequency control for triggering the time base, and the internal and external synchronizing device. The time base velocity ranges from 2 μ sec. to −50,000 μ sec. which can be calibrated by a built-in 1 Mc./s. signal. The amplitude of the signal under observation can be calibrated by internal or external calibrating voltage.

Oscillograph GM 3156/01 (FIG. 6) — The instrument is offered for low frequency work, i.e. mechanical vibration, physiological studies, etc. Time base frequency, 0·25-9,000 c./s., sensitivity, 1 MV. r.m.s./cm., amplifier linear from 0·1 to 40,000 c./s. The cathode-ray tube may be short persistent green or blue or long persistent type.

*Universal p*H *Meter GM* 4491 *with Extension Indicator GM* 4492 — This is offered for measurement of *p*H and oxidation-reduction potential, and for potentiometric titration. The high sensitivity and fully inertia-less indication by cathode-ray indicator make the apparatus suitable for use in the laboratory and in industry. Measuring range, 0-14·15 *p*H or 0-1,415 MV.; accuracy, +0·01 *p*H or 0·5 MV.; measuring electrode, glass, hydrogen, quinhydrone; and reference electrode, calomel.

Electronic Roughness Tester PR 9150 — The measurements are based on a comparative method, the surface of a work piece being compared with that of roughness standards. A crystal pick-up is connected to an amplifier and an indicating meter.

FIG. 4 — GALLENKAMP BOMB CALORIMETER

Due to its simplicity and robust construction the instrument is specially suitable for machine shop and mechanical design work.

Conductivity Measuring Bridge GM 4249 — The apparatus has been specially developed for measuring and comparing specific resistances and conductivities of aqueous solutions, but is equally suitable for measuring ohmic resistance. For conductivity measurement, immersion cell type GM 4221 or flow type of cell GM 4227 is used with the bridge.

The measuring bridge with a cathode-ray indicator may be fed from 50 c./s. mains or by 1,000 c./s. built-in oscillator to avoid polarization. Provision exists for connecting the measuring bridge output to an electronic relay for signalling the change in conductivity. Measuring range 0·5 to 10 megohm; accuracy, normal range, < 0·3-0·8 per cent; extra range, < 0·6-3 per cent.

THE TECHNICAL CORPORATION LTD., SAROJINI NAGAR, LUCKNOW

Brodie-Starling Kymograph — This instrument, manufactured by the firm, has three-speed gear box having ratios 1 : 10 : 100 fitted with special driving motor for use where line-shafting does not exist. Various switches to operate time marking clocks, respiration pumps, etc., are provided.

Hoag Milikan's Oil Drop Apparatus — The instrument is offered for determining the ratio of the electronic charge to the mass of electron. This apparatus is robust and compact in design. The only extra equipment required for operation is a 150 V. dry battery, a d.c. voltmeter (150 V.), and a stop-watch.

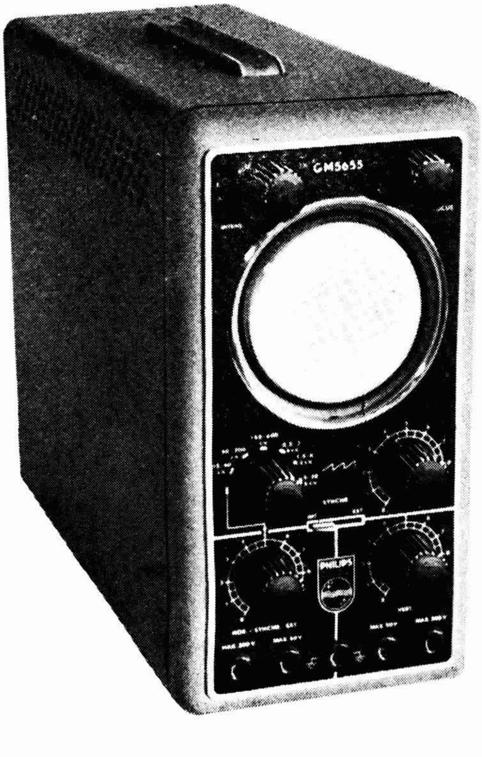

FIG. 5 — PHILIPS FAST TIME BASE OSCILLOSCOPE GM 5660

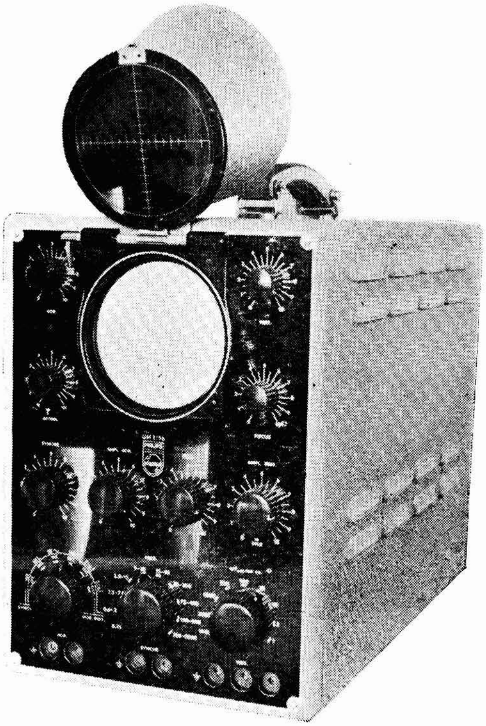

FIG. 6 — PHILIPS OSCILLOGRAPH GM 3156/01

Ripple Projector — This is designed for demonstrating the various wave phenomena such as reflection, refraction, diffraction, and interference by projection on a screen. The picture on the screen is from 2 to 3 ft. in diameter.

Precision spectrometer, electrically driven recording drum and Starling respiration pump are some of the other items manufactured by the firm which were on display.

TOSHNIWAL BROS. LTD., 198 JAMSHEDJI TATA ROAD, FORT, BOMBAY

Dipolemeter DMO 1, manufactured by Wissenschaftlich-Technische Werkstatten, Germany, is an a.c. mains operated instrument with two built-in oscillators, 1,800 and 1,000 kc./s. respectively, for simple and accurate determination of dielectric constants and dipole moments.

Dekameter DKO 3 — This is an a.c. mains operated instrument with built-in 1,875 m. oscillator. It is designed for rapid determination of dielectric constants of liquids, powders and solids; water content of fibres, grains, wood, and purity of plastic materials, solvents, etc. Its use for controlling unit processes such as saponification, distillation,

(*Continued on page* 154)

NOTES & NEWS

Synthesis of oxytocin

OXYTOCIN, THE CHIEF UTERINE contracting and milk releasing hormone secreted by the pituitary gland, has been synthesized by Dr. Vincent du Vigneaud of the Cornell University Medical College, U.S.A. It is the first polypeptide hormone to be produced synthetically. The synthesis of oxytocin paves the way for the possible expansion of its use in clinical medicine, particularly in obstetrics, and in veterinary medicine.

Oxytocin from the pituitary gland was isolated in a pure form by the application of the countercurrent distribution and starch column technique. Subsequently, oxytocin was obtained in crystalline form in combination with flavianic acid. Pure oxytocin, on hydrolysis, gives one equivalent each of leucine, isoleucine, tyrosine, proline, glutamic acid, aspartic acid, glycine and cystine, as well as three equivalents of ammonia. The active principle appears to be a polypeptide having a molecular weight of about 1,000. Degradative studies indicated that the hormone was a cyclic disulphide, five of the amino acids forming the ring structure, the other three being in the side chain.

Reduction of the natural oxytocin results in the breakage of the sulphur link, leaving a straight chain of amino acids. The known amino acids, obtained from other sources, were assembled into a synthetic chain leading to the reduced hormone. The final step in the synthesis was to form the proper ring through the sulphur atoms by oxidation. The resulting product has been shown to possess identical physical, chemical and biological properties as the natural hormone [*Chem. Proc.*, **16** (1953), 477].

A new type of high α-cellulose

RAYOCORD-X, A NEW TYPE OF high α-cellulose produced by the sulphite process, has cellulose chains of uniform length, such that in high-stretch viscose spinning, the chains can be formed in a highly ordered pattern. This imparts unusual strength and toughness to the filaments regenerated from solution. Rayons produced from this cellulose by high-stretch spinning methods possess strengths of up to 4 g. per denier. Conventional rayon fibres have strengths of about 2 g. per denier. With rayon made from the new cellulose, it is possible to stretch the filament at least 100 per cent during spinning. With ordinary textile yarns, the fibres are normally stretched only by 30 per cent, while for tyre cord yarns the stretch is about 60 per cent. Although conventional textile rayons expand about 150 per cent when wet, the rayons produced from Rayocord-X expand only about 65-75 per cent. Because of these properties, the new rayons not only have greater strength and better wearing qualities but readily lend themselves to standard laundering techniques [*Chem. Engng. News*, **31** (1953), 4214].

Transitions of amylose

WATER PLAYS A SIGNIFICANT ROLE in the transitions of the several modifications of amylose. α-Amylose transforms itself to β-amylose at low temperature. Passing through the transient state of α-amylose, amylose-alkali complex likewise transforms itself to β-amylose when alkali is removed. These transitions take place when amylose is exposed to humid atmosphere or immersed in water at the room temperature. When kept in completely dry atmosphere no transition is noticed. β-Form does not undergo any transition even in contact with water at room temperature, but transforms itself to α-form at higher temperature (>60°C.).

The transition of amylose in water may be explained as the phase transition of a binary system of amylose and water. In this phase transition, the interacting units seem to be OH groups of β-glucose of amylose and of water. The OH groups of water seem to be specific for the transition, since OH groups of absolute methanol and ethanol do not react with OH groups of amylose [*Sci. Rep. Tôhoku University, Japan*, **36** (1952), 278].

A new synthesis of 2-deoxy-D-ribose

A SATISFACTORY SYNTHESIS OF 2-deoxy-D-ribose has recently been worked out. 3-Deoxy-D-glucose (0·337 g.) was dissolved in a solution containing 0·19N sodium meta-periodate (1 mole; 21·6 cc.), and after 3 hr., a 5 per cent solution of barium acetate was added, and the resulting precipitate discarded. The solution was kept slightly alkaline by the dropwise addition of ammonium hydroxide until deformylation was complete (about 15 min.). The solution was then deionized by passage through columns of the ion-exchange resins " Amberlite IR-120 " and " IR-4B ". The effluent was evaporated under reduced pressure to a syrup containing 2-deoxy-D-ribose and unchanged 3 - deoxy - D - glucose. This was fractionated by chromatography. 2 - Deoxy - D - ribose was eluted from the strips of paper with cold water and the aqueous solution evaporated to a syrup. The product, after two recrystallizations from ethanol, had melting point and mixed melting point 169°-70°C. [*Nature*, **172** (1953), 1051].

Antifungal substance from *B. subtilis*

A NEW ANTIFUNGAL SUBSTANCE, having a broad antifungal spectrum, is reported from a strain of *B. subtilis* isolated from decomposed foodstuff. The substance differs from bacillomycin, mycosubtilin and fungistatin, the known antifungal products of *B. subtilis*, in its antifungal and antibacterial activities. It resembles the incompletely characterized " *Aspergillus* factor " in its antimicrobial properties.

The substance which was obtained as a dark yellowish mass and appeared homogeneous from chromatographic study, was polypeptide in nature. When kept at 4°C., the antibiotic retained its activity for more than three months. It was found to be stable when autoclaved at 120°C. for 10 min., but less so in alkaline solution. The minimum inhibitory concentration of the substance as determined by the agar cup and agar streak methods for the organisms *A. niger*, *P. notatum*, *A. oryzae*, *Alternaria solani*, *Fusarium* sp., and *B. cinerea*, was found to range between 12 and 30 μg./cc. It was also active against *Curvularia* sp., *Verticillium* sp., *Phoma* sp., *P. rotundum* and *Trichophyton* sp., but inactive against *Epidermophyton* sp. and *Microsporum* sp. at a concentration of 0·2 mg./cc. [*Nature*, **172** (1953), 871].

Chlorparacide

CHLORPARACIDE (*p*-CHLORBENZYL *p*-chlorphenyl sulphide), a new ovicide and insecticide developed, has high specific toxicity for red spider mite. Residues on the foliage exert a persistent ovicidal effect and also act by a " stomach poison effect " on larvae even at concentrations below those at which they are ovicidal. Adult mites are apparently not affected, but the compound is effective in eradicating an infestation due to its persistent toxicity to eggs and larvae. It normally takes 2-3 weeks before an active infestation in the field is reduced to negligible proportions. Its toxicity to human beings is low.

Chlorparacide is a white crystalline compound (m.p. 72°C.). Chemically it is stable and is, therefore, stable in all types of orthodox formulations, and is chemically compatible with all fungicides and insecticides. Chlorparacide is highly lipoid soluble and has an appreciable vapour pressure. The substance is not phytotoxic for most crops attacked by red spider. There is, however, some phytotoxic risk with the *Cucurbitaceae* crops. In field trials, sprays of either miscible oils or dispersible powders, at 0·05 per cent concentration or less, gave outstanding control on apple and pear. The ideal time of application may be as late as the pre-blossom stage, but should be before the main hatch of winter eggs commences. For economic control of summer eggs two applications (0·02 per cent as dispersible powder, and 0·0125 per cent as miscible oil) at intervals were found to give good results [*Chem. Ind.*, No. 45 (1953), 1206].

Movidyn — a colloidal silver disinfectant

MOVIDYN, A NEW COLLOIDAL silver disinfectant now available commercially, has been found to be an effective bactericide in concentrations as low as 0·1 p.p.m. The time required to kill 99·99 per cent of the various test organisms with 1/20,000,000 dilution of this preparation was 1·5 hr. for *S. marcescens*; 3·5 hr. for *S. typhosa*; 11·5 hr. for *M. pyogenes* var. *aureus* and 12 hr. for *E. coli*.

The preparation is composed of approximately 5 per cent by weight of silver (expressed as silver nitrate), colloidally dispersed and stabilized by the addition of a protective agent such as gelatin. The silver is present in a considerably more active form than that of ionic silver, as shown in comparative tests between Movidyn and silver nitrate on *E. coli*. An interesting property of the substance is its residual effect. Glassware in which the tests were made adsorbed silver from the disinfectant solution so that it exhibited a residual bactericidal effect when used again, even though it was treated with sulphuric acid-potassium dichromate solution between tests. There was evidence that its effect was bactericidal rather than bacteriostatic, as in the case of certain heavy metal disinfectants [*Industr. Engng. Chem.*, **45** (1953), 2571].

Chemical modification of wool

SEVERAL METHODS HAVE BEEN employed for the chemical modification of wool — introduction of additional groups in the wool protein molecule — for protecting it against bacterial and fungal attack. The resistance of treated and untreated wool to microbial and fungal attack was evaluated by burying the samples in garden soil for periods up to 3 months and measuring their tensile strength.

The life of the wool can be prolonged by suitably and partially substituting the functional groups in its protein molecules. Both acetylation and esterification of the carboxyl groups with epichlorhydrin considerably lengthen the life of wool. Dinitrophenylation also leads to a higher degree of stabilization, but has the disadvantage of dyeing the wool yellow; it also results in poor light fastness. Reduction of the cystine groups and methylation of the thiol groups leads to a big reduction in the resistance of wool to the action of soil fungi.

Cross-linking of the polypeptide chains in wool with certain bifunctional reagents leads to high resistance to bacterial action. The Kirst method of wool stabilization, which employs bis-chloromethyl-dimethyl-benzene, is promising. The half-life period of the treated wool was four times that of untreated wool.

Studies carried out so far show that nitration, chlorination and heat treatment do not lead to improved stability of wool. No direct relationship exists between the acid and alkali solubilities of wool and its resistance to fungal attack. It is unnecessary to bring about chain-linking in order to obtain a wool resistant to bacterial attack. It is sufficient to substitute the amino and phenol groups in wool protein to make it resistant to bacterial and fungal action. Since wool treated with bifunctional compounds is also more stable to alkali, this method appears to be more promising than others [*Text. Res. J.*, **23** (1953), 604].

Oxidized starch

A PROCESS FOR THE CONTINUOUS electrolytic oxidation of starch has been developed. Oxidized starches are used principally as tub size and coating adhesives in the paper industry, and as warp sizes and finishes in the textile industry. A water slurry of starch (25-33 per cent), containing 5 per cent sodium chloride in solution, is preheated and fed continuously to an electrolyser. In the absence of a diaphragm between the electrodes, the chlorine generated immediately reacts with sodium hydroxide to form sodium hypochlorite. At 40°-50°C., the hypochlorite decomposes to sodium chloride and nascent oxygen which reacts with and splits the starch molecule. Reaction time in the electrolyser depends on the desired degree of split and ranges between 10 and 60 min.

From the electrolyser the starch solution flows to a neutralizing tank and then to a gravity settling or centrifugal separation step. The separated salt solution is recycled to the slurry feed tank.

The electrolyser is a vertical cylindrical vessel partitioned horizontally into a number of individual cells to get uniform treatment of the starch as it flows through the apparatus. A vertical multi-bladed agitator prevents starch particles from settling on the horizontal cell partition walls. To avoid metallic contamination, all parts within the electrolyser are lined with a vinyl resin. The electrodes are water-cooled to avoid local heating. There is also an external cooling jacket.

Salt consumption is of the order of 0·01-0·02 lb. per lb. of dry starch. Consumption of electric power is reported to be 0·05-0·15 kWh. per lb. of product. It is possible to obtain a uniform, homogeneous product of any desired viscosity [*Chem. Tr. J.*, **133** (1953) 968].

Gaseous reduction of iron ore

WITH A VIEW TO CONSERVING metallurgical coke in India, investigations have been undertaken to effect reduction of Indian magnetite and haematite ores with hydrogen, carbon monoxide or a mixture of the two gases. Optimum conditions have been determined for batchwise and continuous reduction.

The optimum temperature at which magnetite could be reduced by hydrogen was found to be 600°C. Though a second maxima for reduction is obtained at 1,000°C., incipient melting of the ore results in the particles coalescing into big lumps and the reduction is retarded. The most efficient temperature for the reduction of haematite ore was found to be 1,000°C. The size of the ore has a minor influence on its rate of reduction in the case of magnetite, sizes between 6 and 10 mesh being most suitable. The optimum rate of flow of hydrogen for the reduction of magnetite at 600°C. was found to be 0·92 cu. ft./min. at atmospheric pressure.

In the case of haematite, the factor limiting the rate of reduction appears mainly to be the rate of supply of hydrogen. Increasing hydrogen pressure was found to improve reduction. The highest pressure which could be obtained in practice is, however, restricted due to the mechanical difficulty of containing hydrogen in the furnace during operation. Carbon monoxide as such, or in admixture with hydrogen, was less effective than hydrogen in bringing about reduction. The amount of reduction of the ore was found, in all cases, to be maximum during the first 3 min. [*Trans. Nat. Inst. Sci., India*, **3** (1953), 211].

Recovery of 2, 3-butanediol

THE RECOVERY OF 2, 3-BUTANEDIOL from fermented beet molasses has been investigated on a pilot-plant scale. The hygroscopic and solubility properties of 2, 3-butanediol suggest its use in printing inks and pastes, dyes, soaps, ointments, and wood and leather skins. With polybasic acids, it condenses to form polyesters of the alkyd type. A more specific use of 2, 3-butanediol is as a chemical intermediate.

Molasses mashes fermented by *Aerobacter aerogenes* and *Pseudomonas hydrophila* contained butanediol, ethanol, acetoin, water, impurities and non-volatile solids. The mash is first stripped of ethanol and then evaporated to a syrup containing 20 per cent butanediol and 28-30 per cent solid. Butanediol is stripped from this syrup at 40 lb./sq. in. pressure in a packed column and then scrubbed from the vapour with water in a similar column. Diol is recovered from the resulting aqueous solution (24 per cent) by a series of distillations, during which the impurities are neutralized by adding sodium hydroxide. The cost of production, working with a plant of capacity 60,000 lb. of molasses per day, has been estimated at 25·6 cents per lb. of 98 per cent butanediol [*Industr. Engng. Chem.*, **45** (1953), 2387].

Hydrogen peroxide by non-electrolytic process

THE PRODUCTION OF HYDROGEN peroxide by the non-electrolytic process — alternate oxidation and reduction of organic compounds — is not dependent for economic success upon cheap power and plants can be located at convenient places near the main consuming industries. In the du Pont process, which is a modification of the German anthraquinone process developed by the I.G., a mixture of alkylated anthraquinones and their tetrahydro derivatives is dissolved in a solvent mixture of primary or secondary nonyl alcohols with methyl or dimethyl alcohol. The anthraquinone mixture is reduced in the presence of activated alumina and the hydrogenated derivative separated by filtration. Oxygen blown through this latter product at 30°-60°C. forms hydrogen peroxide and regenerates the original anthraquinones. The peroxide is extracted with water and the anthraquinones recycled [*Chem. Tr. J.*, **133** (1953), 1015].

Photon printing process

A NEW PRINTING DEVICE DEVELoped — the " photon process "— dispenses with metal types and type moulds. It produces electronically on a film negative, from a typewriter keyboard, a wide variety of types and faces. From this negative any kind of printing plate can be made. The process can be used for any language. At present, studies are being made to adopt it for complex languages, such as those using the Devanagari alphabet and Chinese script. It is believed that the methods developed for the Devanagari alphabet would apply broadly to all Sanskrit-root languages and the Hebrew-Arabic group.

The electronic photon composing machine consists of a typewriter with an extra row of keys and an adjacent panel of dials and push buttons connected with an interior set of photographs and electronic machines. The matter is typed on paper inserted in the carriage in the usual way, the typescript serving as visual record. As each character is typed, the machine's electronic mechanism stores up a code for it. Inside the machine is a replaceable or interchangeable glass matrix disc. The disc contains all the characters, symbols and accents necessary for a particular type of composition. This matrix disc has a capacity of 1,440 individual characters.

When each line of typing is complete, a button is pushed and the disc whirls before a camera. As it whirls, the code device and and electronic eye accentuate the camera to photograph required characters with proper spacings. The line is swiftly photographed and set on the film before the typing of the next line is complete. Corrections can be made by pushing a special " correction key ". When a whole page of copy has been typed and photographed the machine turns out a length of film, ready for immediate development and conversion to a printing plate. The process lends itself to the three major methods of printing: letter press, offset and gravure [*Science Newsletter*, No. 129, Item No. 1898, Scientific Liaison Office, India House, London].

Reclamation of asbestos

SIMPLE AND EFFECTIVE PROCEDURES for reclaiming asbestos from discarded pipe insulation are described. Asbestos or asbestos-cotton fabrics, other than those containing paint, can be freed of adhering cement by first treating it with 5 per cent hydrochloric acid and then rinsing. Fabrics painted on one side are treated with alkali instead of acid to remove the paint as well as the cement. This is accomplished by boiling the asbestos fabric in 5 per cent sodium hydroxide solution for 15-30 min., followed by a preliminary rinsing, a warm wash with a synthetic detergent to remove the paint pigments, and a final rinsing. Removal of cotton from the cleaned cloth is best effected by heat. Thin layers of the material are heated in a muffle furnace at 400°-450°C. After removal of cement, paint and dirt, the asbestos cloth is reduced to fibre in a rotary blender or in a paper pulp beater. Fabric containing glass strands is difficult to process. The recovered asbestos is unchanged chemically, with little or no shortening of the fibres. It can be used for electrical and heat insulation purposes, for making asbestos paper, and as a filler in moulded plastic components [*J. Franklin Inst.*, **256** (1953), 368].

Strength properties of timbers

STRENGTH DATA FROM STANDARD tests, made at the Forest Products Research Laboratory, London, on 122 local and imported softwoods and hardwoods are presented (*The Strength Properties of Timber*, Forest Products Research Bulletin No. 28, H.M.S.O., London, 1953). A brief description is given of the test methods used, as well as explanations of the various strength properties of timber specimens determined. The influence of several factors upon strength of the timber is discussed and the relationships between the strength properties and specific gravity, or density, are examined. Comparison of species and the assessment of their utilization values are made by means of diagrams. A comprehensive table of strength results for all the species of timber tested is appended.

Of the many factors influencing strength of timbers, moisture content and specific gravity are the most important. Within certain limits, the relationship between the logarithm of the strength values and the moisture content can be accurately represented by a straight line. An exponential formula has been derived, which forms the underlying principle on which adjustments of strength values to various moisture contents (below the fibre saturation point) are made. Not all properties of the timbers are affected to the same degree by moisture. While maximum bending strength and maximum comprehensive strength both increase considerably as the wood dries, stiffness (modulus of elasticity) is influenced to a less degree, and toughness as measured by "total work" in bending decreases slightly.

There is a wide variation in the specific gravity values for the different species of timber and also for different specimens of the same species. This variation in density is responsible for the differences observed in the strength properties of the timbers; high density species rank high so far as strength is concerned. Specific gravity affords a much better index to the strength of the individual pieces of the same species than to the average strength of different species. Within the range of specific gravity found in most species, an approximately linear relationship exists between strength and specific gravity, which is particularly good for such properties as maximum compressive strength, maximum bending strength and hardness, but not quite so good for others such as stiffness, shear and cleavage. In general most strength properties, with the exception of shock resistance, are affected by temperature changes and a reduction of strength occurs with the rise of temperature.

Age determination from radioactivity

AN ATOMIC CLOCK FOR DATING mineralogical, archaeological and prehistoric plant and animal remains has been developed. Atomic clocking is based on the observation that radioactive C^{14} being manufactured from the nitrogen in the atmosphere through cosmic-ray bombardment and assimilated as carbon dioxide by living things during life, provides a known percentage of " tagged atoms " whose rate of decay can be checked to determine, within certain limits, how long ago a given plant or animal lived.

As long as an organism is alive, a balance is maintained between radioactive carbon and the ordinary variety. When life ends, no more radioactive carbon is added, and the carbon time clock begins to run down. For the accurate age determination from the carbon found in organic remains, advantage is taken of the fact that as time passes, beta particles are given off at a diminishing rate by C^{14}, its half-life period being 5,568 years. In the method developed, carbon in the specimen is reduced to acetylene gas which can be introduced into a Geiger counter without allowing contamination by air molecules. Age determinations up to 20,000 years can be made fairly accurately [*Science Newsletter*, No. 135, Item No. 1963, Scientific Liaison Office, India House, London].

Two-dimensional paper chromatography of radioactive substances

AN AUTOMATIC SCANNING TECHnique employing a Geiger-Müller tube for the location and estimation of radioactive substances has been successfully employed to the conventional form of two-dimensional paper chromatography for the application of two or more solvent systems to the same labelled mixture. The boundaries of the radioactive zones separated unidimensionally in the first solvent are lightly marked off in pencil while the strip is being scanned radiometrically. The corresponding sections of paper are then cut out and attached by means of stainless steel pins to the bottom of a new strip. Each strip is then wedged lightly between the ground-glass surfaces of the neck of the empty elution unit, which consists of a flat-bottomed flask provided with a side tube and stopper. The extended cone is sealed off at the lower end so that the flask is closed. The strip is adjusted so that the attached section hangs to within 1 cm. or so of the bottom of the flask. The eluting solvent (which must be volatile) is then added through the side tube until the section is immersed to a depth of *c.* 1 mm. The solvent rapidly ascends the strip until it emerges just above the rim of the flask, when it is no longer in equilibrium with its own vapour. It, therefore, evaporates and the eluted substance becomes concentrated in a narrow band (*c.* 0·5 cm.) at the solvent front which is on the new strip of paper. The neck of the elution unit is gently removed, the section detached and the concentrated zone chromatographed in the second solvent and finally scanned. Evaporation may be aided by placing the unit in a gentle air stream (e.g. fume cupboard draught). Subject to the chemical stability of the substances, the whole process can be repeated, thus effecting " multi-dimensional " chromatography. The method also proved to be useful for concentrating the material of several paper sections until sufficient amount was obtained for chemical tests [*Nature*, **172** (1953), 727].

Acetylation of paper for chromatography

IT IS ADVANTAGEOUS IN PAPER chromatography to modify the paper fibres in order to alter the affinity of the paper towards the absorbates, and to modify the retention of the stationary phase in a two-phase system. A number of methods have been proposed by which filter paper may be modified for use in chromatography. A satisfactory method of acetylating Whatman No. 1 paper has been devised, in which acetytation is catalysed by perchloric acid. The filter paper sheet is immersed in a normal (10 per cent) solution of perchloric acid. After an interval of 45 min. the sheets are removed, blotted dry or squeezed, and then immersed for 1¼ hr. in a tank containing a mixture of acetic anhydride (150 parts) and benzene (350 parts) at 0°C.; the mixture is kept agitated during the reaction. The tank is then emptied of fluid and the sheets washed with water, blotted dry and dried in a current of air. Over-exposure to the acetylating liquid causes the paper to weaken to the point where it is difficult to handle.

Another type of esterified paper was produced by adding a small quantity (4 per cent) of sulphuric acid to the tank. In this case the duration of immersion of the catalyst loaded paper was shortened to 15 min. By suitable alignment of immersion tanks and rollers, continuous production of the paper is feasible [*Chem. Ind.*, No. 46 (1953), 1229].

Electrical measurement of butter rancidity

AS A RESULT OF PHYSICAL, CHEMICAL, electrical and organoleptic tests carried out to find a reliable method of assessing the keeping quality of butter-fat, the measurement of electrical resistance of butter-fat has been found to provide a sensitive method of detecting the onset of rancidity. Butter-fat is an almost perfect electrical insulator, but when the emulsion of butter-fat in water is not perfect, channels and drops of water are present which provide conducting paths. The water drops also provide the medium for bacterial growth, and it was expected that a measurement of butter's electrical resistance should provide a correlation between physical and chemical attributes that determine how quickly the butter will go bad. Butter samples of poor quality were successfully graded by measuring their electrical resistance (both high and low voltages can be employed); the butter having the lowest resistance was the first to go rancid. For better quality butter, high voltage measurements gave better correlation [*Science Newsletter*, No. 139, Item No. 1989, Scientific Liaison Office, India House, London].

Hygro-photographic technique

AN EMULSION OF A DOUBLE SALT of mercury and silver iodide in gelatin sensitive to light and water has been developed. The salt undergoes a rapid change of colour from yellow to a violet black when exposed to light. Moisture restores it to its initial yellow colour. A plate or film of a silver bromide emulsion in gelatin is immersed in developer solution in a dark room and then exposed to open daylight and fully developed. The film is then fixed in a solution of hypo to eliminate unreduced bromide and then dipped in a 3 per cent solution of mercuric chloride. Mercuric chloride bleaches the film completely. After washing, it is treated in a 5 per cent solution of potassium iodide, which brings out the yellow colour.

The new plates are capable of direct application in microchemical analyses, e.g. the detection and measurement of traces of water in organic solvents. If a drop of commercial absolute alcohol is placed on an ash-free filter paper and the paper covered with ordinary glass and applied against a hygro-photographic plate, the small quantity of water contained in alcohol passes from the paper into the gelatin. The plate, previously exposed to light, then exhibits a pronounced black ring surrounding a grey area.

When treated for 15-20 min. in a 10 per cent hydrogen peroxide solution, the hygro-sensitive plate loses its light sensitivity, but develops great thermal sensitivity. The thermo-chromic plates thus obtained show thermal effects of ultrasonic waves more conveniently than tetraiodomercurate silver screens [*Chem. Engng. News*, **31** (1953), 4198].

Large-scale continuous extractor

A LABORATORY CONTINUOUS EXtractor of simple construction for the extraction of amounts greater than 500 cc. in volume is described. It consists of a strong bottle of suitable capacity with a ground neck and the bottom cut off. This is evenly ground so that a plastic lid, with an enclosed rubber gasket, fits tightly. The lid is held in position by holding screws attached to a brass band which fits around the bottle. A hole is cut out of the lid for the insertion of the condenser. The vapour tube is placed through the neck and centre of the bottle. The cylindrical part of the bottle is separated from the shoulders by wire netting and a filter paper placed on top of this in order to prevent the material being extracted from passing through. If coarse material is to be extracted, the bottle can be filled directly, otherwise it must be placed in a bag made of suitable cloth. The cooling part of the condenser is similar to a reversed Dewar flask. The water inlet and outlet tubes are sealed through the outside jacket. As the vapour tube passes right into the cooling part of the condenser, exceptionally efficient reflux is obtained with a relatively short length [*Chem. Ind.*, No. 40 (1953), 1053].

Indian Academy of Sciences, Annual Meeting

THE NINETEENTH ANNUAL MEETing of the Indian Academy of Sciences was held in Ahmedabad under the Presidentship of Dr. C. V. Raman, from 27 to 30 December 1953. The venue selected for the meeting was particularly appropriate, as the young University of Gujerat with its many teaching and research institutions together with ATIRA, the research organization of the textile industry of Ahmedabad, provided the visitors an opportunity to come in contact with the growing spirit of science in Gujerat. The three-day session (28-30 Dec.) included the reading of 17 papers in the field of physical, meteorological, mathematical, chemical and geological sciences and two symposia on Cosmic Radiation, and Solar Radiations and the Upper Atmosphere. A feature of special interest for the textile industry was a symposium on the Science of Fibres.

In his presidential address on " The Origin of the Colours in Precious Opal ", Sir C. V. Raman gave an account of the studies which he had recently carried out at the Raman Research Institute, Bangalore, on the multi-layered structure of opal which gives it its fascinating optical properties. The investigations have led to the conclusion that opal consists of alternate layers of two crystalline forms of silica, namely high-cristobalite and low-tridymite, giving rise to selective colours depending on the spacings of the stratifications.

Three papers were presented at the symposium on Cosmic Radiation and four at the symposium on Solar Radiations and Upper Atmosphere.

Professor Bernard Peters and other workers from the Tata Institute of Fundamental Research, Bombay, Dr. R. R. Daniel, and Shri Rama participated in the symposium on Cosmic Radiation and gave an account of their work on the properties of particles discovered with the aid of stuffed emulsions carried up in balloons. They summarized the present state of knowledge on heavy mesons, hyperons, interactions of shower particles and the nature of the charge on primary cosmic radiation. Dr. Vikram Sarabhai of the Physical Research Laboratory, Ahmedabad, gave an account of his recent work on the time variations of cosmic rays and their significance, pointing out the part played by the solar component of the cosmic radiation. The probable diurnal variation of this component as well as its directive effect in the geomagnetic field of earth were also discussed.

During the symposium on Solar Radiation and Upper Atmosphere a discussion was arranged on the ozone content of the atmosphere, its variations during day and night and from season to season, in different latitudes of the earth. Dr. K. R. Ramanathan, Director, Physical Research Laboratory, Ahmedabad, and Dr. L. Ramdas of the Poona Meteorological Observatory participated.

In the symposium on Science of Fibres, discussion centred on the fundamental micro and macromolecular nature of textile fibres. A paper on the statistical distribution of the composite elements was presented by Professor G. Goldfinger of the Buffalo University, U.S.A., and visiting professor to the Ahmedabad Textile Industry's Research Association (ATIRA) and the moisture adsorption characteristics of fibres as revealed by the X-ray diffraction patterns was discussed by Dr. M. K. Sen of the Indian Jute Mills Association Research Institute, Calcutta. Dr. T. Radhakrishnan of the ATIRA dwelt on the visco-elastic properties of the fibres as explained on the Eyring model, while Dr. C. Nanjundayya of the Cotton Technological Laboratory, Matunga, Bombay, drew a picture of the gradual building up of the cotton fibre during its various stages of growth and showed how certain important properties such as fineness, convolutions, strength, wax content, etc., of the fibre were closely interrelated. Dr. P. C. Mehta of the ATIRA surveyed the chemical aspects of the molecular structures of various fibres and discussed the special role played by the active groups in the chain which were responsible for the observed chemical behaviour of the fibres in the wet processing of the textile materials. Dr. M. V. Nimkar of the Calico Mills, Ahmedabad, discussed the moisture adsorption characteristics of the fibres, particularly the regenerated and the synthetic types, in relation to their chemical constitution and morphology.

Of the papers read at the meetings, 5 were devoted to the X-ray, optical and meteorological investigations. Ten papers were devoted to organic chemistry dealing with the work of Professor K. Venkataraman and collaborators at the University Department of Chemical Technology, Bombay, and of Dr. T. R. Seshadri and his coworkers at the University of Delhi. The papers dealt with synthetic and natural organic colouring matters.

Three popular lectures were arranged. The first of these was on " Recent Advances in Colour Chemistry " by Professor K. Venkataraman, the second one by Professor Bernard Peters on " Nature of Cosmic Radiation " and the third by Dr. C. V. Raman on " Colours of Iridiscent Shells ".

Central Laboratories, Hyderabad: Opening Ceremony

THE NEW BUILDING OF THE Central Laboratories for Scientific & Industrial Research was declared open by the Prime Minister, Shri Jawaharlal Nehru, on 2 January 1954 in the presence of distinguished guests, delegates to the Forty-first Session of the Indian Science Congress and eminent industrialists.

The laboratories were established in 1944 by the Hyderabad Government on the initiative of the Council of Scientific & Industrial Research to fulfil the need for a regional scientific and technical development centre which would work in co-ordination with the national laboratories. A grant of Rs. 15 lakhs was sanctioned by the State Government in 1946 for constructing and equipping the laboratories. A further grant of Rs. 18 lakhs was made in 1947. In November 1948 Dr. S. Husain Zaheer, Director of the Laboratories, submitted a detailed scheme for organization and development of the laboratories, which were temporarily housed in the Chemical Technology Department of the Osmania University.

The main building is in the shape of a "T" with the administrative block, the auditorium and the museum forming the two wings and the laboratories, consisting of a basement and four floors, forming the central block. The ancillary buildings consist of four pilot-plant buildings, workshop, electricity substation and the gas house.

The first stage, which has been completed, consists of a basement, ground floor (excluding auditorium and museum), first floor, two pilot-plant buildings, workshop, electricity substation, gas house and store house for inflammable chemicals. The total floor area of these is 86,000 sq. ft. The total expenditure has so far been Rs. 21 lakhs on buildings and Rs. 30 lakhs on pilot plants, equipment and apparatus.

The main purpose of the laboratories is to carry out developmental research of an industrial nature covering both fundamental and applied aspects. The functions assigned to the laboratories include the following:

1. To help and encourage the development of Hyderabad State by organized scientific and industrial research through (a) industrial utilization of raw materials indigenous to Hyderabad State; and (b) devising methods for expansion of existing industries, and for formulating plans for the starting of new industries by carrying out experimental work on a pilot-plant scale in the laboratories.
2. To provide the facilities of a centrally located and well-equipped scientific and industrial research laboratory to the industries in Hyderabad State.
3. To render help and advice to Government departments and industries in matters of scientific interest.
4. To carry out analytical work for Government departments and industries.

The research work carried out at the laboratories is based mainly on the utilization of available resources of Hyderabad State. A brief review of the research activities of the laboratories has been published in an earlier issue of the Journal [*J. sci. industr. Res.*, **12A** (1953), 530].

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THE INDIAN CENTRAL COCONUT COMMITTEE— ANNUAL REPORT, 1951-52

CONSIDERABLE HEADWAY WAS MADE DURING THE year in the reorganization of the Committee's research stations at Kayangulam and Kasaragod. The director of the Kasaragod station was deputed to survey the state of coconut cultivation in Andamans and suggest measures for improving coconut cultivation in the islands. The three-year scheme put forward for improvement of coconut cultivation in Andamans has been approved by the Committee. A similar five-year scheme for development of coconut cultivation in West Bengal was also approved.

The nursery schemes initiated by the Committee have proved popular and the demand for seedlings raised in the nurseries was far in excess of the supply.

Grade specifications for coconut oil and standard contract terms for milling copra have been formulated for adoption by the trade.

A brief account of research work carried out under the auspices of the Committee during the year is given below.

Breeding and morphology — With a view to introducing desirable varieties of coconut from abroad, a detailed study of the morphological and economic characters of a number of varieties planted at the Central Coconut Research Station, Kasaragod, is being made. Observations made so far are: (i) Ganga-bondam and Straits Settlements varieties, Dwarf Green, Laccadive Orange, Laccadive Green, Laccadive Ordinary, Andaman and Fiji varieties produce relatively larger number of leaves and nuts per bunch than the other varieties; (ii) overlapping of male and female phases of the successive inflorescence was found to occur in all the varieties, but there was no overlapping of male and female phases in the same inflorescence of a variety; (iii) Tall Green, Laccadives, Andaman Dwarf, Cochin China, Philippines and Straits Settlements varieties have only few barren axils. Of these, Tall Green, Laccadive Ordinary and Cochin China are high yielders; (iv) 17 out of the 53 varieties did not produce any barren nuts. In Philippines, Leguna, Dwarf Green and Chappadan varieties, the production of barren nuts was fairly high, averaging from 5 to 22 nuts per year.

Button shedding — Study of the sequence of shedding of buttons showed that there was no shedding before the opening of the spathes, and very little between the spathe opening and receptivity of stigma. Maximum shedding occurred in the second and third week after the receptivity of stigma. There was no shedding of the buttons after the sixth week. Anatomical studies undertaken to investigate the factors responsible for the shedding of buttons did not show any lignified or suberized tissue in the region of the junction of embryonic nut and the thalamus. Tests with hormone sprays, like Planofix and Phyomona, for preventing or reducing button shedding were unsuccessful.

In order to test the viability of coconut pollen, a number of artificial media were tested, and one made up of 0·5 per cent agar and 5 per cent sugar was found satisfactory. Complete germination of pollen was obtained in this medium in 12 hr.

Soil analysis — Comparative data on the chemical analysis, mechanical composition and base exchange properties of soil samples belonging to different types from healthy and diseased areas were collected. The data show that most of the soils on which coconuts are grown in Travancore-Cochin are deficient in one or more of the major plant nutrient factors.

To investigate whether the coconut palm disease is a deficiency disease, experiments are in progress with iron, copper, zinc, manganese, magnesium and boron using these as spray in combination and some of them as manure. These experiments, especially where they are used as spray, have given encouraging results.

Copra kilns — Studies carried out during the year have shown that good quality copra can be prepared in the " modified 10-acre Malayan copra kiln ", if the kiln temperature is maintained at 60°C.

Diseases and pests — Investigations on the root and leaf diseases of the coconut in Travancore-Cochin were continued at the Central Coconut Research Station, Kayangulam. Work done so far has shown that the fungi *Botryodiplodia theobromae*, *Rhizoctonia bataticola* and *Rhizoctonia solani* are generally associated with the root disease and the fungi *Helminthosporium halodes*, *Glocosporium* sp. and *Gliocladium roseum* with the leaf disease. Inoculation experiments conducted on healthy seedlings with fungi obtained from the roots of infected trees have indicated that water logging might be a predisposing condition for infection. Individual roots inoculated with these fungi took infection, but in such cases no disease symptoms were manifested on the leaves, etc., of the palms.

The prophylactic effect of application of Bordeaux mixture on fungal infection of palms has been investigated. Tender leaf-bits were sprayed with Bordeaux mixture (full strength) after external sterilization and then inoculated with *Helminthosporium*. Infection took place in the controls and not in the treated bits. The effect of Bordeaux mixture on spore germination, its capacity to initiate infection and the influence of time on the same has also been investigated. It has been observed that the organism takes a minimum of 7 hr. to infect the host.

The grubs of a cockchafer beetle *Lepidiota* sp. have been observed for the first time in India, causing serious damage to the roots of coconut palms in certain areas of Mavalikera and Thiruvella taluks in Travancore. Extensive damage was observed just after the early showers during April, May and June. The grubs attack the roots and completely disconnect them. The nut formation is poor, and in the worst affected cases the palms are barren.

Nurseries and green manuring — There were 31 nurseries functioning during 1951-52 in various States and a total of 214,096 quality coconut seedlings were distributed. The Central Coconut Research Station, Kasaragod, supplied 6,000 seed-nuts from outstanding mother palms to the States of West Bengal and Coorg.

Two schemes for the multiplication and distribution of *Crotalaria striata* seeds were in operation during the year, one in Madras State and the other in Travancore-Cochin. This green manure crop has been found to be eminently suited for growing and incorporation in coconut gardens in the west coast, the soils of which are generally deficient in organic matter.

CHEMICAL RESEARCH LABORATORY, TEDDINGTON — ANNUAL REPORT, 1951-52

THE RADIOCHEMICAL AND MICROBIOLOGICAL GROUPS moved into the two new buildings which were completed during the year. A large amount of work has been undertaken by the laboratory for Government departments in connection with rearmament programme and the laboratory's service to the industry is evidenced by the increasing volume of advice and material help given.

The progress of work in the laboratory's six research groups during the year is briefly described below.

Corrosion research — Accelerated methods of testing are being employed in studies on corrosion of metals. In one such method, electrical capacitance is used to study the absorption of water by the paint film and to detect breakdown of the coating in immersed conditions. A new apparatus has been constructed in which specimens can be subjected to controlled amounts of spray solutions, infra-red and ultraviolet radiations.

Novel temporary protective coatings have been developed. These are based on the incorporation of corrosion inhibitors in thixotropic suspensions of inorganic earths. These coatings, although soft and easily removed when no longer required, do not flow from the protected surfaces on storage. Radioactive techniques are being used to elucidate the mechanism of corrosion inhibition by potassium chromate (containing Cr^{51}) and sodium benzoate (containing C^{14}); the results indicate that the former is more firmly held by the metallic surface.

A clay soil, in which the expected attack on buried pipes had not occurred, was examined and the presence of a species of *Actinomyces* toxic to sulphate-reducing bacteria was revealed — an observation that may have practical implications. Samples of the soil from tannery sites were found toxic to sulphate-reducing bacteria because of the presence of tannates; investigation showed that the activity of the organisms, on which corrosion under such conditions depends, is suppressed by as little as 0·01 per cent tannic acid. This discovery has aroused great interest because of its possible bearing on the protection of buried pipelines and other structures.

Contamination of metal surfaces by particles derived from metal finishing processes has been shown to give rise to a rapid incipient type of corrosion, now termed "filiform", and which may lead to serious deterioration of the prepared metal surface. This work emphasizes the need for air-conditioning to prevent the deposition of such particles when fine precision work is in progress.

Inorganic research — An ion-exchange process for the recovery of gold and other metals from cyanide solutions used in the extraction of gold from ores has been developed. This has arisen from the work of the Radiochemical Group on analysis and recovery of valuable metals from minerals, ores and other materials, in which special attention has been given to the use of ion-exchange resins in separating and concentrating metals from solution.

A chromatographic method has been developed for the separation and determination of niobium and tantalum. This method is a substantial contribution to the analytical chemistry of these metals and is now being used by other laboratories.

Radiochemical research — Three new items of equipment have been designed and constructed by the Radiochemical Group. The first is for determining automatically the life of ion-exchange resins on continuous recycling with different solutions. This provides data to facilitate the design of plant for the recovery of metals. The second is an instrument for scanning filter paper strips on which separation of metal salts, containing radioactive tracers, has been effected; the photographic record thus obtained greatly facilitates analytical work. The third apparatus is a counter, in which scintillations, produced by active radiations on dissolved organic substances, are amplified in a photomultiplier valve. This is employed for the measurement of radioactive material and is particularly valuable for measurement of substances containing radioactive carbon.

Inorganic research — Recent interest in the possible replacement of sulphuric acid by nitric acid for the manufacture of phosphate fertilizers has brought dicalcium phosphate into greater prominence and methods of producing it have been studied. A superphosphate fertilizer made with nitric acid contains monocalcium phosphate and calcium nitrate, both of which are water soluble. The calcium nitrate, being deliquescent, can be an objectionable constituent of the product and it is preferable to remove it. This is easily achieved by converting the soluble monocalcium phosphate into insoluble dicalcium phosphate when the calcium nitrate can be washed away. Processes for recovering the nitrate value of the calcium nitrate as ammonium or potassium nitrate have also been examined. Although insoluble in water, dicalcium phosphate is still a good fertilizer.

Organic research — Many requests for direct assistance have been received by the Organic Group. A notable example is the help being given in connection with the production of benzoic acid of certified calorific value as a thermochemical standard for the calibration of bomb calorimeter equipment. The preparation and distribution of standard samples of organic compounds are being extended to meet the needs of users.

The recent discovery that isonicotinic hydrazide has a chemotherapeutic application revived interest in methods described earlier by the Group for the separation of pyridine homologues from crude tar-base fractions. These individual bases included γ-picoline, an intermediate for the preparation of isonicotinic acid. More recently attention had been given to the quantitative analysis of infra-red spectroscopy of crude and purified pyridine-base fractions. This extension of the work was of practical value since it provided a service for firms which lacked the necessary facilities for the evaluation of synthetic and purified pyridine homologues.

High polymers research — The preparation by the High Polymers Group of semi-permeable membranes with outstanding properties from polyvinyl alcohol, together with the simplification in apparatus made possible by their use, constitute a major advance in osmometry of high polymer solutions. Results of considerable theoretical and industrial significance have been obtained by using highly selective membranes and the molecular weights of simple chemicals of known structure have been determined.

Long-term studies of the behaviour of cation-exchange resins by the High Polymers Group are nearing completion and their practical value has already been proved. The information gained enables critical tests to be applied in assessing the values of new resins, and advice has been given in many cases on the most suitable resin for specific purposes.

Microbiological research — Investigations on the microbiological production of sulphur and sulphide have been intensified. A continuous method for the cultivation of sulphate-reducing bacteria is being employed; a marked increase in the rate of sulphate reduction has been achieved by the use of a suitable nutrient medium. Fundamental work on the sulphate-reducing bacteria has included a study of their use of various carbon sources as reducing agents, and the investigation of " sulphate-free " fermentation with pyruvate as carbon source.

Miscellaneous — Investigations on the oxidation of steel at moderately high temperature have been started with special reference to production of improved steels for boiler superheater tubes. In the work for the British Shipbuilding Research Association, progress has been made in reproducing, in a short period, the types of damage to ships under ordinary seagoing conditions.

The High Polymers Committee, set up to review the work of the High Polymers Group, recommended that investigations on resins possessing complex-forming or other special properties should continue, and that the programme of research on semi-permeable membranes should be extended to include fundamental studies of the factors controlling the degree of semi-permeability of polymer films and their applications in osmometry and dialysis.

On the advice of the Pure Metals Committee nickel, rhenium, thallium and titanium were added to the stock of high purity metals.

INDIAN SCIENCE CONGRESS — SCIENCE EXHIBITION: NEW INSTRUMENTS & APPLIANCES — *Continued from page* 143

etc., is also recommended. The instrument is manufactured by Wissen-schaftlich-Technische Werkstatten, Germany.

Universal Colorimeter, Model V (FIG. 7) — This is a universal photometer having two photocells in balanced circuit and is designed for use in all colorimetric and fluorescent measurements, and photoelectric titration. It is adaptable for use in both deflection and compensation methods. The quantity of liquid required is about 0·2 cc. Mercury lamps and filters are available for fluorescent measurements. The apparatus is designed and manufactured by Dr. B. Lange of Berlin.

Drage Structural Viscometer — The viscometer is designed for measuring viscosities in the range 0-10,000 poises. Viscosity is linearly related to the frictional force acting on the measuring element and this is directly read on the scale. Five different measuring elements are supplied for measuring the viscosities. The instrument is manufactured by Dr. A. G. Epprecht Ltd., Zürich.

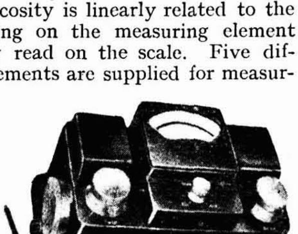


FIG. 7 — LANGE'S UNIVERSAL COLORIMETER

Hartmann & Braun Chopper Bar Controller — The instrument is offered for automatically controlling the temperature of furnaces, heated electrically, by gas or by oil. Small electric furnaces up to 1·2 kVA. can be directly controlled. On and off or step-by-step regulation can also be achieved. The instrument can be used with different thermocouples up to 1,600°C.

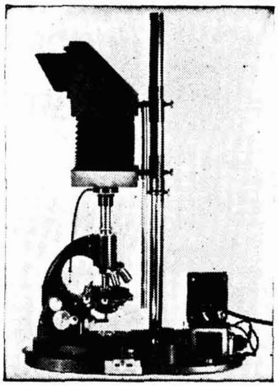


FIG. 8 — PROJECTOLUX ILLUMINATOR

Projectolux Illuminator (FIG. 8) — Manufactured by C. Baker of Holborn Ltd., England, the instrument is useful as an illuminator base for microscope, gives excellent results as a micro-projector for lecture room demonstrations when used with a microscope and a projecting prism. It is also recommended for use in microphotography.

Other instruments displayed were: Rapid Colorimeter; Lange's Multiflex Galvanometer; Drage Ultra Thermostat; Bomb Calorimeter LFA 6330; Frequency Meter and Photoelectric Pick-up.

INDIAN PATENTS

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

Chemicals, plastics, rubber, paints and allied products

47932. Activated carbon, catalysts or catalyst carriers: *Conducting granular carbonaceous substance admixed with activating gases through layers of filling bodies* — Metallgesellschaft Aktiengesellschaft

50150. New crystalline sodium borate: *Heating together sodium borate or a mixture of sodium borates having molar ratio* $Na_2O : B_2O_3$ *between* 0·4 *and* 0·7 *and water to a temperature depending on molar ratio* — Borax Consolidated Ltd.

47597. A process for the preparation of basic aluminium sulphate: *Adding to aluminium sulphate or alum an alkali and a stabilizing agent comprising an aliphatic organic acid or hydroxy acid* — Council of Scientific & Industrial Research

48590. Production of hydrogen peroxide: *Hydrolytic decomposition of persulphuric acid and distillation of hydrogen peroxide formed in apparatus made of graphite* — Deutsche Gold Und Silber-Scheideanstalt Vormals Roessler

49522. Improvements in resin foam and process: *The composition comprises a foamable alkyd resin-organic di-iso-cyanate mixture containing a surface active agent miscible with the mixture and inert with respect thereto* — Wingfoot Corporation

49617. Preparation of 2-4-diamino-pyrimidine derivatives: *Reacting β-keto nitriles of the formula* $R'\text{-}CH(CN)\text{-}CO\text{-}R''$ *with an amine of the formula* $R'''NH_2$ *and condensing the formed product with guanidine* — Carlo Ebra S.p.A.

49799. Manufacture of shaped structures from polymers and copolymers of acrylonitrile: *Solutions of polymer in nitric acid are wet spun in a coagulating bath consisting essentially of water and nitric acid, said bath being maintained at a temperature of* 15°-70°*C.*—Halbig

48112. Process for purifying acetone containing impurities other than methanol: *Acetone is fed to middle section and boiling aqueous liquid to top section of a distilling column* — Les Usines De Melle, Societe Anonyme

48262. Recovery of glycerol: *Mixing concentrated fermentation liquor with granular material continuously agitating said mixture while heating under reduced pressure* — I.C.I. Ltd.

48630. Process for fractionating starch: *Dissolving starch under pressure in aqueous salt solution, precipitating amylose and amylopectine by cooling successively* — Co-operative Verkoop-En Productievereniging Van Aardappelmeel en Derivaten Avebe G.A.

47735. Manufacture of phospho-nitrogenous fertilizers: *Ammonia and air are simultaneously introduced in a solution of natural phosphate with nitric acid* — Societe Anonyme Des Manufactures Des Glaces Et Produits Chimiques De Saint-Gabain Chauny & Cirey

47752. Granulation of fertilizers and the like: *A part of the granulated product is added to the sludge at different stages* — Societe Anonyme Des Manufactures Des Glaces Et Produits Chimiques De Saint-Gabain Chauny & Cirey

47852 and 47853. Process for the production of resinous ester compositions and the esters so produced: *Reacting a higher alkenyl-phenol-aldehyde condensation product with an esterifying agent.*

Etherifying a higher alkenyl-phenol-aldehyde condensation product with a hydrocarbon etherifying agent — British Resin Products Ltd.

49858. Production of guanidine sulphamate and/or melamine: *By reacting a mixture of urea ammonia and sulphur dioxide at temperature above* 220°*C.*— The Consolidated Mining & Smelting Co. of Canada Ltd.

49934. Resinous polyhydric alcohols: *Resinous compositions, useful for the preparation of coating compositions, comprise a resinous polyhydric alcohol and an organic poly-isocyanate* — I.C.I. Ltd.

Chemical processes, engineering and equipment

47550. Grinding apparatus for fibrous, granular and pulverulent materials: *Characterized in that stationary grinding member is adjustably mounted in second support facing first support spaced to accommodate driving pulley and bearings for shaft* — Asplund

50470. Method for granulating urea: *Heating an aqueous solution of urea and maintaining burette content of the solution during heating to less than 5 per cent* — Chemical Construction Corporation

50471. Improvements in granulator: *The granulator has a body with an inlet for the solution nozzles in the body, a chamber in the body for carrying the solution and four chambers in the body for carrying the heating medium* — Chemical Construction Corporation

48851. Method and apparatus for the treatment of finely divided fludizable solid material: *Maintaining a fluidized bed in horizontal flow and trarsmitting heat to the material at successive stages in its flow* — Aluminium Laboratories Ltd.

50666. Pumping apparatus for liquid materials capable of setting: *Downwardly directed mono pump with feed tank located above and connected to pump stator; driving shaft extends upwardly from pump rotor through the tank* — Colcrete Ltd.

Physics — general

47622. Apparatus for investigating a solid capable of being caused to exhibit magnetostrictive properties: *Including means for creating a mechanical wave in the solid and means for detecting the characteristics of the wave propagation* — THE McPHAR ENGINEERING CO. OF CANADA LTD.

47657 and 47682. Thermionic cathodes: *Electron emissive material consisting of a mixture of alkaline earth tungstates with alkaline earth oxides. Electron emissive material formed by heating intimate mixture of finely divided tungsten and alkaline earth oxides* — THE GENERAL ELECTRIC CO. LTD.

47756. Improvements in electrical translating arrangements suitable for use in automatic telephone systems: *Employs a high speed register device common to a plurality of signal sources and involving the scanning of a succession of storage areas* — BRITISH TELECOMMUNICATIONS RESEARCH LTD.

Food and kindred products

48308. Procedure and device for preserving plant and animal products and preservative agents thereof: *Comprising effective ingredients of officinal aromatic plants and adhesive carrier material* — POPP

Drugs and pharmaceuticals

47740. New esters of cycloalkylidene acetic acids: *Aryl cycloalkylidene acetic acids or their derivatives are converted into their N-di-substituted aminoalkyl esters by a known method, or aryl-cycloalkyl-acetic-acid-aminoalkyl ester containing a removable residue is treated to split it off giving cycloalkylidene esters* — CIBA LTD.

48871. Treatment of senna: *The temperature of air is from* 150° *to* 180°*C. and temperature inside the chamber is between* 60° *and* 95°*C.*—COPLANS

49795. Process for the manufacture of new amides: *Quinoline carboxylic acid RO-Q-COOH is converted to an acid amide of formula* $-CON(R^1)-[CH(R_n)-(CHR_{1n})^{-1}]n-ROv$ — CIBA LTD.

49821. Purification of esters of chloramphenicol: *Containing the crude esters in an inert solvent with activated alumina* — THE BRITISH DRUG HOUSES LTD.

47916. Manufacture of unsaturated ketones of the steroid series: *Treating* Δ^{78}-9 : 11-*oxido-steroid with an electrophilic agent in presence of an ether and, if desired, reacting the resulting compound with an acid* — CIBA LTD.

47639. Improvements in carbomycin: *Cultivating Streptomyces halstedii or an equivalent carbomycin-producing organism in an aqueous nutrient medium* — CHAS. PFIZER & CO.

49553. New ox-diazole compounds and process for their manufacture: *Carboxylic acid-N:N'-dihydroazide is reacted with an agent capable of splitting off water* — CIBA LTD.

47961. Process for the manufacture of a new hydrazine compound: *Reacting* 3: 6-*dimercapto pyridazine with hydrazine* — CIBA LTD.

48170. Process for the manufacture of steroids having oxygen in 11-position: *Treating sulphonic acid ester of* 11 β-*acyloxy*-12 α-*hydroxy steroids with hydrolysing agent, splitting resulting* 11:12β *oxides with acids and removing the substituent in* 12-*position of the product by reduction* — CIBA LTD.

Fuels and lubricants

49769. Fuels for internal combustion engines: *Motor fuel containing a minor proportion of a compound of formula* MR_2, *wherein M is iron or nickel and R is a cyclopentadienyl radical* — SHELL REFINING & MARKETING CO. LTD.

49456. Preparation of a mixture of alkyl phenolates and alkyl salicylates having a high content of a polyvalent metal and suitable as lubricant additive: *Reacting a mixture of alkali metal salts of alkyl salicylic acids and alkali metal compounds of alkyl phenol with an inorganic polyvalent metal salt* — N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ

Metals and metal products

46932. Apparatus for continuously casting rimmed steel: *A rod of predetermined length with a solid self-supporting crust and a molten core of the whole length of rod is cast in a chilled mould tube, the predetermined length being more than the length of the mould tube* — JUNGHANS

47496. Electric resistance heating of material in continuous processing lines: *Comprises two transformers connected in phase relation and one end of secondary connected to conductive rolls* — UNITED STATES STEEL CORPORATION

48157. Hydrometallurgical method of extracting metal values: *Dispersing metal-bearing material in an aqueous ammoniacal solution containing ammonia and a sulphur compound, actively agitating the mixture above atmospheric pressure and temperature* — SHERRIT GORDON MINES LTD.

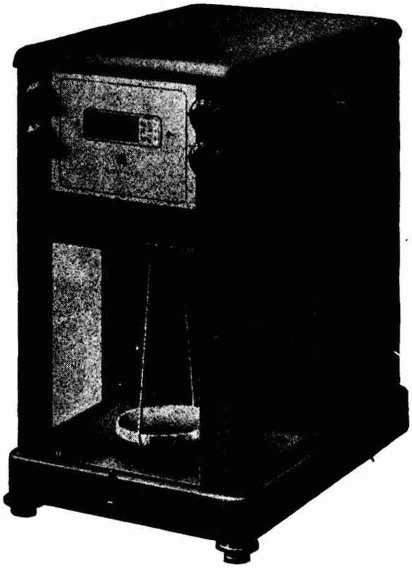
48342. A method for the regeneration of the spent liquid from electrolytic manganese and electrolytic manganese dioxide: *The sulphuric acid present in the spent bath is reacted with an ignited mass obtained by igniting to completion pure manganous sulphate at about* 750°*C.*—COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

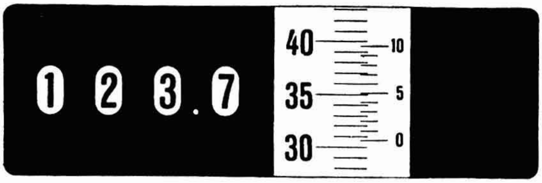
Building materials and methods

50558. Improvements in concrete and concrete mixes: *Concrete mix consisting of portland cement and similar cement such as cement fondu, Roman cement, aluminous cement, sand, mineral aggregate and asbestos* — DUDLER

47002. Improved interlocking building blocks and wall constructions or the like: *A series of interlocking building blocks are formed wherein their vertical ends are returned at similar angles* — STEAD

49353. Construction of floors: *Floor formed on plunger piles and in contact with ground which being allowed to sink transforms floor into suspended structure supported by the piles* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH





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Journal of Scientific & Industrial Research

Vol. 13B, No. 3, MARCH 1954

CONTENTS

PUBLISHED BY THE COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, INDIA
NEW DELHI

J. sci. industr. Res., Vol. 13B, No. 3, Pp. 151-224. March 1954

MARCONI UNIVERSAL BRIDGE

TYPE TF 868

In the Universal Bridge, for the measurement of Inductance, Capacity and Resistance, the multiplying factor is dispensed with and all values can be read directly from a single scale.

The wide ranges covered are:

Inductance (at 1000 c/s)	...	**1 microhenry to 1000 henrys**
Capacity (at 1000 c/s)	...	**1 mmfd. to 100 mfd.**
Resistance (at D.C.)	...	**0·1 ohm to 10 megohms**

The guaranteed accuracy is 1 per cent except at the highest and lowest values.

The 'Q' of inductances and power factor of condensers, both at a frequency of 1000 c/s, can be read directly. An internal valve oscillator supplies the 1000 c/s source.

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On the U-V Emission Spectrum of Toluene*: Emission Observed from Vibrational Levels in the Upper Electronic State to Vibrationless Ground State

SATYA NARAIN GARG
Banaras Hindu University, Banaras

Among other causes, self-absorption by the unexcited vapour near the window of the usual type of discharge tube (where the window has to be kept at least 5 cm. from the discharge to avoid rapid deposition of discharge products) does not allow observation of emission bands from vibrational levels in the upper electronic state to vibrationless ground state in those derivatives of benzene in which emission is observed. It has been possible to reduce the distance between the window and the discharge to 2 cm. by constructing a built-in annular guard ring round the window into which the deposit is secured keeping the window clear.

Employing the modified arrangement, the emission spectrum of toluene has been observed to $\sim$ 1,850 cm.$^{-1}$ on the shorter wave side of the origin. This consists of sharp bands in the positions mostly expected from the corresponding absorption spectrum. A revised analysis of the absorption spectrum of toluene is proposed and a correlation of frequencies with those of benzene has been made.

IN the case of emission spectrum of benzene[1] and a few of its derivatives, e.g. toluene[2,3], benzonitrile[2], fluorobenzene[4] and aniline[5] (in electrical discharge or fluorescence), it is only the transition from the lowest excited singlet electronic level to the singlet ground state which is observed, so far as singlet-singlet transitions are concerned. Even in those derivatives in which emission spectrum is known, it does not extend to shorter wavelengths beyond the 0-0 band. Benzene itself is an exception to this. Occurrence of emission bands of benzene derivatives with wave number differences of $\lesssim$100 from the 0-0 band on the longer wavelength side does show the existence of difference frequencies, most probably 1-1 transitions, but the actual magnitude of the partaking vibration frequency in the upper electronic state remains a matter for conjecture. Of the several causes of non-observation of emission bands on shorter wavelength side of the 0-0 band the following are important: (i) self-absorption, (ii) life-time in the excited electronic state, and (iii) decomposition of the molecule. The purpose of this paper is to focus attention on the *self-absorption* (which is much more in benzene derivatives than in benzene itself) by presenting data on the emission spectrum of toluene extended by $\sim$1,850 cm.$^{-1}$ towards shorter wavelength side of the 0-0 band obtained by reducing the self-absorption.

In the case of emission spectrum excited by electrical discharge, self-absorption occurs due to unexcited vapour present in (1) the path of the discharge and (2) the path

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*Data obtained on the visible spectrum of discharge through toluene vapour have been reported in the paper ' On the " So-called Blue Bands of Benzaldehyde " ' [*J. sci. industr. Res.*, **13B** (1954), 155] wherein it has been shown that the "blue bands" are not due to benzaldehyde but may be due to the radical C_6H_5C. Also, a set of new bands in the visible region are reported and shown, most probably, to belong to toluene itself.

between the discharge and the quartz window of the discharge tube. The former cause cannot be eliminated and a certain amount of the latter is unavoidable in the discharge tube of usual design since the quartz window has to be kept at a reasonable distance (5 cm.) from the discharge to avoid rapid deposition of discharge products and for facilitating observation. The deposit on the quartz window occurs first on its periphery, so that it appears that the discharge products are thrown along the wall of the discharge tube. The modified design for the window and the near electrode of the discharge tube, devised for preventing these products from reaching the window (FIG. 1), permits reduction of the distance of the window from the discharge to ~2 cm. Further reduction in the distance could not be achieved.

Employing this modified arrangement, and a transformer discharge in continuously flowing toluene (B.D.H.; spectroscopically free from benzaldehyde[6]) vapour, a number of weak emission bands have been observed on the shorter wavelength side of the 0-0 band of toluene (FIG. 2). As usual the bands on the longer wavelength side of the 0-0 band are superposed by a strong continuum. No impurities have been detected in the discrete bands on both sides of the 0-0 band. Wave numbers of all the new emission bands are given in Table 1 along with those of bands separated from 0-0 band by ≤800 cm.$^{-1}$, on the longer wavelength side, to show that the emission spectrum obtained definitely belongs to toluene. Practically, most of them correspond to the absorption bands.

TABLE 1 — EMISSION BANDS OF TOLUENE

$\nu_{vac.}$	I	$\nu_{vac.}$— 37481	ASSIGNMENTS
36676*	s	−805	−622 −178
93*	s	−788	−785
36765*	m	−716	−2(622)+530†
82*	m	−699	−521−178†
97*	m	−684	−688
36854*	s	−627	−622
73*	m	−608	−2(233)−622+530−59† −289−233−622+530†
99*	m	−582	−521−59, −2(289)†
36960*	ms	−521	−521
71	m	−510	−2(233)−59†
37030	m	−451	−2(233)†
73*	m	−408	−407
37102*	m	−379	−289−622+530†
24*	m	−357	−2(407)+456
46*	m	−335	−335†
92*	m	−289	−289†
37215*	m	−266	−622+530−178†
48*	m	−233	−178−59, −233†
37305*	ms	−176	−178(=−407+230†)
33*	m	−148	−622+530−59†
62*	m	−119	−2(59)
93*	m	−88	−622+530
37421*	ms	−60	−59(=−233+175†)
81*	s	0	0−0 band
94*	w	13	304−233−59†
37550	w	69	304−233†
37627	w	146	175+304−335†
59*	w	178	175†
65	vw	184	304−2(59)†
37715*	w	234	230†
65*	w	284	280†
85*	w	304	304†
37830*	w	349	2(175)†
89	w	408	230+175†
99	w	418	230+304−2(59)†
37937*	w	456	456
38011*	w	530	530
80*	vw	599	530+304−233†
87	vw	606	926−622+530−233†
38164*	vw	683	926−178−59† 926−233†
38249*	vw	768	926−622+530−59†
38319*	w	838	926−622+530†
50*	vw	869	926−59
38407*	w	926	926
39332*	w	1851	2(926)

* Band corresponding to an absorption and/or fluorescence band.

† Assignment proposed here; s, strong; m, medium; w, weak; vw, very weak.

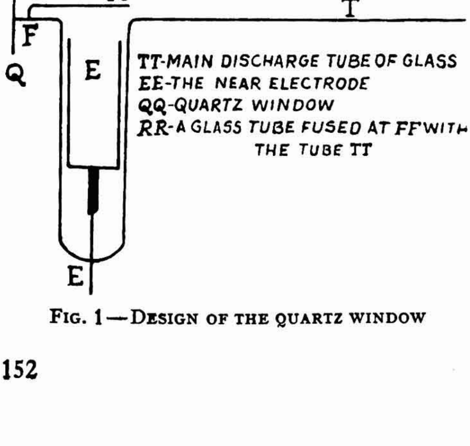

FIG. 1 — DESIGN OF THE QUARTZ WINDOW

Discussion

A partially modified analysis is proposed here in view of the recent work of the author[7-9] summarized below.

1. An investigation[7] of the absorption spectrum of benzaldehyde vapour showed that (i) the vibronic selection rules and depolarization factors of vibrational Raman lines of benzaldehyde point to a symmetry lower than C_{2v} for benzaldehyde molecule and not C_{2v} itself as assumed so far and (ii) all the vibration frequencies of benzaldehyde known from Raman, infra-red and

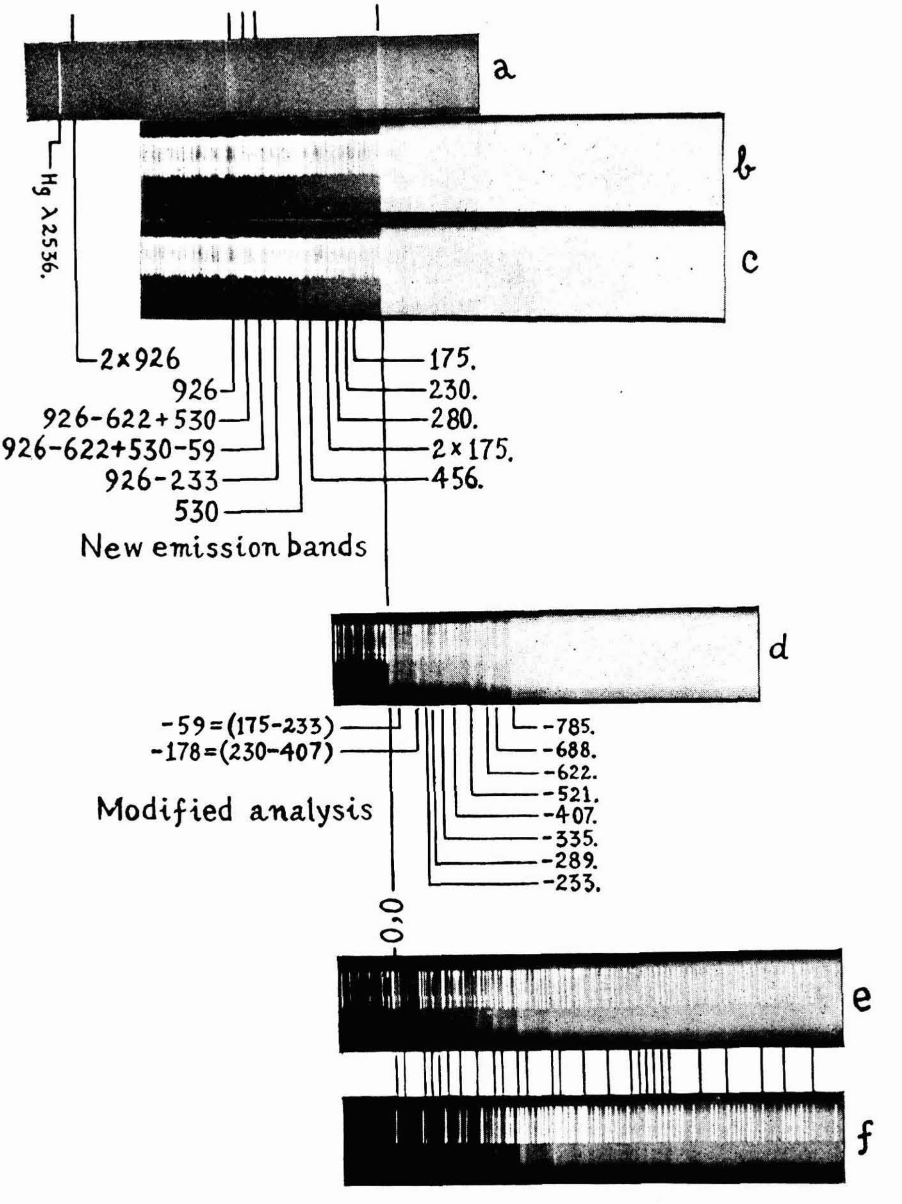

FIG. 2 — EMISSION SPECTRUM OF TOLUENE [(a), Beginning of experiment; slightly impure tube; window clear; (b-e), one and the same plate with difference only in printing; pure spectrum; window very lightly choked; (e and f) a good reproduction of known emission spectrum of toluene showing clearer definition of bands and much less intensity of continuous background]

ultraviolet absorption spectra could be satisfactorily correlated to the corresponding vibrations of benzene and of formaldehyde, and some of the frequencies could actually be calculated from Teller-Radlich product rule.

2. On the basis of similarity, a general theory, correlating the vibration frequencies of a molecule with those of its parts, has been developed[8] and made use of in correlating the vibration frequencies of mono-substituted

TABLE 2 — COMPARISON OF OBSERVED AND CALCULATED VALUES OF A FEW FREQUENCIES OF MONO-SUBSTITUTED BENZENES

MOLECULE	SUBSTITUENT	TOTALLY SYMMETRIC PART OF ν_{18} (606) OF BENZENE		BENDING VIBRATIONS OF SUBSTITUENT			
				In plane		Out of plane	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Toluene	CH_3	558	520	397	—, 335	277	289, 233
Aniline	NH_2	543	533	390	386, —	273	—, 234
Phenol	OH	530	527	384	—, —	270	—, 240
Fluorobenzene	F	506	520	372	368	264	242
Benzonitrile	CN	448	460	346	381, 323	251	264, 170
Benzaldehyde	CHO	431	440	338	328, 281	247	245, 139
Chlorobenzene	Cl	403	418	326	295	241	196
Benzotrifluoride	CF_3	327	338	295	321, 235	226	199, 139
Bromobenzene	Br	315	315	291	250	224	181
Iodobenzene	I	285	267	280	—	219	168

benzenes to all the vibration frequencies of benzene. The relations arising therein show that in mono-substituted benzenes the following frequencies can be correctly represented by simple formulae[*] depending only on the mass of the substituent: (i) The totally symmetric part of ν_{18} e_{2g} (606) of benzene which plays an important role in the spectrum of benzene and its derivatives; (ii) the two bending vibrations of the substituent in the plane of the phenyl group; and (iii) the two bending vibrations of the substituent perpendicular to the plane of the phenyl group. A very wide range of mono-substituted benzenes has been investigated[*] (TABLE 2).

3. Previous workers have assumed a symmetry C_{2v} for the molecules cited above, in general. It has been shown[9] that the assumption of C_{2v} symmetry is not justified on account of the space structure of the particular molecules and/or on account of the contradictions that such an assumption produces in the interpretation of not only the U-V data but also of Raman and infrared spectra data.

Some features of the proposed analysis

The following frequencies have been used in the analysis: (1) *Ground state*: 233, 289, 335, 407, 521, 622, 688, 785; (2) *excited state*: 175, 280, 304, 230, 456, 530, —, —, 926; and (3) 1-1 *transition*: −59, −9, −31, −178, —, −92.

The possibility of occurrence of a singly excited b_2 vibration in the ground or upper electronic state has not been considered by previous workers due to the assumption of symmetry C_{2v} for toluene. It can be seen that the structure of toluene is such that it cannot belong to C_{2v} symmetry but to a lower one. Thus all vibronic transitions are allowed. Ground state vibration frequencies 335 and 289, 233 observed here (corresponding to Raman frequencies 344 and 294, 216) have been assigned[8] to the bending of $-CH_3$ group — the former one to a bending in-plane of the ring and the latter two to out-of-plane bending vibrations. The corresponding frequencies in the excited state are assigned the values 304 and 280, 175. This choice explains the prominently observed but unexplained difference frequencies −9 (= −289+280) and −59 (= −233+175). Ground state frequency 407 corresponds to either e_{2u} 404 vibration or a_{2g} (1,190, calculated) in-plane bending vibration of benzene[8] (vacant space in TABLE 1). Or, it may be that the two frequencies corresponding to the two vibrations of benzene have nearly the same value[8] (∼407). In the analysis, it has been presumed that at least a part of the intensity of the band at ν 37,073 is due to the frequency corresponding to the e_{2u} 404 vibration of benzene, and, similar to the case of benzene, a much reduced frequency 230 has been assigned to this vibration in the excited electronic state. This explains the strong difference frequency −178 as arising out of the 1-1 transition −407+230. The 1-1 transition −622+530 enters into many combinations. Both −622 and +530 have been observed. The other ground state frequencies are 521, 688 and 785. In the excited electronic state the frequency 926 (corresponding to 1,004 in ground state) occurs singly as well as doubly excited. It is seen that the pattern of bands just on the longer wavelength side of 0-0 band is repeated before the band ν 38,407 which involves the excited state

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[*] Actual formulae from which the values are calculated are given elsewhere, e.g. in the paper 'On the "So-called Blue Bands of Benzaldehyde"' [GARG, SATYA NARAIN, *J. sci. industr. Res.*, **13B** (1954), 155].

frequency 926. Many more repetitions of similar nature can be discerned in the analysis. It is also interesting to note the prominent role played by the assigned low frequency vibrations in the majority of bands. By the actual assignment of these low frequency fundamentals in the ground state, the need to interpret them as difference frequencies does not arise and the intensity distribution in the absorption spectrum seems to be put on a more satisfactory basis. The interpretation of the difference frequencies −9, −59 and −178, as arising in 1-1 transitions of low frequencies, explains satisfactorily their intensities in the absorption spectrum.

Acknowledgement

The author wishes to express his thanks to Dr. R. K. Asundi and to Dr. N. L. Singh for their keen interest in the investigation and valuable discussions on the problem, and to the Council of Scientific & Industrial Research, New Delhi, for financial assistance to carry out the investigation.

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On the So-called "Blue Bands of Benzaldehyde"

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The so-called " blue bands " of benzaldehyde have been produced free from any bands due to CO in a simple transformer discharge through flowing vapour of pure toluene free from benzaldehyde. Absence of bands due to CO and absence of benzaldehyde in the source are the evidences against the assignment of the bands to benzaldehyde.

It is suggested that the " blue bands " are due to the radical, C_6H_5C, common to all the compounds in which these bands are known to occur. The strong and prominent frequency 1,730 cm.$^{-1}$, previously supposed to be a carbonyl frequency, it is suggested, may be due to the vibration of C against C_6H_5 with a bond strength of more than one in the radical.

The few weaker, sharp and single-headed additional bands observed may be due to toluene itself. These have been analysed separately from the above bands.

A general correlation of frequencies with those of benzene is given.

THE vapours of a few derivatives of benzene are known to emit (in electrical discharge, or in fluorescence excited by ultraviolet light) a band spectrum in the blue-green region[1]. In all the known cases the structure of this spectrum appears to be the same and is, therefore, attributed to a common emitter. It has been supposed that during excitation of the benzene derivative from the ground state, benzaldehyde is formed by some chemical reaction[1] and is responsible for this spectrum. Hence, the name " blue bands of benzaldehyde " is given for the bands observed. This does not preclude the possibility that the spectrum is due to a common radical[2], such as C_6H_5C. The purpose of the present communication is to present experimental facts to stress the latter view.

Experimental procedure

The " blue " spectrum was produced in transformer discharge in a conventional II-type discharge tube in flowing vapour of pure toluene (B.D.H., spectroscopically free from benzaldehyde[3]). The spectrum obtained was free from bands of CO (Fig. 1). A spectrum of impure tube (containing CO)

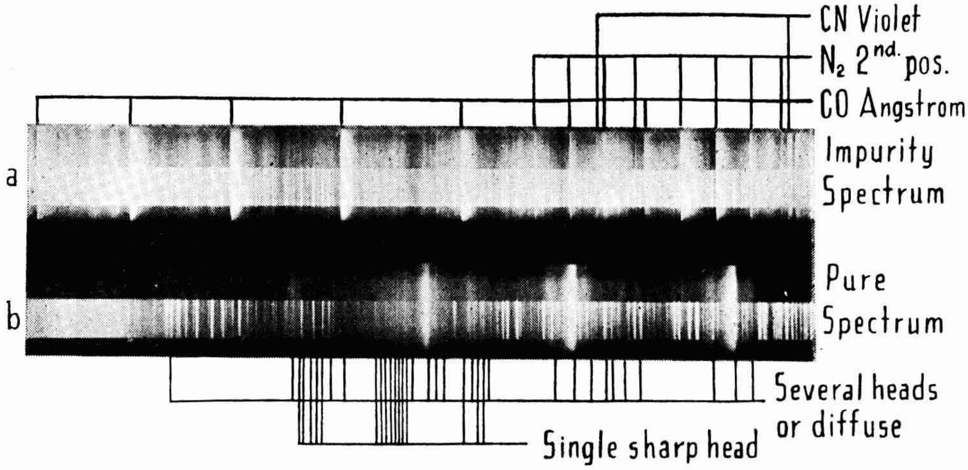

FIG. 1 — SPECTRUM OF DISCHARGE IN (a) IMPURE TUBE AND (b) FLOWING VAPOUR OF PURE TOLUENE

is also reproduced for comparison. A Hilger large quartz spectrograph was used for the purpose. All the bands are degraded to red. Under the dispersion and resolution employed, it was found that some bands show several sharp heads, some are slightly diffuse (probably due to overlapping), while some are sharp bands having a single head. The bands of the first and second type naturally go together and are listed and analysed in Table 1, and the single-headed sharp bands in Table 2. Out of the several heads, the first head (shortest wavelength) was used in analysis.

Discussion

Case against benzaldehyde formation — The data recorded here are more accurate than any previously[4] reported. The freedom of the spectrum from any trace of CO bands indicates the absence of oxygen in the discharge tube as, otherwise, CO bands invariably* appear in this region. Thus it appears impossible for benzaldehyde (even a trace) to be formed from pure toluene under the conditions of excitation employed in the present study. Hence, on this ground alone, the possibility of benzaldehyde being an emitter of these " blue bands " is ruled out.

Criticism of the empirical correlation of the " blue bands " with benzaldehyde — Though this region corresponds to the longest wavelength carbonyl region for a conjugated molecule like benzaldehyde, this does not debar other emitters in this region. The carbonyl absorption in benzaldehyde has the first strong band (of longest wavelength) at ν 26,917[5]. That this absorption system of benzaldehyde is not the counterpart of the " blue bands " is shown firstly by the striking difference in fine structure† of the bands, and secondly by the fact that neither of the first two bands (ν 25,372 and 25,196) of the " blue bands " can be correlated (through possible simple combinations of the frequencies[5] of benzaldehyde) to the absorption band of benzaldehyde at ν 26,917. If such a correlation is attempted through the main frequency (which is 1,730 cm.$^{-1}$ in the first observed quantum) of the " blue bands ", the value of the frequency needed is $\sim$1,755 which does not fit. It seems that apart from the absence of any other concrete

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*The spectrum published by Stewart (*Recent Advances in Physical and Inorganic Chemistry*, 1930, Plate 1) also seems to be free from CO bands, but it has been obtained by using benzaldehyde itself. This fact, therefore, falls out of the way of the argument which follows here.

†From Garg, ref. 5 [Each band (of the carbonyl absorption in benzaldehyde) consists of a central line and three branches on each side degraded away from the line. The successive separations of the six branches are roughly the same, $\sim$28 cm.$^{-1}$, and the central line is unequally spaced between the first branches on the two sides (being nearer to the branch on the longer wavelength side). The intensity of the central line appears to be about half of that of either of the first branch on the two sides and roughly equal to that of the second branch on either side. The third branch on each side is weak].

evidence to support it, the observation of ν 1,730 as the main frequency in the " blue bands " has led to the supposition of a carbonyl group in the emitter. It is suggested that ν 1,730 has a different origin than carbonyl group.

Possible emitter of the " blue bands ": For bands in Table 1 — Since in the absence of oxygen benzaldehyde as emitter is ruled out, and since these bands are observed in a large number of benzene derivatives, the emitter of these bands should be a radical common to these compounds. Apparently, the choice falls on the largest common radical, C_6H_5C. A radical C_6H_5 (or other smaller ones) will not suit since benzene itself does not show the " blue bands ". The choice of C_6H_5C retains the ring and helps in explaining the occurrence of frequencies similar in value to those of benzene.

TABLE 1 — BANDS HAVING SEVERAL SHARP HEADS OR HAVING DIFFUSE APPEARANCE

(*Probable emitter* C_6H_5C)

I	$\nu_{vac.}$	$\nu_{vac.}$ − 25372	ASSIGNMENT
4d	25372 341	0	0−0 band
9	196 180 148 126 093 062	−176	−178, diff. freq.
5d	24974 936 901	−398	−395
3d	190 175 150	−1182	−1182
4	018 23983	−1354	−1360
2	872	−1500	−1500
3	807	−1565	−1500−65, 65 is diff. freq.
3 3 5	642 609 584	−1730	−1730, main freq.
10	464 450 423 394 362	−1908	−1730−178
5	249 214 178	−2123	−1730−395
3	22453	−2919	−1730−1182
4	253	−3119	−1730−1360
3	21938	−3434	−(2×1730)
4	869	−3503	−(2×1730)−65
7	760 749 722 694	−3612	−(2×1730)−178
2	548	−3824	−(2×1730)−395
1	20744	−4628	−(2×1730)−1182
2	578	−4794	−(2×1730)−1360
3	( ) 060 027	−(529−)	−(3×1730)−178
1	18421	−6951	−(4×1730)−178

Values within brackets in the last column are multiple quanta of the frequency and not the arithmetical values.

TABLE 2 — SINGLE-HEADED SHARP BANDS

(*Emitter uncertain; probably toluene itself*)

I	$\nu_{vac.}$	$\nu_{vac.}$ − 22389	ASSIGNMENT
3	22389	0	0−0 band
5	331	−58	−58, diff. freq.
3	185	−204	−204
3	21508	−881	−204−684
5	479	−910	−920
3	418	−971	−58−920
5	386	−1003	−1004
4	326	−1063	−58−1004
3	257	−1132	−204−920
2	207	−1182	−1178
1	149	−1240	−58−1178
2	20459	−1930	−58−1178−684
1	400	−1989	−58−1004−920
1	327	−2062	−58−(2×1004)
1	218	−2171	−1004−1178
2	165	−2224	−58−1004−1178

For bands in Table 2 — These bands are interspersed among the bands recorded in Table 1 and are comparatively weaker. Much attention has not been paid by previous workers* to these bands to show whether or not these too are common to benzene derivatives. Although a few such bands are known to occur, the coincidence of their wavelengths may be just a matter of chance. If the bands given in Table 2 are also common to the benzene derivatives, the suggestion made for the bands given in Table 1 holds good for them also. Otherwise, if they are due to toluene itself (the molecule used in the present experiment), the difference in their structure and the absence of ν 1,730 (observed in the bands in TABLE 1) in their analysis are readily explained, although the absence of ν 1,730 does not come in the way of the suggestion of the emitter being a radical common to the benzene derivatives. The frequencies involved in the analysis are very nearly those already known for toluene in its ground state.

The origin of ν 1,730 — C-C single, double and triple bond frequencies are in the neighbourhood of 900-1,000, 1,650-1,700 and 2,100 respectively. When during the excitation from the ground state (in electrical

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*Specially due to the CO bands unfailingly appearing overlapping the spectrum obtained. This is not so in the present case.

discharge or fluorescence) of a benzene derivative of the type C_6H_5CZ (where Z represents the atoms attached to the C atom), Z is removed, the radical C_6H_5C is left with a bond strength of more than 1 between the phenyl group and the C atom (and certainly with much more than the bond strength existing before the detachment of Z). In compounds of this type (i.e. C_6H_5CZ) it has been shown[6] (see ν_{15} in TABLE 3) that the vibration frequency of C against C_6H_5 is $\approx 1{,}200$ cm.$^{-1}$. Hence, it is not improbable that the vibration frequency of C against C_6H_5 in the radical C_6H_5C be 1,730 cm.$^{-1}$ taking into consideration the large increase in bond strength. The reason *why* ν 1,730 *is the main frequency* of bands in Table 1 can be explained as follows. Consequent on detachment of Z from C_6H_5CZ, the radical C_6H_5C has polarity along its twofold axis (i.e. the line through three C atoms). A change of electronic structure (consequent on change of electronic state) of the radical may affect the effective charge distribution along this axis and, therefore, may affect the bond strength and bond length between the C atom and C_6H_5 group. Thus, the potential energy curves of the radical plotted against the bond length between C_6H_5 and C atom for different electronic states may have sufficiently different forms and positions of minima. If this is so for the two electronic states of the bands given in Table 1, large progression of bands due to the vibration frequency of C against C_6H_5 group arises as a consequence.

TABLE 3 — CORRELATION OF VIBRATION FREQUENCIES OF MONO-SUBSTITUTED BENZENES WITH THOSE OF BENZENE

BENZENE*				MONO-SUBSTITUTED BENZENES
Species	ν_n	Obs.	Cal.†	
A_{1g}	ν_1	3062	—	Practically unchanged
	ν_2	992	—	do
A_{2g}	ν_3	—	1190	Bending vibration of substituent in the plane of ring $=1190\left\{\frac{1}{X}\cdot\frac{78+X-1}{78}\left(1+\frac{487{\cdot}5(X-1)^2+38020(X-1)}{178{\cdot}6(78+X-1)^2}\right)\right\}^{\frac{1}{2}}$ If substituent is a group of atoms, this vibration splits into two of the same order in frequency‡
A_{2u}	ν_4	671	—	Constant at $\sim 670 \pm 20$
B_{1u}	ν_5	—	3063	Practically unchanged
	ν_6	—	1008	Constant at $\sim 770 \pm 20$
B_{2g}	ν_7	—	1520	§
	ν_8	—	538	§
B_{2u}	ν_9	—	1854	Practically unchanged
	ν_{10}	—	1145	do
E_{1g}	ν_{11}	849	—	One part lies between 815 and 849. The other part is the bending vibration of substituent out-of-plane of ring and is $=849\cdot\frac{404}{470}\left\{\frac{1}{X}\cdot\frac{78+X-1}{78}\left(1+\frac{487{\cdot}5(X-1)^2+38020(X-1)}{89{\cdot}3(78+X-1)^2}\right)\right\}^{\frac{1}{2}}$ If substituent is a group of atoms, this vibration splits into two of the same order in frequency‡
E_{1u}	ν_{12}	3099	—	Both the parts have practically unchanged frequency
	ν_{13}	1485	—	Totally symmetric part is ~ 1495. The other part is ~ 1390
	ν_{14}	1037	—	Totally symmetric part is ~ 1030. The other part is ~ 1080
E_{2g}	ν_{15}	3047	—	Totally symmetric part represents valence vibration of the atom linked to phenyl group. It is about 1200 when a C atom is linked to phenyl group. The other part is ~ 3047
	ν_{16}	1600	—	Both the parts have practically unchanged frequency
	ν_{17}	1178	—	do
	ν_{18}	606	—	Totally symmetric part $= 1980\sqrt{(1/X)+(1/78)}$.‡ The other part lies between 610 and 625
E_{2u}	ν_{19}	—	1160	One part supposed to be unchanged. The other part §
	ν_{20}	404	404	One part lies between 404 and 425. The other part constant at $\sim 470 \pm 15$

*Frequency numbering is the same as used by HERZBERG, *Infrared and Raman Spectra of Polyatomic Molecules.*

†Inactive fundamental calculated by LORD and ANDREWS, *J. phys. Chem.*, **41** (1937), 149.

‡For comparison of calculated values with those observed, *see* Table 2 of ref. 7.

§Product of the three frequencies, so marked, remains constant and equal to the product of the three corresponding frequencies of benzene.

Some salient features of the analysis

Before discussing the vibration frequencies used in the proposed analysis it is relevant to give the generalized correlation of vibration frequencies of mono-substituted benzenes with those of benzene derived by the author[6]. X is the weight (on atomic weight scale) of the substituent and is supposed to be ≥ 15 (TABLE 3).

Bands in Table 1 — In benzene (and its derivatives) a difference frequency ν 160 (~178 in toluene[3], ~174 in benzaldehyde[5]) due to 1-1 transition of the vibration ν_{20} 404 (ν_{20} retains nearly unchanged value in the derivatives[6]) is known. Since the ring is supposed to remain intact, ν 178 observed in the " blue bands " has a similar interpretation. The intensification of the bands at ν 25,196, 23,464, 21,760 is due to the superposition of ν 178, the difference frequency of 1-1 transition of a non-totally symmetric vibration. Most probably ν 395 corresponds to ν_{20} 404 of benzene. ν_{17} 1,178 of benzene is observed here as 1,182[6]. ν 1,500 and 1,360 observed here correspond to the totally symmetric and non-totally symmetric parts of ν_{13} 1,485 of benzene[6].

Bands in Table 2 — ν 684 corresponds to the out-of-plane vibration ν_4 671 of benzene[6]. ν 1,004 is known to be a totally symmetric ring frequency corresponding to ν_2 992 of benzene. ν 1,178 corresponds to ν_{17} 1,178 of benzene[6]. ν 920 has various possibilities of being correlated with some inactive fundamental of benzene[6]. In the first ultraviolet band system of toluene a difference frequency of 58 is observed[3]. ν 58 observed here may have a similar interpretation.

Acknowledgement

The author wishes to express his thanks to Dr. R. K. Asundi for his keen interest in the problem and to Dr. N. L. Singh for valuable discussions, and to the Council of Scientific & Industrial Research, New Delhi, for financial assistance to carry out this investigation.

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Synthetic Experiments in the Benzopyrone Series: Part XL — Synthesis of 2-Hydroxymethyl Chromones

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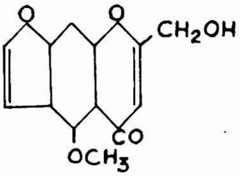
Using N-bromosuccinimide, a method has been worked out for the preparation of 2-hydroxymethyl chromones starting from the corresponding 2-methyl compounds. It is shown that 7-methoxy-2-methyl chromone yields with this reagent a 3-bromo derivative. Bromine also gives the same product. For purpose of comparison the isomeric 2-bromomethyl and 8-bromo compounds have been prepared by unambiguous methods.

With 7-acetoxy-2-methyl chromone, however, N-bromosuccinimide yields the required 2-bromomethyl derivative. This is attributed to the special influence of the acetoxy group which deactivates the benzene ring and enhances the activity of the 2-methyl group. The action of bromine under the same conditions is attended by deacetylation also leading to the formation of 7-hydroxy-8-bromo-2-methyl chromone. The 2-bromomethyl chromone readily undergoes change to 2-hydroxymethyl by the action of silver acetate and subsequent deacetylation. The reactivity of chromone nucleus in these brominations is discussed.

IN an earlier publication[1] a method of synthesis of 2-hydroxymethyl isoflavones was described starting from the simpler 2-methyl isoflavones. The intermediate was the bromomethyl compound which was easily obtained by the use of N-bromosuccinimide. This method was subsequently used for a convenient synthesis of a chromeno-chromone[2]. Though 2-hydroxymethyl isoflavones could be considered to be intermediates in the biogenesis of rotenone derivatives, they have not so far been discovered in natural products. On the other hand, a representative of the simpler chromones belonging to this group is found in chellol (I). Its occurrence[3,4] in the seeds of *Ammi visnaga* along with visnagin (II) is highly significant from the point of view of biogenesis. An attempt has, therefore, been made to prepare 2-hydroxymethyl chromones starting from the corresponding 2-methyl compounds. In the course of this work some interesting results have been obtained on the reactivity of the different positions of the chromone structure towards N-bromosuccinimide.



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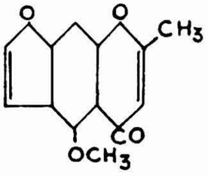
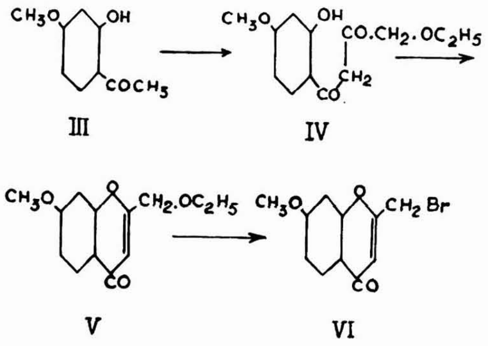


II

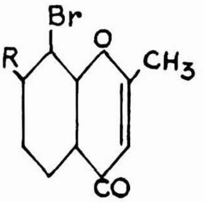
Winter and Hamilton[5] appear to have been the first to use N-bromosuccinimide for the bromination of 2-methyl chromones. They used also bromine and manganese dioxide in glacial acetic acid as the brominating agent. Both methods gave the same product. Though earlier Offe[6] reported the bromination product obtained by the second method to be 2-bromomethyl chromone, Winter and Hamilton produced evidence to show that it must be a 3-bromo compound and identical with the one obtained by using N-bromosuccinimide. Particular emphasis was laid by them on the low reactivity of the bromine atom present in their compound, which is characteristic of α-bromo-α : β-unsaturated carbonyl compounds. This was confirmed by an iodine release study which gave a negative result characteristic of such a system. But they found that it reacted with piperidine to yield a 3-piperidino derivative and this was explained as due to initial 1 : 4-addition and subsequent removal of hydrogen bromide with simultaneous rearrangement. Subsequently, Wiley[7,8], in the course of his studies on the Mannich reaction in the chromone series, carried out the bromination of 7-methoxy-2-methyl chromone and 6-methoxy-2-methyl chromone with N-bromosuccinimide in carbon tetrachloride medium. The products obtained in these cases were monobromo derivatives and were considered to be 7-methoxy-2-bromomethyl chromone and 6-methoxy-2-bromomethyl chromone respectively. In support of this constitution he converted the 6-methoxy compound into the dimethylaminomethyl derivative which was found to be different from the Mannich reaction product of 6-methoxy chromone, formaldehyde and dimethylamine hydrochloride. The Mannich reaction was considered to take place in the 3-position and hence the product obtained in the initial bromination was considered to be substituted in the 2-position. Since there may be other reactive positions in the methoxy chromone nucleus, the above evidence in regard to the constitution of the N-bromosuccinimide product is not conclusive.

In order to clarify the above anomalies, an authentic sample of 2-bromomethyl-7-methoxy chromone has now been prepared by an independent and unambiguous method. For this purpose an extension of the well-known Claisen condensation has been utilized. Peonol (III) is condensed with ethoxyacetic ester in the presence of metallic sodium in dry ether medium and the 1-o-hydroxy-p-methoxy-phenyl-4-ethoxy butane 1: 3-dione (IV) so obtained is subjected to ring closure to yield 2-ethoxymethyl-7-methoxy chromone (V). On treatment with hydrogen bromide in glacial acetic acid the ethoxymethyl compound yields 2-bromomethyl-7-methoxy chromone (VI) melting at 141°-42°. This is different from the reaction product of 7-methoxy-2-methyl chromone and N-bromosuccinimide reported by Wiley (m.p. 160°-61°). Wiley carried out the bromination by heating for only 4 hr. and without using benzoyl peroxide catalyst. Considerably improved yield of the product is obtained by heating for a longer period in the presence of peroxide catalyst. The same substance is obtained by bromination of 7-methoxy-2-methyl chromone with one mole of bromine in glacial acetic acid medium. It should, therefore, be concluded that in 7-methoxy-2-methyl chromone, N-bromosuccinimide does not effect allylic bromination and its reaction is the same as that of bromine.

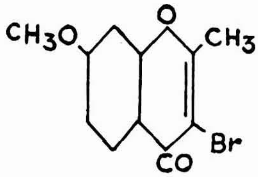


Though there is considerable evidence for the 3-position of chromone being an active one in bromination, other positions in the nucleus cannot altogether be excluded. One such position is the 8-position. In order to provide more conclusive evidence an authentic sample of 7-methoxy-8-bromo-2-methyl chromone (VIIb) has now been prepared by the methylation of the corresponding 7-hydroxy-8-bromo compound (VIIa) whose preparation and constitution have been studied recently[9]. The product melts at 183°-84° and is different from the reaction product of N-bromosuccinimide with 7-methoxy-2-methyl chromone. A degradation reaction carried out subsequently with the latter excluded the possibility of the halogen atom being located in the benzene nucleus. Boiling with absolute alcoholic potash yielded a fission product which did not contain bromine. Consequently the bromine atom should be located in the pyrone ring. Since position-2 is excluded by the synthetic experiment, there is no alternative but to accept position-3 for the bromine atom and the monobromo compound should, therefore, be assigned the structure VIII. This agrees with the results of Winter and Hamilton obtained in the bromination of 2-methyl chromone.

It may be mentioned here that much earlier Wittig[10] carried out the chlorination of 6-chloro-2-methyl chromone and obtained



VIIa: R=OH
VIIb: R=OCH_3



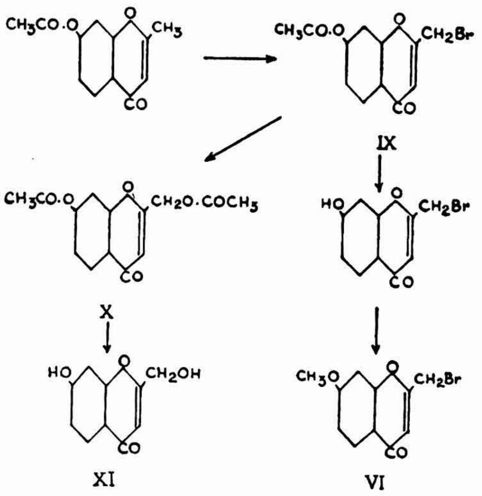
VIII

3 : 6-dichloro-2-methyl chromone which was identical with the product of this constitution obtained by an independent method.

From the experiments discussed above it is clear that the action of N-bromosuccinimide on 7-methoxy-2-methyl chromone differs markedly from that of the isomeric coumarin, 7-methoxy-4-methyl coumarin, in which substitution in the methyl group takes place satisfactorily[11]. In our earlier papers it has been pointed out that an acetyl group is the most convenient for the protection of a nuclear hydroxyl in the Wohl-Ziegler reaction[12] and acetoxy isoflavones and acetoxy coumarins undergo this reaction very smoothly. This is found to be the case when 7-acetoxy-2-methyl chromone is employed. Unlike the 7-methoxy compound this suffers substitution in the 2-methyl group and gives a good yield of 2-bromomethyl-7-acetoxy chromone (IX). The constitution of this product has been confirmed by two definite lines of evidence: (i) When it is deacetylated with alcoholic hydrobromic acid and the product methylated with excess of dimethyl sulphate, 7-methoxy-2-bromomethyl chromone (VI) is obtained melting at 140°-41° either alone or in admixture with the authentic sample prepared from peonol and ethoxyacetic ester; and (ii) the bromine atom of the Wohl-Ziegler product can be replaced by an acetoxy group by the action of silver acetate to give a diacetate (X) which, on deacetylation with alcoholic hydrochloric acid, gives rise to 7-hydroxy-2-hydroxymethyl chromone (XI).

It is clear that the nature of the substituent in the 7-position makes a great difference in the N-bromosuccinimide reaction, the methoxyl leading to the 3-substitution and the acetoxyl to ω-substitution in the 2-position. In order to study the effect of a free hydroxyl group, 2-methyl-7-hydroxy chromone has been subjected to this reaction. This leads to the formation of 7-hydroxy-8-bromo-2-methyl chromone which is already known as the normal product of bromination of the hydroxy compound with bromine. Thus the 8-position becomes predominantly active when there is a hydroxyl in the 7-position.

In summing up the results it should be emphasized that the N-bromosuccinimide reaction is quite successful for the preparation of 2-hydroxymethyl chromones provided nuclear hydroxyl groups are acetylated. The influence of other substituents on this reaction provides an interesting study of the different factors that play their part in regard to the reactivity of the chromone structure.

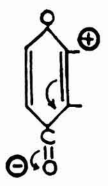


It has been recognized[13,14] that in the simple pyrone structure there are two centres of high reactivity: (i) position-3 (and 5) where electrophilic substitution takes place rapidly; and (ii) position-2 which can suffer nucleophilic attack.

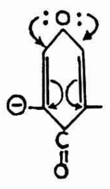
Bromination takes place in the 3 and 3 : 5-positions[15], and when a reagent providing hydroxyl groups attacks the molecule, the ring fission takes place as a result of the attack at the 2-position (e.g. with alkali). The explanation of the specific reactivity in these positions can be found in the formulae XII and XIII. When a 2-methyl group is present, the electrophilic substitution in the 3-position should be enhanced on account of hyperconjugation (XIV).

The characteristic reactivity of these two positions (2 and 3) continues to persist in chromones also and in simple 2-methyl chromone the nuclear positions of the benzene ring are less reactive as indicated by the results of bromination with bromine or N-bromosuccinimide yielding 3-bromo-2-methyl chromone. The presence of a 7-methoxy group does not make any difference. Its effect is just the same as that of a hydrogen atom in the 7-position because 7-methoxy-2-methyl chromone also undergoes substitution with bromine as well as with N-bromosuccinimide in the 3-position.

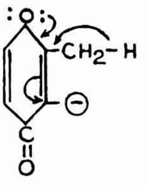
The presence of a hydroxyl group in the 7-position makes considerable difference. It so highly activates the nuclear position-8



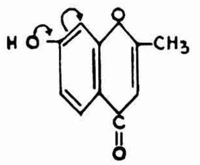
XII



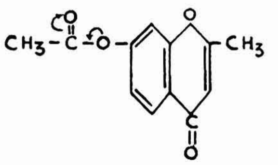
XIII



XIV



XV



XVI

that substitution with bromine as well as with N-bromosuccinimide takes place predominantly inthis position (XV). Its effect on the para carbonyl, in a way deactivating the 2-position also can be imagined. On the other hand, the effect of the acetoxy group will be to deactivate the benzene nucleus and also to activate the para carbonyl group, so that this group exerts its maximum effect on the 2-position (XVI). Consequently the 2-methyl group becomes more reactive and the reaction with N-bromosuccinimide takes place satisfactorily.

Experiments have also been carried out on the bromination of 7-acetoxy-2-methyl chromone using bromine in hot acetic acid medium and in dry carbon tetrachloride medium. The product is found to be 7-hydroxy-8-bromo-2-methyl chromone in both the cases. This is obviously the result of bromination after preliminary deacetylation. Hence the course of bromination with the unhydrolysed acetate itself could not be studied.

The results indicate considerable similarity between bromine and N-bromosuccinimide regarding substitution in the 3-position and in the nuclear position-8. But unlike bromine, the latter reagent has successfully effected substitution in the alkyl group with 7-acetoxy-2-methyl chromone.

Experimental procedure

7-Methoxy-2-bromomethyl chromone (VI) — (*Method I*): (a) *7-Methoxy-2-ethoxymethyl chromone* (V) — Peonol (1·0 g.) and ethoxy acetic ester[16] (2·0 cc.) were dissolved in dry ether (50 cc.) and sodium metal (1·0 g.) was gradually added in small pieces with constant stirring and cooling the mixture in ice water. In the early stages the sodium salt separated out as a cream-coloured solid which gradually dissolved giving a dark red solution. After the addition of half the quantity of sodium metal a further quantity (1·7 cc.) of ethoxy acetic ester was added to the reaction mixture and the addition of sodium continued. The mixture was left overnight and then gently refluxed for 2 hr. in a hot water bath. The dark red viscous mass obtained on evaporation of ether was treated with ice water and the aqueous portion acidified with acetic acid and then extracted with ether (100 cc. lots; 3 times). The combined ether extract was washed with sodium bicarbonate to remove acetic acid and the solvent was distilled off. The oily liquid so obtained was left in the refrigerator for several days, but as it did not solidify it was directly used for the next step. It was taken up in ether, dried over sodium sulphate and the oily mass obtained after distilling off the solvent was refluxed with absolute alcohol (25 cc.) containing 4 drops of concentrated sulphuric acid for 30 min. on a water bath. The alcohol was removed under reduced pressure and the residue taken up in ether. The ether solution was washed with cold dilute sodium hydroxide and then with water. On distilling off the solvent a yellow oil was obtained which gradually solidified when left in the refrigerator for 48 hr. This was extracted with excess of hot petroleum ether and the solvent partially distilled off when a very pale yellow oil separated which solidified on cooling and scratching to a pale yellow solid. When crystallized from petroleum ether, it separated as long and stout rectangular prisms melting at 70°-71°; yield 0·15 g. It did not give any colour with ferric chloride in alcoholic solution and was insoluble in cold dilute sodium hydroxide. With concentrated sulphuric acid it gave a colourless solution without any fluorescence (found: C, 67·1; H, 6·2; $C_{13}H_{14}O_4$ requires: C, 66·7; H, 6·0 per cent).

(b) The above chromone (V, 0·5 g.) was dissolved in glacial acetic acid (1·0 cc.) and treated with 48 per cent hydrobromic acid in glacial acetic acid (6 cc.). The mixture was left at room temperature for 24 hr., then refluxed on a boiling water bath for 45 min., diluted with water (100 cc.) and left in the refrigerator for 24 hr. The solid that separated was crystallized from a mixture of ethyl acetate and petroleum ether when it came out as long and stout rectangular prisms melting at 141°-42°; yield 0·35 g. The compound gave a positive test for bromine and formed pale yellow solutions with aqueous sodium hydroxide and carbonate (found: C, 49·4; H, 3·3; $C_{11}H_9O_3Br$ requires: C, 49·1; H, 3·3 per cent).

In order to prove that no demethylation of the 7-position had occurred in the treatment of 7-methoxy-2-ethoxymethyl chromone with hydrobromic acid, the above product was refluxed with excess of dimethyl sulphate in acetone medium in the presence of anhydrous potassium carbonate for 6 hr. On working up, the product was found to be identical with the original compound and to melt at 141°-42° either alone or in admixture with 7-methoxy-2-bromomethyl chromone.

Method II: (a) *7-Acetoxy-2-bromomethyl chromone* (IX) — 7-Acetoxy-2-methyl chromone (2·18 g.), N-bromosuccinimide (1·78 g.; 1 mole) and benzoyl peroxide (0·12 g.) were taken in dry carbon tetrachloride (150 cc.) and refluxed for 40 hr. on a water bath. A light orange colour developed after refluxing the mixture for 3 hr. which changed to deep orange and finally faded away on the completion of the reaction. The solution was cooled, filtered to remove insoluble succinimide and the solvent was distilled off when a reddish yellow viscous mass was obtained which partially solidified on leaving in the refrigerator for 48 hr. It was collected and washed twice with boiling water to remove the last traces of succinimide. Crystallization from excess of ethyl acetate gave rectangular tablets and prisms melting at 177°-78°; yield 1·3 g. (found: C, 48·7; H, 3·6; $C_{12}H_9O_4Br$ requires: C, 48·5; H, 3·0 per cent). It gave a positive test for bromine.

(b) *Deacetylation* — The above chromone (1·0 g.) was dissolved in boiling alcohol (30 cc.) and to the hot solution was added hydrobromic acid (30 cc., 40 per cent). The mixture was refluxed for 5 min. on a water bath, then diluted with water (100 cc.) and left in the refrigerator for 6 hr. The solid that separated was filtered, dried and crystallized from ethyl acetate when it came out as flat needles and rectangular rods melting at 231°-32° (decomp.); yield 0·72 g. 7-Hydroxy-2-bromomethyl chromone thus obtained gave pale yellow solutions with aqueous sodium hydroxide and sodium carbonate and exhibited no fluorescence with concentrated sulphuric acid. It responded to Lassaigne's test for bromine (found: C, 47·0; H, 2·8; $C_{10}H_7O_3Br$ requires: C, 47·0; H, 2·7 per cent).

(c) *Methylation* — 7 - Hydroxy - 2 - bromomethyl chromone (0·5 g.) obtained above was methylated using dry acetone (75 cc.), dimethyl sulphate (0·6 cc.) and potassium carbonate (3·0 g.) and refluxing on a water bath for 6 hr. 7-Methoxy-2-bromomethyl chromone crystallized from ethyl acetate and melted at 141°-42° either alone or in admixture with the authentic sample obtained by Method I.

7-Hydroxy-2-hydroxymethyl chromone (X) — 7-Acetoxy-2-bromomethyl chromone (IX) (1·0 g.) was dissolved in acetic anhydride (10 cc.) and finely powdered silver acetate (2·0 g.) added. The mixture was refluxed in an oil bath for 5 hr. at 155°-65°. After refluxing for about 15 min. the solution assumed a dark red colour which persisted up to the end of the reaction. The resulting hot liquid was quickly filtered and the residue on the filter paper washed twice with small lots (3 cc.) of hot acetic anhydride. The combined filtrate was poured over crushed ice, mechanically stirred for 4 hr. and then left in the refrigerator for 2 days. As the compound could not be obtained as a crisp solid at this stage, the supernatant liquid was poured off and the pasty mass dissolved in ether. It was dried over anhydrous sodium sulphate and the ether distilled off when again a semi-solid mass was left. Attempts to crystallize this were not successful and hence it was used as such for the next step. The diacetate was dissolved in boiling alcohol (25 cc.) and to the hot solution was added concentrated hydrochloric acid (25 cc.). The mixture was refluxed for 2 hr. on a steam bath, diluted with water (100 cc.) and the whole mass was extracted with ether (50 cc.; 3 times). The ether solution was dried over anhydrous sodium sulphate and the pasty mass obtained on distilling off ether was crystallized from a mixture of benzene and petroleum ether when it appeared as yellow rectangular plates melting at 180°-81°; yield 0·2 g. (found: C, 62·3; H, 3·9; $C_{10}H_8O_4$ requires: C, 62·5; H, 4·2 per cent). The compound exhibited faint green fluorescence with concentrated sulphuric acid and gave no Lassaigne's test for bromine.

7-Methoxy-8-bromo-2-methyl chromone (VIIb)—7-Hydroxy-8-bromo-2-methyl chromone (VIIa, 1·0 g.), prepared according to the method of Naik and Sethna[9] by brominating 7-hydroxy-2-methyl chromone with one mole of bromine in glacial acetic acid, was dissolved in dry acetone (100 cc.) and refluxed with dimethyl sulphate (1·0 cc.) and anhydrous potassium carbonate (3·0 g.) for 6 hr. The acetone solution was filtered off and the residue washed with hot acetone. After distilling off the solvent from the combined filtrate the resulting residue was crystallized from hot alcohol when it separated as yellow stout rhombic prisms melting at 183°-84° (found: C, 39·3; H, 4·9; $C_{11}H_9O_3Br, 4H_2O$ requires: C, 38·7; H, 4·9 per cent).

7-Methoxy-3-bromo-2-methyl chromone (VIII): *Method I* — To a solution of 7-methoxy-2-methyl chromone (1·9 g.) in hot glacial acetic acid (30 cc.) was added a 10 per cent solution of bromine in the same solvent (16 cc.; 1 mole) in small lots with shaking in the course of 30 min. The mixture was kept stoppered overnight and then poured into cold water (200 cc.). The solid that separated on leaving in the refrigerator for 4 hr. was filtered, dried and crystallized from ethyl acetate-petroleum ether mixture when it came out as colourless prismatic rods melting at 157°-58°.

Method II — 7-Methoxy-2-methyl chromone (0·95 g.), N-bromosuccinimide (0·89 g., 1 mole) and benzoyl peroxide (0·05 g.) were taken in dry carbon tetrachloride (100 cc.) and refluxed for 45 hr. on a water bath. The reaction mixture was worked up as in an earlier case. The residue crystallized from a mixture of ethyl acetate and petroleum ether as colourless prismatic rods melting at 157°-58°. Mixed melting point with the sample obtained above by direct bromination remained undepressed. Repeated crystallization did not raise the melting point. Wiley reported the melting point as 160°-61° (found: C, 48·7; H, 3·6; $C_{11}H_9O_3Br$ requires: C, 49·1; H, 3·3 per cent).

Alkali hydrolysis of 7-methoxy-3-bromo-2-methyl chromone — The bromo derivatives (VIII; 1·0 g.) obtained independently by the above two methods were each separately treated with 8 per cent absolute alcoholic potash (30 cc.). The substance dissolved and soon an orange-red solution was obtained. After refluxing the contents for 6 hr. most of the solvent was distilled off and the residue dissolved in water (30 cc.). The clear solution was acidified, when a deep red coloured precipitate was obtained. It was taken up in ether, the ether solution washed with cold sodium bicarbonate solution (5 per cent) and the solvent distilled off when a semisolid mass was left behind which failed to crystallize. It did not give any test for bromine, thereby indicating that the brominated product (VIII) does not contain the bromine atom in the benzene ring of the γ-benzopyrone and thus can be only 3-bromo-2-methyl-7-methoxy chromone.

7-Hydroxy-8-bromo-2-methyl chromone (VIIb): (a) *By NBS reaction of 7-hydroxy-2-methyl chromone*—7-Hydroxy-2-methyl chromone (1·76 g.), N-bromosuccinimide (1·78 g.; 1 mole) and benzoyl peroxide (0·06 g.) were refluxed in dry carbon tetrachloride (100 cc.) for 30 hr. on a water bath and the resulting product worked up as in earlier cases. It crystallized from hot alcohol as stout rhombic prisms melting at 260°-61° (decomp.). The mixed melting point of its methyl ether with the sample prepared by the methylation of 7-hydroxy-8-bromo-2-methyl chromone was undepressed.

(b) *By direct bromination of 7-acetoxy-2-methyl chromone*: (i) *In glacial acetic acid medium* — To a solution of 7-acetoxy-2-methyl chromone (1·0 g.) in hot glacial acetic acid (10 cc.) was added a 10 per cent solution of bromine in the same solvent (7·3 cc.; 1 mole) in small lots with shaking in the course of 10 min. The mixture was left stoppered overnight and then poured over crushed ice. The solid that separated was filtered, dried and crystallized twice from ethyl acetate when it appeared as colourless stout rhombohedral prisms melting at 260°-61° (decomp.) either alone or in admixture with the authentic sample of 7-hydroxy-8-bromo-2-methyl chromone. It was readily soluble in sodium carbonate (5 per cent) and gave a positive test for bromine. On methylation it yielded 7-methoxy-8-bromo-2-methyl chromone melting at 183°-84° either alone or in admixture with an authentic sample.

(ii) *In dry carbon tetrachloride medium* — When a solution of 7-acetoxy-2-methyl chromone in dry carbon tetrachloride was treated with one mole of bromine in dry carbon tetrachloride, 7-hydroxy-8-bromo-2-methyl chromone immediately precipitated out. Mixed melting points of this product and its methyl ether with the authentic samples of 7-hydroxy-8-bromo-2-methyl chromone and 7-methoxy-8-bromo-2-methyl chromone were undepressed.

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Synthetic Experiments in the Benzopyrone Series: Part XLIV—Nuclear Methylation in Hydroxy Isoflavones

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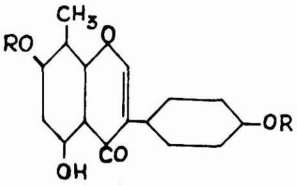
The nuclear methylation of 2-methyl-5:7-dihydroxy isoflavone has been investigated. Authentic samples of 8-C-methyl derivatives have been prepared for comparison by unambiguous methods. Similar 6-C-methyl compounds could not be obtained since 2 : 4 : 6-trihydroxy-3-methyl phenyl benzyl ketone underwent ring closure in an unexpected manner and yielded only 2 : 8-dimethyl-5 : 7-dihydroxy isoflavone. The nuclear methylation product was different from the 8-C-methyl compound and should have undergone nuclear methylation in the 6-position.

The possibility of nuclear methylation introducing two C-methyl groups in the 6- and 8-positions was studied using 2-methyl genistein-4′-methyl ether. When the product was subjected to fission with alkali, 2 : 6-dihydroxy-3-methyl-4 : 4′-dimethoxy phenyl benzyl ketone was obtained showing conclusively that only one methyl group entered the condensed benzene nucleus.

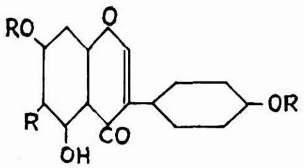
IN Part XXII of this series Seshadri and Varadarajan[1] compared the properties of 8-methyl genistein (Ia) and its dimethyl ether (Ib) with those of similar products obtained by nuclear methylation of genistein (IIa) and concluded that the latter which have higher melting points should be 6-methyl compounds. However, authentic samples of 6-methyl genistein and its dimethyl ether (IIb) were not available for comparison. An attempt was made by the above authors to obtain them by condensing 2 : 4 : 6-trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone (III) with ethyl formate and sodium. Since a hydroxyl para to the methyl, i.e. 6-hydroxyl, is known to be more reactive than the 2-hydroxyl (compare methylation of C-methyl phloroglucinol and phloroacetophenone[2,3] and the acetylation of the latter to yield 2 : 6-dimethyl 5 : 7-diacetoxy chromone[4]), the condensation was expected to give a 6-methyl derivative. This, however, did not proceed satisfactorily and led only to the formation of uncrystallizable products, probably due to the presence of a number of free hydroxyl groups.

The presence of these free hydroxyl groups does not interfere in the synthesis of 2-methyl isoflavones in which the appropriate ketone is boiled with acetic anhydride and



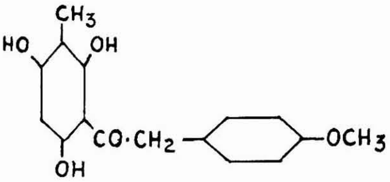
I

(a) R = H
(b) R = CH_3

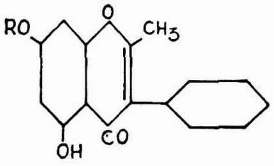


II

(a) R = H
(b) R = CH_3

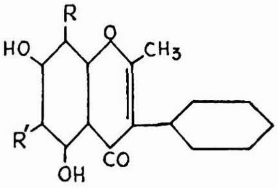


III



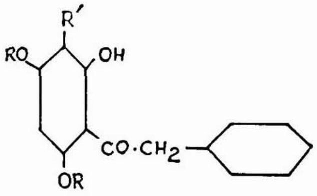
IV

(a) R = H
(b) R = CH_3



V

(a) R = H; R′ = CH_3
(b) R = CH_3; R′ = H



VI

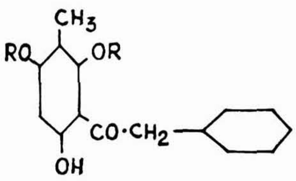
(a) R = R′ = H
(b) R = R′ = CH_3
(c) R = CH_3; R′ = H

sodium acetate. Hence, these 2-methyl compounds have now been chosen as convenient examples for the fuller study of nuclear methylation in isoflavones. The simplest of these, i.e. 2-methyl-5 : 7-dihydroxy isoflavone[5] (IVa), when methylated by means of methyl iodide and anhydrous potassium carbonate in acetone solutionor with one mole of dimethyl sulphate in the same solvent, gives rise to a crystalline product (m.p. 171°-73°) giving a deep pink colour with alcoholic ferric chloride. The analytical values and ferric chloride colour indicate that it is 2-methyl-5-hydroxy-7-methoxy isoflavone (IVb). Earlier, Baker *et al.*[5] recorded for a compound of this constitution (method of preparation not recorded) a m.p. of 186°-87° and also mentioned that it gave a bluish green colour with alcoholic ferric chloride. This colour reaction seems to be characteristic of C-methyl isoflavones[1,6] and the melting point also agrees with that of the nuclear methylation product of IVa described below. The nuclear methylation has been carried out using excess of methyl iodide and sodium methoxide under the conditions adopted by Baker *et al.*[7] for genistein. It is, however, found that boiling the mixture for 4 hr. gives a better yield than refluxing it for 12 hr. as was done by Baker *et al.*[7] in the case of genistein. In the present case, the only product that could be isolated is a C-methyl derivative (m.p. 187°-88°) which gives with alcoholic ferric chloride an initial deep pink colour changing to deep green.

In order to establish the constitution of the nuclear methylation product, authentic samples of 2 : 6-dimethyl-5 : 7-dihydroxy isoflavone (Va) and 2 : 8-dimethyl-5 : 7-dihydroxy isoflavone (Vb) and their methyl ethers were required. The starting point for the synthesis of Vb is 2 : 4 : 6-trihydroxy phenyl benzyl ketone (VIa). On treatment with methyl iodide and anhydrous potassium carbonate in acetone solution, it gives rise to two substances which are separated by fractional crystallization from alcohol. The more sparingly soluble fraction melts at 153°-55° and does not give any blue or green colour with concentrated nitric acid. By analogy with the nuclear methylation of phloroacetophenone[2] and of 2 : 4 : 6-trihydroxy-4′-methoxy phenyl benzyl ketone[1,8], the product in the present case is considered to be 2-hydroxy-3-methyl-4 : 6-dimethoxy phenyl benzyl ketone (VIb). It has, however, been confirmed by rigid and unequivocal synthesis as given below. The more soluble fraction melts at 116° and gives a blue colour with concentrated nitric acid. It is identical with an authentic sample of 2-hydroxy-4 : 6-dimethoxy phenyl benzyl ketone (VIc) prepared according to the method of Aghoramurthy *et al.*[9]. The ketone (VIb) has also been prepared in a different manner using C-methyl phloroglucinol which itself has been obtained according to the method of Shriner and Hull[10]. Its condensation with phenyl acetonitrile yields 2 : 4 : 6-trihydroxy-3-methyl phenyl benzyl ketone (VIIa) which on methylation with excess of methyl iodide and anhydrous potassium carbonate in acetone solution furnishes the desired ketone (VIb). That there is only one C-methyl group in the above compound, i.e. no further nuclear methylation takes place with methyl iodide, is established by carrying out the methylation of VIIa with two moles of dimethyl sulphate when the same dimethyl ether (VIb) is produced.

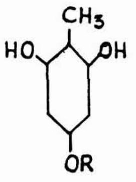
It is possible that the methylation of the trihydroxy ketone (VIIa) might have taken an alternative route, and the product has the constitution VIIb and not VIb. This possibility has been eliminated in the following manner. Treatment of C-methyl phloroglucinol (VIIIa) with methyl alcohol and hydrogen chloride yields the α-methyl ether (VIIIb), the structure of which was earlier established by Curd and Robertson[2] by its synthesis. Interaction of the α-methyl ether (VIIIb) with phenyl acetonitrile under the conditions of Hoesch reaction gives rise to 2 : 4-dihydroxy-3-methyl-6-methoxy phenyl benzyl ketone (IX) which on methylation with one mole of dimethyl sulphate yields VIb. When VIb is boiled with acetic anhydride and sodium acetate 2 : 8-dimethyl-5 : 7-dimethoxy isoflavone (Xa) is obtained. This could be partially demethylated to 2 : 8-dimethyl-5-hydroxy-7-methoxy isoflavone (Xb) by treating with hydriodic acid at 110° for half an hour according to the method of Aghoramurthy *et al.*[9]. It melts at 151°-53° (m.p. of the acetate 198°-200°C.) and gives an initial violet colour with alcoholic ferric chloride changing to deep green with excess of the reagent.

It is possible that during the above demethylation with hydriodic acid the γ-pyrone ring might have opened and an isomeric change to 2 : 6-dimethyl-5-hydroxy-7-methoxy isoflavone (XI) might have taken place. The absence of any such isomerization in this case has been established in two ways: (1) The dimethyl ether (Xa) has also been partially demethylated with anhydrous aluminium chloride in ether solution. This reagent is known not to cause isomeric change. The product is identical with the one obtained by using hydriodic acid. (2) The hydriodic acid demethylated product has also been remethylated; the resulting dimethyl ether is found to be identical with the original 2 : 8-dimethyl-5 : 7-dimethoxy isoflavone (Xa) in every respect. The product of nuclear methylation of 2-methyl-5 : 7-dihydroxy isoflavone (IVa) is quite different from 2 : 8-dimethyl-5-hydroxy-7-methoxy isoflavone (Xb). In order to synthesize an authentic sample of the 2 : 6-dimethyl compound (XI) the vigorous acetylation of 2 : 4 : 6-trihydroxy-3-methyl phenyl benzyl ketone (VIIa) has been attempted. As already mentioned in this paper, since the hydroxyl para to the methyl group is more reactive than the one ortho to it, the ketone



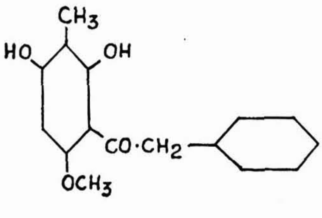
VII

(a) R = H
(b) R = CH_3

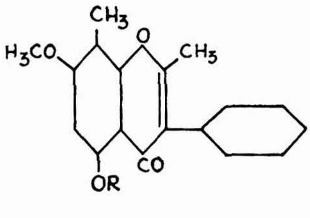


VIII

(a) R = H
(b) R = CH_3

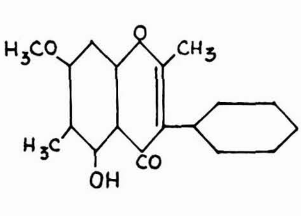


IX



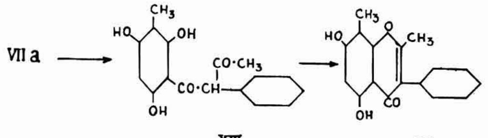
X

(a) R = CH_3
(b) R = H



XI

VIIa was expected to give 2: 6-dimethyl-5: 7-diacetoxy isoflavone. But the vigorous acetylation of the ketone VIIa yields a diacetoxy dimethyl isoflavone which could be hydrolysed to the corresponding dihydroxy compound (m.p. 256°-57°). On methylation with one mole of dimethyl sulphate, it furnishes a partial methyl ether melting at 151°-53° which is identical with 2 : 8-dimethyl 5-hydroxy-7-methoxy isoflavone (Xb) described above. The identity has been confirmed by the preparation of the acetate. Therefore, the parent dihydroxy dimethyl isoflavone obtained by the deacetylation of the diacetoxy compound is 2 : 8-dimethyl-5 : 7-dihydroxy isoflavone (XII). In this vigorous acetylation of the ketone, the hydroxyl ortho to the methyl group has unexpectedly proved to be more reactive than the one para to it. The course of acetylation should be as shown below and the intermediate in the formation of isoflavone should be a derivative of the diketone XIII.



The presence of an α-acetyl group in the ketone seems to alter the relative reactivities of the hydroxyl groups present in the benzene ring. Such a type of ring closure involving the hydroxyl groups ortho to an alkyl group is not unknown. The conversion of the tetrahydro sumatrolic acid into a chromano-chromone by means of acetic anhydride and fused sodium acetate yields only the 8-alkyl derivative[11]. Similarly dehydro dihydro toxicarol[12] is said to be formed from dihydro toxicarolic acid. In more recent work[13] the Allan-Robinson benzoylation of 3-methyl phloroacetophenone has given rise to two products, viz. 6-methyl-chrysin and 8-methyl-chrysin.

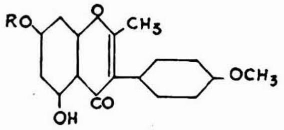
Although it has not been possible to synthesize the 6-methyl compounds for comparison, on the basis of the evidence adduced above and by analogy with the behaviour of chromones[14,15] in nuclear methylation, it can be concluded that the nuclear methylation of 2-methyl-5 : 7-dihydroxy isoflavone has taken place in the 6-position. The higher melting point (187°-88°) of the nuclear methylation product of IVa as compared with that of 2 : 8-dimethyl-5-hydroxy-7-methoxy isoflavone (Xb) (m.p. 151°-53°) further supports the above conclusion.

In the foregoing discussion, it has been proved that the nuclear methylation products are not 8-methyl compounds; hence it is concluded that they are 6-methyl compounds. The only objection to this view is that in nuclear methylation of genistein (IIa) and of 2-methyl-5 : 7-dihydroxy-isoflavone (IVa), instead of one methyl group two methyl groups might have entered the benzene nucleus of the benzo-γ-pyrone thereby giving rise to 6 : 8-dimethyl compounds. This point could not be settled by analysis because in both C-mono and dimethyl compounds carbon and hydrogen values lie close to each other. It could, however, be easily settled by carrying out the degradation of the product of nuclear methylation of genistein (IIa) and of 8-methyl genistein dimethyl ether (Ib) itself by means of alkali. If the resulting ketones obtained are found to be identical, then the product of nuclear methylation of genistein (IIa) should contain only one C-methyl group and should be definitely 5-hydroxy-6-methyl-7 : 4′-dimethoxy isoflavone (IIb).

For this purpose the nuclear methylation of genistein (IIa) has been done with excess of methyl iodide and sodium methoxide under the conditions adopted by Baker and coworkers[7], but the yield of the product is very poor. However, in the nuclear methylation of nor-eugenin, chrysin[13,15], and of 2-methyl-5 : 7-dihydroxy isoflavone a yield of 12 per cent of the nuclear methylated product is obtained. These three pyrone derivatives have a substituent in the 2-position. It would appear, therefore, that benzo-γ-pyrones unsubstituted in the 2-position suffer decomposition readily in alkaline medium and this may account for the poor yields in the nuclear methylation of genistein (IIa).

Therefore, as a suitable alternative the nuclear methylation of 2-methyl genistein, 4′-methyl ether[7] (XIVa) has been carried out. The mixture could be separated into two fractions. The sparingly soluble fraction is the nuclear methylated product (m.p. 198°-200°) and gives a deep pink colour with alcoholic ferric chloride which changes to deep green with excess of the reagent. The more soluble fraction melts at 162°-63°

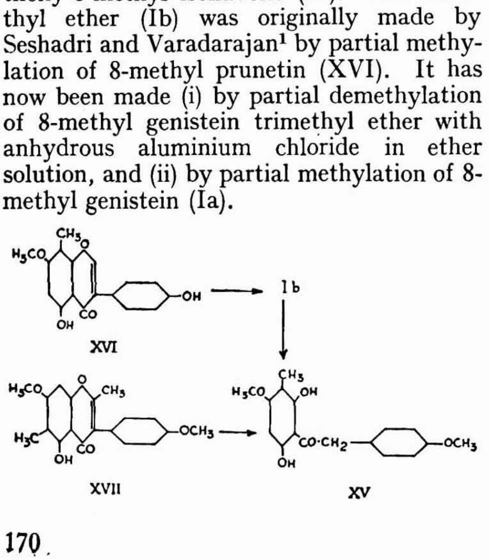
and gives a deep violet colour with alcoholic ferric chloride; it is identical with an authentic sample of 2-methyl-5-hydroxy-7 : 4′-dimethoxy isoflavone (XIVb) prepared by methylation of XIVa with dimethyl sulphate (1 mole) and anhydrous potassium carbonate in dry acetone solution. Baker *et al.*[7] carried out the methylation of XIVa using dimethyl sulphate and aqueous alkali and have reported 197° as the melting point of the product obtained thereby. They, however, have not recorded the ferric chloride reaction for their methylated product. Its melting point, however, agrees with that of the nuclear methylated product mentioned above and it would appear that they obtained the nuclear methylated product by this method.



XIV

(a) R = H
(b) R = CH_3

The nuclear methylated product (m.p. 198°-200°) described above when subjected to alkali degradation gave rise to a hydroxy ketone (m.p. 196°-97°) which is identical in every respect with an authentic sample of 2 : 6 - dihydroxy - 3 - methyl - 4 : 4′ - dimethoxy phenyl benzyl ketone (XV) obtained by the alkali degradation of 5-hydroxy-7 : 4′-dimethoxy-8-methyl isoflavone (Ib). The dimethyl ether (Ib) was originally made by Seshadri and Varadarajan[1] by partial methylation of 8-methyl prunetin (XVI). It has now been made (i) by partial demethylation of 8-methyl genistein trimethyl ether with anhydrous aluminium chloride in ether solution, and (ii) by partial methylation of 8-methyl genistein (Ia).



The identity of the fission ketones described above definitely proves that in the nuclear methylation of 2-methyl genistein-4′-methyl ether (XIVa) only one methyl group has entered, and that in the 6-position of the condensed benzene ring, and hence the nuclear methylated product is XVII. A similar behaviour could be expected in case of genistein (IIa) and 2-methyl-5 : 7-dihydroxy isoflavone (IVa). Hence it is established that nuclear methylation in hydroxy isoflavones described above takes place in the 6-position of the condensed benzene ring.

Experimental procedure

2 - Methyl - 5 - hydroxy - 7 - methoxy isoflavone (IVb) — 2-Methyl-5 : 7-dihydroxy isoflavone[5] (IVa) (0·86 g.) in dry acetone (100 cc.) was refluxed with dimethyl sulphate (0·35 cc.) in presence of ignited potassium carbonate (2 g.) for 3 hr. The solution was filtered off and the potassium salts washed with warm acetone. After distilling off the solvent the residue was treated with water. The colourless solid was filtered, washed with water and crystallized from alcohol. The methyl ether separated as long stout rectangular prisms, melting at 171°-73°. Further crystallization did not raise the melting point. It gave in alcoholic solution a deep pink colour with ferric chloride. The same product was obtained by using a large excess of methyl iodide in place of dimethyl sulphate in the above methylation (found: C, 72·7; H, 5·1; $C_{17}H_{14}O_4$ requires: C, 72·4; H, 5·0 per cent).

The acetate obtained by heating the above isoflavone with acetic anhydride (5 cc.) and pyridine (10 drops) at 150° for 2 hr. crystallized from alcohol as colourless flat needles and rectangular rods melting at 202°-3° (found: C, 70·2; H, 5·1; $C_{19}H_{16}O_5$ requires: C, 70·4; H, 4·9 per cent).

2-Hydroxy-3-methyl-4 : 6-dimethoxy phenyl benzyl ketone (VIb) : (a) *Nuclear methylation of* 2:4: 6-*trihydroxy phenyl benzyl ketone* (VIa)— 2: 4: 6-Trihydroxy phenyl benzyl ketone[16] (VIa) (5 g.) was dissolved in dry acetone (100 cc.) and gently refluxed with methyl iodide (11·5 cc.) in presence of ignited potassium carbonate (20 g.) for 6 hr. The acetone was distilled off. Water was added to the residue and the undissolved solid filtered. It was repeatedly crystallized from alcohol until there was no further rise in the melting point. The product was obtained as colourless square plates melting at 153°-55°. Its alcoholic solution gave a brown colour with ferric chloride. No blue colour was obtained with concentrated nitric acid; yield 0·65 g. The alcoholic mother liquors after removal of the nuclear methylated ketone were concentrated when a brownish semi-solid was obtained. It was filtered and crystallized from alcohol when it separated as colourless prisms melting at 116°. It gave a reddish brown colour with ferric chloride in alcoholic solution and a blue colour with concentrated nitric acid. Mixed melting point with an authentic sample of 2-hydroxy-4:6-dimethoxy phenyl benzyl ketone[9] (VIc) was not depressed.

(b) (i) 2:4:6-*Trihydroxy*-3-*methyl phenyl benzyl ketone* (VIIa) — Dry C-methyl phloroglucinol[10] (5 g.) and benzyl cyanide (6·5 g.) were dissolved in dry ether (20 cc.) and freshly fused zinc chloride (2 g.) added. The solution was cooled to 0° and a stream of dry hydrogen chloride passed through it for 4 hr. The mixture was then left overnight at 0°. The ethereal layer was decanted off and the oily ketimine hydrochloride washed twice with dry ether. It was hydrolysed by heating with water (150 cc.) for 2 hr. in a boiling water bath. On cooling in ice a dark solid separated. It was crystallized once from boiling water and twice from dilute alcohol when it separated in the form of buff-coloured flat needles and narrow rectangular plates. It melted at 200° and gave with alcoholic ferric chloride a greenish brown colouration.

(ii) *Methylation of* VIIa *to* VIb — The above trihydroxy ketone (0·82 g.) was dissolved in dry acetone (100 cc.) and refluxed gently with dimethyl sulphate (0·65 cc.) in presence of ignited potassium carbonate (3 g.) for 3 hr. The acetone was distilled off and the product worked up as in the previous case. It crystallized from alcohol as colourless square plates melting at 153°-55°. The same ketone (VIb) was obtained by employing an excess of methyl iodide in place of dimethyl sulphate in the above methylation.

(c) (i) 2:4-*Dihydroxy*-3-*methyl*-6-*methoxy phenyl benzyl ketone* (IX) — C-Methyl phloroglucinol-α-methyl ether[2] (VIIIb) (1·1 g.) and phenyl acetonitrile (2 cc.) were dissolved in dry ether (80 cc.) and fused zinc chloride (0·5 g.) added. The mixture was cooled to 0° and a stream of dry hydrogen chloride was passed for 4 hr. After 15 hr. the upper layer of ether was decanted off and the residual ketimine hydrochloride was washed with dry ether. It was then heated with water (60 cc.) for 2 hr. on a boiling water bath. The mixture was cooled and the precipitate collected and crystallized from alcohol. 2:4-Dihydroxy-3-methyl-6-methoxy phenyl benzyl ketone separated as pale short prisms, melting at 141°-43°; yield 1·0 g. It gave a pink colour with alcoholic ferric chloride and was easily soluble in aqueous sodium hydroxide. It was readily soluble in hot alcohol, ethyl acetate and acetone (found: C, 70·7; H, 5·7; $C_{16}H_{16}O_4$ requires: C, 70·6; H, 5·9 per cent).

(ii) *Methylation of* IX — The above dihydroxy ketone (0·7 g.) was dissolved in acetone (100 cc.) and treated with methyl iodide (5 cc.) and potassium carbonate (5·0 g.) and the mixture refluxed for 4 hr. Acetone and unreacted methyl iodide were then distilled off and the product worked up as in the previous case. When crystallized from alcohol, VIb separated as colourless square plates, melting at 153°-55°; yield 0·6 g. (found: C, 71·5; H, 6·3; $C_{17}H_{18}O_4$ requires: C, 71·3; H, 6·3 per cent).

2:8-*Dimethyl*-5:7-*dimethoxy isoflavone* (Xa) — 2-Hydroxy-3-methyl-4:6-dimethoxy phenyl benzyl ketone (VIb) (1·2 g.) was mixed with fused sodium acetate (2 g.) and refluxed for 10 hr. with excess of acetic anhydride at 170°-80°. The mixture was allowed to cool and then poured into ice cold water (400 cc.). After 6 hr., the crystalline solid was filtered and washed well with water. When crystallized from alcohol twice, it separated as stout prisms melting at 184°-86°; yield 0·5 g. (found: C, 74·0; H, 5·8; $C_{19}H_{18}O_4$ requires: C, 73·5; H, 5·8 per cent).

2:8-*Dimethyl*-5-*hydroxy*-7-*methoxy isoflavone* (Xb) — (a) 2:8-Dimethyl-5:7-dimethoxy isoflavone (Xa, 0·75 g.) obtained above was dissolved in acetic anhydride (15 cc.) and then hydriodic acid (15 cc.; d. 1·7) cautiously added with cooling. The mixture was heated for exactly half an hour at 110° in an oil bath. The contents were cooled and poured into a saturated solution of sodium bisulphate and left overnight. The solid was filtered and washed with water. The residue was then thoroughly macerated with excess of cold 10 per cent sodium carbonate solution repeatedly and the undissolved portion filtered and washed with water.

It was crystallized from alcohol twice, when it separated in the form of long yellow stout prismatic rods melting at 151°-53°. It gave an initial violet colouration with ferric chloride in alcoholic solution which changed to green with excess of the reagent.

(b) The above dimethoxy isoflavone (Xa, 0·6 g.) was dissolved in dry ether (400 cc.). The solution was cooled to 0° and a solution of anhydrous aluminium chloride (1 g.) in dry ether (50 cc.) added in small lots with shaking, in the course of 15 min. The flask was left in an ice bath for 2 hr. with occasional shaking and then left at room temperature for 48 hr. The ether was then distilled off. The aluminium chloride complex which remained behind was decomposed by adding pieces of ice and some hydrochloric acid. The flask was shaken thoroughly and left aside for 1 hr. The colourless solid obtained was filtered off and crystallized from alcohol. 2:8-Dimethyl-5-hydroxy-7-methoxy isoflavone (Xb) separated as long yellow stout prismatic rods melting at 151°-53° either alone or when mixed with a sample obtained in (a) above (found: C, 72·9; H, 5·2; $C_{18}H_{16}O_4$ requires: C, 73·0; H, 5·4 per cent).

The acetate prepared by heating the isoflavone obtained above with acetic anhydride and pyridine crystallized from alcohol as colourless long rectangular plates, and melted at 198°-200° (found: C, 71·5; H, 5·6; $C_{20}H_{18}O_5$ requires: C, 71·0; H, 5·3 per cent).

Remethylation of Xb *to* Xa — The above isoflavone (Xb, 0·96 g.) was dissolved in dry acetone (100 cc.) and refluxed with excess of dimethyl sulphate (8 cc.) for 60 hr. in presence of ignited potassium carbonate (8 g.). Acetone was then distilled off and the product worked up as in the previous case. When crystallized from alcohol it separated as stout prisms melting at 184°-86°. It was identical with 2:8-dimethyl-5:7-dimethoxy isoflavone (Xa) and its mixed melting point was not depressed.

(c) (i) 2 : 8-*Dimethyl*-5 : 7-*diacetoxy isoflavone* — 2: 4 : 6-Trihydroxy-3-methyl phenyl benzyl ketone (VIIa, 5 g.) was mixed with fused sodium acetate (5 g.) and refluxed for 12 hr. with acetic anhydride (35 cc.) at 170°-80°. The contents were cooled to room temperature and poured into crushed ice (300 g.) and the mixture set aside overnight. Most of the acetic acid was neutralized with aqueous sodium hydroxide. After 4 hr. the dark sticky solid was filtered and washed with water. It was macerated with 25 cc. of cold alcohol to dissolve out resinous impurities, filtered and washed again with cold alcohol. The product was then crystallized twice from boiling alcohol and once from ethyl acetate. It was obtained as colourless rectangular tablets melting at 188°-89° (found: C, 69·0; H, 4·8; $C_{21}H_{18}O_6$ requires: C, 68·9; H, 4·9 per cent).

(ii) *Deacetylation* — The above diacetoxy isoflavone (m.p. 188°-89°, 1·75 g.) was dissolved in alcohol (100 cc.) and concentrated sulphuric acid (4 cc.) added. The mixture was refluxed for 2 hr. The solution was diluted with an equal amount of water and as much alcohol as possible was distilled off. The crystalline solid obtained on cooling was filtered and recrystallized from alcohol twice. The compound (XII) separated in the form of shining stout rectangular prisms melting at 256°-57°. With alcoholic ferric chloride, it gave an initial violet colour which changed to deep green on adding excess of the reagent; yield 0·95 g. (found: C, 72·8; H, 5·1; $C_{17}H_{14}O_4$ requires: C, 72·4; H, 5·0 per cent).

(iii) *Partial methylation of* XII *to* Xb — The above dihydroxy isoflavone (XII, 0·5 g.) was dissolved in dry acetone (50 cc.) and refluxed with dimethyl sulphate (0·2 cc.) in presence of ignited potassium carbonate (2 g.) for 3 hr. and the product worked up as in the previous cases. Monomethyl ether (Xb) separated from alcohol as long yellow stout prismatic rods melting at 151°-53°. The same compound (Xb) was also obtained by employing a large excess of methyl iodide instead of dimethyl sulphate in the above methylation. It gave the same colour reaction and acetate as described earlier.

Nuclear methylation of 2-methyl-5: *7-dihydroxy isoflavone* (IVa) — Sodium (8 g.) was added in small pieces to absolute methanol (220 cc.) contained in a flask fitted with a reflux condenser. When all the sodium had dissolved, the solution was cooled to 0° and 2-methyl-5 : 7-dihydroxy isoflavone[5] (IVa, 6·9 g.) was added with stirring followed by methyl iodide (24 cc.). The solution was refluxed for 3 hr. and then the solvent distilled off. The residue was treated with water (300 cc.) and extracted with ether thrice. The ether solution was washed with 10 per cent sodium hydroxide solution and then with water. The yellowish solid that remained on evaporation of the ether solution was crystallized thrice from alcohol. The nuclear methylated isoflavone was obtained as colourless flat needles melting at 187°-88°. It gave with alcoholic ferric chloride an initial deep pink colouration which changed to green on further addition of the reagent (found: C, 72·5; H, 5·2; $C_{18}H_{16}O_4$ requires: C, 73·0; H, 5·4 per cent). The acetate of the nuclear methylated isoflavone (m.p. 187°-88°) prepared by the acetic anhydride pyridine method crystallized from alcohol as colourless rectangular rods and prisms melting at 227°-28° (found: C, 71·0; H, 5·6; $C_{20}H_{18}O_5$ requires: C, 71·0; H, 5·3 per cent).

5-*Hydroxy*-7 : 4′-*dimethoxy*-8-*methyl isoflavone* (Ib) — (a) 8-Methyl genistein (Ia, 1 g.) was taken in dry acetone (100 cc.) and freshly ignited potassium carbonate (2 g.) and methyl iodide (0·9 cc.) were added. The solution was refluxed for 4 hr. The product was worked up as described earlier. When crystallized from alcohol, Ib separated as pale brown needles melting at 164°-66°; yield 0·44 g.

(b) *Partial demethylation of* 8-*methyl genistein trimethyl ether*[1] *to* Ib — 8-Methyl genistein trimethyl ether (0·85 g.) was dissolved in dry ether (300 cc.) and the solution cooled to 0°. An ice cold solution of anhydrous aluminium chloride (1 g.) in dry ether (50 cc.) was then added with shaking in small lots. The mixture was stirred from time to time for 2 hr. and then set aside for 24 hr. at room temperature and worked up as in the previous case of partial demethylation with aluminium chloride. The yellow product, when crystallized from alcohol, separated as light brown needles melting at 164°-66° either alone or when mixed with an authentic sample of the substance reported earlier by Seshadri and Varadarajan[1]; yield 0·5 g. The acetate prepared by heating the compound with acetic anhydride and pyridine crystallized from alcohol as cream-coloured stout rectangular prisms melting at 170°-72° (found: C, 68·1; H, 5·3; $C_{20}H_{18}O_6$ requires: C, 67·9; H, 5·1 per cent).

Alkaline hydrolysis of 5-*hydroxy*-7:4′-*dimethoxy*-8-*methyl isoflavone* (Ib) — Potassium hydroxide (4 g.) was dissolved in absolute ethanol (50 cc.) and to this solution 0·5 g. of 5-hydroxy-7: 4′-dimethoxy-8-methyl isoflavone (Ib) was added. The mixture was refluxed for 30 min. Water (50 cc.) was added to the solution and the alcohol distilled off. The solution was filtered to remove the undissolved matter and the filtrate acidified when a bright yellow solid separated out. It was filtered and crystallized from dilute alcohol when 2:6-dihydroxy-3-methyl-4 : 4′-dimethoxy phenyl benzyl ketone (XV) was obtained as pale brown needles melting at 196°-97°. It did not give any colour with alcoholic ferric chloride; yield 0·15 g. (found: C, 67·4; H, 6·3; $C_{17}H_{18}O_5$ requires: C, 67·6; H, 6·0 per cent).

Nuclear methylation of genistein — The method of Baker and Robinson[7] was adopted for the nuclear methylation of genistein. The yield of the nuclear methylated product (m.p. 198°-200°) was 0·05 g. from 5 g. of genistein. It was also found that unlike the nuclear methylation of IVa, the decrease in the refluxing period from 12 to 4 hr. did not bring about any improvement in the yield.

2-*Methyl*-5-*hydroxy*-7: 4′-*dimethoxy isoflavone* (XIVb) — 2-Methyl-5: 7-dihydroxy-4′-methoxy isoflavone[7] (XIVa, 1 g.) was dissolved in dry acetone (100 cc.). Freshly ignited potassium carbonate (1·9 g.) and dimethyl sulphate (0·35 cc.; 1·1 mole) were added. The mixture was refluxed for 4 hr. and the product worked up as in the previous cases. When crystallized from alcohol 2-methyl-5-hydroxy-7:4′-dimethoxy isoflavone (XIVb) separated as shining colourless needles melting at 162°-63°. It gave a deep violet colour with alcoholic ferric chloride; yield 0·85 g. (found: C, 68·8; H, 5·0; $C_{18}H_{16}O_5$ requires: C, 69·2; H, 5·1 per cent). The acetate obtained by heating with acetic anhydride and pyridine at 140° crystallized from alcohol as rectangular rods melting at 185°.

Nuclear methylation of 2-*methyl*-5 : 7-*dihydroxy*-4′-*methoxy isoflavone* (XIVa) *to* (XVII) — Sodium (7 g.) was added in small pieces to absolute methanol (195 cc.) contained in a flask fitted with a reflux condenser. When all the sodium had dissolved the solution was cooled to 0° and 2-methyl-5:7-dihydroxy-4′-methoxy isoflavone (XIVa, 5 g.) was added with stirring followed by methyl iodide (35 cc.; 30 moles). The solution was refluxed for 4 hr. and the product worked up as in the previous case of nuclear methylation of IVa. When crystallized from alcohol a mixture of two products was obtained; these were separated from each other by fractional crystallization from alcohol. The sparingly soluble portion

(i.e. the nuclear methylated product XVII) separated as colourless flat needles and long rectangular plates melting at 198°-200° and gave a deep pink colour with alcoholic ferric chloride which changed to deep green with excess of the reagent; yield 0·35 g. (found: C, 69·7; H, 5·8; $C_{19}H_{18}O_5$ requires: C, 69·9; H, 5·5 per cent).

The alcoholic mother liquor when concentrated deposited colourless needles melting at 162°-63° alone or when mixed with the authentic sample of 2-methyl-5-hydroxy-7:4′-dimethoxy isoflavone (XIVb) described earlier in this paper.

Alkaline hydrolysis of nuclear methylation product (XVII) — The above C-methylated isoflavone (XVII, m.p. 198°-200°, 0·1 g.) was refluxed with 25 cc. of 8 per cent alcoholic potassium hydroxide for 30 min. Water (25 cc.) was added to the solution and the product worked up as described earlier. When crystallized from dilute alcohol it separated as pale brown needles melting at 196°-97°. The mixed melting point with an authentic sample of 2:6-dihydroxy-3-methyl-4:4′-dimethoxy phenyl benzyl ketone (XV) described earlier in this paper was not depressed.

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Studies in Xanthones: Part III*— Constitution of Decussatin & Swertinin

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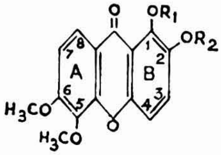
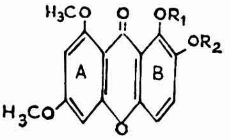
On the basis of chemical evidence previously recorded and on the basis of ultraviolet spectrum analysis, the naturally occurring xanthones, decussatin and swertinin, have been assigned structures 1-hydorxy-2, 6, 8-trimethoxy xanthone and 1, 2-dihydroxy 6, 8-dimethoxy xanthone respectively.

THE xanthones — decussatin and swertinin — isolated from *Swertia decussata*[1] were provisionally assigned the structures (I) and (II).



I $R_1 = H$
$R_2 = CH_3$
II $R_1 = R_2 = H$



III $R_1 = H$
$R_2 = CH_3$
IV $R_1 = R_2 = H$

Colour reactions given by decussatin and swertinin with alcoholic ferric chloride and the conversion of swertinin to decussatin by methylation established the position of the hydroxy group in decussatin — a trimethoxy hydroxy xanthone as 1, and the two hydroxy groups of swertinin — a dimethoxy-dihydroxy-xanthone as 1 and 2. Further evidence that completely demethylated swertinin (i) does not develop a deeper colour on exposure of its alkaline solution to air, and (ii) does not form addition compound with p-benzoquinone[2,3] eliminated positions 3 and 4 in ring (B) for the remaining two hydroxy groups which, therefore, must be in ring (A). Observation (ii) also eliminates the 5, 8-dihydroxy structure. Therefore, there remain only five possibilities, (i) 5, 6-, (ii) 5, 7-, (iii) 6, 7-, (iv) 6, 8-, and (v) 7, 8-, of which 5, 6-dihydroxy structure was proposed on the basis that the alkaline fusion product gave red colouration with concentrated sulphuric acid and glycerol like that of pyrogallol. Since migration[4] of hydroxy groups during alkali fusion of polyhydroxy phenol derivatives is not uncommon and glycerol-sulphuric acid colouration test for pyrogallol may not be considered as decisive, and sufficient quantity of decussatin or swertinin was not available for fusion with alkali and isolation of pure pyrogallol, if any, spectroscopic investigation of these xanthones and their derivatives was undertaken to locate the position of hydroxy or methoxy groups in the molecule.

Ultraviolet absorption curves for a few xanthones have been recorded in the literature[5-7]; however, only a single attempt has been made in the past to correlate absorption curves of polyhydroxy xanthones with their molecular structure. Mull and Nord[8,9] have given a number of curves for a series of known xanthones and by comparison of the curves of rubrofusarin and nor-rubrofusarin with the spectra of these xanthones they suggested possible structures for them.

Absorption curves of decussatin (FIG. 1) and swertinin (FIGS. 2 and 3) are characteristic of xanthones. The maximum present in xanthones at approximately 3,370-3,636A is present in decussatin at 3,150A and in swertinin at 3,290A, though a little shifted towards shorter wavelength. The characteristic minimum at about 3,000-3,200A is also present in decussatin at 2,780A and in swertinin at 2,820A. However, they are at slightly shorter wavelength. As observed by Mull and Nord, this shift towards shorter wavelength is characteristic of 3-hydroxy xanthone which has the maximum at 3,077A and minimum at 2,790A. This evidence, therefore, indicates that decussatin and swertinin are 3-hydroxy xanthone derivatives (cf. FIGS. 2 and 3 with FIG. 5 of Mull and Nord).

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*The two papers on "Chemical Investigation of *Swertia decussata*" published in *J. Indian chem. Soc.* form Parts I and II of the series.

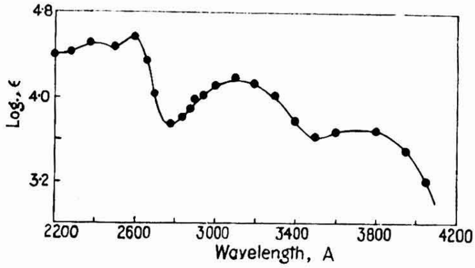


FIG. 1 — ULTRAVIOLET SPECTRUM CURVE OF DECUSSATIN IN ALCOHOL (C = 0·0062 g./l.)

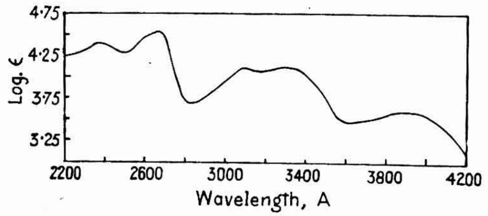


FIG. 2 — ULTRAVIOLET SPECTRUM CURVE OF SWERTININ IN CYCLOHEXANE (C = 0·01175 g./l.)

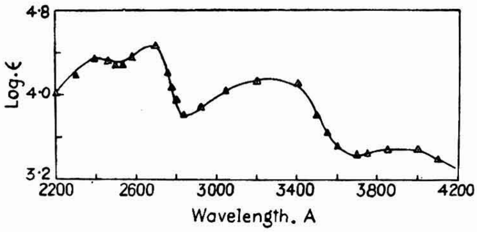


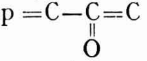
FIG. 3 — ULTRAVIOLET SPECTRUM CURVE OF SWERTININ IN ALCOHOL (C = 0·00825 g./l.)

In the region of shorter wavelength a slight dip in the curve at about 2,550A in the case of 1, 8-dihydroxy xanthone (cf. FIGS. 9-12 of Mull and Nord) is present at about 2,600A in decussatin and at about 2,670A in swertinin. Ravenelin which is 1, 8-dihydroxy xanthone derivative has this maximum at about 2,650A. The slight minimum at about 2,400A characteristic of 1-hydroxy group of 1-hydroxy xanthone is also present at 2,460A in decussatin and at about 2,520A in swertinin (cf. FIGS. 2-4, 8-12 of Mull and Nord). It is at about 2,400A in ravenelin. General nature of the curve of swertinin in this region (2,400A to 2,700A) of the spectrum is very similar to that of 1-8-dihydroxy xanthone (cf. FIGS. 9-11 of Mull and Nord). In the region of longer wavelength 1, 8-dihydroxy xanthone has an additional minimum at about 3,700A and maximum at 3,800A. This minimum and maximum are characteristic of 1, 8-dihydroxy xanthone and are absent in other hydroxy xanthones (cf. FIG. 9 of Mull and Nord with his other curves). Corresponding to these characteristics, swertinin has a minimum at 3,600A and maximum at 3,900A, and decussatin has this minimum at 3,500A and maximum at 3,750A. This evidence, therefore, indicates that decussatin and swertinin are 1, 8-dihydroxy xanthones.

Further comparison of the absorption spectra of swertinin with that of 1, 6-dihydroxy xanthone shows a marked similarity. Both have a minimum at about 2,400A (cf. FIG. 8 of Mull and Nord). The nature of the curve of swertinin between 2,800A and 3,600A is very similar to that of 1, 6-dihydroxy xanthone and is quite different from that of ravenelin which is 1, 4-dihydroxy xanthone (cf. FIG. 10 of Mull and Nord). The maximum at 3,090A in swertinin is characteristic of 3-hydroxy xanthone (cf. FIG. 5 of Mull and Nord). Since positions 3 and 6 are identical in xanthones, this part of the curves further supports the conclusion that decussatin and swertinin are 3-hydroxy xanthone derivatives.

Absorption curves of completely methylated swertinin and completely demethylated swertinin are shown in Figs. 4 and 5 respectively.

Thus ultraviolet spectrum analysis along with the chemical evidence put forth by the previous workers[1] indicates that decussatin is 1-hydroxy-2, 6, 8-trimethoxy xanthone (III), and swertinin is 1, 2-dihydroxy-6, 8-dimethoxy xanthone (IV).

Reduction of methyl ether of decussatin with lithium aluminium hydride to a xanthene derivative will be communicated later. This xanthene derivative being devoid of the strong chromophoric group  $=C-\underset{\underset{O}{\|}}{C}=C$ originally present in xanthone can be spectroscopically compared with the three trimethyl ethers of pyrogallol, phloroglucinol and 1, 2, 4-benzene triol[10]. The ultraviolet spectrum curve (FIG. 6) of the xanthene obtained from decussatin methyl ether has maxima at 2,540A, 2,760A and 2,900A. Maximum at 2,540A is characteristic of xanthene[11] (IV). Maximum at 2,760A is characteristic of phloroglucinol trimethyl ether[12] representing part B of the molecule (III), and maximum

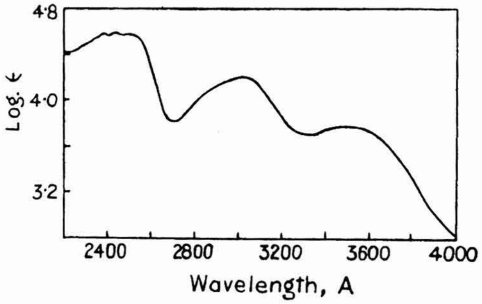


FIG. 4 — ULTRAVIOLET SPECTRUM CURVE OF DECUSSATIN METHYL ETHER IN ALCOHOL (C = 0·00570 g./l.)

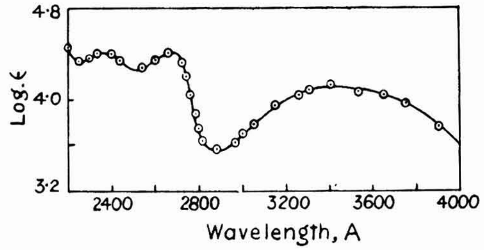


FIG. 5 — ULTRAVIOLET SPECTRUM CURVE OF DEMETHYLATED SWERTININ IN ALCOHOL (C = 0·0065 g./l.)

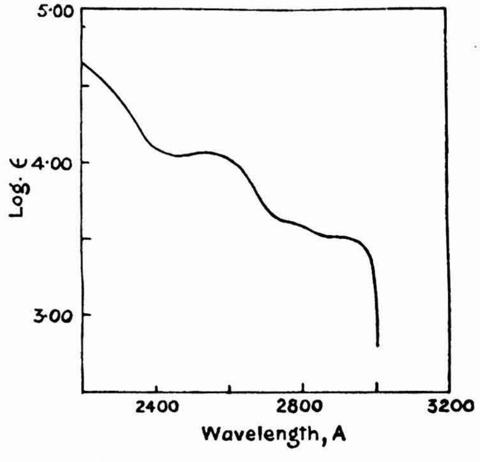


FIG. 6 — ULTRAVIOLET SPECTRUM CURVE OF THE XANTHENE FROM DECUSSATIN METHYL ETHER (C = 0·00968 g./l.)

at 2,900A is characteristic of 1, 2, 4-benzene triol trimethyl ether[13], representing part A of the molecule (III). No absorption characteristic of pyrogallol trimethyl ether[12] at 2,670A is observed. The presence of a maximum at this wavelength is expected if decussatin had the structure (I). This spectral evidence of reduced decussatin derivative gives additional support to the conclusion that decussatin is 1-hydroxy-2, 6-8-trioxy xanthone (III).

Thus on the basis of spectrum analysis and chemical evidence, the structures assigned to decussatin as 1-hydroxy-2, 6, 8-trimethoxy xanthone and to swertinin as 1, 2-dihydroxy 6, 8-dimethoxy xanthone seem to be more probable than those previously proposed on the basis that alkali fusion product of swertinin gave with glycerine and sulphuric acid colouration similar to that of pyrogallol.

Work on isolation and identification of alkali fusion products of these xanthones by partition paper chromatography is in progress.

Acknowledgement

The authors are grateful to Dr. M. G. Marathe of Poona University for sparing some flavones used in this investigation.

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The Fries Reaction: Part IV—The Rearrangement of the Derivatives of Salicylic Acid & Substituted Benzoic Acids

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The Fries migration of benzoyl salicylic acid, methyl acetyl-salicylate, methyl benzoyl-salicylate, acetyl-salol, benzoyl-salol, acetyl-salicylanilide and benzoyl-salicylanilide shows that the migration of acetyl and benzoyl groups is not hindered by the carboxyl, carbomethoxy, carbophenoxy and carbanilido groups in the ortho position to the phenolic group. The aryl esters of salicylic acid undergo Fries rearrangement at 140°C., in presence of four moles of aluminium chloride. The phenyl esters of o-nitro- and p-nitrobenzoic acids failed to give any definite products.

ROSENMUND and Schnurr[1] carried out the Fries rearrangement of aspirin to 5-acetyl-2-hydroxybenzoic acid, but the corresponding o-benzoyl salicylic acid did not give the migration product. Cox[2] prepared 5-caproyl-2-hydroxybenzoic acid and its ester from o-caproyl salicylic acid and its methyl ester showing that the carboxyl as well as the carbomethoxy groups in the ortho position were not inhibitory to the Fries reaction. Brown[3] carried out successfully the migration of o-nitrophenylacetate while Shah and Shah[4] rearranged aspirin and p-acetoxy-benzoic acid. Recently Amin and Shah[5] have studied the Fries migration of the acetyl and benzoyl esters of methyl β-resorcylate and β-resorcylic acid. With a view to getting more evidence on the structural factors affecting the phenolic part of the ester, we studied the rearrangement of (1) o-acetyl salicylic acid, (2) o-benzoyl salicylic acid, (3) methyl o-acetyl-salicylate, (4) methyl o-benzoyl-salicylate, (5) phenyl o-acetyl-salicylate, (6) phenyl o-benzoyl-salicylate, (7) o-acetyl-salicylanilide, and (8) o-benzoyl-salicylanilide at the room temperature in nitrobenzene solution using two moles of aluminium chloride for one mole of the ester. All of them with the exception of (7) and (8) underwent the migration of the acyl group, but the acetyl group migrated more easily than the benzoyl group, and gave higher yields of the migration product. Acetyl- and benzoyl-salicylanilides required the temperature of 130°-40°C. for the migration as only the deacylated products were obtained at the room temperature.

Rosenmund and Schnurr[1] have studied the migration of the phenyl esters of bromo- and alkoxybenzoic acids. Reynolds, Fuson, Scott and Speck[6] studied the esters of xylic and mesitoic acids. We studied the phenyl esters of o-nitro- and p-nitrobenzoic acids, and found that the reaction did not take place at the ordinary temperature, while the reaction at 50°C. was so vigorous that neither mechanical stirring nor dilution with the solvent was effective in preventing the charring of the mass, and nothing definite could be obtained. Using four moles of aluminium chloride the phenyl and o-cresyl esters of salicylic acid at 140°C. gave 2-4′-dihydroxy-benzophenone and 2-4′-dihydroxy 3′-methyl-benzophenone, thus giving the para migration products. Both of these ketones were characterized by the formation of their 2:4-dinitrophenylhydrazones. As the ketones obtained by the rearrangement of m-cresyl and p-cresyl salicylates did not give the 2: 4-dinitrophenylhydrazones, we assumed them to be 2: 4′-dihydroxy-2′-methylbenzophenone and 2: 2′-dihydroxy-5′-methylbenzophenone formed by the para and ortho migration of the salicyl group. The Fries migration of α-naphthyl and β-naphthyl salicylates gave complex resinous masses from which nothing definite could be isolated.

Experimental procedure

The Fries migration of benzoyl salicylic acid and formation of 5-benzoyl-2-hydroxybenzoic acid — The following method was found to be the most convenient for benzoylating salicylic acid.

To a solution of salicylic acid (14 g.) in acetone (50 cc.) dry sodium bicarbonate (20 g.) and benzoyl chloride (12 cc.) were added, and the mixture was refluxed on water bath for 2 hr. After the removal of acetone, the sodium salt of benzoyl salicylic acid was dissolved in water and the acid precipitated on the addition of concentrated ice-cold hydrochloric acid. It crystallized from hot water in plates, m.p. 132°C., and gave a negative test with ferric chloride solution (yield 85 per cent).

After keeping the solution of benzoyl salicylic acid (5·2 g., 1 mole) and aluminium chloride (6 g., 2 moles) in nitrobenzene (40 cc.) for 48 hr., and working up the product as usual, 5-benzoyl-2-hydroxybenzoic acid (1·7 g.) was obtained. It crystallized from dilute alcohol in needles, m.p. 207°C., and gave deep brown colour with ferric chloride. The melting point was undepressed by an authentic sample prepared by the method of Limpricht[7] (found: C, 67·0; H, 7·3; calculated for $C_{14}H_{10}O_4$: C, 67·2; H, 7·2 per cent).

The Fries migration of methyl acetyl-salicylate — The acetylation of methyl salicylate was carried out by heating on a sand bath with a mixture of the ester (10 cc.) and acetic anhydride (15 cc.) for 3 hr. It crystallized from dilute alcohol in plates, m.p. 49°-50°C., as recorded by Erdmann[8].

The Fries migration product obtained by using two moles of aluminium chloride gave methyl-5-acetyl-2-hydroxybenzoate (yield 75 per cent) after 48 hr. It crystallized from dilute alcohol in needles, m.p. 55°C., and its alcoholic solution gave a reddish brown colour with ferric chloride (found: C, 61·6; H, 5·2; $C_{10}H_{10}O_4$ requires: C, 61·9; H, 5·1 per cent).

On hydrolysis with alkali, it gave 5-acetyl-2-hydroxybenzoic acid, m.p. 217°C., undepressed by an authentic specimen, prepared by the method of Rosenmund and Schnurr[1].

The Fries migration of methyl benzoyl-salicylate gave methyl-5-benzoyl-2-hydroxybenzoate (yield 52 per cent) which crystallized from dilute alcohol in needles, m.p. 95°C. It gave reddish brown colour with ferric chloride, and on alkaline hydrolysis gave 5-benzoyl-2-hydroxybenzoic acid, m.p. 207°C., identified by mixed melting point, with an authentic specimen. The melting point of the ester is given as 94°-95°C. by Lowenstein[9].

The Fries migration of phenyl-acetyl-salicylate at ordinary temperature gave a sticky mass which was taken up in warm 0·5 per cent solution of sodium hydroxide. The alkaline filtrate on acidification with hydrochloric acid gave 5-acetyl-2-hydroxybenzoic acid, m.p. 217°C. (yield 70 per cent).

The Fries migration of phenyl-benzoyl-salicylate at ordinary temperature gave a resinous mass which was extracted with 0·5 per cent solution of sodium hydroxide. On acidification with hydrochloric acid 5-benzoyl-2-hydroxybenzoic acid, m.p. 207°C., was obtained (yield 45 pr cent).

The Fries migration of acetyl-salicylanilide — An intimate mixture of acetyl-salicylanilide (5·1 g.) and powdered aluminium chloride (5·3 g.) was heated in an oil bath at 130°-40°C. for 1½ hr. After decomposing the contents of the flask with ice-cold hydrochloric acid, the viscous residue was extracted with 0·5 per cent solution of sodium hydroxide. The solid obtained by acidifying the alkaline extract with hydrochloric acid was collected and treated with sodium bicarbonate solution to remove the free acid. 5-Acetyl-2-hydroxybenzanilide crystallized from dilute alcohol in prisms, m.p. 117°C., and its alcoholic solution gave deep reddish brown colouration with ferric chloride (yield 40 per cent) (found: N, 5·7; $C_{15}H_{13}O_3N$ requires: N, 5·5 per cent). The Fries migration of the same product at ordinary temperature gave the original salicylanilide.

The Fries migration of benzoyl-salicylanilide did not take place at ordinary temperature but by heating at 140°C., for 1½ hr. (yield 25 per cent). 5-Benzoyl-2-hydroxybenzanilide crystallized from dilute alcohol in plates, m.p. 175°C., and its alcoholic solution gave reddish brown red colouration with ferric chloride (found: N, 4·1; $C_{20}H_{15}O_3N$ requires: N, 4·4 per cent).

The Fries migration of phenyl-salicylate (salol) and the formation of 2 : 4′*-dihydroxybenzophenone* — An intimate mixture of salol (4·3 g., 1 mole) and aluminium chloride (11·0 g., 4 moles) was heated in an oil bath at 140°C. for 3 hr. The cooled mass was decomposed with ice-cold hydrochloric acid, and the solid filtered off. It was shaken up with sodium bicarbonate solution to remove salicylic acid, and the residue purified through 0·5 per cent sodium hydroxide solution. The solid obtained on acidification crystallized from dilute alcohol in colourless plates, m.p. 145°C. (yield 75 per cent). Its alcoholic solution gave red colour with ferric chloride. The melting point for 2 : 4′-dihydroxybenzophenone as given by Baeyer[10] is 144°C. (found: C, 72·8; H, 4·7; $C_{13}H_{10}O_3$ requires: C, 72·9; H, 4·7 per cent).

2: 4-*Dinitrophenylhydrazone* crystallized from alcohol in red plates, m.p. 250°C. (found: N, 13·8; $C_{19}H_{14}O_6N_4$ requires: N, 14·2 per cent).

The Fries migration of o-cresyl-salicylate under similar conditions gave 2 : 4′-dihydroxy-3′-methyl-benzophenone which crystallized from dilute alcohol in yellowish prisms, m.p. 112°C. (yield 80 per cent). Its alcoholic solution gave violet colour with ferric chloride (found: C, 73·3; H, 5·7; $C_{14}H_{12}O_3$ requires: C, 73·7; H, 5·3 per cent).

2 : 4-*Dinitrophenylhydrazone* crystallized from alcohol in red plates, m.p. 245°C. (found: N, 13·5; $C_{20}H_{16}O_6N_4$ requires: N, 13·7 per cent).

The Fries migration of m-cresyl-salicylate gave 2 : 4′-dihydroxy-2′-methyl-benzophenone which crystallized from dilute alcohol in plates, m.p. 146°C. (yield 80 per cent). It dissolved in alkali solution with a yellow colour, and its alcoholic solution gave violet colouration with ferric chloride. It did not react with 2 : 4-dinitrophenylhydrazine (found: C, 73·4; H, 5·0; $C_{14}H_{12}O_3$ requires: C, 73·7; H, 5·3 per cent).

The Fries migration of p-cresyl-salicylate gave 2 : 2′-dihydroxy-5′-methyl-benzophenone which crystallized from dilute alcohol in triangular plates, m.p. 143°-44°C. (yield 70 per cent). It dissolved in alkali solution with a yellow colour, and its alcoholic solution gave violet colouration with ferric chloride. It did not give the 2 : 4-dinitrophenylhydrazone (found: C, 73·4; H, 5·0; $C_{14}H_{12}O_3$ requires: C, 73·7; H, 5·3 per cent).

The preparation of phenyl o-nitrobenzoate — A mixture of o-nitrobenzoic acid (15 g.), thionyl chloride (12 cc.) and a drop of pyridine was warmed up to 60°C. for 3 hr. The excess of thionyl chloride was removed under vacuum, and the crude o-nitrobenzoyl chloride was added gradually to phenol (15 g.) dissolved in 10 per cent sodium hydroxide solution (100 cc.). The solid crystallized from dilute alcohol in prisms, m.p. 52°C. (yield 80 per cent) (found: N, 6·0; $C_{13}H_9O_4N$ requires: N, 5·8 per cent).

Phenyl p-nitrobenzoate prepared in an identical manner using p-nitrobenzoic acid crystallized from dilute alcohol in prisms, m.p. 132°C. (yield 90 per cent) (found: N, 5·9; $C_{13}H_9O_4N$ requires: N, 5·8 per cent).

Attempted Fries migration of phenyl o-nitrobenzoate — A solution of phenyl o-nitrobenzoate (5 g.) and aluminium chloride (4 g.) in nitrobenzene (50 cc.) was kept at the room temperature for 24 hr. There was no visible sign of the evolution of hydrogen chloride when the solution was warmed up to 50°C., but the reaction later became extremely violent resulting in the charring of all the products. The reaction did not occur without the use of the solvent also. Similarly phenyl p-nitrobenzoate failed to undergo the rearrangement.

Acknowledgement

We are thankful to Dr. T. S. Gore for the microanalysis.

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The Fries Reaction: Part VI—The Rearrangement of Aryl p-Toluenesulphonates & a Convenient Method for the Synthesis of Hydroxy-diarylsulphones

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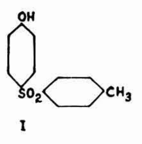
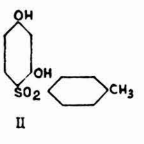
The Fries migration of the aryl p-toluenesulphonates of phenol, o-cresol, m-cresol, p-cresol, methyl salicylate and salicylanilide (Shirlan) has been studied at 130°-40°C. The migrations were smooth at this temperature, providing a convenient method for the synthesis of hydroxy-diarylsulphonates, which are useful as antiseptics and dyestuff intermediates. The migration in the case of salicylanilide took place smoothly in nitrobenzene solution. It is found that most of these migrations take place in the para position to the hydroxyl group.

THE Fries migration of the aryl esters of aliphatic as well as aromatic acids has been extensively studied by various workers, but the literature is very scanty with regard to the rearrangement of the arylsulphonates. Rittler[1] has claimed, in a German patent, the migrations of phenyl p-toluenesulphonate and phenyl-2-naphthalenesulphonate to p-hydroxyphenyl-p-tolylsulphone and p-hydroxyphenyl-2-naphthylsulphone in the presence of anhydrous aluminium chloride. Simons, Archer and Randall[2] carried out the migration of p-cresylbenzenesulphonate to 2-hydroxy-4-methyldiphenylsulphone in the presence of hydrogen fluoride. As hydroxy arylsulphones are useful as antiseptics and as coupling components for azoic dyestuffs, we investigated this reaction exhaustively with p-toluenesulphonyl derivatives of phenol, o-, m- and p-cresols, methyl salicylate, and salicylanilide (Shirlan) in presence of anhydrous aluminium chloride, and found the migrations taking place smoothly in presence of two moles of aluminium chloride for one mole of the ester at elevated temperature (130°-40°C.). The reaction did not take place at ordinary temperature, while the use of nitrobenzene as a solvent did not offer any advantage in yields of the resulting products. Zinc chloride was not an efficient catalyst in this reaction.

Phenyl p-toluenesulphonate gave a product (m.p. 125°C.) which Rittler assumed to be p-hydroxyphenyl-p-tolylsulphone (I) without adducing any chemical proof. Rittler[3] obtained also the isomeric product (m.p. 138°C.) by the Friedel-Crafts' reaction between phenol and p-toluenesulphonyl chloride. According to our observations, both the reactions yield the same product, and there is, therefore, the possibility of the product obtained by the Fries migration of phenyl-p-toluenesulphonate being o-hydroxyphenyl-p-tolylsulphone (II). The product coupled with 2:4-dichlorobenzene-diazonium chloride, giving an orange dye (III) which could not be methylated by dimethyl sulphate in presence of acetone and anhydrous potassium carbonate. The dye, therefore, had the chelated o-hydroxy-azo structure, whereas if (II) had been the structure of the hydroxysulphone, the dye would have the p-hydroxy-azo structure. Thus it is beyond doubt that the p-toluenesulphonyl group migrates to the position para to the hydroxyl. o-Cresyl- and m-cresyl-p-toluenesulphonates underwent similar migrations with the formation of 3-methyl-4-hydroxyphenyl-p-tolylsulphone and 2-methyl-4-hydroxyphenyl-p-tolylsulphone, while p-cresyl-p-toluenesulphonate gave 5-methyl-4-hydroxy-p-tolylsulphone which is the only expected product. Each sulphone could be readily methylated by dimethyl sulphate in presence of aqueous sodium hydroxide showing the absence of



I



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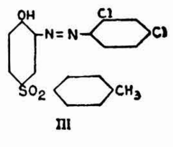

III

chelation even in the case of those sulphones which contained the hydroxyl and p-toluenesulphonyl groups in the ortho position. Similarly such a sulphone gave a negative colour reaction with aqueous or alcoholic ferric chloride. They condensed smoothly with chloracetic acid and coupled readily with diazonium salts. The p-toluenesulphonyl derivative of methyl salicylate responded to the reaction, but the isolated product was 5-p-toluenesulphonyl-2-hydroxybenzoic acid, the intermediate methyl ester having undergone hydrolysis, either during the Fries migration or subsequent treatment with dilute alkali solution. The Fries migration of the p-toluenesulphonyl derivative of salicyl-anilide (Shirlan) in nitrobenzene solution gave the expected sulphone 5-p-toluenesulphonyl-2-hydroxy-benzanilide.

Experimental procedure

Fries migration of phenyl-p-toluenesulphonate and formation of p-hydroxyphenyl-p-tolylsulphone (I) — When a mixture of phenyl-p-toluenesulphonate (5·0 g.) and anhydrous aluminium chloride (5·3 g.) was heated in an oil bath, the evolution of hydrogen chloride fumes started at 75°C. The temperature was slowly raised to 140°C., and the reaction mixture maintained at that temperature for 1 hr. The dark violet liquid formed solidified on cooling and was decomposed with ice-cold hydrochloric acid. The crude solid that separated out was filtered off, and dissolved in 1 per cent sodium hydroxide solution. The clear filtrate on acidification gave a solid (2·5 g.) which crystallized from dilute alcohol or ligroin in plates, m.p. 125°C. It was free from any other isomeric product (found: C, 62·4; H, 4·6; S, 13·3; $C_{13}H_{12}SO_3$ requires: C, 62·4; H, 4·8; S, 12·9 per cent).

4-*Methoxyphenyl-p-tolylsulphone* was prepared by the action of dimethyl sulphate (5 cc.) on the solution of the hydroxysulphone (1·0 g.) in 10 per cent sodium hydroxide (25 cc.), and crystallized from dilute alcohol in plates, m.p. 122°C. (depressed to 100°C. by admixture with the parent compound) (found: C, 64·3; H, 5·4; $C_{14}H_{14}O_3S$ requires: C, 64·1; H, 5·3 per cent).

4-*p-Toluenesulphonyl-phenoxyacetic acid* — Monochloracetic acid (1·2 g.) was added to the solution of 4-hydroxyphenyl-p-tolylsulphone in 30 per cent caustic soda solution (4 cc.) and the mixture heated on water bath for 1 hr. The solution was diluted with water, cooled, acidified with hydrochloric acid and extracted with ether. The ethereal extract was treated with dilute sodium carbonate solution, and the solid that separated out on acidification with hydrochloric acid was collected. It crystallized from dilute alcohol (charcoal) in needles, m.p. 177°C. (found: S, 10·7; $C_{15}H_{14}O_5S$ requires: S, 10·5 per cent).

2′-5′-*Dichlorobenzene-azo*-4-*hydroxyphenyl-p-tolylsulphone* — A cold filtered diazotized solution of 2: 5-dichloraniline (0·8 g.) was slowly added to a cold solution of 4-hydroxyphenyl-p-tolylsulphone (1·2 g.) in 10 per cent sodium hydroxide (15 cc.) when an orange dye began to separate out slowly. The precipitate was filtered off after 1 hr., and crystallized from alcohol in orange needles, m.p. 179°-80°C. (yield 1·6 g.) (found: S, 8·0; $C_{19}H_{14}O_3N_2Cl_2S$ requires: S, 7·6 per cent).

Attempted methylation of the above azo dye— The azo dye (1 g.) dissolved in boiling anhydrous acetone (20 cc.) was treated with dimethylsulphate (1·3 cc.) and freshly ignited potassium carbonate during 24 hr. On pouring into water and after removing acetone, the product obtained was crystallized from dilute alcohol in orange needles, m.p. 179°-80°C.; undepressed by the original dye.

4-*Hydroxy*-3-*methylphenyl*-*p*-*tolylsulphone* was obtained by the Fries migration of o-cresyl-p-toluenesulphonate (yield 40 per cent) and crystallized from dilute alcohol in plates, m.p. 132°C. (found: C, 63·8; H, 5·3; S, 12·4; $C_{14}H_{14}O_3S$ requires: C, 64·1; H, 5·3; S, 12·2 per cent). It coupled with diazotized 2 : 5-dichloraniline giving an orange-red dye, which crystallized from alcohol in orange scales, m.p. 188°-89°C. This dye resisted methylation by the usual methods (found: S, 7·3; $C_{20}H_{16}O_3N_2Cl_2S$ requires: S, 7·3 per cent).

The methyl ether crystallized from dilute alcohol in rhombic plates, m.p. 110°C. (found: C, 64·9; H, 5·8; $C_{15}H_{16}O_3S$ requires: C, 65·2; H, 5·8 per cent).

4-*Hydroxy*-2-*methylphenyl*-*p*-*tolylsulphone* was obtained by the Fries migration of m-cresyl p-toluenesulphonate (yield 30 per cent) and crystallized from dilute alcohol in needles, m.p. 144°C. (found: C, 63·6; H, 5·4; S, 12·3; $C_{14}H_{14}O_3S$ requires: C, 64·1; H, 5·3; S, 12·2 per cent).

The methyl ether crystallized from dilute alcohol in needles, m.p. 132°C. (found: C, 64·9; H, 5·7; $C_{15}H_{16}O_3S$ requires: C, 65·2; H, 5·8 per cent).

2-*Hydroxy-5-methylphenyl-p-tolylsulphone* was obtained by the Fries migration of p-cresyl-p-toluenesulphonate (yield 30 per cent) and crystallized from dilute alcohol in plates, m.p. 130°C. (found: C, 63·8; H, 5·3; S, 12·0; $C_{14}H_{14}O_3S$ requires: C, 64·1; H, 5·3; S, 12·2 per cent).

The methyl ether crystallized from dilute alcohol in needles, m.p. 143°-44°C. (found: C, 65·1; H, 5·7; $C_{15}H_{16}O_3S$ requires: C, 65·2; H, 5·8 per cent).

4-*Methyl-2-p-toluenesulphonyl-phenyl acetic acid* was prepared by the action of the above hydroxysulphone in chloracetic acid as usual. It crystallized from dilute alcohol in needles, m.p. 174°C. (found: S, 10·3; $C_{16}H_{16}O_5S$ requires: S, 10·0 per cent).

The azo dye obtained by coupling the diazotized 2: 5-dichloraniline with the hydroxysulphone crystallized from alcohol in dark red needles, m.p. 250°C. It resisted methylation with dimethyl sulphate by usual methods (found: S, 7·3; $C_{20}H_{16}O_3N_2Cl_2S$ requires: S, 7·3 per cent).

Preparation of o-p-toluenesulphonyl methyl salicylate — Methyl salicylate (10 g.) and p-toluenesulphonyl chloride (20 g.) were dissolved in ether (50 cc.) in a round bottom flask. A 20 per cent solution of sodium carbonate (40 cc.) was added gradually with mechanical stirring. There was evolution of carbon dioxide, and after the removal of ether, the flask was kept on the water bath for 2 hr. The precipitated solid was filtered off, washed with 1 per cent solution of alkali in the cold and crystallized from alcohol, when needles, m.p. 88°C., were obtained (yield 50 per cent). Its alcoholic solution did not give any colouration with ferric chloride (found: S, 10·5; $C_{15}H_{14}O_5S$ requires: S, 10·6 per cent).

5-*p-Toluenesulphonyl salicylic acid* was obtained by the usual Fries migration of the above ester. The product purified through 0·5 per cent sodium hydroxide solution was also soluble in sodium bicarbonate solution (yield 35 per cent). It crystallized from dilute alcohol in thick needles, m.p. 239°-40°C. (found: C, 58·2; H, 4·4; S, 11·1; $C_{14}H_{12}O_5S$ requires: C, 57·8; H, 4·0; S, 11·0 per cent).

o-p-Toluenesulphonyl salicylanilide — Salicylanilide (10 g.) and p-toluenesulphonyl chloride (20 g.) were dissolved in acetone (50 cc.) in a round bottom flask. A 25 per cent solution of potassium carbonate (40 cc.) was added gradually with mechanical stirring, when a solid began to separate out gradually, and the separation was complete after 1 hr. The solid was filtered off and washed with 1 per cent sodium hydroxide solution (yield 50 per cent). It crystallized from dilute alcohol in needles, m.p. 105°C., and its alcoholic solution gave a negative test with ferric chloride solution (found: N, 3·5; S, 9·0; $C_{20}H_{17}O_4SN$ requires: N, 3·8; S, 8·7 per cent).

5-*p-Toluenesulphonyl salicylanilide* — A solution of the above p-toluenesulphonyl derivative (5 g.), anhydrous aluminium chloride (5 g.) in freshly distilled nitrobenzene (50 cc.) was heated in an oil bath at 125°C. for 2 hr. After decomposing the cold solution with ice-cold hydrocloric acid, nitrobenzene was removed under steam distillation and the solid was filtered off. The dry residue was extracted with benzene to remove insoluble impurities, and the concentrated solution of benzene deposited a brown solid which crystallized from alcohol in flat needles, m.p. 225°C. (yield 25 per cent). Its alcoholic solution gave reddish brown colour with ferric chloride (found: N, 4·2; S, 9·0; $C_{20}H_{17}O_4SN$ requires: N, 3·8; S, 8·7 per cent).

The methyl ether prepared by refluxing the solution of the above compound (0·5 g.) in acetone (20 cc.) with dimethyl sulphate (1 g.) in presence of anhydrous potassium carbonate (2 g.) for 12 hr., crystallized from dilute alcohol in fluffy plates, m.p. 185°C. (found: N, 3·5; $C_{21}H_{19}O_4SN$ requires: N, 3·7 per cent).

Acknowledgement

We take this opportunity of thanking Dr. T. S. Gore for the microanalysis.

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A Method for the Preparation of Diiodotyrosine

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A method is described for the preparation of diiodotyrosine by reacting tyrosine with iodine at *p*H 7 (phosphate buffer) and room temperature (25°-27°C.). The yield is 85 per cent.

MANY methods have been described in literature for the iodination of tyrosine to diiodotyrosine. Jamieson[1] was the first to carry out the preparation of diiodotyrosine by adding solid iodine to a solution of tyrosine in sodium hydroxide. By carrying out the reaction at 0°C., Ostwald[2] improved the yield of diiodotyrosine. Harington[3] iodinated a solution of tyrosine in concentrated ammonia at 0°C. employing theoretical quantity of iodine and obtained an yield of 60 per cent of diiodotyrosine. Bauer, Strauss and Maschmann[4] carried out the reaction in a medium containing sodium bicarbonate, but the yield was only 56 per cent. In all these methods the reactions were carried out at alkaline *p*H and at 0°C. and the quantity of tyrosine used for iodination was of the order of 5 g. or less. By employing a larger quantity of tyrosine (90 g.), but otherwise retaining broadly the conditions of the earlier methods, Savitskii[5] obtained an yield of 88 per cent of diiodotyrosine. He was the first to point out that diiodotyrosine crystallizes as the dihydrate. According to the meagre details available of another method patented by the same author[6], iodination of tyrosine was carried out in a solution of benzene or toluene at −8° to −10°C. Pierre Sue[7], using radioactive iodine, reported an yield of 65 per cent. The yield in the method ascribed to Zeynek[8] is not available.

Quite a departure from the methods described above was made by Bauer and Strauss[9] when they used iodine monochloride (in the vapour form) as iodinating agent. They reported an yield of 38·5 per cent. Following this method, Barkdoll and Ross[10] reported an yield of 66 per cent. Block and Powell[11] improved upon this method and obtained an yield of 80-85 per cent. A similar yield (86 per cent) using iodine monochloride is recorded by Borrows, Clayton and Hems[12].

From our experience based on the semimicro-volumetric estimation of phenolphthalein by iodination[13], it occurred to us to study the iodination of tyrosine in buffered media, especially from the point of view of developing a simple method for the preparation of diiodotyrosine with fairly quantitative yields. If the iodination could be achieved under physiological conditions of *p*H, it would have added significance.

Our finding that the iodination of phenolphthalein to tetraiodophenolphthalein takes place quantitatively and with great facility at *p*H 9·9 using sodium carbonate-bicarbonate buffer (SUBRAHMANYAM, D. and SRINIVASAN, M., unpublished data) was made use of for the conversion of tyrosine to diiodotyrosine. In the various experiments carried out at different *p*H levels in the alkaline range using carbonate buffer, it was found that, although iodination of tyrosine was complete almost instantaneously as measured by the iodine uptake, the resulting product was highly coloured, indicating that secondary reactions had simultaneously taken place. We, therefore, decided to employ the phosphate buffer. Li[14] has studied the kinetics and mechanism of the formation of diiodotyrosine using phosphate buffer (*p*H 5·0-6·0). Besides the buffer action, Li has suggested that the phosphate ion might be involved in the reaction. He has not, however, dealt with the actual conditions for the preparation of diiodotyrosine.

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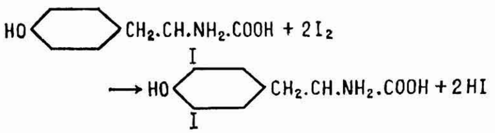
*C.S.I.R. Scholar.

Experiments using phosphate buffer at pH 5, 6 and 7 — To 10 cc. of a hydrochloric acid solution of tyrosine (10 mg./cc.) and 2/5M phosphate buffer (40-100 cc.) contained in a 250 cc. standard flask, 50 cc. 0·1N iodine were added under shaking and the solution then made up to volume. The rate of reaction was studied by determining the consumption of iodine in aliquots at different time intervals at the room temperature (26°-28°C.). The main findings of these experiments were:

(1) In conformity with the findings of Painter and Soper[15] on the iodination of phenols, iodination of tyrosine also is a function of the concentration of buffer and is inhibited by excess iodide.

(2) The volume of 2/5M buffer required for maximum rate of reaction and the time for 100 per cent conversion at *p*H 5, 6·2 and 7 are: 100 cc. and 16 hr.; 75 cc. and 2½ hr.; and 40 cc. and 10 min. respectively. The results obtained at *p*H 7 are significant physiologically.

(3) That the following reaction



has taken place was shown by (a) the characterization of the crystals obtained at the end of the reaction at *p*H 7 as diiodotyrosine and (b) the formation in the medium of the theoretical quantity of iodide as determined by the Andrews procedure[16].

(4) Use of iodine far in excess of the theoretical requirements results in a coloured product.

(5) Minimum amount of water in the reaction mixture is conducive to maximum separation of diiodotyrosine formed. Under these conditions, the diiodotyrosine separates out when about half the theoretical quantity of iodine has been added. This simultaneous separation of diiodotyrosine from the medium, with the progress of the reaction, results in a pure product and obviates further steps in purification.

(6) The yield of diiodotyrosine at *p*H 7 is about 85 per cent.

(7) Diiodotyrosine obtained under these conditions is optically active. This is also significant physiologically.

Preparation of diiodotyrosine — Based on these findings, the method adopted for the preparation of diiodotyrosine was as follows.

Buffer mixture — Phosphate buffer, 4/5M; *p*H 7, 11.

Tyrosine solution — Five grams L-tyrosine (B.D.H.) in 5 cc. concentrated hydrochloric acid and diluted to 40 cc. with water.

Iodine solution — 1N, 115 cc.

To the buffer mixture kept well stirred in a pyrex beaker (2·5 l.) were added, in small increments, tyrosine and iodine solutions alternatively. After the iodine previously added had been nearly consumed (pale yellow colour in the medium), more of tyrosine and iodine solutions were added. When about half the quantity of tyrosine added in this manner had been iodinated (about 20 min. from the start), diiodotyrosine (silky needles) crystallized out of the reaction mixture almost instantaneously. At the end of the reaction (about an hour from the start), the crystals were centrifuged off and transferred to a tared sintered glass septum. The supernatant solution on stirring yielded a further crop of crystals (glistening spangles; the yield of the second crop of crystals was facilitated by cooling in the ice chest overnight). The combined crop of crystals was washed on the filter with ice-cold water and dried; yield 85 per cent.

The final product was pale yellow in colour, melted at 199°-200° (decomp.), was chromatographically pure and optically active; $[\alpha]_D^{28°} = +2.3°$; 5·016 in 1·1N HCl (cf. ABDERHALDEN and GUGGENHEIM[17]).

Acknowledgement

The authors' thanks are due to Dr. V. Subrahmanyan, Director of this Institute, for his kind interest.

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Lithium Aluminium Hydride as a Reducing Agent for Anthoxanthins: Part I

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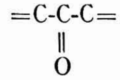
It is known that carbonyl compounds are generally reduced to carbinols by reduction with lithium aluminium hydride. Very little work has been done on this reduction in the field of anthoxanthins, which contain a carbonyl group. It has been reported recently that some γ-pyrones on reduction by this reagent gives γ-pyranols. It has now been found that methyl ether of decussatin, a naturally occurring xanthone, and some flavones are reduced to the xanthene derivative and flavenes respectively in good yields.

IN continuation of our studies on the constitution of xanthones — decussatin and swertinin — isolated from *Swertia decussata*[1], it has been found that the methyl ether of decussatin, for which formula (I) was provisionally assigned, on reduction with lithium aluminium hydride gives a xanthene derivative (II) and not a xanthydrol derivative (III). This was rather unexpected because carbonyl compounds on reduction with this reagent are generally known to give carbinols. This anomalous behaviour of a xanthone was thought of importance for the study of naturally occurring plant pigments of anthoxanthin group for the following reasons: (1) this method of reduction would give a direct chemical evidence for the presence of a carbonyl group in anthoxanthins, particularly xanthones; (2) this would be an elegant method for the synthesis of catechin-type compounds; (3) the reduced anthoxanthins which are devoid of their original



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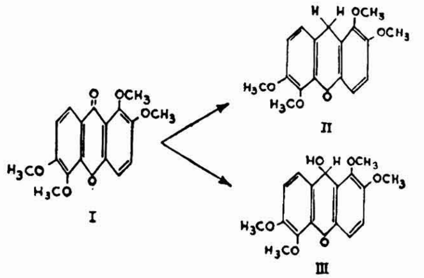
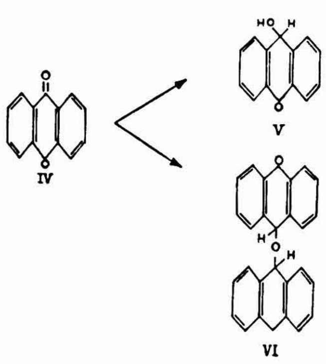
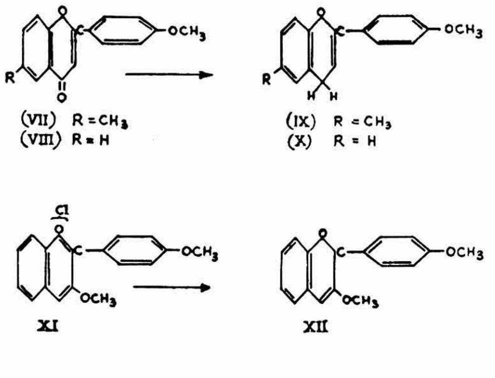
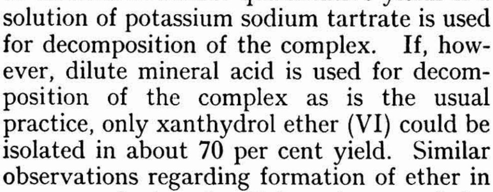
chromophoric grouping may serve as a simpler material for ultraviolet spectrum analysis and hence comparison of U.V. curves of these reduced compounds with those of polyhydroxy phenols or their methyl ethers may give valuable information regarding the orientation of hydroxy groups in the original anthoxanthins; (4) in case the reduction goes from -CO- to -CH-OH and not -CO- to -CH_2, this would be an excellent method for the preparation of pyrylium salts. Since very little information was available on this subject when these investigations were undertaken, a systematic investigation on the reduction of anthoxanthins with lithium aluminium hydride was undertaken. While the work was in progress, Mirza and R. Robinson[2] in their preliminary note reported for the first time the reduction of γ-pyrones with lithium aluminium hydride to γ-pyranols and their conversion to pyrylium salts.

Decussatin methyl ether (I) on boiling with excess of lithium aluminium hydride in ether for about 12 hr. gave the xanthene derivative (II). However, xanthone (IV) is reduced by this reagent to xanthydrol (V). This can









be isolated in almost quantitative yields if a solution of potassium sodium tartrate is used for decomposition of the complex. If, however, dilute mineral acid is used for decomposition of the complex as is the usual practice, only xanthydrol ether (VI) could be isolated in about 70 per cent yield. Similar observations regarding formation of ether in presence of mineral acid have been made by Woodward and co-workers[3]. 4'-Methoxy-6-methyl flavone (VII) and 4'-methoxyflavone (VIII) on reduction with lithium aluminium hydride gave the corresponding reduced products, presumably flavenes, (IX) and (X), when the complex was decomposed with sulphuric acid (10 per cent). In this connection it is interesting to note that Karrer and Seyhan[4] and Elstow and Platt[5] have recently reported on the reduction of flavylium salts with lithium aluminium hydride. Karrer suggests the formula (XII) to the dihydro derivative obtained from 3, 4'-dimethoxy-2-phenyl benzopyrylium chloride (XI); however, the latter authors presume that flavenes are formed in the process of reduction.

Generally, carbonyl compounds are reduced to carbinols by lithium aluminium hydride; however, as described in this paper, this reduction has gone a step further and corresponding xanthenes and flavenes have been isolated in the cases described above. A few isolated observations have been made in the past wherein further reduction of carbinol to methylene derivative has been reported. Witkop[6] observed "hydrogenolysis" of a spiro-[cyclopentane-1-2'-ψ-indoxyl] to spiro-[cyclopentane-1, 2'-dihydroindole]. Conover and Trabell[7] observed that *o*- and *p*-substituted amino carbonyl compounds on reduction with lithium aluminium hydride gave amino alkyd derivatives. They further reported that *p*- and *o*-hydroxy carbonyl compounds did not give the corresponding alkyl derivatives probably due to precipitation phenomenon, but 4, 4'-dimethoxy benzophenone gave 4, 4'-dimethoxy diphenyl methane. Reduction of decussatin methyl ether is similar to that of the methoxy benzophenone.

A systematic investigation of the reduction of anthoxanthins with lithium aluminium hydride and synthesis of catechin-type compounds is in progress; however, since the results obtained so far are unusual and of interest, it is thought worth while to communicate them at this stage.

Experimental procedure

Xanthene derivative from methyl ether of decussatin (II) — Decussatin monomethyl ether (I), m.p. 165°C. (120 mg.), was suspended in ether (50 cc.) and lithium aluminium hydride (500 mg.) was added. The mass was refluxed for 18 hr. The excess lithium aluminium hydride was decomposed with 10 per cent sulphuric acid. Ethereal solution was washed with water and dried over anhydrous sodium sulphate. Grey solid residue obtained after removal of ether melts at 105°-12°C. It was crystallized twice from alcohol when 51 mg. material, m.p. 125°-26°C., were obtained. This was dried under high vacuum (found: C, 67·5, 67·6; H, 6·2, 6·2; $C_{17}H_{18}O_5$ requires: C, 67·55; H, 5·96 per cent).

Xanthydrol ether from xanthone (VI) — Xanthone (II), m.p. 173°C. (600 mg.), was dissolved in ether and added to the ethereal solution of lithium aluminium hydride (60 mg.). The resulting complex was decomposed with 10 per cent sulphuric acid and the product extracted with ether. The ethereal solution was worked up as above. The residue melted at 150°-60°C. When washed with alcohol, a compound (420 mg.), m.p. 199°-202°C., was obtained. This was crystallized from xylene, and dried; m.p. 202°-3°C. Its melting point and properties are the same as described in literature[8] (found: C, 82·4; H, 4·5; $C_{26}H_{18}O_3$ requires: C, 82·54; H, 4·76 per cent). The same compound was obtained if dilute hydrochloric acid instead of dilute sulphuric acid was used for decomposition of complex.

Xanthydrol from xanthone (V) — Xanthone (IV) (600 mg.) was reduced as described above. The complex was decomposed with Rochelle salt and the reaction product was worked up as above. The crude residue melted at 123°-24°C. It was crystallized from alcohol when a compound, m.p. 125°C. (550 mg.), was obtained. Its melting point and properties are the same as described for xanthydrol in literature[8].

4'-Methoxy-6-methyl flavene from 4'-methoxy-6-methyl flavone (IX) — 4'-Methoxy-6-methyl flavone (VII), m.p. 170°C. (200 mg.), was dissolved in ether and added to the ethereal solution of lithium aluminium hydride (50 mg.). After about 10 min. the complex was decomposed with dilute sulphuric acid (10 per cent) and the product extracted with ether and worked up as described above. The crude material melted at 95°-112°C. It was crystallized twice from alcohol, dried and analysed; m.p. 130°C. The yield of the pure product was 70 mg. (found: C, 81·4; H, 6·5; $C_{17}H_{16}O_2$ requires: C, 80·95; H, 6·35 per cent).

4'-Methoxy flavene from 4'-methoxy-flavone (X) — 4'-Methoxy flavone (VIII), m.p. 157°C. (252 mg.), was dissolved in ether and reduced with lithium aluminium hydride (50 mg.). The complex was decomposed with dilute sulphuric acid and the reaction product worked up as described before. The crude material was crystallized from alcohol, m.p. 123°-24°C., and analysed after drying. The yield of the pure product was 55 mg. (found: C, 80·4; H, 5·8; $C_{16}H_{14}O_2$ requires: C, 80·67; H, 5·88 per cent).

Acknowledgement

The authors are thankful to Dr. M. G. Marathe of Poona University for the supply of some flavones.

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Studies in Indian Turpentine: Part IX — Hydroxylation of Higher Boiling Fractions

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Hydroxylation of the higher boiling fraction (>180°C.) of third grade Jallo turpentine was carried out by saturating it with dry hydrogen chloride and replacing the chlorine in the resultant product by hydroxyl group with the aid of alkaline reagents. The best results were obtained when slaked lime was used as the hydroxylating agent.

A new method for the estimation of chlorine in the chloroterpenes has been standardized.

SPENT turpentine, obtained in the production of terpin hydrate, was found by Bhushan, Gulati and Joshi[1] to contain 13·97 per cent alcohols (calculated as $C_{10}H_{17}OH$) to which they attributed its pleasant but penetrating odour. Even though terpineol was not a constituent of the " spent " oil, the higher boiling fractions of the latter could be used as a pine oil substitute. Attempts were, therefore, made to hydroxylate the higher boiling and at present industrially less useful fractions of Indian turpentine (*Pinus longifolia* Roxb.) with a view to obtaining products which may find application in ore flotation processes, in the textile industry or as insecticide-aids.

Experimental procedure

Turpentine oil used in this investigation was obtained from the Government Rosin & Turpentine Factory, Jallo (Punjab). The third grade oil was fractionated in an atmosphere of carbon dioxide and the fraction boiling below 180°C. tapped off; the residual light brown oil (40 per cent by volume) had the following characteristics: n_D^{32}, 1·4950; d_{33}^{33}, 0·9200; iod. No., 162; mean mol. wt., 202; boiling range, 180°-270°C./ 745 mm.

Preparation of chloroterpenes — The residual oil was cooled to about −5°C. and saturated with a steady stream of dry hydrogen chloride. The resultant dark brown liquid was washed free of acid and after drying over anhydrous sodium sulphate had the following characteristics: n_D^{33}, 1·4996; d_{34}^{34}, 1·008; iod. No., 60; mean mol. wt., 233; chlorine content, 12·86 per cent.

Hydroxylation with alcoholic potash — The chloroterpenes (240 g.) were taken up in alcohol (500 cc.) and to the solution were added 57·6 g. of potassium hydroxide dissolved in 562 cc. of alcohol (to give an overall concentration of 5 per cent KOH in the solution) in an autoclave (5 l. capacity) and the mass heated under pressure for 9 hr. After distilling off alcohol and filtering off the precipitated potassium chloride, the product was washed with water to remove the last traces of soluble impurities. The hydroxylated product was dried over anhydrous sodium sulphate and distilled under reduced pressure.

The effect of pressure, period of reaction and concentration of alcoholic potash on the hydroxylation of chloroterpenes is recorded in Tables 1-3.

The results in Tables 1-3 show that the optimum conditions for hydroxylation of chloroterpenes are to heat the chlorinated terpenes with 2·5 per cent alcoholic potash for 9 hr. at 75 lb./sq. in. The product so obtained had the following characteristics: n_D^{30}, 1·4924; d_{26}^{26}, 0·927; mean mol. wt., 201·4; iod. No., 132; hydroxyl content (Zerevitinoff method[2]), 1·378 per cent (corresponding to 18·02 per cent alcohols as $C_{15}H_{25}OH$); boiling range, 230°-67°C./745 mm., 59 per cent boiling between 247° and 258°C. The product contained no chlorine.

Hydroxylation of chloroterpenes with aqueous sodium hydroxide and soap — The method of Ayres[3] and Padgett and Degening[4] for the hydroxylation of alkyl chlorides was extended to chloroterpenes. Sodium oleate (480 g.)

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TABLE 1 — EFFECT OF PRESSURE ON THE HYDROXYLATION OF THE CHLOROTERPENES

(*Conc. of alcoholic potash, 5 per cent; period of reaction, 9 hr.*)

PRESSURE lb./sq. in.	YIELD OF HYDROXYLATED PRODUCT %	ANALYSIS OF THE PRODUCT				
		OH %	Calculated as $C_{15}H_{25}OH$ %	n_D^{30}	Iod. No.	Cl %
—	98·7	nil	nil	1·4989	61·5	12·79
50	98·2	1·150	15·03	1·4940	133·8	nil
75	98·3	1·337	17·48	1·4928	133·6	nil
100	98·2	1·189	15·55	1·4935	132·2	nil
125	90·5	0·971	12·70	1·4940	129·8	nil
150	87·7	0·904	11·89	1·4943	128·0	nil

TABLE 2 — EFFECT OF PERIOD OF REACTION ON HYDROXYLATION OF CHLOROTERPENES

(*Conc. of alc. potash,* 5%; *pressure,* 75 *lb./sq. in.*)

REACTION PERIOD hr.	YIELD OF HYDROXYLATED PRODUCT %	ANALYSIS OF THE PRODUCT			
		OH %	Calculated as $C_{15}H_{25}OH$ %	n_D^{30}	Iod. No.
3	98·6	0·821	10·74	1·4954	137·5
6	98·0	0·831	10·86	1·4952	134·1
9	98·3	1·337	17·48	1·4928	133·6
12	95·1	1·295	16·93	1·4935	130·9
18	80·0	1·339	17·51	1·4930	125·6

TABLE 3 — EFFECT OF CONCENTRATION OF ALCOHOLIC POTASH ON HYDROXYLATION OF CHLOROTERPENES

(*Pressure,* 75 *lb./sq. in.; period of reaction,* 9 *hr.*)

CONC. OF POTASH %	YIELD OF HYDROXYLATED PRODUCT %	ANALYSIS OF THE PRODUCT			
		OH %	Calculated as $C_{15}H_{25}OH$ %	n_D^{30}	Iod. No.
10·0	98·5	0·956	12·50	1·4945	132·8
5·0	98·5	1·337	17·48	1·4928	133·6
2·5	98·6	1·378	18·02	1·4924	132·1
0·5	98·4	1·054	13·78	1·4939	132·6

TABLE 4 — CHLORINE CONTENT OF CHLORINATED TERPENES

CHLORO COMPOUND	CHLORINE %		
	Stepanow's method	Alcoholic potash method	
Longifolene hydrochloride ($C_{15}H_{25}Cl$)	10·59 12·31	14·64 14·61	14·73 (theory)
Residual turpentine saturated with dry hydrogen chloride	8·81 9·97	14·21 14·23	14·27 (Carius)
Mother liquor left after removal of longifolene hydrochloride	6·71 5·98	11·72 11·73	11·74 (Carius)

and caustic soda (75 g.) in 150 cc. of water were mixed with isoamyl alcohol (300 g.), followed by addition of chloroterpenes (200 g.) in small lots. The mixture was stirred and slightly warmed to obtain a uniform emulsion and autoclaved under varying conditions of time and pressure. The resulting jelly-like product was freed of isoamyl alcohol and water by distillation and the residue extracted with acetone. After the removal of acetone, the product was dried over anhydrous sodium sulphate and purified by distillation under reduced pressure.

The pleasant-smelling oil obtained by autoclaving for 8 hr. under a pressure of 135 lb./sq. in. had the following characteristics: n_D^{30}, 1·4976; iod. No., 133; hydroxyl content, 2·162 per cent (corresponding to 28·27 per cent alcohols as $C_{15}H_{25}OH$). The product did not contain chlorine, but had 4·8 per cent soap (estimated as Na_2O).

Hydroxylation with lime — Unslaked lime (available lime, 50 per cent) (57 g.) was made into a paste with water (1,150 cc.) and the chloroterpenes (240 g.) were added in small lots with constant stirring to effect a uniform suspension. The reaction mixture was heated for 9 hr. at a pressure of 75 lb./sq. in. The autoclaved product was filtered under suction and the solid extracted with ether to recover a further quantity of oil. The dried product was distilled under reduced pressure to yield a pleasant-smelling distillate having the following characteristics: n_D^{30}, 1·4930; iod. No., 138; hydroxyl content, 3·1210 per cent (corresponding to 40·81 per cent alcohols as $C_{15}H_{25}OH$). The product did not contain chlorine.

Estimation of chlorine — Since the commonly used Stepanow's method was not found reliable in the case of chloroterpenes, heating with alcoholic alkali under pressure was made use of to determine chlorine in these compounds. Thirty to fifty milligrams of the chloro compound were taken in a 50 cc. Jena flask and 10 cc. of 10 per cent alcoholic potash added. After loosely plugging the mouth with glass wool, the flask was placed in an autoclave one-third filled with alcohol. The autoclave was then heated to a pressure of 75 lb./sq. in. for 9-10 hr. After cooling, the mixture was heated on a water bath to distil alcohol remaining over, 20 cc. water added, the solution acidified with 6N nitric acid and chlorine estimated by Volhard's method. The comparative results obtained by this method and Stepanow's method are given in Table 4.

Conclusions

1. When tertiary chloroterpenes are hydroxylated with alcoholic potash under pressure, the equilibrium tends towards dehydrochlorination.
2. Aqueous suspensions of lime are more suitable for effecting hydroxylation.
3. Alcoholic potash effects a more complete removal of organic chlorine than sodium metal used in Stepanow's method and furnishes a better method for the estimation of chlorine in chloroterpenes.

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Enzyme Systems of the Silk-worm, *Bombyx mori* Linn.: Part II—A Papyrographic Micro-method for the Detection & Characterization of Peptidases

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A simple papyrographic micro-method for the detection and characterization of peptidases is described; the method which has been found to have a precision comparable to that of the ultra-micro-method of Linderstrom-Lang, has been successfully applied for a study of the peptidase activity of the tissues and body fluids of the silk-worm, *Bombyx mori* **Linn.**

IN the course of our studies on the enzymatic make up of the eggs, the glandular and intestinal tissues and the haemolymph of the silk-worm, *Bombyx mori* Linn., we had to deal with micro-quantities of research material. Micro and ultra-micro-methods for carrying out such studies have been developed chiefly by Linderstrom-Lang, Holter, Kirk[1] and their associates. These cyto- and histo-chemical methods[2], however, involve micro-titrimetric[3,4], dilatometric[5], manometric[6,7] and spectrophotometric[8] techniques which demand specialized equipment and manipulative skill of a high order.

Papyrographic (paper chromatographic) techniques have not so far been utilized for the detection and characterization of enzymes in micro-quantities of tissues and tissue fluids, although the technique has been applied for a study of the enzymatic degradation of proteins[9,10] and peptides with a view to determine the arrangement of amino acids in the substrates[11,12]. The method, which is simple, elegant and reproducible,

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has recently been applied for the separation and characterization of the penicillins in fermented beers[13]. By a careful choice of peptides whose R_F values lie distinctly far from those of their constituent amino acids, it should be possible to develop papyrographic methods for the detection and characterization of peptidases associated with the different tissues and tissue fluids of the silk-worm. The present communication describes a suitable method for the purpose.

Experimental procedure

Material for these studies was collected from well-fed and disease-free silk-worms in the fourth and fifth instars. Haemolymph was obtained by pricking the worm at the third segment with a finely drawn capillary pipette. About 0·03-0·05 cc. of the fluid per worm could be drawn without any permanent damage to the organism. The haemolymph was diluted with twice the volume of M/15 ice cold, toluene saturated, phosphate buffer of *p*H 7·2, and preserved in the ice chest. The entire operation of collecting and diluting the fluid should be carried out as quickly as possible (within a minute or two), since exposure of the sample to room temperature results in a darkening of the mixture. If the sampling is carried out quickly, the sample should exhibit a pale straw colour.

The glands and the intestines are each dissected out and separately ground up with 2 volumes of the ice cold phosphate buffer (*p*H 7·2). These homogenates were preserved in a refrigerator under toluene. The substrates for these studies were employed in M/25 concentration and were prepared in M/15 phosphate buffer of *p*H 7·2. For determining the carboxy peptidase activity, chloracetyl peptides of tyrosine, tryptophane and leucine were used, while for amino peptidase activity other peptides (*see* TABLE 1) were employed.

The reaction mixtures consisted of 0·25 cc. of the buffered substrate and 0·05 cc. of the enzyme preparation; the mixture in each case was made up to a final volume of 0·5 cc. and incubated at 37°C. At the end of every hour, 2·5 μl. of the reaction mixture was spotted on to a filter paper (Whatman No. 1, 20 × 23 cm.). The method of developing, printing, spraying, etc., was similar to that described earlier[14]. Butanol-acetic acid-water in the ratio of 10 : 2·5 : 10 was employed as the developing solvent.

The ultraviolet print of the papyrogram as also the ninhydrin treated papyrograms are diagrammatically represented in Figs. 1 and 2.

TABLE 1 — R_F VALUES AND OTHER SPECIFIC TESTS OF SOME PEPTIDES AND CONSTITUENT AMINO ACIDS

SUBSTRATE	R_F VALUE (WITH BUTANOL ACETIC ACID AS SOLVENT)	COLOUR WITH NINHYDRIN	AMINO ACID	R_F VALUE (BUTANOL ACETIC ACID)	COLOUR WITH NINHYDRIN	SPECIFIC COLOUR TESTS
L-Alanyl glycine	0·33	Pink	Alanine	0·39	Pink	—
Glycyl-glycine	0·26	Yellow	Glycine	0·33	Brick-red	—
Glycyl L-leucine	0·66	do	L-Leucine	0·72	Pink	—
Glycyl-L-tyrosine	0·46	do	L-Tyrosine	0·53	do	U.V.P.
Glycyl-L-tryptophane	0·54	do	L-Tryptophane	0·61	Brownish pink	U.V.P. Erlich's reaction — blue purple
L-Leucyl-glycine	0·60	Pink	—	—	—	—
L-Prolyl-phenyl alanine	0·97 (phenol H_2O)	Yellow	L-Phenyl alanine	0·66	Pink	U.V.P.
			L-Proline	0·41	Yellow	Blue green with isatin
L-Seryl-serine	0·25 (phenol H_2O)	do	L-Serine	0·19	Brick-red	Cherry-red with Pauly's diazo reaction
L-Alanyl-histidine	—	—	Histidine	0·19	Pink	Red with Sakaguchi's reaction
Benzoyl-L-arginine	—	—	Arginine	0·17	do	—
Diglycyl glycine	0·22	Yellow	—	See above	—	—
L-Leucyl-glycyl-glycine	0·52	Pink	—	do	—	—
Glutathione	—	do	Glutamic acid	0·37	Pink	—
Chloracetyl-leucine	—	No colour	—	See above	—	—
Chloracetyl-tryptophane	0·98	do	—	do	—	—
Chloracetyl-tyrosine	0·97	do	—	do	—	—

U.V.P., ultraviolet printing possible.

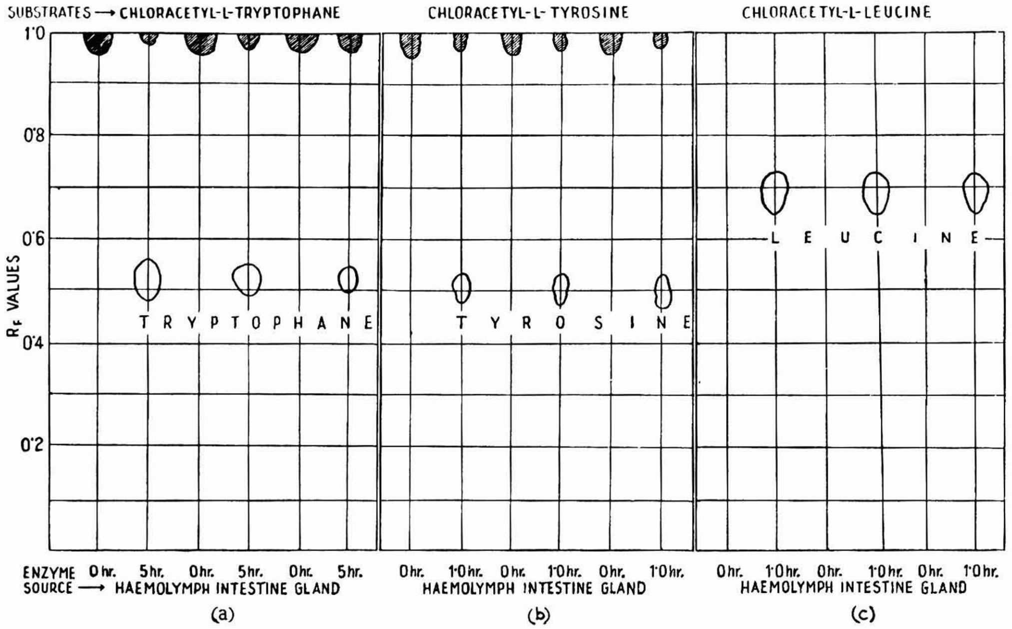

FIG. 1 — PAPYROGRAM OF CARBOXY-PEPTIDASE ACTIVITY [(a) and (b), diagrammatic reproduction of ultraviolet prints; (c), ninhydrin sprayed papyrogram]

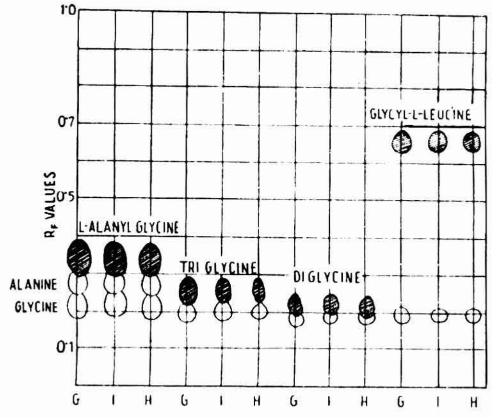

FIG. 2 — PAPYROGRAM OF AMINO-PEPTIDASE ACTIVITY [G, gland; I, intestine; H, haemolymph; shaded portions represent spots of unreacted substrate]

Discussion

It will be seen from Figs. 1 and 2 that with a given source of the enzyme there is a considerable variation in its activity towards the different types of substrates employed in our studies. This fact is strikingly noticeable in the case of the homogenates of the silk-worm gland and intestines. A reference to Fig. 1 (a, b and c) will show the exceptional convenience offered by the chloracetyl derivatives when they are employed as substrates for a study of the carboxy peptidase activity. All of them have high R_F values[14], approaching 1·0, while the amino acid component of the derivative possesses values which are far lower (TABLE 1). It is thus possible to obtain a " clean " papyrogram with only a single spot representing the released amino acid, while the substrate is carried along with the solvent front. This is particularly noticeable in the case of the enzymic splitting of chloracetyl-L-leucine which does not react with ninhydrin (FIG. 1c). The chloracetyl derivatives of the two aromatic amino acids, tryptophane and tyrosine, offer certain additional advantages. Firstly, being opaque to ultraviolet light, the papyrograms which carry their spots lend themselves to ultraviolet printing by which they could be located without interference from any other " transparent " amino acids which may be associated with the reaction mixture. Secondly, tryptophane and tyrosine react with ninhydrin giving coloured spots characteristically different and easily distinguishable from those of other amino acids; further confirmation of their presence could be obtained by treating the papyrograms with spraying reagents exclusively specific to these two amino acids. There are a few other peptides which on hydrolysis release an amino acid component characterizable by treating the spots with a specific reagent; in this connection, mention should be made of the peptides of proline, histidine and arginine (TABLE 1).

A comparison of the relative precision of the method with those of the micro-titrimetric and the micro-dilatometric methods of Linderstrom-Lang[5,6] shows that the minimum concentration of the enzymatically liberated amino acid that can be detected and estimated is of the order of 0·5-30·0 μg. corresponding to $5\text{-}23 \times 10^{-5}$ mg. of amino nitrogen which compares favourably with the micro-titrimetric method which gives a precision of $5{\cdot}6 \times 10^{-5}$ mg. of amino nitrogen.

The precision attainable by the microdilatometric method is, however, about 50 times greater.

The papyrographic method possesses one additional advantage; it is helpful in elucidating the nature of the reaction while dealing with enzyme preparations of the type described in this communication; we have to take into account the possible side reactions, in the nature of trans-aminations and trans-peptidases which might occur in the reaction mixture; while titrimetric and dilatometric methods would not reveal such side reactions, they can be detected by papyrographic methods.

Summary

1. A papyrographic micro-method for the detection and characterization of peptidases has been described; the precision attainable by this method is comparable to that of the ultra-micro-titrimetric method of Linderstrom-Lang.

2. The technique, while being simple, elegant and reproducible, does not involve either the use of expensive and specialized equipment or demand manipulative skill of a high order.

3. The method is applicable to microquantities of tissues and pin prick quantities of body fluids and has been successfully applied for a study of the peptidase activity of the tissues and body fluids of the silkworm.

4. By the choice of appropriate substrates, the type of the peptidase present can be characterized.

5. Successful accomplishment of the technique depends upon (i) the choice of a suitable peptide whose R_F value is placed distinctly far from those of its constituent amino acids and/or (ii) the employment of a peptide one of whose components is characterizable by an exclusively specific reaction or has an absorption in the ultraviolet region.

6. The method offers the additional facility for side reactions, like trans-aminations and trans-peptidations, to reveal themselves, if any of them occur in the reaction mixture.

Acknowledgement

Our grateful thanks are due to the Central Silk Board for financing a scheme of which this forms a part and to the Director, Indian Institute of Science, Bangalore, for his kind interest.

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Determination of Carbon & Hydrogen by Calorimeter Bomb

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A method is described by which carbon and hydrogen in fuel can be determined using the calorimeter bomb. The effects of sulphur, nitrogen and mineral matter in the fuel are allowed for. The determination of calorific value and carbon, or carbon and hydrogen, can be combined in one experiment. The proposed method is especially suitable for the analysis of volatile fuels difficult to handle in the normal combustion technique, but it can be used for all fuels.

THE determination of carbon and hydrogen in fuels, using the calorimeter bomb, was carried out by Kroker[1] and by Berthelot[2] more than 50 years ago; the water formed during the combustion was driven out as water vapour, absorbed and weighed. Hempel[3] made use of soda-lime for carbon dioxide absorption. Kroker[1] and Fries[4] used a 2-valve bomb. Zuntz and Frentzel[5] suggested the weighing of the bomb before and after discharge and also finding its volume. Hempel[3] attempted to improve the precision of weighing by making use of a small bomb. Higgins and Johnson[6] also employed the method of weighing suggested by Kroker. As the bombs normally weigh several hundred grams, an error of even 0·01 g. in weighing causes a serious error in the determinations. Langbein[7] used phosphorus pentoxide for the absorption of water formed inside the bomb and displaced the nitric acid by blowing air through the bomb; sulphuric acid was determined by titration. Broadly speaking, however, these methods do not give the required accuracy, because:

(1) the presence of nitric and sulphuric acids makes it difficult to expel all water;

(2) errors are involved in weighing the bomb;

(3) the acids attack the inner lining of the bomb and the valve connections;

(4) the sulphuric acid obtained on expelling nitric acid retains some moisture; and

(5) the humidity in the bomb air and the water of hydration from the mineral matter of coal present difficulties.

In order to overcome the drawbacks and to evolve a reliable method, researches have been undertaken in this laboratory and a method has been developed which gives results with an accuracy of ±0·15 in the percentage of carbon and ±0·05 in the percentage of hydrogen. The accuracy of the determination is not affected when sulphur is present even in large concentrations. Further, the method developed has been found to be suitable for the analysis of volatile fuels difficult to handle by the normal combustion technique, e.g. Liebig's or Fenton's. The new method is recommended for laboratories equipped with calorimeter bombs and precise gas analysis apparatus, e.g. fuel laboratories, and laboratories of collieries, oil refineries, thermal power stations, gas works and coke oven plants.

Determination of carbon

This method is a modification of that used by Whitaker[8] 25 years ago. The bomb is charged in the usual manner with oxygen to 25 atm. pressure, the fuel being in position, and 1 cc. of water being on the floor of the bomb. Ignition is effected by a weighed length (6 in.) of sewing cotton hanging from the nickel or platinum fuse wire. The calorific value is determined as usual, if required. After the determination, and when the bomb has definitely attained the room temperature, it is discharged through a gas sampling tube (FIG. 1) and through a little water in a wash bottle to saturate the gas with moisture before metering. The moisture saturation can be satisfactorily effected by using a relatively small quantity of water (20 cc.) inside a cylinder or flask packed with moist glass wool. The water in the wash bottle is made just acid to methyl orange with a drop of dilute sulphuric acid and saturated with oxygen containing about

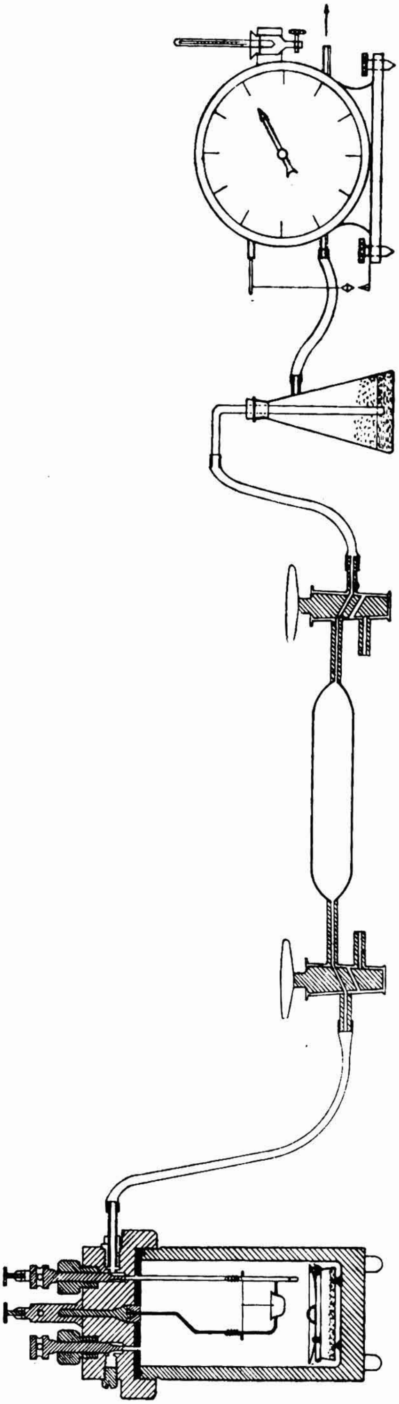

FIG. 1 — APPARATUS FOR DETERMINING CARBON IN COAL

10-12 per cent of carbon dioxide by first discharging through it several times the exhaust gases from the bomb generated in earlier (ordinary calorimetric) experiments. The gases are then passed through the meter to effect the saturation of the meter water equally.

In actual experiments, the barometric pressure and the temperature (of the meter water) are required. The gases are discharged from the bomb at a slow and steady rate (to avoid water surge in the meter), two or three minutes being taken for the complete discharge. They pass first through the sampling tube (FIG. 1). The gas sample is immediately analysed for carbon dioxide, preferably in the 21 cc. Haldane apparatus[9], in which the gas may also be tested for any combustible constituent in order to verify that combustion in the bomb has been complete. If more than 1 or 2 cc. of water are used in the bomb, the solubility of carbon dioxide in the water causes difficulties arising from small variations in the gas sample composition on discharge. These variations are less when there is some sulphur in the fuel, the acidic products of combustion apparently preventing undue solubility of carbon dioxide, even when 5 cc. of water are used in the bomb (TABLE 1). It is, of course, not necessary to introduce into the bomb any water at all; the hydrogen of the fuel yields enough water to absorb the acid fumes (from sulphur and nitrogen) in all normal cases. It is possible to determine carbon and hydrogen in the fuel in the same experiment if the bomb is quite dry.

Samples of the discharging gas were taken (1) near the beginning of the bomb discharge; (2) in the mid-period and (3) towards the end of the discharge. The total volume of the discharged gas is about 10 litres.

To calculate the weight of carbon present, it is necessary to find the density of carbon dioxide in the gas mixtures. When the proportion of carbon dioxide is less than 10 per cent by volume, there is no appreciable correction to be applied to the theoretical value of 1·965 g. per litre at N.T.P. If, however, the concentration is greater than 10 per cent, the following values are to be taken for density: (1) at 10 per cent carbon dioxide, 1·965 g. per litre at N.T.P.; (2) at 16 per cent carbon dioxide, 1·966 g. per litre at N.T.P.; and (3) at 20 per cent carbon

TABLE 1 — EFFECT OF SOLUBILITY OF CARBON DIOXIDE ON DETERMINATION OF CARBON

(*Substance combusted, benzoic acid*)

QTY. OF BENZOIC ACID g.	SULPHUR ADDED g.	SULPHUR %	WATER IN BOMB cc.	CO_2 % IN SAMPLING TUBE 1	2	3
0·7200	—	—	5	10·27	10·35	10·46
0·7100	—	—	5	10·20	10·21	10·26
0·4100	—	—	5	5·81	5·86	5·90
0·4960	—	—	5	7·03	7·11	7·22
0·7550	—	—	—	10·70	10·69	10·69
0·7300	—	—	—	10·30	10·31	10·29
0·6400	—	—	—	9·08	9·09	9·08
0·7500	—	—	—	10·67	10·65	10·65
0·5000	0·0020	0·4	5	7·18	7·19	7·19
0·5000	0·0020	0·4	5	7·23	7·22	7·23
0·7203	0·0073	1·0	5	10·20	10·21	10·22
0·6359	0·0065	1·0	5	8·46	8·46	8·44
0·7781	0·0074	0·9	5	10·26	10·27	10·25
0·7060	0·0153	2·1	5	8·86	8·85	8·85

dioxide, 1·967 g. per litre at N.T.P. (The observed density at N.T.P. of pure carbon dioxide is 1·9768 g. per litre.) It is necessary to know also the volume of the bomb itself which is normally between 300 and 400 cc.

A convenient meter for use is the meter of the Boys' gas calorimeter in which one revolution corresponds to $\frac{1}{10}$ or $\frac{1}{12}$ cu. ft. The meter is first tested for its accuracy and carefully adjusted and corrected if necessary. A room of relatively constant temperature is desirable. Standard substances such as sucrose, benzoic acid and naphthalene can be indirectly but effectively used for checking the meter calibration by burning them in the bomb. These indeed provide " overall " checks.

Example

Substance (benzoic acid) taken	0·4281 g.
Vol. of bomb	300 cc.
Vol. of exhaust gas	2·827 × $\frac{1}{12}$ cu. ft.
Carbon dioxide in the gas	9·754% by vol.
Barometric pressure	733·60 mm.
Meter temperature	32·1°C.
Aq. tension at 32·1°	35·87 mm. mercury
Vol. of exhaust gas	$\frac{2\cdot827\times28\cdot32}{12}$ = 6·671 litres
Vol. of gas in bomb	0·300 litres
Total volume	6·971 litres
Vol. at N.T.P.	$\frac{6\cdot971\times273\times697\cdot7}{305\cdot1\times760}$ = 5·727 litres

Carbon content	$\frac{5\cdot727\times9\cdot754\times1\cdot965\times12\cdot01}{100\times44\cdot01}$ = 0·2995 g.
Ignition thread	0·0051 g. carbon
Net carbon	0·2944 g.
Carbon in benzoic acid	$\frac{0\cdot2944\times100}{0\cdot4281}$ = 68·77%
Theoretical value	68·87%

The amounts of carbon in sucrose and benzoic acid with and without added sulphur were determined using the bomb as above. The results given in Tables 2 and 3 show good agreement with the theoretical values, even in the presence of as much as 16 per cent of sulphur.

It may be observed from Table 3 that a high concentration of sulphur (such as may be met with in Assam, Punjab and Kashmir coals) does not affect the carbon values determined by this method, even with 5 cc. of added water present in the bomb.

To apply the method directly to coal, samples of coal were analysed for their carbon contents both by the bomb method described above and by ultimate analysis in the standard method. The sulphur content of the samples was about 1 per cent. The carbonates in coal were also determined by Beet's method[10]. The analyses of exhaust gases from the bomb were carried out in Haldane 21 cc. gas analysis apparatus. It is useful to pass the gas sample after carbon dioxide absorption into the combustion pipette as a check on complete combustion to verify the absence of combustible gas.

TABLE 2 — DETERMINATION OF CARBON IN BENZOIC ACID AND SUCROSE

Wt. of sample g.	CO_2 in exhaust gas %	Density of CO_2	Carbon determined %	Theoretical value %	Difference
Benzoic acid (1 cc. of water in the bomb)					
0·5062	9·05	1·965	68·89	68·87	+0·02
0·4281	9·75	1·965	68·77	68·87	−0·10
0·6086	11·10	1·965	68·87	68·87	nil
1·0671	17·23	1·967	69·00	68·87	+0·13
0·9967	17·65	1·967	68·87	68·87	nil
1·0883	19·22	1·967	69·00	68·87	+0·13
1·0755	19·28	1·967	68·85	68·87	−0·02
1·2343	20·10	1·967	68·89	68·87	+0·02
1·3612	22·53	1·967	68·89	68·87	+0·02
Standard sucrose (1 cc. of water in the bomb)					
0·9356	8·58	1·965	42·06	42·10	−0·04
0·9283	9·96	1·965	42·02	42·10	−0·08
0·9628	10·24	1·965	42·09	42·10	−0·01

TABLE 3 — EFFECT OF SULPHUR ON CARBON DETERMINATION

(*5 cc. of water in bomb*)

Wt. of sample g.	Wt. of sulphur added g.	Sulphur present %	CO_2 %	Density of CO_2	Carbon determined %	Theoretical value %	Difference
0·3980	0·0069	1·70	8·57	1·965	68·80	68·87	−0·07
0·7567	0·0151	1·96	13·89	1·966	68·73	68·87	−0·14
0·3975	0·0158	3·82	8·54	1·965	69·00	68·87	+0·13
1·0193	0·0548	5·10	16·95	1·967	68·90	68·87	+0·03
0·7757	0·0775	9·08	12·25	1·966	69·01	68·87	+0·14
0·7030	0·1406	16·66	11·42	1·967	68·87	68·87	nil

TABLE 4 — CARBON CONTENTS OF COAL SAMPLES

(*As received basis*)

Sample No.	Moisture %	Ash %	CO_2 as carbonates %	Carbon by ultimate analysis (Liebig) %	Carbon by bomb method %	Average difference
CAJ/52/B	1·10	28·07	1·26	61·01 61·02 av. 61·015	61·06 60·99 60·94 av. 60·997	−0·018
CAJ/49/C	1·10	22·66	0·79	66·67 66·71 av. 66·69	66·74 66·71 av. 66·725	+0·035
CAJ/49/D	1·00	21·14	1·30	67·67 67·47 av. 67·57	67·61 67·59 av. 67·60	+0·030
CAJ/53/A	1·10	29·30	0·83	60·30 60·19 av. 60·245	60·36 60·23 av. 60·295	+0·050
CAJ/52/D	0·99	26·30	2·06	62·65 62·59 av. 62·62	62·78 62·58 av. 62·68	+0·060
CAJ/289	1·11	14·09	0·48	74·03 73·98 av. 74·005	73·86 73·98 av. 73·92	−0·085
CAJ/289/blend	0·92	14·94	0·48	73·19 73·28 av. 73·235	73·13 73·13 av. 73·13	−0·105
CAJ/49/A	1·00	14·57	0·80	73·94 74·08 av. 74·01	74·09 74·08 av. 74·085	+0·075

Table 4 gives the results obtained. The ash remaining in the bomb crucible was examined in each case. Sometimes a small amount of carbon was found but it never exceeded 0·0003 g. Complete combustion can be ensured by placing a small amount of ignited sand in the crucible below the coal pellet.

Determination of hydrogen

Whitaker[8] using Goutal's bomb (100 cc.), which is much smaller than the usual calorimetric bomb (cap., 200-400 cc.), used smaller weights of fuel and measured and analysed the exhaust gas for carbon dioxide content. The water formed was partly absorbed inside the bomb and partly absorbed from the discharged gases. The quantity of nitric acid formed was small; and the water vapour (in U.K.) arising from the air in the bomb was negligible and did not seriously affect the values for hydrogen. In India the atmospheric humidity varies from 30 to 80 per cent and the temperature may be 90°F. or more; hence allowance is essential for such moisture in a 300-400 cc. bomb. Nor can it be simply included in an overall blank.

The moisture in Indian coals varies from 0·5 to 15 per cent. For lignites it is still higher. The ash of coals lies between 10 and 30 per cent, and in using an internal absorbent, care is needed to guard against ash contamination. The water of hydration of the mineral matter must also be allowed for in calculating the hydrogen to unit coal basis as the ash is high.

The sulphur content of most Indian coals is about 0·5 per cent but coals from Assam may contain up to 5·0 per cent or even more sulphur. As a result of a number of trials, calcite powder was found to be satisfactory for overcoming the interference from sulphuric acid. The nitrogen in the bomb air is displaced to avoid interference from nitric acid.

Procedure

Drying — Clean and dry the bomb and its connections and dry it completely by placing inside the bomb the squat weighing bottle (B) containing the absorbent (pumice soaked in concentrated sulphuric acid), sealing the bomb and connecting to a vacuum pump for 20 min. B rests on a thin glass triangle so that no moisture remains entrapped under it. The bottle B is a glass weighing bottle 2 in. in diameter and $\frac{1}{2}$ in. tall and carries a ground stopper (S) which fits with a quarter turn on the thread (screw). The arrangement is important as it enables one to lift the bottle out of the bomb after inserting the lid, and/or to place the bottle in the bomb and remove the lid without contamination from the moisture of the air, the stopper (S) being then quickly withdrawn. Vacuum drying for 20 min. in the presence of the absorbent is found adequate. The bomb is now dry. It is opened and the absorbent bottle B removed after inserting the stopper (S).

Blank — No fuel is used for the blank except the ignition thread. Connect the ignition wire and the weighed thread. Weigh B containing the absorbent with S covering it. Insert B, remove S, and quickly seal the bomb. Now displace the bomb air three times with oxygen (6 atm. each time) discharging after each charge. Finally charge the bomb to 20 atm. with oxygen. Fire the thread and allow the bomb to stand for 2 or 3 hr. on the water oven at a temperature of about 70 or 80°C. Allow to cool for 1 hr., open the bomb, quickly insert S, remove B and S together, and weigh. The gain in weight measures the moisture in the bomb air + moisture from (all) the oxygen used + the water from the combustion of the thread. This gain is deducted from the values obtained in the actual experiment for hydrogen in the fuel. This " blank " requires checking periodically, especially if the wet and dry bulb temperatures vary.

In burning the fuel in the bomb, there is danger that fly ash may get into the absorbent. Accordingly, a watch glass cover W is supported $\frac{1}{8}$ in. above the bottle (B) inside the bomb. The watch glass is $2\frac{1}{4}$ in. in diameter, the bomb (Mahler Cook type, cap., 400 cc.) being $2\frac{1}{2}$ in. in internal diameter. This cover is found to give adequate protection from contamination with fly ash and allows enough space for the circulation of bomb gases and thus permits absorption of water produced. The watch glass cover (W) has to be rapidly inserted and removed, and should be made accordingly with a vertical piece fused to it in the middle for convenient handling (FIG. 2).

Use of calcite — It is necessary to add 0·1-0·2 g. of powdered calcite to the fuel as a covering layer. The object is to absorb the sulphuric acid produced, which otherwise finds its way, partly or wholly, into the

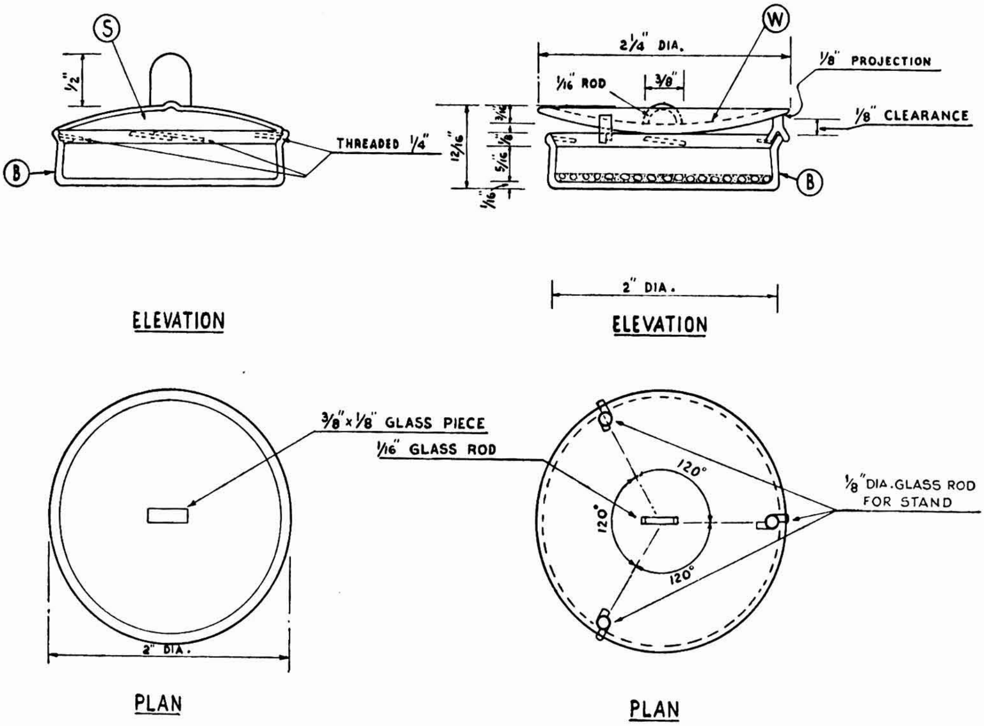

FIG. 2 — WEIGHING BOTTLE FOR THE ABSORBENT

absorbent in bottle B. The watch glass (W) prevents contamination of the absorbent with calcite.

Experiments — After obtaining the blank for the bomb as above, and the bomb being dry, proceed as follows. Weigh 0·5 g. of the fuel, preferably in powdered form, and cover it with 0·1-0·2 g. of calcite, powdered to pass 72 B.S. mesh. Place a small silica cap (loose fitting) over the fuel and calcite to prevent the fuel from being ejected from the crucible on ignition. Fix the ignition wire and thread as usual, the thread touching the fuel. Now insert the weighed bottle B (with S) carrying the absorbent. Quickly remove S, place the watch glass cover in position, and seal the bomb without delay. Charge three times with oxygen at 6 atm. and discharge each time as for blank. Next fill with oxygen at 20 atm. Ignite in the usual way. Immersion in water is not necessary nor advantageous, unless the bomb has a rubber washer which may decompose if hot. Allow to stand on the water oven for 4 or 5 hr. and then to cool for one hour. Open the bomb, remove W, quickly insert S, and remove B with S and weigh. The gain in weight of the dish and absorbent, minus the blank, gives the weight of water produced by the fuel. To obtain the hydrogen, deduct the weight of water present as moisture in the fuel and also any water of hydration of any mineral matter present if hydrogen in unit coal is required.

The bomb is now washed with a little distilled water and the washings filtered and titrated. The nitric acid is negligible and an overall allowance of 0·0009 g. of water is made for each cc. of N/10 acids found (mainly sulphuric). This allowance is added to the gain in weight of the absorbent, as this hydrogen has not been absorbed.

The moisture in coal is determined simultaneously if the coal is of high (>3 per cent) moisture type. Dry and wet bulb readings are required for the blank, etc., as stated earlier.

Example

Coal taken	0·4619 g.
Coal ash	16·70% = 0·0077 g. H_2O
Moisture in coal	6·80% = 0·0314 g. H_2O
Dry bulb	87°F. } same as for blank
Wet bulb	80°F.

Water absorbent

Initial wt.	42·1710 g.
Final wt.	42·4120 g.
Wt. of water absorbed	0·2410 g.

Deduct

(1) Wt. of moisture in coal	0·0314 g.
(2) Water of hydration taken as 10 per cent of ash	0·0077 g.
(3) Blank for oxygen and thread and bomb air	0·0448 g.
Total	0·0839 g.
∴ Water from hydrogen of coal (unit)	0·2410—0·0839 =0·1571 g.
N/10 H_2SO_4 from bomb washings	1 cc.
∴ Add	0·0009 g.
Total	0·1580 g. water
or	0·0177 g. hydrogen
Hydrogen in unit coal	$\frac{0{\cdot}0177\times100}{0{\cdot}4619}=3{\cdot}83\%$
Hydrogen in unit coal from ultimate analysis (Liebig)	3·82%

Comparison with Liebig's method — To show the error range, several analyses were carried out. The results in Table 5 show the comparison of hydrogen values obtained by this method with those obtained by ultimate analysis by the standard method.

In many experiments where nitrogen (as bomb air) was not displaced the percentage hydrogen values were invariably higher by 0·15-0·20 per cent in comparison to those obtained by the standard method. It is, therefore, necessary first to displace the nitrogen from the bomb air as recommended.

Effect of (added) sulphur — To test the applicability of the procedure to standard organic compounds, such as sucrose and

TABLE 5 — HYDROGEN IN COAL

COAL SAMPLE	MOISTURE %	ASH %	TOTAL SULPHUR %	HYDROGEN BY BOMB METHOD %	HYDROGEN BY STANDARD METHOD %
CAU/17*	6·80	16·7	1·38	3·82	3·81
CAJ/29*	1·00	18·5	0·63	4·11	4·12
CAU/9*	4·85	—	0·45	4·35	4·30
CAC/498*	3·30	15·2	—	4·74	4·79
CAC/214	5·40	20·5	1·10	3·58 3·60	3·57 3·58
CAJ/54+55+56/C	1·10	17·7	0·50	3·96 3·98 3·94	3·94 3·95 —
CAU/54	2·20	16·5	0·60	4·35 4·33	4·32 4·30
Rakhikol	1·40	21·5	—	4·41 4·36	4·39 4·38
CAJ/54+55+56/E	0·90	22·4	0·50	3·99 3·96	4·02 4·01
Gaslitan XVI	1·40	13·2	0·42	4·42 4·38	4·40 4·42
CAC/641	4·40	—	0·42	5·03 4·98	5·02 5·03
Namdang coal	1·99	—	2·72	5·95 5·94	5·94 5·95
Assam coal	2·80	3·8	3·76	5·17 5·18	5·20 5·22
Ledo coal	2·42	—	4·73	5·80 5·82	5·78 5·82
Cherra coal	2·80	18·1	7·80	4·85 4·82	4·86 4·86

*In the first four samples, simultaneous determinations were made by both the methods on the same day.

TABLE 6 — EFFECT OF ADDED SULPHUR ON DETERMINATION OF HYDROGEN

	SULPHUR ADDED g.	SULPHUR %	HYDROGEN		REMARKS
			By bomb method %	Calculated %	
Benzoic acid, g.					
0·4000	—	—	4·95	4·95	Sulphur and benzoic acid in fused form; calcite powder used
0·8482	0·0112	1·42	4·99	4·95	
0·5294	0·0141	2·59	4·95	4·95	
0·6161	0·0167	2·64	4·97	4·95	
0·6285	0·0184	2·84	5·00	4·95	
0·4572	0·0152	3·22	4·92	4·95	
0·3791	0·0146	3·71	4·93	4·95	
Sucrose, g.					
0·4523	—	—	6·42	6·43	Sulphur kept in the bottom of crucible and sucrose spread over it; calcite powder used
0·8282	0·0118	1·41	6·42	6·43	
0·6342	0·0100	1·55	6·38	6·43	
0·6087	0·0119	1·92	6·46	6·43	
0·3668	0·0090	2·39	6·39	6·43	

TABLE 7 — ACIDS FORMED IN THE BOMB

(*Mahler Cook bomb used; bomb air not displaced*)

WT. OF BENZOIC ACID g.	WT. OF S TAKEN g.	SULPHUR %	WT. OF SULPHUR RECOVERED g.	RECOVERY %	TOTAL ACIDS N/10	SULPHURIC ACID N/10	NITRIC ACID N/10
0·9597	0·0093	0·96	0·0088	94·62	10·52	5·50	5·02
1·0005	0·0155	1·53	0·0153	98·72	14·14	9·56	4·58
1·0008	0·0200	1·96	0·0195	97·50	20·60	12·19	8·41
0·9099	0·0201	2·16	0·0190	94·54	16·07	11·89	4·18
1·3371	0·0368	2·68	0·0333	90·48	26·80	20·81	5·99
0·7730	0·0287	3·58	0·0282	98·24	19·60	17·63	1·97
1·0800	0·0442	3·93	0·0436	98·65	30·18	27·25	2·93
1·0695	0·0518	4·62	0·0481	92·85	32·00	30·06	1·94
0·9841	0·0481	4·66	0·0480	99·79	31·95	30·00	1·95
1·0610	0·0520	4·67	0·0485	93·26	37·50	30·31	7·19
0·7174	0·0377	4·99	0·0375	99·47	27·63	23·44	4·19
0·8553	0·0478	5·29	0·0423	88·49	25·82	20·20	5·62
1·0392	0·1039	9·09	0·1028	98·95	73·00	64·25	8·75
1·0004	0·1000	9·09	0·0939	93·90	65·00	58·69	6·31
0·9963	0·1006	9·17	0·0883	87·80	56·20	55·02	1·18
0·9589	0·1024	9·65	0·0990	96·76	70·90	61·88	9·02
1·0009	0·1500	13·03	0·1456	97·06	91·40	90·10	1·30
1·0185	0·1973	16·23	0·1888	95·70	119·70	118·00	1·70
1·0191	0·2021	16·55	0·1935	95·74	127·40	120·94	6·46
0·7256	0·1451	16·66	0·1392	95·94	89·00	87·00	2·00
Without sulphur							
1·0016	—	—	—	—	—	—	7·00
1·4599	—	—	—	—	—	—	8·50
1·0340 (naphthalene)	—	—	—	—	—	—	10·00

benzoic acid, samples of 99·98 per cent purity were mixed with sulphur in varying concentrations. The bomb air was displaced before each determination. Table 6 gives the results.

It is clear that the effects of added sulphur are negligible, as long as calcite is used.

Effect of nitrogen — The effect of oxides of nitrogen in the oxidation of sulphur dioxide to sulphur trioxide has been shown by Regester[11] and later by Kohout[12]. In the bomb method, the nitrogen is retained in the bomb air for the determination of carbon dioxide, since sulphur dioxide as such would interfere with the correct estimation of carbon dioxide by potash absorption in the analysis of the exhaust gas. For the hydrogen determination, the nitrogen of the bomb air is removed because nitric oxide and sulphur trioxide are both soluble in sulphuric acid. In order to avoid errors from this source, the use of calcite was explored and found experimentally to give reliable results.

Bomb acids (*variability*) — The extent of the variability in the acids (sulphuric and nitric) formed in the bomb is shown in Table 7. The bomb air was not displaced.

The quantity of nitric acid formed depends to a degree upon the quantity of fuel burnt. If a small quantity of benzoic acid is combusted, the value of hydrogen obtained

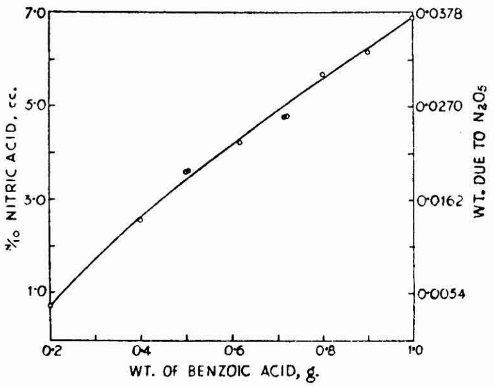

FIG. 3 — NITRIC ACID FORMED DURING COMBUSTION OF BENZOIC ACID

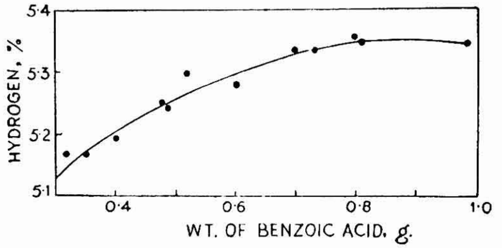

FIG. 4 — HYDROGEN DETERMINED IN BENZOIC ACID

will be affected to a less extent. Fig. 3 shows the amount of nitric acid formed with different quantities of benzoic acid, and Fig. 4 gives the hydrogen values found. Both show a successive rise. In fact, it was found that by giving nitric oxide free access to the pumice absorbent (using platinum rhodium wire gauze in place of watch glass as cover) an allowance of 0·0054 g. made for each cc. of N/10 nitric acid seems to give correct values.

Moisture from oxygen in cylinders — That compressed oxygen may contain a little moisture has been verified by blank experiments with the bomb, and by passing the same volume of oxygen through absorbent anhydrone U tubes direct from oxygen cylinder. Such moisture present in the oxygen tends to increase slightly as the oxygen pressure in the supply cylinder falls. Periodic blank determinations are, therefore, necessary.

Weighing — An error is involved in using sealed weighing bottles unless the gases (rich in carbon dioxide) in the bottles are displaced by air before each weighing. The vessel is initially weighed with air, but when the final weight is taken it contains 10 per cent or more of carbon dioxide. This would give high values on account of the heavy vapour density of carbon dioxide. The error is avoided if the cover of the bottle is removed (in a desiccator) and it is momentarily opened and sealed again.

Acknowledgement

The author would like to thank Dr. J. W. Whitaker for much help and advice throughout this work, and Dr. N. G. Basak, Dr. R. P. Puri and Mr. G. N. Badami who have scrutinized the manuscript and made useful suggestions.

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Mixed Fertilizer & Light Magnesia from Sea Bitterns

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The reaction between ammonium carbonate and magnesium salts has been made use of for fixing free ammonia with bittern in the preparation of a nitrogenous fertilizer containing potash. Bittern of density 34·5°Be. yields a product containing available nitrogen 22 per cent and potash (K_2O) 3 per cent. Light basic magnesium carbonate and light magnesia are obtained as useful byproducts.

THE well-known reaction between ammonium carbonate and gypsum is used by the fixed nitrogen industry for converting ammonia into ammonium sulphate fertilizer. Sodium sulphate[1] and magnesium sulphate are possible alternatives to gypsum. Sea bittern, left over after the crystallization of common salt, contains principally magnesium sulphate and magnesium chloride with smaller amounts of sodium and potassium chlorides. Large quantities of sea bitterns are at present thrown back into the sea and not exploited.

The total quantity of bittern produced is of the order of 380 million gallons of 29°Be. ($\equiv$190 million gallons of 34·5°Be.) on the basis of an annual production of 1·7 million tons of salt from sea brine[2]. Many swamps containing brines, similar in composition to the sea bittern, exist in south-east India (e.g. Vaidyanarayan Swamp, Tanjore) and in the Rann of Kutch at Kharaghoda. They are extensive and the quantity of bitterns available in them is almost unlimited. Not much attention has been paid to these sources because magnesium chloride and magnesium sulphate, even if recovered, do not find a ready market in India or abroad owing to foreign competition. The loss of sulphate expressed in terms of sulphur in the bitterns annually produced amounts to 1,04,690 tons[2]. An inexpensive process, which will convert the natural sulphates in sea water to ammonium sulphate and also recover all the potash it contains, will have an important significance.

The compositions of some bitterns from a few localities are shown in Table 1. The distribution of components in Wadala bittern when concentrated to 34·5°Be. is given in Table 2.

The pre-treatment of brine by (i) ammonia and carbon dioxide, (ii) lime and carbon dioxide or (iii) soda to remove magnesium and calcium, is a step in the purification of brine in the ammonia-soda process[3]. Commercially, brine or bittern is treated with any of the two latter methods for the manufacture of light magnesium carbonate and calcined light magnesia[4,5]. Since ammonium carbonate fails to completely precipitate magnesium in presence of ammonium salts formed *in situ*, the treatment of bittern with ammonia and carbon dioxide has not been sufficiently studied. However, the reaction has been used in Germany[6] for the production of ammonium salts and basic or neutral magnesium carbonate from magnesium minerals, such as glauberite. An American patent[7] describes the preparation of magnesia and a nitrogenous fertilizer from dolomite, in which the mineral is digested with nitric acid, followed by treatment with ammonia and carbon dioxide. The present investigation was undertaken to determine the optimum conditions for the removal of magnesium from sea bittern by treatment with ammonium carbonate and to ascertain the nature of the product obtained with bitterns from different sources.

Sea bittern contains little of calcium. Magnesium in it is precipitated by ammonia and carbon dioxide from hot solutions as $MgCO_3$ or $MgCO_3.Mg(OH)_2.3H_2O$ or as a double salt of ammonium, depending on the conditions of reaction.

$$MgX_2+2NH_3+2H_2O=Mg(OH)_2+2NH_4X$$

$$MgX_2+2NH_3+CO_2+H_2O=MgCO_3+2NH_4X$$

$$xMgCO_3+yMg(OH)_2= (x+y)MgO_2.xCO_2.zH_2O+(y-z)H_2O$$

where X stands for Cl or $\frac{1}{2}$ SO_4.

TABLE 1 — COMPOSITION OF BITTERNS FROM DIFFERENT SOURCES IN INDIA

	CHUNAMPET SALT WORKS, MADRAS (1)	TATA CHEMICALS, MITHAPUR (2)	WADALA SALT WORKS, BOMBAY (3)	KHARAGHODA (4)	TATA CHEMICALS, MITHAPUR (5)	WADALA SALT WORKS, BOMBAY (6)
Density, °Be.	29·00	29·00	30·00	30·00	34·50	34·50
Sp. gr.	1·25	1·25	1·27	1·27	1·32	1·32
Temp., °C.	25·00	*	34·00	*	34·00	34·00
1. NaCl, %	17·25	9·20	10·50	7·50	1·60	1·60
2. $CaSO_4$, %	*	0·30	0·30	*	—	—
3. $MgSO_4$, %	7·40	5·60	5·90	6·70	7·01	10·10
4. $MgCl_2$, %	10·50	12·00	10·10	15·00	22·10	17·90
5. KCl, %	1·90	2·10	2·10	4·90	2·30	2·40
6. Br, %	0·02	0·18	0·18	*	0·30	*
7. Water, %	62·98	70·62	70·62	65·90	66·70	68·00

(1) B. SHAH, *Ph.D. Thesis*, Bombay Univ. (1944); (2) analysis by C. B. Joshi of the works; (4) K. H. VAKIL, *Salt*, p. 16; (3), (5) and (6), analyses by authors.

*Not recorded.

TABLE 2 — DISTRIBUTION OF COMPONENTS IN WADALA BITTERN (31·05°Be.) CONCENTRATED TO 34·5°Be. AT 35°C. (CONCENTRATED IN THE LABORATORY)

COMPONENTS	31·05°BE. BITTERN (SP. GR., 1·273; VOL., 1,000 CC.)			34·5°BE. BITTERN (SP. GR., 1·315; VOL., 590 CC.)			LOSS ON CONCENTRATION	
	w/v %	w/w %	g.	w/v %	w/w %	g.	g.	%
NaCl	11·8	9·3	118·0	2·9	1·7	17·1	100·9	85·7
KCl	2·0	1·5	20·0	3·1	2·5	18·5	1·5	7·5
$MgCl_2$	14·8	11·6	148·0	23·4	17·8	138·0	10·0	6·7
$MgSO_4$	8·6	6·8	86·0	13·3	10·1	.78·5	7·5	8·8

The reaction between bittern and ammonium carbonate was studied under different conditions of dilution, temperature and molar ratio for obtaining a solution of the fixed ammonium salts associated with the minimum amount of magnesium. Preliminary studies showed that magnesium could be largely precipitated out by adding one molar quantity of ammonium carbonate in excess of the stoichiometric requirement to a saturated bittern at a temperature not exceeding 50°C. Based on this observation, a process for obtaining a mixed N-K fertilizer from Wadala and Tata bitterns has been worked out.

Two litres of the bittern were treated simultaneously with gaseous ammonia and carbon dioxide in the molar ratio of 2 : 1 at such a rate as to maintain the temperature of the solution at 50°C. Magnesium carbonate separated as a white bulky precipitate. To avoid blocking of the inlet tubes, the reaction was carried out in two or three batches. The precipitate from each batch was washed with the minimum quantity of water to remove the adhering ammonium salts and the washings added to the next batch. Finally, all the carbonate precipitate was well washed with water, filtered by suction and the washings added to the original filtrate. The total filtrate was either heated to 80°C. for 5 min. or allowed to stand overnight to precipitate any magnesium carbonate present. The excess of ammonia and ammonium carbonate were recovered by distillation and were added to the next batch. The residual liquor from the distillation was crystallized to obtain the mixed nitrogenous fertilizer. The results are given in Table 3.

TABLE 3 — ACTION OF AMMONIA AND CARBON DIOXIDE ON SEA BITTERNS

(*Volume of bittern, 2 l.; temp., 50°C.; rate of ammonia gas feed, 32 g./hr.*)

DESCRIPTION	WADALA BITTERN (30°Be.)	WADALA BITTERN (34·5°Be.)	TATA BITTERN (34·5°Be.)
1. Mg ion, g./l.	47	87·5	93
2. Reactants			
(i) NH_3, g.	260	370	390
(ii) CO_2, g.	340	470	500
(iii) Molar ratio $(NH_4)_2CO_3$: Mg salt	2	1·5	1·5
3. No. of batches	2	4	4
4. Final volume, l.	2·5	4·0	4·0
5. Unprecipitated Mg salt as Mg, g./l.	1·5-2·0	4·1	4·1
6. Mg precipitated, %	95-98	91	91
7. Yield:			
(i) Basic $MgCO_3$, g.	384	650	670
(ii) Nitrogenous product, g.	700	880	890
8. Loss of final product during processing, %	10·0	6·0	6·0
9. Composition of 7(ii):			
NH_4Cl, %	31·2	58·4	69·5
$(NH_4)_2SO_4$, %	21·8	25·5	15·6
NaCl, %	37·0	4·4	4·1
KCl, %	6·4	6·3	6·8
$MgCl_2.6H_2O$, %	3·6	nil	nil
$MgSO_4.7H_2O$, %	—	5·4	3·9
10. Available nitrogen (N)-potash (K_2O), %	13-4	21-4	21-4

TABLE 4 — COMPOSITION OF CRYSTALLIZED FRACTIONS FROM 34·5°Be. BITTERN AFTER TREATMENT WITH AMMONIA AND CARBON DIOXIDE

[*Yield from 4 l. of solution (diluted)*]

CROP NO.	I	II	III	IV	V	VI	VII
Volume, cc.	1300·00	600·00	575·00	350·00	250·00	105·00	Dried
Density of soln. after separation of solid (original density 13·2°Be.), °Be.	16·70	18·90	20·50	23·24	26·20	27·10	—
Wt. of crystals separating between densities, g.	105·00	210·00	40·00	80·00	25·00	75·00	35·00
NH_4Cl, %	91·34	72·50	91·02	80·01	88·88	44·00	28·46
$(NH_4)_2SO_4$, %	5·90	15·91	6·04	15·39	6·92	30·60	28·86
$MgSO_4.7H_2O$, %	1·64	6·30	—	—	—	—	—
$MgCl_2.6H_2O$, %	—	2·46	0·92	0·85	—	—	—
KCl, %	0·76	1·93	1·56	2·48	2·86	15·26	8·84
NaCl, %	0·38	0·92	0·46	1·27	1·34	10·17	33·84

TABLE 5 — COMPOSITIONS OF FRACTIONS FROM 30°Be. BITTERN

(*About 150 g. of mixed fertilizer employed*)

Crop No.	I	II	III	IV
Density, °Be. (hot)	26·10	28·60	26·10	28·0
Wt. of crystals separating out, g.	18·00	20·00	10·00	66·0
NaCl, %	86·00	40·00	0·90	8·3
KCl, %	0·57	1·40	0·42	4·8
NH_4Cl, %	6·20	48·64	79·00	56·5
$(NH_4)_2SO_4$, %	6·50	9·96	19·48	30·2
Balance, %	0·73	—	0·20	0·2

I and II, solid separated at boiling point; III and IV, solid obtained while cooling at the respective densities; residual solution (40 cc.) was not analysed.

Fractional crystallization of the mixed fertilizers

The product obtained from 30°Be. bittern contained a large amount of sodium chloride (TABLE 3), which is an objectionable constituent in the fertilizer. Fractional crystallization of the 30° and 34·5°Be. products from solutions was tried to remove the greater part of sodium chloride and magnesium salts. Three procedures were examined based on the solubility relationships of the components:

(1) Crystallization from a hot (boiling) saturated solution by cooling. Compositions of the fractions at various stages (density) from 34·5°Be. product are presented in Table 4.

(2) Evaporation and separation of solid at the boiling point of the solution, followed by cooling the hot filtrate to crystallize out the highly soluble salt. The process was repeated. The results obtained with 30°Be. product are given in Table 5.

(3) Extraction of the solid, obtained on complete evaporation, by the solution at its boiling point, leaving a solid richer in sodium chloride. On cooling the hot filtrate, the dissolved constituents, namely ammonium chloride and ammonium sulphate, would crystallize out. The process was repeated. The results are given in Table 6.

Gypsum treatment — In the procedures described above, the excess of ammonium carbonate was recovered by distillation and returned to cycle. In order to economize on the equipment and the fuel cost for distillation, the ammoniacal liquor was treated with gypsum, a byproduct of the salt industry. The procedure is described below.

Two litres of the ammoniacal liquor (alkalinity 2·5N), containing 270 g. fixed solid per litre, were treated with 400 g. of finely ground mineral gypsum ($CaSO_4.2H_2O$, 87; $CaCO_3$, 2·1 per cent) and kept in suspension by stirring. The temperature of the reaction mixture was maintained between 50° and 60°C. Carbon dioxide was bubbled direct into the mixture at the rate of 20 g./hr. in order to convert free ammonia into carbonate. The reaction, which was brisk in the beginning, was complete in 4-5 hr. The reaction proceeded smoothly up to a residual alkalinity of 0·3N; alkalinity of the reaction mixture could not be reduced further even with an excess of gypsum. The precipitated calcium carbonate (84 per cent purity) was separated by filtration and the solution evaporated to crystallization. Small losses were unavoidable due to batch working. The compositions of the mixed fertilizers obtained from Tata (34·5°Be.) and Wadala (30°Be. concentrated to 34·5°Be.) bitterns are as follows:

	Tata %	*Wadala* %
$(NH_4)_2SO_4$	44·9	50·8
NH_4Cl	47·1	40·0
NaCl	3·5	3·5
KCl	4·2	4·2
Magnesium salt	0·3	1·5
N, K_2O	22, 3	21, 3

The final composition, in each case, agrees within 2 per cent of the expected composition,

TABLE 6 — COMPOSITION OF CRYSTALLIZED FRACTIONS FROM MIXED FERTILIZER (30°Be. PRODUCT)

(*About* 300 *g. of fertilizer*)

CROP No.	I	II	III	IV	V	VI	VII	VIII	TOTAL CONSTITUENTS IN 300 G.	RECOVERY % OF FRACTIONS I-VI
Wt. of crystals separating out, g.	40·0	25·0	22·0	35·0	26·0	15·0	55·0	35·0	300·0	—
NaCl	3·8	3·8	3·9	5·7	5·7	10·8	87·4	93·6	122·3	5·5
KCl	3·2	3·6	2·5	3·4	3·4	8·6	0·6	0·9	18·2	31·0
NH_4Cl	54·3	56·3	54·3	48·3	47·3	44·6	7·2	4·1	93·6	82·2
$(NH_4)_2SO_4$	30·2	30·0	35·3	36·5	38·5	32·0	4·8	1·5	65·4	83·8
$MgCl_2.6H_2O$	8·5	6·3	4·0	6·1	5·1	4·0	—	—	—	—

I-VI, crystals obtained by cooling; VII-VIII, solid residue; mother liquor residue (85 cc.) not analysed.

Treatment of the carbonate precipitate — Calcined magnesia is an article of commerce, and is used as a refractory material and in the manufacture of Sorel cement. The light variety is an excellent lagging material for thermal insulation. The physical properties of magnesia are dependent on the conditions employed during its preparation, which can be varied to suit its specific use[8].

In the present study, light carbonate and light magnesia of the best variety were obtained by suitably varying the experimental conditions during their production. The precipitate of the basic carbonate, which was contaminated with sodium chloride and ammonium salts, was washed with water, filtered under suction and dried. The characteristics of the products obtained under different conditions are given in Table 7.

Air-dried samples gave a hard mass which was difficult to grind, whereas samples dried at 110°C. could be easily powdered to pass through 80 mesh sieve. A fine powder was obtained by drying the wet cake at 250°C. The hardness was apparently due to the particles adhering to each other.

Calcination of the carbonate gave pure white magnesia whose bulk density was approximately half that of the carbonate; Table 8 shows the effect of the temperature of calcination of sample No. 4 on the bulk density of calcined magnesia.

The analysis of the magnesia obtained from sample 5, calcined at 600°C., is given in Table 9.

The calcined light magnesia compares favourably with Darlington's calcined light magnesia manufactured by the Pattinson process. The sample, tested by the Central Glass & Ceramic Research Institute, Calcutta, was reported to form periclase crystals at 1,550°C. when fired with Fe_2O_3, indicating that the material could be used for making refractories after proper heat treatment,

TABLE 7 — CHARACTERISTICS OF LIGHT CARBONATE AND LIGHT MAGNESIA OBTAINED UNDER DIFFERENT CONDITIONS

SAMPLE No.	BULK DENSITY g./l.	COMPOSITION	TREATMENT	
			Washing	Drying
1	220	$3\ MgCO_3.Mg(OH)_2.4H_2O$	Cold	110°C.
2	330	$3\ MgCO_3.Mg(OH)_2.7H_2O$	Hot	110°C.
3	410	$MgCO_3.H_2O$	From $Mg(HCO_3)_2$	110°C.
4	200	$3\ MgCO_3.Mg(OH)_2.3H_2O$	Boiled for 6 hr.	110°C.
5	180	$MgCO_3.Mg(OH)_2.3H_2O$	Boiled and expanded for two days	Wet cake dried at 250°C.

TABLE 8 — EFFECT OF TEMPERATURE OF CALCINATION ON THE BULK DENSITY OF CALCINED MAGNESIA

[*Sample No.* 4 (*Table* 7) *employed; duration of calcination,* 1 *hr.*]

TEMP. °C.	CO_2 %	BULK DENSITY (LOOSE METHOD) g./l.
500	2·640	120
600	0·141	106
700	0·143	114
800	0·130	118
900	0·128	129

TABLE 9 — ANALYSES OF MAGNESIA CALCINED AT 600°C.

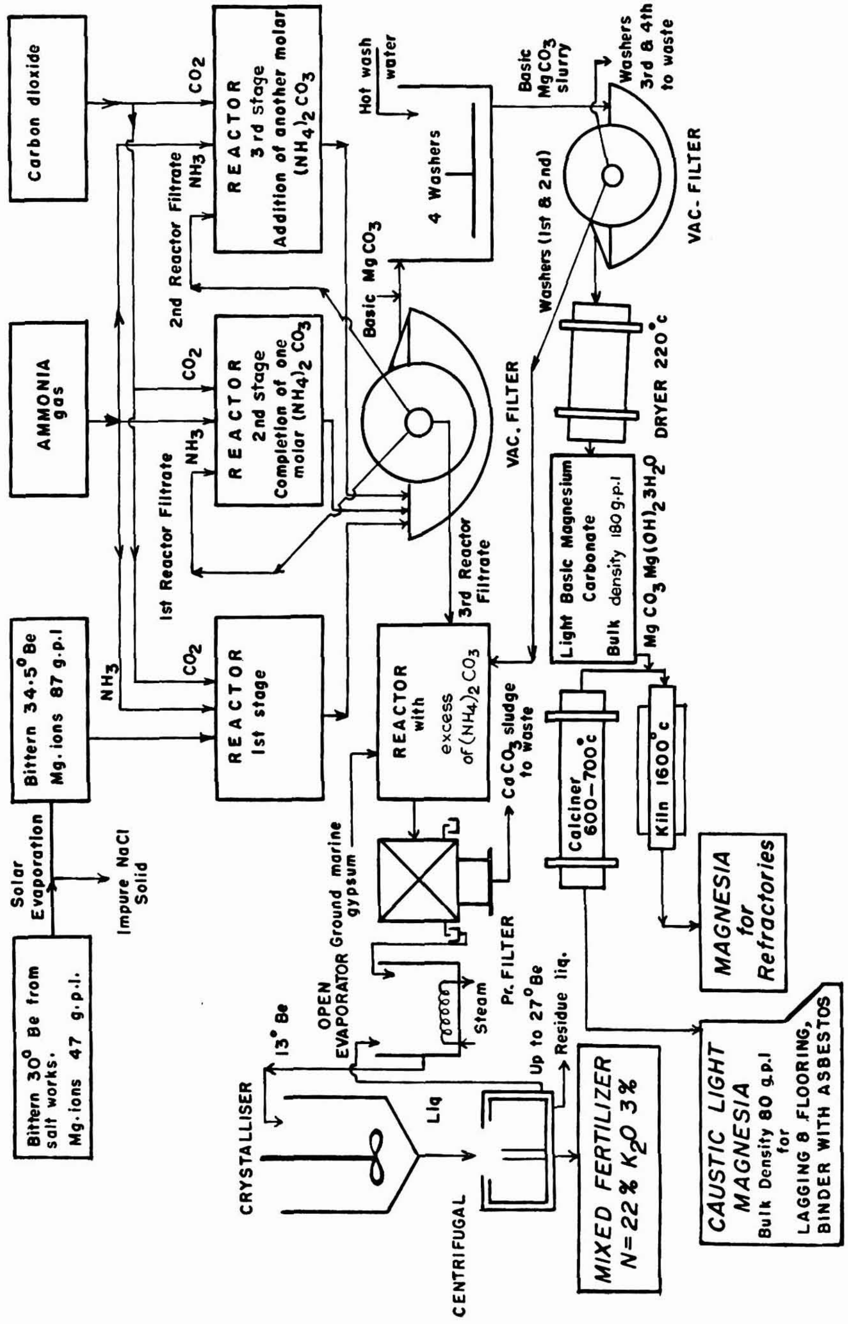
(*Assay,* 98·62% *MgO; loss on ignition,* 3·16%; *bulk density,* 80 *g./l.; fineness,* —200 *mesh*)

	%
Insoluble in acid	0·071
Fe_2O_3	0·050
R_2O_3	0·060
CO_2	0·143
Ca	0·464
Na	0·021
SO_4	0·435

Discussion

The extent of removal of magnesium from 30° and 34·5°Be. bitterns was about 74 per cent with one molar quantity of ammonium carbonate, and increases to 95 and 91 per cent respectively with an equal amount of ammonium carbonate added in excess. The unprecipitated magnesium in solution at the end of the reaction was of the order of 2 and 4 g./l. respectively. The double advantage of carrying out the reaction with

MIXED FERTILIZER & MAGNESIA FROM SEA BITTERNS



ammonia gas is that it yields a concentrated filtrate and removes magnesium ions more effectively from the solutions. The treated liquor contains not more than 5 and 9 per cent (w/v) free ammonia respectively. Hence, the expected loss of ammonia during the processing would be small. The excess of ammonia and ammonium carbonate, recovered by distillation, was added to the subsequent batches which were treated with only the theoretical quantity of ammonia and carbon dioxide. Some difficulty was experienced with 34·5°Be. bittern, because the precipitate obtained was bulky and tended to form a thick slurry. This was overcome by increasing the rate of flow of ammonia to 200 g./hr. and carrying out ammonation in two or three batches. Working with 2 gal. of bittern, reproducible results were obtained with respect to the composition of the final products. The results of these trials indicate that the process can be successfully adopted to large-scale operation.

Some interesting results were obtained when an attempt was made to remove sodium and ammonium chlorides from the mixed fertilizers by fractional crystallization from water. The first crop of crystals separating between 13° and 17°Be. was mainly ammonium chloride (91 per cent pure). When magnesium was present in the mixture, its sulphate separated out between 17° and 19°Be. Recrystallization of these two crops gave ammonium chloride of 98 per cent purity. Sodium chloride did not separate out until the solution reached a density of 27°Be. The last fraction after 27°Be. contained only 6 per cent of the total solid which was practically all sodium chloride. Only 2·5 per cent of the total ammonia is lost in discarding this fraction, but it can be recovered by distillation with lime. Ammonium sulphate was present in all fractions along with ammonium chloride. It thus appears practicable to permutate various desired compositions of sulphate and chloride in the mixed fertilizer by simple fractional crystallization. Small amounts of magnesium salts would not be harmful and, in fact, have been lately considered as a desirable constituent in mixed commercial fertilizers (N-P-K-Mg).

In the present communication, a more complete study was made with the 34·5°Be. bittern, in which the concentration of sodium chloride was already much lower than in the 30°Be. bittern. The loss of magnesium chloride and sulphate in concentrating 30° to 34·5°Be. bittern was 6·7 and 8·8 per cent respectively. A higher concentration of the bittern, namely 36°Be., could not be achieved by direct solar evaporation and was, in fact, undesirable because the greater part of magnesium sulphate was removed from the solution. Working with dechlorinated Tata's bittern (after the recovery of bromine), a product very similar to that from Tata's 34·5°Be. bittern was obtained. This bittern, therefore, could also be used in the process. The Wadala bittern (30°Be.) has a slightly higher content of SO_4 ions, but it has to be concentrated to 34·5°Be. before processing.

In the gypsum treatment for fixing the excess of ammonium carbonate, as described above, the reaction proceeds smoothly with both the natural mineral as well as with the marine gypsum from salt works. In this process, the final product becomes fortified with more ammonium sulphate. A nearly equal proportion of ammonium sulphate and ammonium chloride was obtained in the mixed fertilizer. Calculation shows that the above modification utilizes all the gypsum obtained as a byproduct in the manufacture of salt from sea water.

Summary

The magnesium salts in the bitterns of 30° and 34·5°Be. were precipitated by treatment with ammonia and carbon dioxide to form normal or basic magnesium carbonate. This resulted in the formation of an equivalent amount of ammonium salts in solution and yielded, on evaporation, a mixed nitrogenous fertilizer $[NH_4Cl+(NH_4)_2SO_4+KCl]$. The optimum condition for the reaction is a simultaneous treatment of the undiluted bittern at 50°C. with ammonia and carbon dioxide to precipitate insoluble basic magnesium carbonate from a saturated solution with a small amount of ammonium salt. The removal of magnesium was 90-95 per cent when 2 molar quantities of ammonium carbonate are added. An yield of 3·2 lb. of pure white basic magnesium carbonate/gal. of 34·5°Be. bittern, having a bulk density of 180 g./l., was obtained, which, on calcination at 600°-700°C., gave light magnesia of bulk density 80 g./l. The filtrate was treated with gypsum (natural mineral or marine) to fix

the excess of ammonium carbonate, the precipitate of calcium carbonate filtered off, and the solution evaporated to give 7 lb. of a mixed fertilizer per gallon of 34·5°Be. bittern. The product contains equal proportions of ammonium sulphate and ammonium chloride, with a total nitrogen content of 21-22 per cent. The process provides a useful method for the manufacture of an ammonium sulphate-chloride-potash mixed fertilizer without the use of sulphuric acid.

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Carbonization of South Arcot Lignite

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Carbonization of South Arcot lignite briquettes at temperatures from 500° to 720°C. reveals that the yield of char decreases and that of tar and gas increases as the temperature of carbonization rises. The char and tar obtained compare favourably with those obtained from other lignites.

SOUTH Arcot lignite deposits are estimated at 2,000 million tons[1] and their exploitation is of great importance to South India. Carbonized lignite with properties similar to those of charcoal is an ideal domestic and industrial fuel. The new thermal station in Milam County, Texas, built by Messrs Texas Power & Light Co., carbonizing 9,000 tons of Texas lignite per day[2], is the latest example in this field.

This paper reports results on the carbonization of South Arcot lignite at temperatures from 500° to 720°C. The raw lignite was crushed and briquetted in a hand-operated press and the briquettes were carbonized at 500°, 550°, 600°, 650°, 700° and 720°C.

The carbonized briquettes were analysed and their proximate analyses and calorific values determined. The tar was subjected to fractional distillation and the ash content, specific gravity, etc., of the pitch determined.

Experimental procedure

Raw lignite containing about 40 per cent moisture was air dried to 13·8 per cent moisture and used in these studies. Table 1 gives the results of proximate analysis and the calorific value of the sample.

The air-dried lignite was crushed to −60 mesh and the material briquetted in a hand-operated press. No binder was added during briquetting. Three to four briquettes were carbonized at a time in a locally fabricated rectangular carbonizer heated by a muffle furnace. After the desired temperature was attained, it was maintained for 1 hr. The volatiles were condensed and tar was separated from the non-condensing gases. The temperature of the carbonizer was measured by a chromel-alumel thermocouple. The furnace was allowed to cool and the weight of the carbonized briquettes and the condensate determined.

TABLE 1 — PROXIMATE ANALYSIS AND CALORIFIC VALUE OF RAW LIGNITE

	PROXIMATE ANALYSIS	
	Actual	Moisture-free basis
Moisture, %	13·8	—
Volatile matter, %	47·4	54·9
Ash, %	2·5	2·9
Fixed carbons, %	36·3	42·2
Calorific value, B.t.u./lb.	9650	11200

The proximate analysis and the calorific value, true specific gravity and porosity determinations of the carbonized briquettes were carried out according to A.S.T.M. methods[3,4]. The apparent specific gravity was determined from the volume and the weight of the briquettes. The strength of the briquette was determined by dropping it from a height of 7 ft.

A composite sample of the condensate was dewatered and its specific gravity determined. It was then subjected to fractional distillation[5]. The specific gravity of the pitch and its volatile matter[6] and ash contents were also determined.

Results and discussion

Table 2 gives the product distribution obtained by the carbonization of lignite briquettes at various temperatures.

The yields (on moisture-free basis) of char, tar and non-condensing gas at various temperatures of carbonization are given in Table 3. These results show that the yield of char decreases and the yield of condensate and gases increases as the temperature of carbonization rises.

The carbonized briquettes were dark grey in colour and preserved their shape well. The size of the briquette got reduced due to shrinkage of lignite particles during their carbonization. The tar was light and floated on water.

Table 4 gives the proximate analysis and calorific value of char obtained at different carbonization temperatures.

The data presented in Table 4 show that the volatile matter in the char decreases and its calorific value increases with increasing temperature of carbonization. The moisture content of the carbonized briquettes increases with temperature. This may be explained from the fact that the briquettes carbonized at higher temperature are more porous and this facilitates greater absorption of moisture from the atmosphere.

Table 5 gives the apparent specific gravity, the true specific gravity and the porosity of carbonized briquettes at various temperatures. The true specific gravity increases with the temperature of carbonization.

The results of fractional distillation of the condensate are given in Table 6.

The pitch obtained during the distillation of the condensate had an ash content of 0·19 per cent, volatile matter, 65·4 per cent and specific gravity (92°F./92°F.), 1·108.

TABLE 2 — PRODUCT DISTRIBUTION DURING CARBONIZATION

TEMP. OF CARBONIZATION °C.	WT. OF RAW BRIQUETTES g.	WT. OF CARBONIZED BRIQUETTES g.	CONDENSATE (INCLUDING MOISTURE) g.	NON-CONDENSING GASES (BY DIFFERENCE) g.
500	68·5	31·8	15·5	21·2
500	69·9	32·7	15·7	21·5
550	47·7	21·8	11·4	14·5
600	50·3	22·5	12·2	15·6
600	56·1	26·2	13·6	16·3
650	63·3	26·9	16·5	19·9
700	68·6	29·4	17·5	21·7
700	70·6	29·9	17·4	23·3
720	67·6	28·7	17·5	21·4

TABLE 3 — YIELD OF PRODUCTS OF CARBONIZATION

(Percentage by weight of moisture-free lignite)

TEMP. OF CARBONIZATION °C.	CARBONIZED BRIQUETTES %	CONDENSATE %	NON-CONDENSABLE GASES %
500	53·7	10·2	36·1
500	54·1	10·2	35·7
550	53·0	11·8	35·2
600	51·8	12·6	35·6
600	54·2	12·3	33·5
650	49·2	14·3	36·5
650	49·4	12·0	37·6
700	49·6	13·7	36·7
700	49·1	12·8	38·1
720	49·1	14·4	36·5

TABLE 4 — PROXIMATE ANALYSIS AND CALORIFIC VALUE OF CARBONIZED BRIQUETTES

TEMP. OF CARBONIZATION °C.	PROXIMATE ANALYSIS (ACTUAL)				CAL. VAL. (B.t.u./lb.)	PROXIMATE ANALYSIS (MOISTURE-FREE BASIS)			CAL. VAL. (MOISTURE-FREE BASIS) B.t.u./lb.
	Moisture %	Vol. matter %	Ash %	Fixed carbon %		Vol. matter %	Ash %	Fixed carbon %	
500	3·4	14·6	4·6	77·4	—	15·2	4·8	80·0	—
500	3·8	14·2	5·0	77·0	12545	14·7	4·2	80·1	13030
550	3·5	13·2	4·8	78·5	—	13·7	5·0	81·3	—
600	4·2	11·0	5·0	79·8	13110	11·4	5·3	83·3	13310
600	3·8	9·9	4·9	81·4	—	10·3	5·1	84·6	—
650	6·3	7·0	5·1	81·5	12845	7·5	5·5	87·0	13710
650	6·4	7·1	4·8	81·7	12480	7·6	5·1	87·3	13330
700	7·8	7·0	5·4	79·8	12850	7·6	5·8	86·6	13940
700	7·4	7·2	4·8	80·6	12845	7·8	5·2	87·0	13880
720	7·7	7·2	6·0	79·1	12050	7·8	6·5	85·7	13050

TABLE 5 — CHARACTERISTICS OF THE CHARS

TEMP. OF CARBONIZATION °C.	APPARENT SP. GR. (92°F./92°F.)	TRUE SP. GR. (92°F./92°F.)	POROSITY %
500	—	1·09	—
550	0·72	1·20	40·0
600	0·82	1·25	34·4
650	0·82	1·20	31·7
700	—	1·46	—
720	—	1·26	—

TABLE 6 — FRACTIONAL DISTILLATION OF TAR

(*Sp. gr. of tar*, 0·969)

TEMP. RANGE °C.	DISTILLATE %	CUMULATIVE %
Up to 170	0·82	—
170-200	0·83	1·65
200·210	1·29	2·94
210-235	2·64	5·58
235·270	6·78	12·36
270-300	10·00	22·36
300-315	3·62	25·98
315-335	8·15	34·13
Residue (pitch)	53·33	87·46
Loss (by difference)	12·54	100·00

TABLE 7 — YIELDS OF CHAR AND TAR FROM COALS AND LIGNITES

TEMP. OF CARBONIZATION °C.	NATURE OF COAL	CHAR (BY WT. OF MOISTURE-FREE COAL)	TAR (BY WT. OF MOISTURE-FREE COAL)
500	Bituminous coal[7] (Disco process)	72·0	7·5
	Texas lignite[8]	70·2	10·1
	North Dakota lignite[9]	74·0	1·8
	South Arcot lignite	53·9	10·2
550	Sub-bituminous coal[10]	66·5	12·0
	Texas lignite[8]	67·4	9·3
	South Arcot lignite	53·0	11·8
600	North Dakota lignite[9]	67·2	1·2
	German lignite[11]	59·0	12·9
	South Arcot lignite	52·0	12·4
700	North Dakota lignite[9]	64·4	0·4
	South Arcot lignite	49·4	13·3

Table 7 gives comparative data on the yields of char and primary tar from different types of coal and lignite.

The data presented in Table 7 are not strictly comparable since they are obtained in various types of carbonizers under varying carbonizing conditions. They, however, indicate that the yield of tar from South Arcot lignite is good, while the yield of char is generally low. In this respect South Arcot lignite resembles German lignite.

Summary

South Arcot lignite was briquetted and carbonized at 500°, 550°, 600°, 650°, 700° and 720°C.

The yield of char decreased and the yield of tar and gas increased as the temperature of carbonization increased. The volatile matter in the carbonized briquette decreased and its fixed carbon content and calorific values increased.

The true specific gravity of carbonized char increased with the temperature of carbonization.

The strength of carbonized briquette was satisfactory and was as good as that of raw briquettes.

The ash content of the pitch was low.

The yields of tar and char from South Arcot lignite compare favouraby with those from coals and lignites from other sources.

Acknowledgement

The authors wish to express their thanks to the Government of Madras for permission to publish this paper, to Mr. Paul R. Eyrich, Chairman of the Committee of Experts, Lignite Investigation, Neyveli, and Mr. H. K. Ghose, Officer-in-charge, Lignite Investigation, Neyveli, for their interest in this work, and to Dr. P. P. Reddy, Chief Chemist, Chemical Testing and Analytical Laboratory, Madras, for determining the calorific value of chars reported in this investigation.

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Beneficiation Studies on a Pyrite Sample A from Alpha Mine, Wynaad, Nilgiris

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Beneficiation of a pyrite sample from Alpha Mine, Wynaad, Nilgiris, has been studied by tabling as well as flotation, primarily with a view to utilizing it as a source of sulphur. The sample was found to contain 1·7 per cent sulphur and 0·6 dwt. of gold per ton. The principal gangue minerals were quartz and pyrophyllite and tabling has given a concentrate of grade 37·8 per cent sulphur, recovery being 62·1 per cent. Optimum conditions for the flotation of pyrite have been worked out. Both ethyl and amyl xanthates have been used as collectors, the latter yielding a better grade of concentrate with 39·8 per cent sulphur, recovery being 90 per cent at *p*H 8·0.

ABOUT 1½ tons of pyrite-bearing material containing quartz, pyrophyllite, dolomite, traces of magnetite and limonitic material were received for investigation. The sample was crushed in the jaw crusher and a representative portion from this was further reduced to –8 mesh in the roll crusher and used in all the experiments.

Results and discussion

Chemical analysis — The results of chemical analysis of the sample are given in Table 1.

Sieve analysis — The sieve analysis of the roll-crushed product (TABLE 2) and microscopic examination of the various fractions show that most of the pyrite is free at –35 mesh. At coarser sizes, pyrite is mostly interlocked.

Tabling — As most of the pyrite is released at –35 mesh, the ore was roll-crushed to this size and passed over the Wilfley table after hydraulic classification. The results of tabling are presented in Table 3.

It is found from tabling data (TABLE 3) that most of the pyrite is in the coarse fraction representing 30·8 per cent by weight and containing 70·2 per cent of the total sulphur. Tabling of this coarse product recovers 62·1 per cent of the total sulphur, with the grade assaying 37·8 per cent sulphur.

Flotation — The *p*H of the ore pulp used in the flotation tests was 7·4, without the addition of any *p*H regulator and using distilled water for making the pulp. Although the *p*H of the pulp can be brought to 7·0 with the use of 2 lb./ton of sulphuric acid, a very large excess was found necessary to bring the *p*H to the acid range on account of the presence of carbonates; hence experiments in the acid range were not carried out although pyrite is known to float well in this range.

Feed for flotation was prepared by wet grinding the ore in the ball mill for different

TABLE 1 — CHEMICAL ANALYSIS

	%
Total S	1·46
SiO_2	74·60
Al_2O_3 Fe_2O_3	17·20
CaO	2·50
MgO	1·70
As	nil
Cu	nil
Gold	0·6 dwt./ton (by fire assay)

TABLE 2 — SIEVE ANALYSIS OF –8 MESH PRODUCT

SIZE (mesh)	WT. %
+ 10	5·3
– 10 + 14	17·1
– 14 + 20	19·5
– 20 + 28	14·2
– 28 + 35	9·4
– 35 + 48	7·1
– 48 + 65	4·9
– 65 + 100	4·8
– 100 + 150	3·1
– 150 + 200	2·2
– 200	12·4

TABLE 3 — TABLING OF –35 MESH PRODUCT AFTER HYDRAULIC CLASSIFICATION

PRODUCT	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
Coarse concentrate	2·3	37·8	62·1
Medium concentrate	0·2	32·4	6·9
Fine concentrate	0·1		
Coarse tailing	28·5	0·4	8·1
Medium and fine tailing	46·5	0·4	13·3
Slime	22·4	0·6	9·6
	100·0	1·4	100·0

periods. Sieve analyses of two of the products employed for the flotation tests are given in Table 4.

*Effect of p*H *on the flotation of pyrite* — The results given in Table 5 show that with increase of *p*H from 7 to 8·2, recovery of sulphur increases but the grade gradually falls after an initial increase. At *p*H 9·3 both grade and recovery are low. Flotation at a *p*H range of 7·4-7·8 gives the best results. Lower concentration of xanthate is ineffective in floating pyrite.

Effect of higher concentration of ethyl xanthate — Higher concentration of ethyl xanthate (0·5 lb./ton) shifts the optimum *p*H more to the alkaline range as is evident from the results given in Table 6. Probably the higher concentration of xanthate overcomes the depressing effect of alkalies.

Effect of amyl xanthate — The results of flotation with amyl xanthate (0·3 lb./ton) in the *p*H range 7·4-8·0 are recorded in Table 7. Both grade and recovery are better and the optimum *p*H for good results is raised from 7·8 to 8·0 when ethyl xanthate is replaced by amyl xanthate.

Effect of particle size — The results of flotation experiments employing 18 min. grind and using 0·15 lb./ton of ethyl xanthate (TABLE 8) indicate the importance of the size of particles on the flotation characteristics. The results are better than with 0·3 lb./ton of collector at a coarser size.

Cyanidation — The original sample assays only 0·6 dwt. of gold per ton and all the flotation tailings of the tests reported earlier assay less than 0·1 dwt./ton. Straight cyanidation of the ore recovers almost all the gold, the consumption of lime and potassium cyanide being 1·4 and 1·1 lb. per ton respectively. As the gold content in the ore is too low for economic recovery, no further tests were performed.

TABLE 4 — SIEVE ANALYSES OF ORE GROUND IN BALL MILL

SIZE (mesh)	12 MIN., WT. %	18 MIN., WT. %
+ 65	4·1	2·0
− 65+100	9·2	4·6
−100+150	14·1	9·4
−150+200	12·6	9·4
−200+270	11·2	14·2
−270	48·8	60·4

TABLE 5 — EFFECT OF *p*H ON THE FLOTATION OF PYRITE

(*Collector: ethyl xanthate,* 0·3 *lb./ton; grinding time,* 12 *min.*)

*p*H	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
7·0	3·8	30·8	80·2
7·4	3·1	39·7	84·3
7·8	2·9	41·4	82·2
8·0	4·1	31·1	87·3
8·2	4·5	29·9	92·2
9·3	4·6	25·4	80·0

TABLE 6 — FLOTATION WITH ETHYL XANTHATE

(0·5 *lb./ton*)

*p*H	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
7·4	3·2	37·3	81·7
7·9	2·6	43·9	78·2
8·0	3·8	37·1	96·6
8·2	3·6	35·9	88·5

TABLE 7 — FLOTATION WITH AMYL XANTHATE

(0·3 *lb./ton*)

*p*H	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
7·4	3·5	35·6	84·6
7·9	3·2	39·5	86·6
8·0	3·3	39·8	90·0

TABLE 8 — FLOTATION WITH ETHYL XANTHATE

(*Ethyl xanthate,* 0·15 *lb./ton; grinding time,* 18 *min.*)

*p*H	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
7·4	2·9	41·9	83·2
7·8	2·8	42·7	81·9
8·0	2·9	40·3	80·0

Summary

The principal gangue mineral in the pyrite sample is quartz, followed by pyrophyllite, dolomite and traces of magnesite and limonitic material. Pyrite is liberated from the gangue at a size of —35 mesh.

Tabling recovers 62·1 per cent sulphur in a concentrate assaying 37·8 per cent sulphur. Flotation at a *p*H of 7·8 using 0·15 lb./ton of ethyl xanthate yields a concentrate of grade 42·7 per cent sulphur with a recovery in this product of 81·9 per cent. Use of amyl xanthate (0·03 lb./ton) at a *p*H of 8·0 gives a concentrate assaying 39·8 per cent sulphur, the recovery being 90 per cent.

As there was little gold in the ore, no cyanidation tests were performed in detail.

Acknowledgement

The authors' thanks are due to Dr. G. P. Contractor, formerly Acting Director, for his keen interest during the progress of this work; to Mr. E. H. Bucknall, Director, National Metallurgical Laboratory, for his comments on the report; to the Director, Geological Survey of India, for financing this research scheme and to the Director, Council of Scientific & Industrial Research, for permission to publish the results.

Beneficiation Studies on a Pyrite Sample B from Alpha Mine, Wynaad, Nilgiris

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Beneficiation of a second pyrite sample from Alpha Mine, Wynaad, Nilgiris, has been studied by gravity as well as flotation methods. The sample was found to contain 1·46 per cent sulphur and only traces of gold. The main gangue minerals were pyrophyllite and quartz. Tabling recovers 72·7 per cent sulphur, the grade of concentrate being 39·3 per cent sulphur. Tabling followed by flotation of table middlings recovers 89 per cent sulphur in a combined concentrate assaying 43·76 per cent sulphur.

Straight flotation with ethyl xanthate as collector recovers 94·0 per cent sulphur in a pyrite concentrate assaying 47·1 per cent sulphur when pyrophyllite, which is an inherently flotable mineral, is deflocculated using sodium carbonate and sodium metasilicate.

THE ore was very soft and soapy to the touch. Sulphur in the ore was present in the form of cubical pyrite. The main gangue was pyrophyllite, followed by quartz, dolomite and limonitic material. The sample was crushed in a jaw crusher and a portion of this was further reduced to —10 mesh in a roll crusher and used in all the experiments.

Results and discussion

Chemical analysis — The analysis of the sample given in Table 1 shows that it contains only 1·7 per cent sulphur. The sample does not contain any gold.

Sieve analysis — The sieve analysis of the roll-crushed product (TABLE 2) and microscopic examination of the various fractions indicate that all the pyrite is free from interlocked particle at —35 mesh and more than 80 per cent is liberated even at about 28 mesh.

Tabling a —28 mesh feed — Tabling of a material roll-crushed to —28 mesh was carried out after hydraulic classification into two fractions. The results (TABLE 3) of the test indicate the presence of only 7·3 per cent of the total sulphur in the finer classified

TABLE 1 — CHEMICAL ANALYSIS OF THE ORE SAMPLE

	%
Total S	1·7
SiO_2	56·4
Al_2O_3	15·6
Fe_2O_3	7·0
CaO	5·9
MgO	4·5
Loss on ignition	8·7

TABLE 2—SIEVE ANALYSIS OF —10 MESH PRODUCT

SIZE (mesh)	WT. %
+ 14	21·3
− 14 + 20	21·2
− 20 + 28	13·2
− 28 + 35	7·2
− 35 + 48	5·6
− 48 + 65	5·2
− 65 + 100	5·1
−100 + 150	3·7
−150 + 200	1·6
−200	15·9

TABLE 3—TABLING AFTER GRINDING TO —28 MESH

PRODUCT	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
Concentrate 1 (coarse)	3·1	39·3	72·7
Concentrate 2 (fine)	0·3	13·0	2·3
Coarse tailing	54·5	0·6	20·0
Fine tailing	42·1	0·2	5·0
	100·0	1·68	100·0

fraction, whereas 92·7 per cent is present in the coarser fraction which constitutes 67·6 per cent by weight of the total feed. Tabling the coarse fraction recovers 72·7 per cent of total sulphur in a concentrate of grade 39·3 per cent sulphur.

Tabling followed by flotation of table middlings — Tabling of the —35 mesh material after hydraulic classification recovers 61·5 per cent of the total sulphur (TABLE 4) in a concentrate assaying 43·76 per cent sulphur, whereas flotation of the table middling after grinding increases the recovery to 89·0 per cent, the grade remaining almost the same.

Flotation — The main gangue mineral, pyrophyllite, belongs to the class of minerals which are inherently flotable. Particular attention was given to depressing this mineral during flotation of pyrite.

The *p*H of the pulp obtained after grinding the ore in distilled water was found to be alkaline due to the presence of carbonate minerals.

The flotation results using ethyl xanthate (0·2 lb./ton) and pine oil (0·08 lb./ton) are given in Table 5.

Although the recovery is 92·4 per cent, the grade is only 18·27 per cent sulphur, due to the flotation of gangue material. Selective flotation of pyrite is achieved by dispersing pyrophyllite by the addition of sodium metasilicate. The results of tests carried out with a feed ground for 6 min. in a rod mill (sieve analysis recorded in TABLE 6) are given in Table 7. The results indicate the beneficial effect of sodium carbonate and sodium metasilicate using ethyl or amyl xanthates as collectors. The tailings in all cases assayed less than 0·1 per cent sulphur.

TABLE 4 — TABLING FOLLOWED BY FLOTATION OF TABLE MIDDLING

PRODUCT	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
Table concentrate	2·35	43·76	61·5
Flotation concentrate	1·06	43·46	27·5
Table tailing 1 (coarse)	39·76	0·13	3·1
Table tailing 2 (fine)	42·12	0·24	6·0
Flotation tailing (mixed)	14·71	0·21	1·9
	100·00	1·67	100·0

TABLE 5—FLOTATION WITH AMYL XANTHATE AND PINE OIL

(*Grinding time, 7 min.*)

PRODUCT	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
Flotation concentrate	8·0	18·27	92·4
Flotation tailing	92·0	0·13	7·6
	100·0	1·57	100·0

TABLE 6 — SIEVE ANALYSIS OF FEED USED IN FLOTATION

[*Grinding time, 6 min. (rod mill)*]

SIZE (mesh)	WT. %
+100	8·1
−100+150	14·3
−150+200	10·7
−200+270	9·5
−270	57·4

TABLE 7 — FLOTATION WITH ETHYL AND AMYL XANTHATES

Conditioner in (1) 1·0 *lb./ton of* Na_2CO_3; (2) 1·0 *lb./ton of* Na_2CO_3 + 0·5 *lb./ton of sodium metasilicate*]

	COLLECTOR	WT. %	ASSAY, SULPHUR %	RECOVERY, SULPHUR %
1	(a) Ethyl xanthate	3·9	41·7	92·4
	(b) Amyl xanthate	3·1	46·0	93·1
2	(a) Ethyl xanthate	2·9	47·1	94·1
	(b) Amyl xanthate	3·7	43·2	95·6

The best result was obtained by using ethyl xanthate as collector and sodium carbonate and sodium metasilicate as modifying agents, when a concentrate of grade 47·1 per cent sulphur with a recovery of 94·1 per cent is obtained.

There was practically no flotation of pyrite with 0·15 lb./ton of ethyl xanthate when copper sulphate was used as activator. Probably the unadsorbed copper in solution reacted with xanthate reducing the concentration of xanthate necessary to float pyrite. This was borne out by the increased amount of the collector necessary to float pyrite.

Summary

The principal gangue minerals in the ore are pyrophyllite and quartz.

Tabling a —28 mesh feed recovers 72·7 per cent of the total sulphur, the grade of concentrate being 39·3 per cent sulphur. Tabling a finer feed (—35 mesh) followed by flotation of table middlings recovers 89·0 per cent of sulphur in a combined concentrate assaying 43·76 per cent sulphur.

Straight flotation recovers more than 90 per cent of the total sulphur, the concentrate assaying more than 40 per cent sulphur. The best result is obtained when the gangue is deflocculated using sodium carbonate and sodium metasilicate and flotation carried out using ethyl xanthate as collector.

Recovery is 94 per cent with the pyrite concentrate assaying 47·1 per cent sulphur.

As there was no gold present in the ore, no cyanidation tests were performed.

Acknowledgement

The authors' thanks are due to Dr. G. P. Contractor, formerly Acting Director, for his keen interest during the progress of this work; Mr. E. H. Bucknall, Director, National Metallurgical Laboratory, for his comments on the report; to the Director, Geological Survey of India, for financing this research scheme and to the Director, Council of Scientific & Industrial Research, for permission to publish the results.

Letters to the Editor

POLAROGRAPHIC STUDIES ON FERRIPHOSPHATE COMPLEXES IN SOLUTION

THE INTENSITY OF COLOURS IMPARTED BY iron compounds to glasses is known to be suppressed by the incorporation of phosphates in the batches. Recently, investigations were initiated in this laboratory to study the mechanism of the phenomenon. Quite often, similarity in the behaviour of aqueous solutions and glasses containing the same colorants has provided useful background in such work.

It is known that phosphates have a bleaching effect on the colour produced by iron salts in aqueous systems, due possibly to the formation of complexes between ferric iron and phosphates[1]. The present study, including spectrophotometric, polarographic and magnetic measurements on ferriphosphate complexes in aqueous solutions, was undertaken as a part of these investigations.

A solution containing ferric ions is reduced by mercury; consequently, a well-defined polarographic wave due to ferric-ferrous reduction cannot be obtained[2]. There are, however, certain complex forming agents such as sodium oxalate[3], fluoride[4], tartarate[5] which exercise some stabilizing influence and the reduction of ferric complex takes place at a more negative potential so that well-defined polarographic waves can be obtained by using these salts as the supporting electrolytes.

For polarographic study of ferriphosphate complexes in solution, several series of solutions were prepared by dissolving ferric phosphate in phosphoric acid and sodium hydrogen phosphate buffer, and their polarograms were taken using Heyrovskey photographic recording polarograph. The chemicals used were of A.R. quality.

Since the half-wave potential is expressed against saturated calomel electrode, the e.m.f. at the mercury pool anode of the polarographic cell was measured against that of a saturated calomel electrode using a Cambridge *p*H meter. Hydrogen ion concentration of the solution was also determined with the same instrument using a quinhydrone electrode. The results are given in Table 1.

With 0·01 per cent pure gelatin in the test solution to suppress the maxima, a well-defined polarographic wave, due to the reduction of ferriphosphate complex, was obtained. Following the method outlined by Lingane[3], thermodynamic equations have been derived for the evaluation of half-wave potential and other related quantities from

TABLE 1 — POLAROGRAPHIC DATA ON IRON PHOSPHATE

(Supporting electrolyte, mixtures of varying proportions of 0·704M NaH_2PO_4 and 1·620M H_3PO_4 solutions; molar concentration of Fe^{+++} 0·00335)

SOLN. No.	NaH_2PO_4 SOLN. CC.	H_3PO_4 SOLN. CC.	*p*H	$(E_{\frac{1}{2}})$ S.C.E.	LOG C $(H_2PO_4)^-$
1	1	99	0·76	+0·157	−2·15
2	20	80	1·08	+0·144	−0·85
3	40	60	1·38	+0·137	−0·55
4	50	50	1·55	+0·110	−0·45
5	70	30	1·96	+0·086	−0·31
6	80	20	2·22	+0·067	−0·25
7	85	15	2·39	+0·059	−0·22
8	90	10	2·59	+0·062	−0·20
9	95	5	2·94	+0·048	−0·18

the experimental results. The data obtained from the polarographic wave were found to conform to thermodynamic relations and the reversibility of reduction of ferriphosphate complex has been established. Half-wave potentials ($E_{\frac{1}{2}}$) for the reduction waves, obtained under different experimental conditions, were calculated and these correspond, in each case, to the reduction of ferric to the ferrous state.

Even though the value of $E_{\frac{1}{2}}$ as expressed against saturated calomel electrode (S.C.E.) was positive, well-defined polarographic waves could be obtained on application of a negative e.m.f. across the cell due to the potential at the mercury pool anode being positive with respect to S.C.E. The value of $E_{\frac{1}{2}}$ (S.C.E.) for the complex was, however, more negative than that for simple ferric-ferrous reduction, due to more electropositive character of the ferriphosphate complex. Also, the half-wave potential was found to be dependent upon the concentration of $(H_2PO_4)^-$ ion in the solution and not on the *p*H of the solutions used. Fig. 1 shows the relation between half-wave potential ($E_{\frac{1}{2}}$) of ferriphosphate complex and concentration of the complex forming $(H_2PO_4)^-$ ion.

$$E_{\frac{1}{2}} = 0{\cdot}525 + 0{\cdot}061 \log K - 0{\cdot}061\ n.\ \log C_{(H_2PO_4)^-} \text{ at } 35°C.$$

Number of $(H_2PO_4)^-$ ions in the complex

$$n = \frac{-\Delta E_{\frac{1}{2}}}{0{\cdot}061\ \Delta \log C_{(H_2PO_4)^-}} = 4{\cdot}0$$

Dissociation constant

$$K = \log^{-1} \frac{E_{\frac{1}{2}} - 0{\cdot}525}{0{\cdot}061} = 0{\cdot}7 \times 10^{-9}$$

when $\log C_{(H_2PO_4)^-} = 0$.

In the series of solutions studied, two complexes were detected. Assuming that reduction has taken place directly from ferriphosphate complex to free ferrous ion, the first complex was found to have the formula $[\,Fe(H_2PO_4)_4\,]^-$. This was, however, stable only up to a certain concentration of $(H_2PO_4)^-$ ion in solution below which another complex, containing either a smaller number of or no $(H_2PO_4)^-$ ions, was found. This second complex was less stable than the first one and the polarographic wave for this was not so well defined. From the shift of the half-wave potentials with changing concentration of $(H_2PO_4)^-$ ions, the dissociation constant of the first complex was found to be $0{\cdot}7 \times 10^{-9}$.

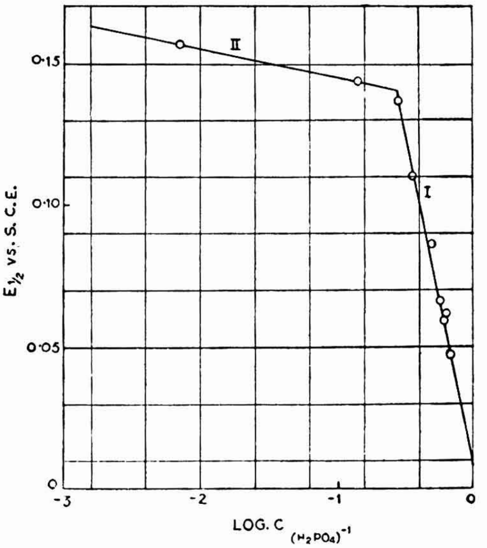

FIG. 1 — RELATION BETWEEN HALF-WAVE POTENTIAL ($E_{\frac{1}{2}}$) AND CONCENTRATION OF $(H_2PO_4)^-$ ION

Ilkovic's relation between diffusion current and concentration of iron could also be established within the concentration range studied, i.e. 0·0008 to 0·0063[M]Fe and the diffusion coefficient for the ferriphosphate ion has been calculated from it. Comparing the value of diffusion coefficient for the ferriphosphate ion ($0{\cdot}206 \times 10^{-5}$ sq. cm. sec.$^{-1}$ at 25°C.) with that for simple ions like Cd^{++}, Al^{+++}, etc., it was found that the mobility of ferriphosphate ion was much less than that for the simple ions, presumably due to its larger size. Linear relationship between diffusion current and concentration of iron suggests the possibility of using the method for the estimation of iron.

These studies on ferriphosphate complexes have revealed that (1) the reduction of the complexes was reversible and change in valency was one; (2) two complexes were formed one of which contained four $(H_2PO_4)^-$ groups; (3) dissociation constant of the complex containing four $(H_2PO_4)^-$ groups was of the order of 10^{-9}; (4) Ilkovic's relation between diffusion current and concentration of iron holds good within the concentration range studied. The method could, therefore, be employed for the determination of iron;

and (5) diffusion coefficient of the complex was much smaller than that for simple ions, which indicates that the size of the complex is larger than that of simple ions.

Further work along these lines is in progress and a detailed account of the results obtained will be published elsewhere.

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ELECTROLYTIC PRODUCTION OF CUPROUS OXIDE

CUPROUS OXIDE IS AN IMPORTANT INGREDIENT in the manufacture of antifouling paints. During World War II most of the output of this product was utilized by the U.S. Navy in antifouling formulations. It is also used in the production of copper salts, in ceramics and in the development of porcelain red glaze and red glass. The yellow form of cuprous oxide finds considerable application in agriculture[1]. The rectifying characteristic of cuprous oxide is made use of in the manufacture of rectifiers in which the cuprous oxide is formed *in situ*. These rectifiers are widely used in electrochemical industries.

Industrial manufacture of cuprous oxide is usually based on thermal or electrolytic methods. In either case, one of the main difficulties seems to be to obtain cuprous oxide free from cupric oxide and metallic copper. Depending on the purity of the product, specifications for two grades of cuprous oxide have been detailed in U.S. Navy specification 52C4c. The chemical composition established for each grade and the I.S.I. specification for a similar grade of cuprous oxide is given in Table 1.

Cuprous oxide was prepared by electrolytic method for the first time by Lorenz[4] in 1896. Various aspects of the problem have been studied by others subsequently[5-7]. A recent French patent[8] claims an yield of 1 kg. of cuprous oxide of 93 per cent purity for an energy consumption of 1·25 kWh. Addition of glue to the electrolyte during electrolysis is reported to yield the yellow form of cuprous oxide[9].

Large quantities of cuprous oxide could be manufactured by the electrolytic method using copper scrap available in the country. Investigation of this process was, therefore, undertaken to study the essential details for the economic operation of a cell on a commercial scale to produce a product of the required standard.

An alkaline solution of sodium chloride was used as electrolyte. Refined copper scrap was used as anode and electrolytic copper sheet as cathode. The influence of such factors as concentration of sodium chloride and sodium hydroxide, *p*H, temperature and current density on the purity and colour of the product, as well as on the current efficiency, was studied. Optimum conditions have been determined to produce cuprous oxide of the required standard.

Small-scale experiments were carried out in a 2 l. pyrex basin containing 1·5 l. sodium chloride solution maintained at the desired temperature. Alkali content of the electrolyte was varied to study its effect on the colour of the product as well as on the purity and current efficiency. A copper sheet (10 × 5 cm.) inside a cloth diaphragm served as cathode. A similar sheet of copper made from scrap served as anode. Direct current for the electrolysis was supplied by a generator (25 amp. at 6 V.). Using a 10 per cent sodium chloride solution at 80°C. with the addition of the optimum amount of alkali and passing a current of 2·5 amp. (current density 5 amp./sq. dm.), 6·5 g. of cuprous oxide was obtained in an hour. Under these conditions the current efficiency was 97·5 per cent, and the product obtained was found to be of the purity and colour as

TABLE 1

	U.S. NAVY SPECIFICATION[2]		I.S.I. SPECIFICATION[3] %
	Grade I %	Grade II %	
Cuprous oxide (Cu_2O)	97	90	96
Total copper (Cu)	86	80	—
Total reducing power as Cu_2O	97	90	—

the standard specimen received from the U.K. Coal Board.

The large-scale cell consisted of a vessel made of monel metal containing 6 l. of 10 per cent sodium chloride solution having the desired alkalinity. Four cathodes (15 × 12·5 cm.), each separately supported inside a cloth diaphragm and connected together, were supported from a wooden lid provided for the vessel. Three anodes of the same dimensions were similarly connected together and supported from the lid with the cathodes on either side of them. The electrolyte was maintained at 80°C. and, during electrolysis, an additional quantity of the electrolyte was circulated through the diaphragms at the rate of approximately 10 l./hr. The overflow was continuously filtered and the cuprous oxide recovered. From a motor-generator set, a current of 52 amp. was passed through the cell at a cell voltage varying from 1·5 to 1·9 V., maintaining the current density at approximately the same value as in the case of the small-scale experiment.

The cell has been run for periods of 1-4 hr. several times and current efficiencies of 94-96 per cent were obtained. Cuprous oxide thus prepared was washed thoroughly and dried at 80°-100°C. under reduced pressure after a stabilizing treatment. The product obtained is comparable to the imported sample of cuprous oxide. The energy consumption varies from 0·275 to 0·35 kWh. per pound of cuprous oxide (0·78 kWh./kg.), which is lower than the figure claimed in the French patent[8].

A semi-pilot plant unit has been set up for studying the operational technique of the process on a commercial scale. Full details of the work will be published at a later date.

The authors wish to express their thanks to Messrs India Alkalies Ltd., Calcutta, for a generous supply of copper scrap.

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CATALYTIC VAPOUR PHASE OXIDATION OF PHENANTHRENE

INVESTIGATIONS ON RAW MATERIALS OTHER than naphthalene for the production of phthalic anhydride have revealed that other aromatic hydrocarbons such as phenanthrene, anthracene, etc., can also be used for the purpose. Zalkind and Kesarev[1] studied the oxidation of phenanthrene over pumice-vanadium pentoxide catalyst under various conditions and obtained 21 per cent total acids, containing mainly phthalic acid. They also found that a mixture of uranium and vanadium oxides (30 : 70) catalysed the reaction, yielding 41 per cent total acids. Kinney and Pincus[2] oxidized anthracene, phenanthrene and specific fractions of tar oil rich in napththalene, using two types of commercially available catalysts, viz. (1) German type: silica-based vanadium pentoxide-potassium sulphate, and (2) American type: alumina-based vanadium pentoxide. With phenanthrene as the raw material, they obtained 18·1 and 35·2 per cent yields of phthalic anhydride respectively, using the above catalysts. Brooks[3], in an attempt to obtain diphenic acid from phenanthrene using a fluidized bed of vanadium pentoxide-potassium sulphate-silica gel catalyst, obtained 13·5 per cent of phthalic anhydride besides a number of other products. Shelmerdine and collaborators[4] reported the results of their investigation on the oxidation of coal-tar oil, rich in naphthalene and its derivatives, to phthalic anhydride, and have indicated the possibility of commercial exploitation of the process. Recently Gulati and Bhattacharyya[5] have obtained varying percentages of phthalic acid from *o*-xylene using various catalysts.

The heavy oil fraction of coal-tar, containing appreciable amounts of phenanthrene and anthracene, has been used by us for the

TABLE 1 — CATALYTIC OXIDATION OF PHENANTHRENE USING AIR AS THE OXIDIZING MEDIUM

(*Temp. of catalyst*, 450°C.)

CATALYST	TEMP. OF THE CARBURETTER °C.	SPACE VELOCITY OF THE AIR cc./hr./unit vol. of catalyst	VOL. OF AIR PASSED/G. OF PHENANTHRENE cu. ft.	YIELD OF PHTHALIC ANHYDRIDE WITH RESPECT TO PHENANTHRENE %	YIELD OF MALEIC ANHYDRIDE WITH RESPECT TO PHENANTHRENE %	YIELD OF PHTHALIC ANHYDRIDE CALCULATED ON THEORETICAL YIELD %
V_2O_5-K_2SO_4 on silica	240	2294	6·08	50·35	4·16	60·54
do	220	2294	13·35	49·12	4·33	59·07
V_2O_5 on Al_2O_3	240	2071	5·30	35·17	0·51	42·29
do	240	2071	4·66	35·28	0·67	42·41

production of phthalic anhydride. Using phenanthrene as the starting material we have investigated the conditions for obtaining better yields. The catalysts used were prepared in the laboratory with varying percentages of vanadium pentoxide. In some cases ammonium vanadate was used. Maximum yield of phthalic anhydride was obtained with vanadium pentoxide deposited on silica gel and promoted by potassium sulphate. At a reaction temperature of 450°C. and a space velocity of air 2,294 cc./hr./unit volume of the catalyst, the percentage yield of phthalic anhydride was 60·54 of theory. The alumina-based vanadium pentoxide catalyst gave an yield of 42·41 per cent at a space velocity of air 2,071 cc./hr./unit volume of catalyst. The experimental procedure employed was similar to that of Kinney and Pincus[2] (with certain modifications), and the vapours of the substance to be oxidized in admixture with the air were passed over a bed of catalyst maintained at the desired temperature.

The yields of phthalic anhydride obtained show a marked improvement on the yields obtained so far. From a number of runs under different conditions, it was observed that the optimum temperature for oxidation was 450°C. Higher temperatures gave more vigorous oxidation, resulting in increased percentages of carbon dioxide in the exit gases and consequently lower yields. Below 450°C., some unconverted phenanthrene and some yellowish quinone type of compounds were obtained. Production of maleic anhydride, which invariably accompanies phthalic anhydride, was also lowest at 450°C.

It has been found that under optimum conditions, only 30 per cent carbon of the phenanthrene vaporized was utilized in the formation of phthalic anhydride. About 44 per cent is accounted for as carbon dioxide, and the remaining 25 per cent is obtained as carbon monoxide, maleic anhydride and quinone type of compounds.

The results of a few typical experiments are given in Table 1.

Details of preparation and treatment of the catalyst are the subject-matter of a patent and will be published later.

Grateful thanks are due to Dr. J. W. Whitaker, Director, and Dr. A. Lahiri, Deputy Director, Fuel Research Institute, for their keen interest in the work.

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CHEMICAL INVESTIGATION OF *HYOSCYAMUS MUTICUS*

DUNSTAN AND BROWN[1], GADAMER[2] AND Poljewijd[3] found that *Hyoscyamus muticus* contains hyoscyamine along with traces of atropine. Our study has revealed that the plant contains, besides hyoscyamine and atropine, 0·02 per cent of hyoscine and a large amount of potassium chloride.

The drug, which was obtained from Egypt, contained 1·09 per cent of total alkaloids. Finely powdered material (5·5 kg.) was exhausted with alcohol and the extract concentrated under vacuum when a large amount of a crystalline product, mainly potassium chloride, separated out. After removing this, the alkaloids were extracted with chloroform in the usual way and worked up according to the method of King[4]. A partial separation of weakly and strongly basic alkaloids was thus effected. In the weakly basic fraction, 1·3 g. of a syrupy mass was obtained which gave gold chloride, m.p. 204°-5°C., and gold bromide, m.p. 191°-92°C.; a mixed melting point with authentic specimen of hyoscine gold chloride and gold bromide showed no depression. From the strongly basic fraction hyoscyamine crystallized out when chloroform was removed. On repeated crystallizations from benzene and acetone, white needles, m.p. 106°-7°C., were obtained and gave gold chloride, m.p. 164°-65°C. From the mother liquors of the above, after repeated crystallizations from benzene and dilute alcohol, atropine in silky white needles (0·2 g.), m.p. 114°-15°C., was obtained. This was characterized through gold chloride which melted at 138°-40°C.

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L-GLUTAMIC ACID CONTENT OF SOME OILSEED CAKES

GLUTAMIC ACID, AS ITS MONOSODIUM SALT, IS extensively used as a condiment for enhancement of taste and flavour. The world production for this purpose amounts to about 15 million lb. per annum, 6 million lb. being manufactured in the U.S.A.[1] and the remainder in Japan and China[2]. It is also used in its free form as a drug in the treatment of mental deficiencies in infants and adolescents[3]. In connection with a scheme for the preparation of amino acids on a commercial scale, it was found necessary, as a preliminary, to carry out a survey of the glutamic acid content of various raw materials. The investigation was confined to the indigenously available oilseeds and seed cakes which are cheap and rich in protein.

In the classical methods of protein analysis, glutamic acid is estimated either by isolation of the hydrochloride or by precipitating the calcium or barium salt[4]. In the latter procedure aspartic acid is separated as copper aspartate. The methods are not very reliable[5,6] as the precipitation of glutamic acid is incomplete, and also amino acids such as serine[7] are precipitated along with the dicarboxylic acids. The methods are still more untrustworthy when applied directly to hydrolysates of complex materials such as oil cakes.

Among the modern methods of analysis, the most reliable is the use of an enzyme from a strain of *Clostridium welchii*-SR12 which specifically decarboxylates glutamic acid. The carbon dioxide liberated by the action of the enzyme gives a measure of the glutamic acid content. The method, which is quick and reliable, has been used in the present work for the determination of glutamic acid in hydrolysates obtained from oil cakes.

The decarboxylase used in this experiment was prepared, as described by Gale[8], from a strain of *Clostridium welchii*-SR12 supplied by American Type Culture Collection. The preparation of the hydrolysates and the manometric measurements of carbon dioxide evolved were carried out as described in a previous communication from this laboratory[9].

Most of the oil cakes examined have a high content of glutamic acid. From the point of view of commercial availability groundnut cake is the most suitable for the manufacture of this amino acid (TABLE 1).

TABLE 1 — L-GLUTAMIC ACID CONTENT OF OILSEED CAKES

OIL CAKE	NITROGEN IN CAKE %	GLUTAMIC ACID IN CAKE	
		g./100 g. dry wt. (present work)	Values reported in literature†
Water melon (*Citrullus vulgaris*)*	11·1	17·2	—
Holoptelea (*Holoptelea integrifolia*)*	10·3	13·0	—
Groundnut (*Arachis hypogea*)	7·8	10·4	8·5[10]*
Tobacco (*Nicotiana tabacum*)*	6·3	9·5	—
Mustard (*Brassica campestris*)	5·4	8·2	—
Til (*Sesamum indicum*)	5·9	7·9	—
Sunflower (*Helianthus annuus*)	5·0	7·0	3·5[11]‡
Argemone (*Argemone mexicana*)*	4·7	6·1	—
Castor (*Ricinus communis*)	4·7	5·2	—
Mowra (*Bassia latifolia*)	2·8	5·1	—
Safflower (*Carthamus indicus*)	2·8	4·7	—
Linseed (*Linum usitatissimum*)	4·0	4·2	2·5[12]‡
Coconut (*Cocos nucifera*)	2·9	3·9	3·6[11]‡
Cotton (*Gossypium herbaceum*)	3·0	3·8	3·3[10]*

* Defatted meal. † Recalculated to the same nitrogen basis as in the present work. ‡ Protein isolated from material.

On the basis of these results glutamic acid has been prepared on a large laboratory scale from this source; the results of the work will be published elsewhere.

The authors wish to thank Dr. M. Damodaran for suggesting the investigation.

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STARCH-SYNTHESIZING ENZYMES IN TAPIOCA (*MANIHOT UTILISSIMA*) ROOTS

THE NATURE AND PROPERTIES OF THE ENzymes concerned in the synthesis of starch in potato, pea and bean have been the subject of investigation by different groups of workers[1]. Hanes[2] first discovered in 1940 the presence of phosphorylase in potato and peas and showed that the enzyme catalysed the formation of amylose from glucose-l-phosphate. Later, Haworth, Peat and Bourne[3] reported the isolation from potato of an enzyme (Q-enzyme) which in association with potato phosphorylase, catalysed the synthesis of amylopectin from glucose-l-phosphate. In a series of papers, Peat and his collaborators[4-10] presented evidence that the Q-enzyme converted linear amylose into branched amylopectin. More recently Sri Ram and Giri[11] reported the presence of phosphorylase and Q-enzyme in green gram (*Phaseolus aureus*). In the present note, a preliminary account of our work on the starch-synthesizing enzymes of tapioca root is reported.

An extract of tapioca roots containing the different enzymes was prepared as follows: Fresh tapioca roots were peeled and sliced using a stainless steel knife. Five hundred grams of this material were soaked for 10 min. in 1 litre of 0·05 per cent sodium hydrosulphite solution. The liquid was drained off and the slices suspended in 150 cc. of distilled water and mashed in a Waring blender. The extract was expressed through a muslin cloth, clarified by centrifuging and preserved at 0°C. after the addition of toluene.

Preliminary tests on the juice showed the presence of phosphorylase, Q-enzyme, and pyro- and glycerophosphatases. When the juice was incubated at *p*H 6 with glucose-l-phosphate[8], the mixture did not develop any reducing power, thereby showing the absence of phosphatase activity with respect to glucose-l-phosphate. Alpha and beta-amylase activities were not present to any detectable extent. The phosphorylase and Q-enzyme were fractionated from the extract by following the procedure described by Bourne and Peat[4] for the separation of the enzymes from potato juice.

The phosphorylase activity of the extract was determined according to Hanes[2], with slight modifications. Di-potassium-glucose-l-phosphate used as the substrate was prepared by the method of Sumner and Somers[12]. The reaction mixture was made up as follows: 10 cc. of 0·1M di-potassium-glucose-l-phosphate were added to 25 cc. of 0·1M citrate buffer (*p*H 6·0). Fifteen cc. of the phosphorylase solution were then added. The mixture was maintained at 25°C. Suitable blanks were run at the same time for making appropriate corrections. The quantity of inorganic phosphate formed was determined by the method of Fiske and Subbarow[13] in aliquots of the reaction mixture after removing the proteins by treatment with 10 per cent trichloracetic acid. The quantity of amylose formed was determined by reacting aliquots of the mixture with iodine according to the conditions described by Hanes[2] and determining the blue colour in a Klett-Summerson photoelectric colorimeter using filter No. 66. The amylose equivalent was calculated using as standard, amylose prepared from tapioca starch by the thymol method described by Bourne, Donnison, Haworth and Peat[14]. The results are given in Table 1. It is evident

TABLE 1 — ACTION OF PHOSPHORYLASE ON GLUCOSE-L-PHOSPHATE

Time (min.)	0	30	60	90	120	150
Increase in free inorganic phosphorus, in 5 cc. reaction mixture, mg.	—	0·038	0·084	0·137	0·179	0·202
Iodine colour* with polysaccharide present in 5 cc. of reaction mixture, $D\frac{66}{1\ \text{cm.}}$	—	0·074	0·180	0·304	0·392	0·480
Amylose equivalent†, mg.	—	0·154	0·375	0·633	0·816	1·000

*Determined with Klett-Summerson photoelectric colorimeter using filter No. 66, and 1 cm. cell.

†Calculated using amylose prepared from tapioca starch as standard; the optical density of iodine colour obtained with 1·0 mg. of amylose was 0·480.

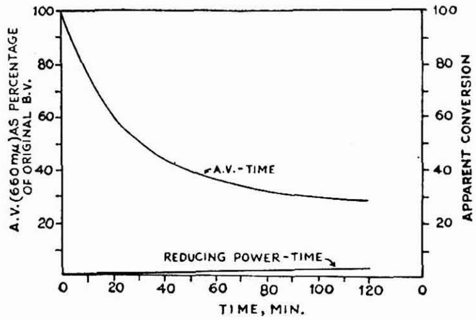

FIG. 1 — ACTION OF Q-ENZYME ON AMYLOSE

from Table 1 that the data obtained are similar to that reported by Hanes[2] with potato phosphorylase.

The method adopted for the determination of Q-enzyme activity was the same as that described by Barker, Bourne and Peat[6] by following the action of the enzyme on amylose at *p*H 7 in citrate buffer. The optical density of the colour obtained with iodine was measured in a Klett-Summerson photoelectric colorimeter using filter No. 66 at known intervals of time. The quantity of reducing sugar formed was also determined in aliquots using the micro-method of Somogyi[15]. The results are presented in Fig. 1. It is evident that the Q-enzyme effects about 70 per cent diminution of the absorption value of amylose with the liberation of only 2 per cent of reducing sugars (as maltose). The results obtained are similar to that reported by Barker, Bourne and Peat with potato Q-enzyme.

Further work on the factors affecting the activities of phosphorylase and Q-enzyme and the nature of the polysaccharides synthesized by the enzymes is in progress and will be reported elsewhere.

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18 *Jan.* 1954

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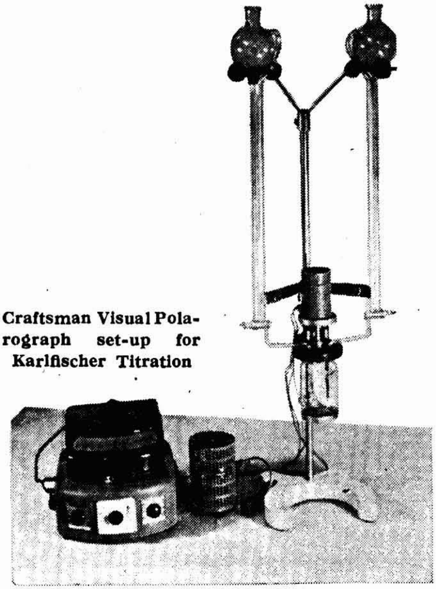

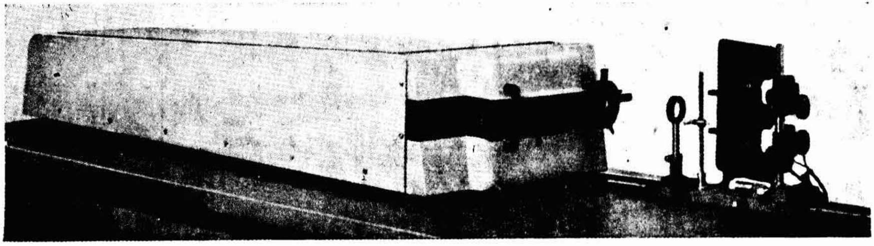

Printed by H. Jacquemotte, S.J., at the Catholic Press, Ranchi, India
Published by the Council of Scientific & Industrial Research, India. Editor : B. N. Sastri, M.Sc.