JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

VOLUME XIV. APRIL, 1950. No. 2.

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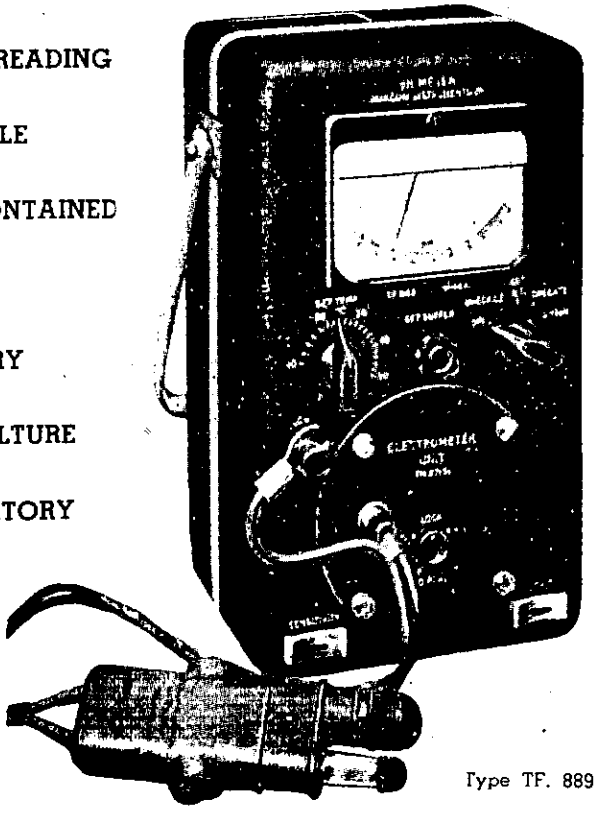

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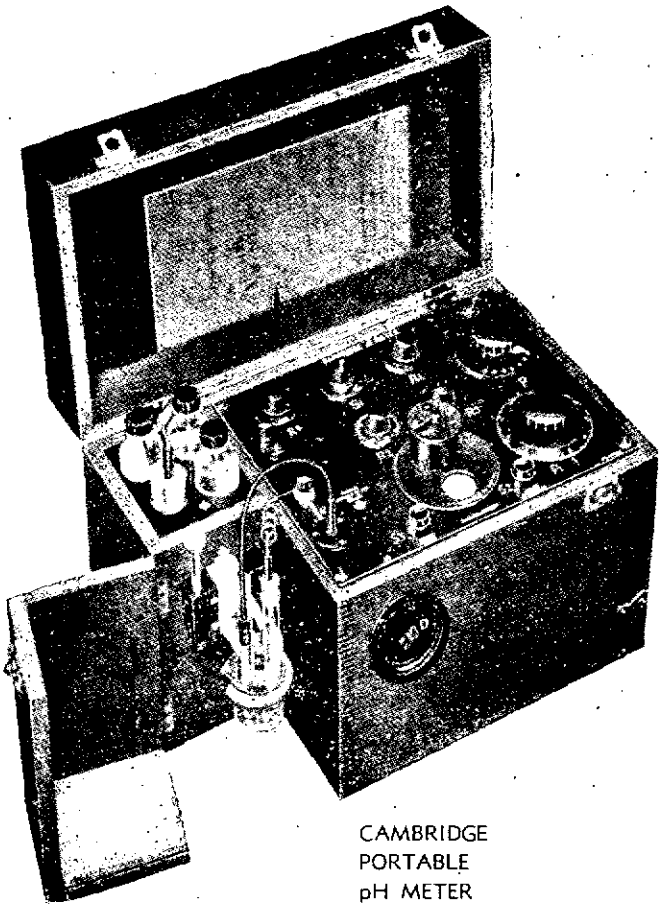

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JOURNAL OF THE
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VOLUME XIV APRIL, 1950 No. 2

IN THE NEW YEAR HONOURS

—LEFT

PROF. F. G. SOPER, C.B.E., Ph.D., D.Sc., F.R.I.C., F.N.Z.I.C.,
University of Otago.

DR. H. E. ANNETT, O.B.E., B.Sc. Agric., D.Sc., F.R.I.C., F.N.Z.I.C.,
Soil Fertility Research Station, Hamilton.

RIGHT—

Editorial . . .

THE HYDROGEN BOMB

The most surprising feature about President Truman's announcement of his Government's decision to proceed with the manufacture of the hydrogen bomb, was that it surprised no one. Prepared beforehand by a few newspaper articles, the public accepted with seeming equanimity the announcement of its probable impending doom. As Einstein says, "Every step (in the armament race between the United States and Russia) appears as an unavoidable consequence of the preceding one. In the end there beckons more and more clearly the general annihilation."

The public cannot now be unaware of the deadliness of the proposed new weapons, but their reaction is based either on the optimistic view that New Zealand is too far away, or a fatalism leading them to believe that annihilation is unavoidable. The weakness of the first attitude is obvious, but the second has a firmer basis. We feel that Professor Einstein is right when he condemns the idea of security through armaments as an illusion. With the new weapons this is particularly true, for there may be no survivors, let alone victors.

It bodes ill that a great nation such as the United States should have to acquiesce in the failure of its diplomacy and employ the mailed fist, a gesture which must be interpreted in many quarters as a lack of faith in the United Nations Organisation, now hospitised on its own soil. It is also sad to realise that despite the boasted internationalism of science, no difficulty is apparent in finding staff to make scientific weapons, either in the United States or elsewhere.

How then can mankind escape? Only the foolhardy would have a ready answer, but whatever the real answer be, we are confident that the fight for man's survival and sanity cannot be won with material weapons, but by drawing on our spiritual resources which seem to be so underestimated and neglected. We are proud of the fact that many scientists show such devotion to the tasks of and loyalty to the ideals of science, thus indicating possession of those resources of the spirit that should enable us to give some leadership and hope in a darkened age. If we are interested in the survival of ourselves, our fellows and our children, it seems incumbent on us to give a little more time to the development of these resources.

CONFERENCE, 1950

Christchurch, August 22nd - 25th

N.Z.I.C. - R.I.C.

Accommodation

Up to March 1st only 147 cards had been returned out of 520 which were sent out. Of these, 132 members have indicated their intention of attending the Conference (approximately half desiring to have accommodation arranged), while 15 have let the Committee know that they are definitely unable to attend. Will the remaining 373 who have not already returned cards, please do so as soon as possible.

Owing to some uncertainty with regard to the dates of Race Meetings, it is already becoming apparent that accurate information regarding accommodation requirements will be essential at an early date. This is particularly the case where members wish to be accommodated at some particular hotel. Hotels will probably insist upon members confirming their bookings and paying a deposit. It appears that very few single rooms will be available.

A further Circular will be sent out not later than April and prompt replies will be essential.

Times of arrival in Christchurch will need to be notified in reply to the April Circular. The Committee will arrange accommodation from Monday night until Saturday morning. Those, however, who want additional accommodation apart from this period will need to make their own arrangements—but please let the Secretary know.

Programme

A symposium has been arranged on "Isotopes" with particular emphasis on techniques.

Papers are invited for additional symposia on:—

"Agricultural and Biological Chemistry."

"Physical and Structural Chemistry."

"Industrial Processes Utilising Organic Materials of N.Z. Origin."

"Analytical Chemistry."

Provision will also be made for suitable papers on other subjects.

THE CONTRIBUTION BY NEW ZEALAND WORKERS TO THE CHEMISTRY OF PLANTS

PART II.—INVESTIGATION OF THE NATIVE FLORA*

By J. Murray.

Resin Acids and Related Compounds:

With two exceptions, the New Zealand members of this group show a close structural similarity to diterpenes, and like the solid diterpenes, they are largely restricted to the pines among the native flora.

One of the key compounds in the series is agathic dicarboxylic acid, first isolated in a pure state from Kauri gum and Manila copal by Hosking in 1929. Kauri gum contains also a few terpene compounds, at least one other resin acid and possibly several neutral diterpenoids as yet uncharacterised. The constitution of the acid has been completely elucidated by the work of Ruzicka with Hosking, and later co-workers in Switzerland (1929-48).

The basic structure of the substance was shown by dehydrogenation, when three products were obtained, agathalene (1:2:5—trimethylnaphthalene), pimanthrene (1:7—dimethyl phenanthrene) and a liquid substance later shown to be a substituted acenaphthene. Agathic acid contains two double bonds and readily cyclises with loss of CO_2 to isonoragathic acid. Taking these facts in conjunction with the isoprene rule, Ruzicka and Hosking were able to put forward a probable formula for agathic dicarboxylic acid; a rigorous proof of the structure and of the finer points of its stereochemistry are dealt with in the work of Ruzicka and later collaborators.

The kauri resin acid is not known to be related in structure to the diterpene kaurene obtained from the essential oil of the tree.

Three other New Zealand pines yield compounds with the same carbon skeleton as agathic acid. From the heart wood of **Dacrydium colensoi**, Hosking and Brandt (1934) isolated manyl oxide, ketomanoyl oxide and a hydroxylated diterpenoid of undetermined affinities. **D. biforme and D. kirkii** yielded one neutral compound, manoöl.

Hosking and Brandt found that both manoöl and manoyl oxide with dry HCl formed manoene trihydrochloride, derived from the parent dicyclic triene. This was identical with a trichloro compound obtained similarly from the dihydric alcohol sclareol, a product of **Salvia sclarea.** All three compounds, too, on dehydrogenation gave agathalene and 1 : 2 : 8—trimethyl phenanthrene.

Ketomanoyl oxide is converted to manoyl oxide by Clemmensen reduction. The chemistry of this group of substances was described in several papers from 1934-7, leading to the structures given below.

A diterpene oxide which may belong to this group is olearyl oxide, present in the high-boiling residues of the essential oil of **Olearia paniculata** (1945). The reactions and derivatives parallel those of manoyl oxide, except that on dehydrogenation the only product obtained is agathalene, even after cyclisation to a tricyclic diterpene.

Perhaps the most notable feature of this small group of diterpenoids is their presence in plants belonging to quite unrelated families—manoöl, manoyl oxide and ketomanoyl oxide in the **Podocarpaceæ**, sclareol in the **Labiatæ** and olearyl oxide in the **Compositæ.** To these can probably be added marrubin, a lactone from horehound (Labiatæ).

***Note:** In the first section of this part (October, p. 130) the discovery of the identity of dacrene, sciadopitene and phyllocladene was erroneously attributed to Brandt. The identification was actually due to Dr. Briggs.

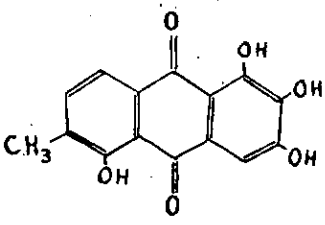
The resin from the wood of the miro **(Podocarpus ferrugineus)** was subjected to a preliminary study by Easterfield in 1910, while a more complete investigation was carried out by Brandt and Neubauer (1939-40). The main constituent is a phenolic diterpenoid, ferruginol, which dehydrogenates with selenium to pimanthrene and a retenol, thought to be 8-hydroxy-retene. The production of pimanthrene is anomalous and is presumably due to the presence of the adjacent phenolic group. Retene was obtained by dehydrogenation of the fully hydrogenated material. Ferruginol is closely related in structure to hinokiol, obtained from a Japanese pine. In addition to ferruginol, the resin of the miro contains a-pinene and possibly other terpenes, and a mixture of two resin acids, miropinic and isomiropinic acids, $C_{20}H_{30}O_2$. On dehydrogenation they yield pimanthrene, but their precise structures remain to be determined. Miropinic acid is believed to be identical wfth resin acids obtained in small amount from the wood of **Dacrydium biforme, Dacrydium kirkii** and perhaps other **Dacrydium** species (1937). A minor modification in the proposed structure of ferruginol followed from a partial synthesis by American workers (1940).

A substance which may be similar to ferruginol is totarol, a secondary alcohol isolated from the resin of **Podocarpus totara,** by Easterfield (1903-10). Further work was carried out by Short and Stromberg (1937), at Manchester, but this research has apparently not yet been completed. Dehydrogenation with selenium gives 1-methyl-7-hydroxyphenanthrene, while the reduced substance gives a methyl isopropyl phenanthrene not identical with retene.

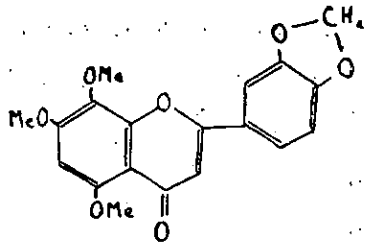
The heart-shakes of kahikatea **(Podocarpus dacrydioides)** and of rimu **(Dacrydium cupressinum)** consist almost entirely of podocarpic acid. The chemistry of this substance has been studied by several workers, including Easterfield and Aston (1910) and Sherwood and Short (1938), and a mixture of stereoisomers of podocarpic acid has since been synthesised. A recent development of interest is the preparation from podocarpic acid of a substance with strong oestrogenic properties (Brandt, 1948). This was not unexpected, since a similar compound has been prepared from abietic acid. It seems quite possible that useful compounds of this nature could be readily and economically prepared from podocarpic acid or similar New Zealand diterpenoids; podocarpic acid in particular could be obtained in considerable quantity, and in a very satisfactory state of purity. The possibilities of this should be more thoroughly explored than has been the case up to the present.

The three remaining resinols belong to an entirely different type. They are matairesinol and conidendrin from the matai **(Podocarpus spicatus)** and isoölivil from maire **(Olea cunninghamii).** The first two were obtained by Briggs and co-workers in 1935, and they verified the structure given for matairesinol by Haworth and Richardson about the same time. A small amount of an acid was isolated also. The resinol in the heart-shakes of the maire was found to be isoölivil by Briggs and Frieberg (1937), and support was obtained for the formula proposed shortly before. A number of resinols belonging to this group are rather widely distributed among plant families, and some of them have useful applications in medicine and agriculture. Matairesinol has anti-mitotic properties and tumour necrotising action in cancer of mice.

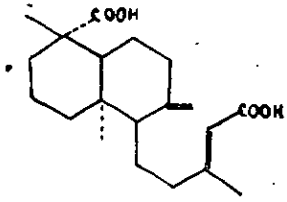
There is much scope for future research in this field, both in the investigation of new compounds and in seeking applications for those already known. Probably there are a considerable number of minor constituents present in the pines which have not yet been reported.



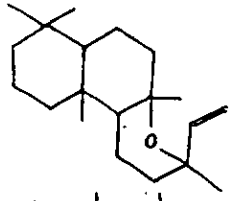
Areolatin



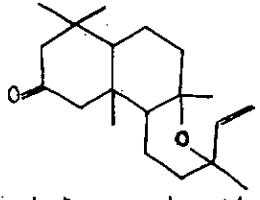
Heliternin



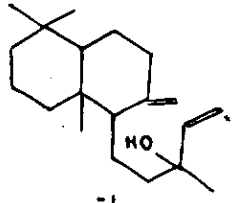
agathic acid



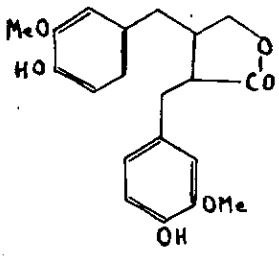
manoyl oxide



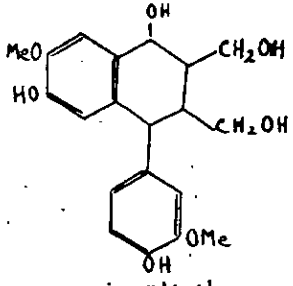
kelomanoyl oxide



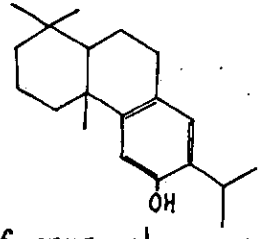
manoöl



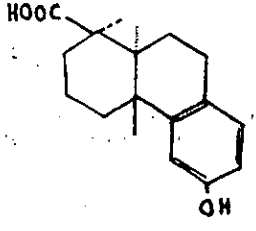
malairesinol



isoölivil



ferruginol



podocarpic acid

COLOURING MATTERS

Until recently, the chemistry of the New Zealand plant pigments was largely neglected, the only published work being that of Perkin on vitexin and exploratory experiments on the Coprosma genus by Aston (1917-23). However, research on several plant pigments is progressing in different centres at the present time, particularly at Auckland University College, where Dr. Briggs is engaged on a comprehensive study of the Coprosma pigments. Four **Coprosma** species have now been investigated (1948-9) in detail, and all contain pigments belonging to the anthraquinone series, both free and as glycosides. Some of these species are notable for the very high yields (up to 24% by weight of the dried bark), and for the number of separate substances which they contain. The separation of these complex mixtures of pigments has been made possible largely by the use of chromatography with magnesia as absorbent. In this way as many as a dozen pure compounds could be obtained from a crude extract.

Coprosma australis: Three substances were identified in the crude pigments—morindin, the corresponding aglycone morindone, and rubiadin-1-methyl ether, in a total yield of 17%.

Coprosma areolata: The dried bark of this tree contains no less than 23% by weight of pigments comprising rubiadin-1-methyl ether and a new anthraquinone colouring matter, areolatin. The structure of the latter was shown by degradation and synthesis to be that of 1:5:6:7-tetrahydroxy-2-methyl anthraquinone.

Coprosma lucida: This plant contains a large number of individual pigments, both in the free state and combined as glycosides. Only the sugar-free pigments are considered in the initial publication (1949), and seven of the eight were identified. One of these, lucidin, is a new compound and is probably 1:3:5-trihydroxy-2-methyl anthraquinone. Four of the remaining colouring matters, namely anthragallol, anthragallol-2-methyl ether, rubiadin and 3-hydroxy-2-methylanthraquinone have not previously been reported to occur free in nature.

Coprosma acerosa: Although the most recent botanical studies indicate that this plant and **C. lucida** are widely separated phylogenetically, their pigment compositions are very similar. C. acerosa differs from the preceding species in containing a smaller proportion of lucidin, and in yielding rubiadin-1-methyl ether with only a trace of the unmethylated pigment. Anthragallol is present only in the form of its methylated derivatives.

Coprosma rubra yields three pigments, including rubiadin-1-methyl ether.

In addition to the anthraquinone colouring matters, all the Coprosma species examined contain asperuloside, a colourless glycoside probably of a furane type of uncertain affinities. It is known that most of the remaining species of this genus contain pigments apparently belonging to the same class, and we look forward with interest to further work in this field.

Vitex littoralis 'Puriri.' Some of the yellow wood of this tree was sent to Perkin, who extracted from it two colouring matters, vitexin and homovitex as glucosides. The researches of Perkin (1900), Barger (1906), and Peteri (1939) have led to two alternative structures for vitexin.

Melicope ternata "Wharangi." Briggs and Locker (1949) have isolated four new methylated flavonols from the bark of the wharangi, elucidated their structures and synthesised one of them, together with other related flavonols. These substances, meliternin, meliternatin, ternatin and wharangin are closely related in structure, differing only in the number and arrangement of methoxy and methylenedioxy groups; the first mentioned was prepared by synthesis.

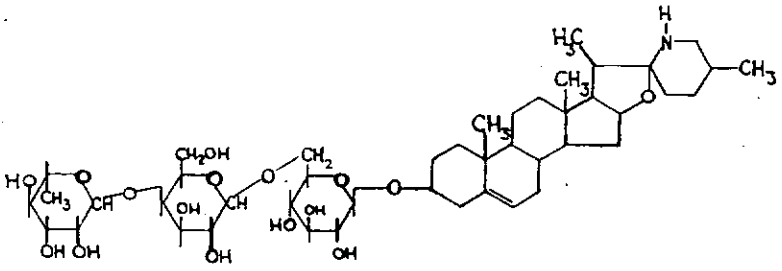
No other research on the colouring matters of New Zealand plants has been published, although several have been and are being investigated. In a few cases pigments have been obtained in the course of other work (e.g.), quercetin was shown to be present in tutin extract (1910) and later in the wood of matai. Anthocyanin pigments are known to be widespread, but they do not normally repay extensive investigation.

ALKALOIDS

The New Zealand flora, unlike that of Australia, is apparently rather deficient in alkaloid-containing species. Even families and genera which are noted for the production of alkaloids are commonly found in this country to be free of basic constituents. To date seven species are known to yield alkaloids, and there are a few others which contain small percentages of bases. Some native plants are believed to be poisonous, although the toxic principles have not been identified.

Laurelia novæ-zelandiæ 'Pukatea.' The pharmacological properties of this tree have been known since at least 1870, although it was not until 1910 that Aston isolated a crystalline alkaloid (pukateine) from the bark, and showed that two others (laureline and laurepukine) were also present. These substances were subsequently investigated by Barger and Swiss workers (1931-2), who succeeded in elucidating their constitutions and in confirming two of these by synthesis. Pukateine is a strong analgesic with a similar action to that of morphine, which, indeed, it resembles in structure.

Solanum aviculare 'Poroporo.' Levi (1930) extracted the green berries and leaves, obtaining a glucosidic alkaloid, which was later (1942) identified as solasonine by Briggs and co-workers. A considerable amount of work has been done by Briggs and his school on this alkaloid, which is present also in the species **S. xanthocarpum** and **sodomæum**, while closely related alkaloids are solauricine from **S. auriculatum** and solmargine from **S. marginatum**. Solasonine differs from solanine, the poisonous principle of the



SOLASONINE

potato, only in having an extra oxygen atom, and the structure shown has been put forward by Briggs, based partly on work subsequent to 1942 (when a different formula was proposed), and partly on the structure of solanidine elucidated by Swiss and American workers (1942-1945). Solmargine differs from solanine in having two extra oxygen atoms, and in having a disaccharide residue instead of a trisaccharide, while solauricine is isomeric with solasonine and very similar both physically and chemically to it.

Sophora species. Several New Zealand species have been investigated by Briggs and co-workers (1937-48), and found to contain alkaloids commonly

noted in this genus. The results are particularly interesting in the light they throw on the botanical classification of the species. Thus **S. microphylla** seeds yield mainly methylcytisine and matrine with a small amount of cytisine and sophochrysine, while the chief constituent of the alkaloid fraction of the seeds of **S. tetraptera** is matrine. A little methylcytisine and sophochrysine are also present. The kowhai of the Chatham Is. is normally listed as a separate species, **S. chathamica**, but the alkaloids in the plant are identical both in nature and proportion to those in **S. microphylla**. It seems likely from this that the two species are identical, or at least that the difference between them does not warrant species rank. A variety of **S. microphylla** growing near Auckland was analysed in the same way (1948) and the major alkaloid is methyl cytisine, with some cytisine but only a very low percentage of matrine. This notable difference from the normal constitution of **S. microphylla** is probably sufficient to establish the Auckland plant as a separate species.

The Leguminosæ family (other than Sophora). White (1943-6) has published the results of an extensive survey of more than 200 species, both native and introduced. No alkaloids were detected in the New Zealand species examined (genera **Corallospartium, Carmichælia, Chordospartium, Clianthus** and **Notospartium**). A number of Acacia species examined were found to contain β-phenylethylamine and tryptamine; the latter has not previously been reported to occur in plants. A new alkaloid, calycotomine, was isolated from **Calycotome** and **Cytisus** species, and some structural work on it is reported. Otherwise, the plants examined were found to contain the alkaloids common to this family. Some of the plants had been studied in Europe, and in a few cases White's results differ from those reported in the literature. Generally, however, the alkaloid content of these naturalised species was very similar both here and in their native habitat. With some of the common plants, the distribution of alkaloid throughout the plant was studied, general conclusions being that in the **Papilionaceæ** alkaloid moves upwards and outwards in the plant, particularly at flowering, and usually accumulates in the seeds. There is a definite time-lag between rapid growth and the accumulation of alkaloid in the plant tissues.

Senecio kirkii: The members of the **Senecio** genus very frequently produce alkaloids, but thus far only one of the 30 or so New Zealand species has been investigated. Briggs, Mangan and Russell (1948) have isolated a new alkaloid from **S. kirkii**, and have reported initial degradative experiments. This substance, senkirkine, resembles some of the alkaloids found in other species in giving on hydrolysis an acid (senecic acid) and an alkanolamine. Senecic acid has been found in the alkaloids of four other species, but the base was not identified.

At least three other New Zealand **Senecio** species contain alkaloids, so an interesting field is likely to be opened up.

Ergot alkaloids. There has been a certain amount of work done with New Zealand ergot samples, notably by Metcalf (1943) and Hassall (1944). The alkaloidal content is similar to that of European specimens, except that ergometrine appears to be absent.

A few other New Zealand plants are known to contain alkaloids, usually in small amounts, but they have not been thoroughly examined as yet.

MISCELLANEOUS COMPOUNDS

Tutin.

Easterfield and Aston (1900-1) isolated the exceedingly poisonous substance, tutin ($C_{15}H_{18}O_6$) from the seeds and leaves of the 'tutu' plant (**Coriaria**

species). This plant has been responsible for much poisoning of stock in New Zealand, particularly in the early days of the colony, and most of the related species in other countries are believed to be toxic also. The European species yields a closely-related substance, coriamyrtin, while the Japanese varieties contain another very similar compound. These poisons are members of a small group of compounds which are apparently oxygenated sesquiterpenoids. A large volume of work has appeared on picrotoxinin, the most important member of the group, the most recent of which is due to Slater (1943-9) in New Zealand and Suter and Schlittler (1949) in Switzerland, but the structure of the substance has not yet been elucidated. Tutin is a lactone with a terminal methylene group and at least one alcoholic hydroxyl group, but its relationship to picrotoxinin is still obscure. All three species of tutu contain about 0.05% of tutin.

Occasionally certain areas in New Zealand produce poisoned honey, and recently Sutherland was able to isolate the principle causing this (1946). The poisoned honey yielded a new substance, mellitoxin, which appears to be a hydroxylated tutin, $C_{15}H_{18}O_7$. A search for this substance in the tutu plant gave negative results, but it was found in the honey-dew secreted by the hopper Scolypopa australis when feeding on the plant and it was obtained from this by the bees.

Karakin. The poisonous kernels of the karaka tree, **Corynocarpus lævigata**, contain among other substances a glycoside, karakin. This was first isolated by Skey (1871) and has been the subject of study by several New Zealand chemists, including Easterfield and Aston (1901-3), Carrie (1934) and Carter (1943-9). The hydrolysis of karakin is evidently a complex process, but the first step is believed to result in the production of hiptagenic acid glucose derivatives and CO_2, while the final hydrolytic products are glucose and hiptagenic acid. Hiptagenic acid is also obtained from a glycoside present in an East Indian tree **(Hiptage mandablota)**, and the recent identification of it with β-nitropropionic acid will be of interest to plant biologists. There are only two compounds containing a nitro group known to be produced in nature, the other being the antibiotic chloromycetin, in which the nitro group is attached to a benzene nucleus. It is not yet known whether the free nitro group is present in the parent karakin, and it will undoubtedly be very interesting to see the results of the further investigations now proceeding.

The poisonous nature of the glycoside is presumably due to the β-nitropropionic residue.

Methyl mercaptan. The unpleasant odour of the Hupiro (**Coprosma foetidissima**) has been shown by Sutherland (1948) to be due to methyl mercaptan, which was obtained in small yield. This is an unusual plant constituent, and it would be interesting to determine whether it is really present in the plant in a free state, or is liberated from some more complex form by enzymatic hydrolysis.

Methyl salicylate was shown by Briggs and Taylor (1947) to be responsible for the odour of the leaf stalks of the fern **Asplenium lamprophyllum.** The closely related species **A. bulbiferum** apparently does not contain the ester.

Carbohydrates, etc. The gums present in many New Zealand plants have been almost entirely neglected in this country, probably because of the very considerable difficulties encountered in working with these substances. McIlroy (1944) obtained from **Phormium tenax** gum an aldobionic acid yielding a uronic acid and a pentose. The calcium salt of the acid was also present. Despite the fact that an important New Zealand industry was

founded on Phormium tenax, it is surprising to find so little known of its chemistry, although there are many references to various industrial applications. The hemicellulose of the plant has been studied by Brandt (1937) and by McIlroy and co-workers (1945-9). The latter have put forward evidence for the formulation of the hemicellulose as an aldotrionic acid with probably two nine-unit xylose chains attached to its terminal xylose residue. The aldotrionic acid itself consists of two xylose units and one glucuronic acid residue. It may be mentioned in passing that various parts of Phormium tenax contain pigments and a fixed oil, although there is little or no published work on them.

Saponins. There is no published research on any saponin constituent of a New Zealand plant, although tests have shown that the following species probably contain appreciable amounts:—**Tetragonia expansa, Dodonea viscosa, Knightia excelsa, Chenopodium** species, **Pittosporum crassifolium, P. eugenioides** and other species, **Pseudopanax** species, **Olearia macrodonta** and **Pomaderris** species.

In concluding this survey, it may be pointed out that it was impossible in the space available to give an adequate account of the chemistry of any particular plant, and frequently no reference has been made to early workers or published material. However, normally, the early literature is reviewed in the later papers on each subject. Many articles and papers have been written dealing with practical aspects of the extraction, uses, etc., of kauri gum, Phormium fibre and tannins, but in this survey only work directly related to the chemistry of these substances has been noted. In addition there is a very considerable volume of unpublished work and partly-completed researches, particularly on plant oils and pigments which for various reasons have not been mentioned. However, it is hoped that sufficient has been given to indicate the work which has been done, and perhaps some of the directions in which it could profitably be continued or extended. No doubt there are many plants yet untried, but which will yield results both interesting and valuable (e.g., saponin-containing species).

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Paesia scaberula (Scented fern).
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Phyllocladus trichomanoides (Tanekaha, Celery Pine).
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Pittosporum eugenioides (Tarata, Lemonwood).
Carter and Heazlewood, J.S.C.I. (1949), **68**, 34.
Podocarpus dacrydioides (Kahikatea, White Pine).
Brandt, Nature (1949), 892 (Podocarpic acid).
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Briggs, Mangan and Russell, J.C.S. (1948), 1891.
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ITEMS OF INTEREST.

We have been receiving a number of Unesco publications, including the "Courier" (published monthly), a pamphlet on "The Question of Establishing United Nations Research Laboratories," and a specimen copy of the "Bulletin on Narcotics," which will be published quarterly at $2.00 per year. Any reader who is further interested should write to the Editor. We also receive on exchange the publications of the other Institutes in the British Empire and the French "Chimie Analytique."

Dr. H. Bloom, who has been promoted to the status of Senior Lecturer at Auckland University College, and Mr. G. M. Wallace have joined the Journal Committee.

Mr. and Mrs. D. D. Perrin have returned to New Zealand and are stationed at Ruakura Animal Research Station.

Dr. I. Reifer, who has returned to Poland after some years at the Plant Chemistry Laboratory, Palmerston North, has been compelled to resign as a Fellow owing to difficulties over exchange. In a letter to the Hon. General Secretary, Dr. Reifer extends his good wishes to members of the Institute, and thanks them for the honour done in electing him to the Fellowship. His address is: Warszawa, Wiejska 15/3, Poland.

Mr. M. L. McGlashan, formerly Canterbury Branch Editor, and Mrs. McGlashan are living at Reading, where he is doing post-graduate research in thermodynamics under Prof. Guggenheim.

Although priority has been granted to the faculty of engineering in the plans for the new Canterbury College at Riccarton, no announcement has been made about the Chemistry Department, which is at present grossly overcrowded.

ION EXCHANGE AND SOME ANALYTICAL APPLICATIONS.

W. S. Fyfe, University of Otago.

(Summary of a lecture delivered at the Annual Conference, 1949.)

All ionic solids exhibit ion exchange to some extent. Surface ions are bound to the lattice with a lower energy than similar ions in the interior of the crystal. When placed in a polar solvent surface ions become solvated, which further decreases the bonding. A marked dissociation may thus result. If a foreign electrolyte is added, it is logical to expect a certain amount of exchange to occur, particularly when the foreign ion is held by the lattice with a larger bonding energy than the original ion. It would thus appear that the amount of exchange might be proportional to the area of crystal surface available. This is why certain structural types with the so-called zeolite lattice are so well suited for exchange reactions. The extent of exchange depends largely on the following factors:—

1. Forces binding ions in the lattice.
2. Relative valence of the exchanging ions.
3. Concentration of the exchanging ions.
4. Relative size of the ions (solvated).
5. Accessibility of the lattice to entering ions.

Types of Substances with Useful Exchange Properties.

Natural and Synthetic Aluminosilicates.

These belong chiefly to the clay and zeolite families. Feldspars also show marked exchange, particularly at high temperatures. Synthetic zeolites are prepared either by fusion or precipitation by adding sodium silicate to aluminium sulphate or sodium aluminate. Gel materials have a higher capacity for exchange than fusion prepared materials.

Carbonaceous Exchangers.

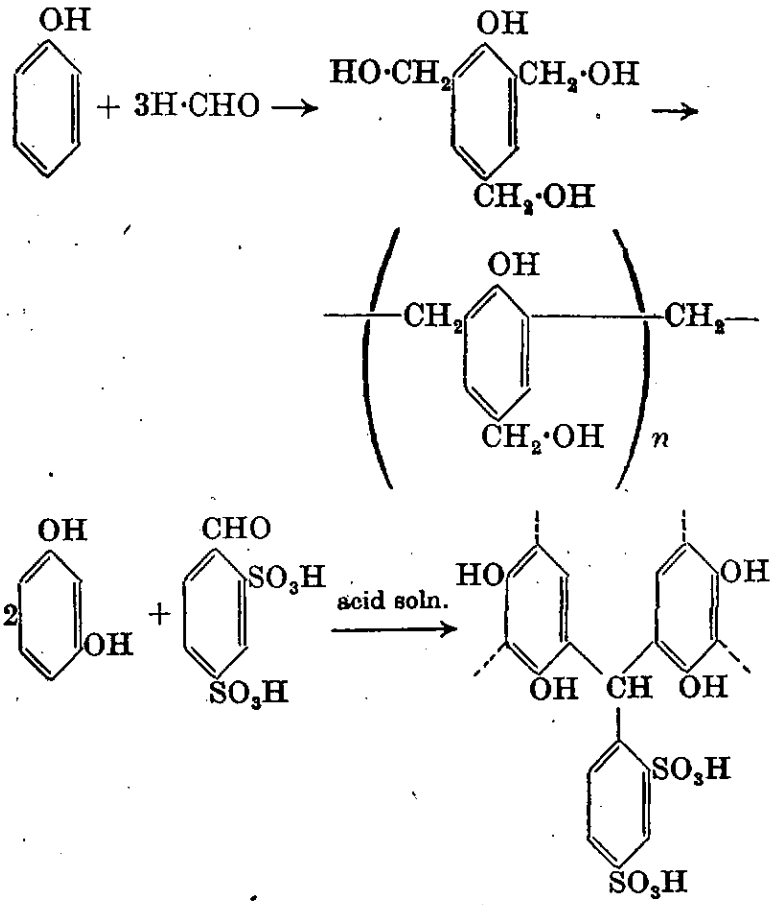
These materials preceded the true exchange resins and were first prepared by Adams and Holmes, who later synthesised the first high polymer exchangers. Commercially such materials are made by the partial sulphonation of coals. They are completely stable in acid solution. A marked advantage of such materials is that they do not impart silica to water passing through them. In physical properties they resemble the graphitic acids.

Resinous Exchangers.

These types have proved most suitable for fundamental studies on ion exchange as an exact knowledge of active groups and purity can be obtained. It is also becoming possible to produce "tailor made" resins to fit a particular process. The essential feature of an exchange resin is a highly-polymerised hydrocarbon skeleton of low solubility carrying as large a number as possible of active exchange groupings. The synthesis of two typical resins is illustrated in fig. 1. The ionisable exchanging groups are the carboxylic, sulphonic and phenolic groupings. These groups are active at different pH values.

Anion Exchangers.

Adams and Holmes also synthesised the first anion exchangers which contained active amino groups. They are generally produced by the condensation of aromatic amines with formaldehyde.



The various types of exchangers have their particular advantages and limitations. Silicates seldom have a large capacity and little modification of the original structure can be made. However, the writer has found that in the zeolite natrolite, the sodium could be almost entirely replaced by copper, chromium and ferric iron. They are completely unstable to acids, but can be used over a wide temperature range.

The activity of organic resins depends on the degree of ionisation of the active groups, which in turn depends on pH. Thus it is possible to control the exchange process to some extent. They are generally completely stable to acids and alkali. Exchange in resins is generally more rapid than in silicate types. In column separations some resins show troublesome swelling properties and may be rather soluble, which is undesirable in tracer work. Most resins cannot be used above 60° C., but zeolites are quite stable up to 200°, and feldspars could be used at even higher temperatures.

The Exchange Process.

To illustrate the exchange process the case of a natural zeolite and an exchange resin will be briefly considered.

(a) Exchange in the natural zeolite analcite—

Analcite ($NaAlSi_2O_6.H_2O$) is a typical cubic zeolite with an open framework formed by linked silicon-oxygen and aluminium-oxygen tetrahedra. The structure contains large channels and cavities forming an interstitial space of about 30% of the crystal volume. Those channels are normally occupied by water molecules. These water molecules can be replaced by other neutral molecules like ammonia, mercury and iodine, and the cations can be replaced with little alteration of the unit cell dimensions. A point of particular interest arises from the position of the sodium ions. In the unit cell (Z, the number of molecules = 16) there are twenty-four equivalent positions in which these can be placed and it is necessary to fill only sixteen. This conclusion was checked by replacing the sodium atoms with silver. It was found that the sixteen silver atoms distributed themselves among the twenty-four positions. This distribution must be random for the substance still maintained cubic symmetry. Whether this random distribution is an average in space alone, or in space and time, cannot be determined by X-rays. The possibility of replacing the ions suggests that the latter is true. It is this movement which permits sodium to diffuse out of the lattice and silver to diffuse in when the zeolite is placed in a solution of silver nitrate. It appears that base exchange in zeolites is due to the channels, the presence of water molecules, and to empty spaces in the lattice which allow more diffusion than if all the spaces were occupied. It is of considerable interest that R. M. Barrer has recently synthesised hydrogen silicate types.

(b) Exchange in the resin Dowex-50—

This is a recently developed cation exchange resin containing sulphonic acid groupings only. The simple constitution of this resin has made it one of the most suitable for fundamental studies. It is an aromatic high polymer stable in both acid and alkaline solutions. It is produced in small spherical particles of a gel nature. To obtain the exchange capacity, Dowex can be titrated as a strong acid with alkali. If a particle of the resin is placed in a solution of sodium chloride an equilibrium is set up. Two points of view are held regarding this equilibrium; (1) that it is a Donnan type equilibrium in which the surface of the particle acts as a membrane and the resin is the non-diffusible anion, and (2) that the equilibrium is governed by the law of mass action and that the concentration differences are due to the different activities in the solution and resin-gel phase.

When the hydrogen form of the resin is placed in a solution of sodium chloride equilibrium is established as follows:—

$$H\,(resin) + Na\,(soln) \rightleftharpoons H\,(soln) + Na\,(resin)$$

On the Donnan concept

$$aNa\,(resin).\ aCl\,(resin) = aNa\,(soln).\ aCl\,(soln)$$

$$aH\,(resin).\ aCl\,(resin) = aH\,(soln).\ aCl\,(soln)$$

$$K = \frac{Na\,(resin).\ H\,(soln)}{Na\,(soln).\ H\,(resin)}$$

This latter result is exactly what would be expected from mass action. At the present time the mass action conception is favoured.

Both types of substance have in common the large non-diffusible anionic framework with ionised cations ready for exchange. Cellulose compounds for the same reason show exchange. In all cases diffusion into the substance is facilitated by wide capillaries.

A feature of some interest is the order of exchange among cations. Some of the established series are as follows:—

Cs, Rb, K, Na, Li

Ba, Sr, Ca, Mg

Th^{4}, La^{3}, Ba^{2}, Na.

Two features are obvious; firstly that with ions of different valencies the ion with the higher charge is held more strongly, secondly that among ions of the same charge the order is the converse of the ionic size. It would appear that the critical factor is the ionic potential of the hydrated ion. The order has also been predicted from considerations of a°, the distance of closest approach of the ions given by the Debye-Huckel equation. A difference between the state of affairs in a natural zeolite and a resin may arise from the different dimensions of the channels into the interior of the crystal. In most zeolites these channels are seldom more than about 3A° in diameter, which would mean that most of the water around the solvated ion would be stripped off before the ion could enter a channel. In the case of resins the channels are of various diameters and some large molecules have been shown to enter quite easily.

Analytical Aspects of Ion Exchange.

Only brief mention of these will be made here as full details may be found in the various references.

One of the major uses of resins has been in the concentration of solutions too dilute to be analysed by ordinary means. The process generally involves a primary concentration on the resin followed by elution and polarographic analysis. Accuracy at least equal to that obtained spectrographically is claimed. (1)

In three outstanding cases ion-exchange resins have proved valuable in the separation of substances of similar analytical properties—

(a) The rare earths. (2)

(b) The amino acids. (1)

(c) Radio-active fission products. (2)

The sharpness of a separation depends on the following factors:—

1. Difference in exchange potential of the substances.
2. Nature of eluent.
3. Length of column. Isotopes have been separated on very long columns.)
4. Degree of column loading.
5. Flow rate.
6. Physical state of exchanger.

Separations may be very sharp when one of the substances is too large to enter the structure. This has been reported in the separation on natural zeolite of NH_4 and $N(CH_3)_4$ ions.

Resins have also found use in the removal of ions that normally interfere in an analytical procedure. For example, the phosphate ion interferes in the determination of sodium by the zinc uranyl acetate method and in the determination of calcium by oxalate. In such a case the anion would be removed by an anion exchange resin.

In qualitative analysis the use of exchangers can simplify many separations. Thus the writer has found it possible to rapidly separate the metals of group II. and such mixtures as Fe, Ni, Co, Cu, Cr.

As yet the number of quantitative analytical procedures based on ion exchange are small. A great deal of research has to be carried out on the determinations of equilibrium states reached under ordinary conditions of flow rate to estimate the accuracy attainable. In many cases ion exchange methods cannot be expected to improve on standard methods, their chief advantage being that they may greatly shorten the time of analysis where maximum accuracy is not necessary.

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General.

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ELECTION OF FELLOW.

Professor J. Ivon Graham, who came to New Zealand in August last to take up the chair of Coal Mining at the School of Mines, University of Otago, has been elected a Fellow of the New Zealand Institute of Chemistry.

Before leaving England Professor Graham was Adviser on Scientific Aspects of Underground Problems, in the Scientific Department of the National Coal Board of Great Britain and has had extensive experience conducting investigations on spontaneous combustion and atmospheric conditions in coal-mines, and on the treatment of coal by high-pressure hydrogenation.

Professor Graham is a Fellow of the Royal College of Science, Ireland, an M.A. of Cambridge, an M.Sc. of London, and an 1851 Science Research Scholar. He is also a Fellow of the Royal Institute of Chemistry, a Fellow of the Institute of Fuel, and has been a member of the Council of the Institution of Mining Engineers for the past twenty years.

New appointments at Canterbury College are Dr. T. Hagyard as Senior Lecturer in applied chemistry, and Messrs J. Austin, J. Beckwith, and M. Christensen as Junior Lecturers.

Dr. R. E. Corbett returned to Dunedin last month after gaining his Ph.D. at Cambridge. Mr. C. L. Carter has also returned after doing some research at Edinburgh.

Mr. A. I. Biggs, of Singapore, is spending his furlough at Canterbury College.

Dr. O. F. Nauen has left S. W. Peterson and Co., Wellington, on being appointed an examiner in the Patent Office.

Mr. G. Dingley, lately of Dominion Breweries, Otahuhu, has been appointed Chemist to Messrs Newdick Bros., manufacturers of cake and biscuits, Auckland.

LABORATORY ASSISTANTS' EXAMINATIONS.

1949 PASSES.

Theoretical Chemistry.

Bush, L. S.; Cross, J. A.; Hornby, D. W.; Johnston, D. M.; Trewern, Lillian C.

Elementary Colculations.

Bush, L. S.; Cross, J. A.; Gee, Beverley C.; George. J. S.; Hornby, D. W.; McLean, A. J.; O'Callaghan, M. L.; Taylor, June S.; Underhill, A. P.; Wood, R. D.

Elementary Physics.

George, J. S.; Johnston, D. M.; Loftus, J. M.; Trewern, Lillian C.

Practical Chemistry.

Cross, J. A.; Dickinson, G. W.; Fisher, Judith E.; Henry, D. F.; Hornby, D. W.; Hull-Brown, I.; McLean, A. J.; Mincher, P. R.; Russell, Vigette V.; Taylor, June S.

Photography.

Saunders, I. D.; Trewern, Lillian C.

We publish below some of the papers set in the 1949 Laboratory Assistants' Examination.

CHEMISTRY.

November, 1949. Time: Three (3) Hours.

Six Questions. Attempt Question 1 and 5 others.

1. (a) 0.267 grams of a metallic oxide on reduction gave 0.230 grams of metal. Find the equivalent of the metal.
   (b) Excess phosphorus is burnt in jars of nitrous oxide, nitric oxide and air—80% Nitrogen, 20% Oxygen. What volume of Nitrogen will be left in each case? Express your answer as a fraction of the original gas.
   (c) 10 ml of Caustic Soda are completely neutralised by 14.5 ml of standard acid, 10 ml of which in turn are neutralised by 8.8 ml of N/10 Sodium Carbonate. Find the strength of the Caustic Soda in grams per litre: Na = 23. O = 16. H = 1. C = 12.
2. How would you distinguish between the various oxides of lead, copper and iron?
   In your answer, describe their appearance and their reaction with alkali, mineral acid and on heating.
3. **Define:** Elements, Acid, Valence.
   State: Charles' Law, Law of Multiple Proportions.
   Explain the process and principles underlying:—
   Separation of Gases by diffusion.
   Purification of salts by fractional crystallisation.
4. What are the principal commercial sources of Sucrose?
   Plant A contains Glucose and plant B Sucrose:
   Describe the tests that would confirm this.
   How is White Sugar obtained from Raw Sugar?
   How is Glucose obtained commercially?
   How is Alcohol obtained from a Sugar?

5. Write a short chemical account of **one** of the following:—
   (a) Fixation of atmospheric nitrogen.
   (b) Ionic dissociation theory applied to Acids and Alkalis and Salts.
   (c) Uses of Coke in Industrial Chemical processes.
6. (a) How is Magnesium obtained from the common natural sources?
   (b) What are some of its principal alloys and their uses?
   (c) Give Name, Formula and brief description of three of its compounds.
7. How would you prepare a small quantity of bromine in a laboratory? Write the equation and describe the visual changes when:—
   (a) Bromine Water is added to acidified potassium iodide solution.
   (b) Burning phosphorus is plunged into bromine vapour.
   (c) Sulphuretted Hydrogen is bubbled through bromine water.
   (d) Given a glass jar of bromine vapour and one of nitrogen peroxide, what chemical test would you make to distinguish them?

ELEMENTARY PHYSICS.

November, 1949. Time: Two (2) Hours.

Attempt all questions which are of equal value.

1. Define Force and explain the resolution of forces.
   Distinguish between weight and mass.
   A weight of 5 tons is supported from the jib of a crane which makes an angle of 30° with the vertical post. The top of jib is level with the top of the post and is supported by a rope fixed to the top of the post and to the top of the Jib.
   Calculate the stress in the Jib and the pull on the rope supporting the Jib.
2. (a) Define Surface tension and give an account of some simple experiment to demonstrate the existence of surface tension.
   (b) What effects are observed when a clean tube open at each end is placed vertically in (a) Mercury; (b) Water.
   (c) What is the effect on surface tension of adding substances such as soap to water? What use is made of this effect?
3. For what purposes are thermostats used? Describe the construction and operation of any type with which you may be acquainted.
4. (a) Define Latent Heats.
   (b) What is the effect of pressure on the Boiling point of a liquid.
   (c) Explain an elementary refrigeration cycle.
5. State laws of reflection and define and give formula for the focal point of a curved mirror.
   Discuss and illustrate by diagrams the formation of images by (a) plane; (b) concave (spherical and paraboloid) mirrors.
6. What do you understand by Electromagnetic induction?
   How is this principle made use of in the operation of an induction coil and an A.C. motor?

ELEMENTARY CALCULATIONS.

November, 1949. Time: Two (2) Hours.

All questions should be attempted.

1. What is the formula for finding the volume of a sphere?
   If the lifting power of a hydrogen-filled balloon equals the difference of the weights of its own volume of air and of hydrogen, what will be the lifting power in tons, of a spherical balloon of diameter 200 feet?

Given 1 cubic foot of air weighs 0.08 lbs and is 14.4 times as heavy as hydrogen. $\pi = 3.14$.

2. (a) Taking 1 litre = 61 cubic inches, find the capacity in cubic inches of a car engine rated at 2500 cubic centimetres.

   (b) The price of 4 metres of material is 250 francs and 20 yards of the same material costs £5. Given that 1 metre = 39.37 ins., find the current no. of francs to the £.

3. The following 37 results represent exam marks,

   (51 64 33 40 41 39 61 77 85 68 29 42 32
   (57 17 31 31 86 69 33 40 59 59 42 71 75
   (68 25 40 45 38 79 31 55 88 27 58

   (i.) Arrange in groups 0-9, 10-19, etc.

   (ii.) Find the Median; Upper and Lower quartile; and the quartile deviation.

   (iii.) Draw the frequency curve.

4. (a) In judging cream, points were allotted for flavour, texture and colour in the proportion 6 : 3 : 1. One sample scored the maximum for flavour and colour and half-points for texture. What percentage of total points did it score?

   (b) If the price of gas is reduced from 8d. to 7d. a unit, but consumption in a home increased from 140 to 180 units, in what ratio will the bill be increased?

5. A rectangular sink is 3 ft. long, 2 ft. broad and 6 inches deep. What is the area of the inner surface? If this surface is covered with sheet lead 1/32 inch thick, what volume of lead is needed?

   If the specific gravity of lead is 11.36, what weight of lead is used?

6. (a) Divide $x^4 - 7x^2 + 1$ by $x^2 - 3x + 1$

   (b) The equation $(x - a)(x + 2) = 3x(x + 3) - 2x(x + a)$ is satisfied when $x = 4$
   What then is the value of a?

7. (a) In the triangle A B C side a = 12 cm, side b = 5 cm and angle C = 90°.
   Calculate to four places of decimals (1) Cos A, (2) Tan B; and find from your tables the value of angles A and B.

   (b) A building casts a shadow 120 ft. long on flat ground. The angle of the elevation of the top of the building from the end of the shadow is 50° 30'. Find the height of the building.

MINUTES OF COUNCIL MEETING OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY HELD AT THE DOMINION LABORATORY ON WEDNESDAY, FEBRUARY 22nd, 1950, at 10 a.m.

Present: Dr. J. Melville, President (Chairman), Messrs P. R. Parr (Vice-President), F. H. G. Johnstone (Canterbury Delegate), F. J. T. Grigg (Proxy for Otago), S. E. Wright (Wellington Delegate), W. G. Hughson (Hon. General Secretary), A. P. Oliver (Assistant Secretary).

Apologies: Received from Professor Llewellyn (Auckland Delegate) and Mr. O. H. Keys (Otago Delegate). Mr. Parr acted for Professor Llewellyn and Mr. Grigg acted for Mr. James, who had been nominated by Mr. Keys but was unable to attend.

Minutes: Of Council Meeting on 25/11/49, M.526-533 were confirmed.

REPORTS FROM SUB-COMMITTEES.

Conference 1950.

Minutes of three Meetings of 1950 Conference Committee were received. Hamilton is favoured by delegates to Council as the venue of the 1951 Conference, and the Hon. General Secretary has been asked to approach members in Hamilton to see if a Conference could conveniently be held there.

Royal Society Congress.

Professor Packer is to be asked to represent the Institute on the Royal Society Congress Committee for May 1951, Christchurch. Our Institute will collaborate in running the Chemical Section of the Royal Society Congress, but will not organise specific Institute activities.

Australia and New Zealand Association for Advancement of Science:

Will hold its next meeting in Brisbane, May 23rd-30th, 1951.

Employment Committee:

Moved Canterbury/Auckland—"That Mr. G. M. Smith be appointed Hon. Secretary of the Committee and that Mr. Borthwick be thanked for his long period of service."—Carried.

Members on the Employment Register receive regular circulars, and notifications of positions are received regularly from C.S.I.R. Australia.

Examinations Committee:

The report from the Examinations Committee for 1949 was received. The records of the Committee have been forwarded to the 1950 Dunedin Committee.

Moved Auckland/Canterbury—"That the results of the November, 1949, examinations be approved, and that Laboratory Assistants' Certificates be issued to Messrs I. D. Sanders and J. S. George and that the granting of a certificate to Miss L. Trewern be held over until March, 1950, by which time she will have completed three years' service, and that her case be referred to the Dunedin Committee to be brought up again later."—Carried.

Moved Chair/Otago—"That the outgoing 1949 Examination Committee be thanked for their services."—Carried.

A letter was received from Dr. I. J. Cunningham asking whether Bacteriology could be taken as a major subject for the Laboratory Assistants' Certificate.

Moved Canterbury/Auckland—"That Dr. Cunningham be informed that Bacteriology may not be taken as a major subject and that this decision be communicated to the Examinations Committee, Dunedin."—Carried.

A letter was received from Mr. C. Roberts, Education Department, Christchurch, stating that he will be unable to act on the 1950 Examinations Committee because of a transfer. The matter was referred to the Dunedin Branch to appoint another member in consultation with the Examinations Committee.

Journal:

Report received from the Editor. It was decided not to procure any further reprints of Professor Packer's Presidential Address.

Moved Chairman/Auckland—"That Mr. Salmon's quote on the basis of £30/5/0 for the printing of the revised List of Members be accepted."—Carried.

Branches are reminded that changes of address of members should be notified promptly to the Editor.

Abstracting:

No reply from Department Scientific and Industrial Research to the Editor's proposals for abstracting can be expected until the American Chemical Abstracts inform the Department of their requirements.

Industrial Chemical Essay Prize:

Entries for 1950 close on June 30th.

New Prize Offer:

Prize offered by Mr. Edwards and Mr. Morcom Green. Report received from Professor Llewellyn and Dr. Briggs on an interview with Mr. Edwards.

The prize will be of an annual value of £25, and it is suggested that the recipients should be young chemists working in New Zealand who show particular aptitude in pure chemistry, applied chemistry or Chemical Engineering. The donors wish the terms of reference to be as wide as possible so that a candidate may be assessed on published work, by the product he produces, by the process he designs, or by any other means appropriate to his circumstances. It is proposed that the age limit be 30 years, and that the prize be awarded on work carried out during the year preceding the award.

The Vice-President agreed to ask the Auckland Branch to form a subcommittee to formulate rules governing the award of the Prize, and to find a suitable name for the prize. The Canterbury delegate felt that this and the I.C.I. Prize should not necessarily bear the name of the donors. Suggestions from Branches would be welcomed.

Standards Institute:

The Timber Preservation Committee is proceeding with Standards for several woods. Further letter to come from Mr. R. T. Wright.

Standard Method of Analysis:

Dr. Melville reported that the meeting of the Committee, held on February 21st, 1950, had passed six methods. Further methods, mainly in connection with minor elements, would be further investigated.

The Soils and Fertilizers Sub-Committee is continuing its work, but the Animal Tissues Sub-Committee may cease to function.

U.N.E.S.C.O.—Food and People:

Reports received from delegates outlining activities proposed for 1950 on the development of this theme.

Science Abstracting:

It was decided to await the reply from Department Scientific and Industrial Research (see above) before deciding what action to take.

International Union of Chemistry:

A copy of Statutes and Regulations is still awaited. The annual subscription would probably be 375 dollars.

Patents Committee:

Report received from the Sub-committee stating that Dr. Nauen had been appointed to the position of Patents Examiner in Chemistry. In applying for the position he knew it was class 5, Clerical Division.

It was the opinion of the Sub-committee that nothing could be done about a change of classification. The matter will be referred to the Professional Status Committee, to consider discussing with the Public Service Commission the principle of appointing Professional Officers under the control of clerical officers.

Manpower Report:

A report was received from the Wellington Branch re research work for the Ph.D. Degree in Institutions outside the University. Canterbury was opposed to the suggestion. Auckland was in sympathy with the aims expressed, but considered the steps proposed were premature.

Moved Wellington/Chairman—"That no further action be taken meantime pending further discussions and the accumulation of further information by the Branches."—Carried.

P.C.I.L.S.

A proposal for closer relations between the Royal Institute Chemistry and Commonwealth Chemical Institutes was received from the Royal Institute of Chemistry in England, and was amplified by Mr. Grigg, who had recently discussed the matter personally with officers of the Royal Institute of Chemistry. As a first step it was moved Chairman/Auckland—"That Council authorize the transmission to Royal Institute of Chemistry of a list of names of members of Royal Institute of Chemistry (New Zealand Section), who are also members of the New Zealand Institute of Chemistry."—Carried.

The Dunedin Branch has, up to the present, been examining the problem, but since the Royal Institute of Chemistry (New Zealand Section) has formed a sub-committee to examine the matter and has asked Council to appoint three Wellington members to a sub-committee, Council decided to ask Dunedin to transfer their sub-committee activities to Wellington.

The New Zealand Institute of Chemistry Sub-committee members are Messrs J. M. C. Tingey, S. E. Wright and W. G. Hughson.

Membership:

Moved Auckland/Canterbury—"That the resignations of Messrs Rainnie and D. J. O'D. Davis be accepted.

BOOKS RECEIVED

COLLOID SCIENCE. Vols. I. and II. by A. E. Alexander and J. Johnson (Oxford, at the Clarendon Press, 1949). Pp. 837. Price 60/-.

A very well-written general account of surface properties dealing with, first, the theoretical aspects of the subject and then the experimental methods applied. Topics discussed include osmotic pressure and membrane phenomena, sedimentation equilibria, electrophoresis and allied phenomena, viscosity, diffusion, optical, X-ray, electron diffraction and other methods, plastic flow and elasticity, the study of air-water, oil-water, gas-liquid, liquid-liquid and solid-liquid interfaces, sols, gels, pastes, foams, emulsions, colloidal electrolytes, clays and zeolites, proteins, polymers and membranes. The symbols used are uniform throughout and set out in an introductory table.

It may perhaps be argued that certain sections, e.g., that on thermodynamics, might well have been left out in view of the large size of the work, but because of the excellent manner in which the relevant theory has been condensed into these sections, their inclusion is amply justified.

The scope of the book precludes the detailed discussion of all topics chosen, but an excellent general treatment is provided. —H.B.

AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY. Volume I. (Fundamental principles and the properties of gases), by J. R. Partington, Professor of Chemistry in the University of London (Queen Mary College). Longmans, Green and Co., London 1949. Pp. xlii + 943. Price 80/-.

An excellent treatment of thermodynamics, kinetic theory of gases statistical mechanics and quantum theory, wave mechanics, thermometry, high temperatures, low temperatures and the properties of gases, including pressure-volume-temperature relations, characteristic equations, critical phenomena, densities and molecular weights of gases and vapours, specific heats of gases, viscosities of gases, conduction of heat through gases, diffusion and gases at low pressures.

A full mathematical treatment of the topics selected is given, but to understand it, very little previous knowledge of mathematics is necessary because of an excellent introduction which gives a resume (in 114 pages) of most of the mathematics required. It includes the fundamental concepts of differential and integral calculus as well as trigonometric and hyperbolic functions.

Perhaps the best section of the book is the excellent treatment of thermodynamics. In the section on the kinetic theory of gases the distribution laws are logically deduced and applications given. Statistical theory is particularly well handled, including critical accounts of Maxwell-Boltzman, Bose-Einstein, Fermi-Dirac and Gentile statistics, in which the limitations are clearly discussed. Examples are given of the calculation of entropies of gases by statistical methods. A concise treatment of wave mechanics is given.

The section on temperature and thermometry is dealt with much more fully than in most advanced works on physical chemistry and should be of great interest to practical chemists, as should the excellent critical account of the properties of gases.

Throughout the work an emphasis has been placed on the experimental side as instanced by the numerous tables and graphs which appear. They are particularly valuable, as they are up-to-date and many of the sources of information are not accessible in this country. Descriptions are given of apparatus and experimental methods and of empirical and semi-empirical formulæ likely to be of great use to experimental chemists and chemical engineers.

Very full references to the literature up to the end of 1948 are given and each topic is preceded by a bibliography. The index is, however, not as complete as could be desired. One excellent feature of the book is its uniformity of symbols, a full list being given. It is very clearly printed, symbols and diagrams are excellent and mistakes have been virtually eliminated. As a first-class critical account of the topics dealt with it cannot be bettered, and subsequent volumes of this series will be awaited with interest. —H.B.

The Practice of Research in the Chemical Industries, by R. H. Griffith, Senior Research Chemist, North Thames Gas Board. Pp. 184. London: Oxford University Press. 12/6. At first sight it would appear that there are few industrial laboratories in New Zealand large enough for this book to have any application, but it can be read with profit by any chemist in charge of an industrial laboratory, as it contains useful suggestions on all aspects of laboratory organisation. The information frequently applies just as much where the bulk of the work is routine. Subjects discussed include staff, design and location of the laboratory, costs and profits, library research, welfare and safety, records, small and large-scale experimental work, and the relationship of the laboratory and its staff to the rest of the firm. Apart from the more practical value of this volume, it presents an ideal of harmonious and successful industrial laboratory work, which can be a tonic in judicious doses.

The latest volume of **Organic Syntheses,** Vol. 29 (John Wiley and Sons and Chapman and Hall, $2.50) is now available. It contains 35 new preparations, the most interesting probably being that of Raney nickel catalyst from nickel-aluminium alloy.

Volume V. of Organic Reactions, edited by Roger Adams (John Wiley and Sons and Chapman and Hall, $6.00), contains the following chapters:— The synthesis of acetylenes; cyanoethylation; the Diels-Alder with quinones and other cyclenones; the preparation of aromatic fluorine compounds from diazonium fluoborates; the Friedel-Crafts with aliphatic dibasic acids and their anhydrides; the Gattermann-Koch; the Leuckart; selenium dioxide oxidations; the Hoesch synthesis and the Darzens glycidic ester condensation. After a general discussion, each article lists the compounds to which the reactions have been applied, with an indication of the conditions and yields.

Advanced Organic Chemistry, by G. W. Wheland, University of Chicago. Second edition, 1949. Pp. 799. John Wiley and Sons, New York; Chapman and Hall, London. $8.00. Any textbook of advanced organic chemistry in a single volume can only deal with a certain number of topics, and with this limitation, Wheland has produced an excellent volume. The topics are: Modern views on the various types of valence bonds; addition compounds; acids and bases; structural isomerism; stereoisomerism; configuration of carbon compounds; strain theory and steric hindrance; the theory of resonance; electrostatic effects; molecular rearrangements; tautomerism and free radicals. Each section is well illustrated with equations and formulæ and references are given up to 1948. Only one minor error was noted, in the formula of phenol-isatin, p. 559.

Carotenoids, by P. Karrer and E. Jucker (published in German by Birkhauser, Basel, Switzerland, 1948). Paper covers, 39 Swiss francs; bound, 43 Swiss francs.

This is the third monograph which has been published on carotenoids. The first was published by L. S. Palmer in 1922, at a time when the constitution of even the most common of carotenoids—β-carotene, was unknown. Next Zechmeister and Cholnoky published their book in 1934, at a time

when the development of chromatographic techniques made feasible the isolation of pure carotenoids, and due to the efforts of Continental chemists, particularly Kuhn, Zechmeister and Karrer, the constitution of several of these had been determined.

Now more than 70 carotenoids have been identified and the constitution of about half of these is known. Probably no one has contributed more to this result than Professor P. Karrer and co-workers at the Chemical Institute of the University of Zurich. The work which he has written with E. Jucker, the latter having been associated with Karrer in many recent papers in the Helvetica Chimica Acta, bears the mark of being authoritative and lucid, and has detailed lists of references. The book serves well the research worker as well as the student.

The occurrence, estimation and functions of carotenoids in plants and animals are treated in detail. Methods of isolation and determination of constitution are described as illustrative of the research techniques used, while typical absorption spectra and coloured prints showing the crystal forms of several carotenoids are included in the appendix.

The book is remarkably free from errors, with only a small oversight such as on page 320. The reference (1) J. M. Heilbron and R. E. Phipers, Biochem. J., **29**, 1369 (1935) is repeated under (3). This seems unnecessary.

The book is to be wholeheartedly commended, and no chemical library dealing with plant or animal products can afford to be without a copy. It is to be hoped that an English translation will soon be made available.

—F.B.S.

Tin—its Mining, Production, Technology, and Applications. by C. L. Mantell. American Chemical Society Monograph Series. Second Edition. Pp. 573. 1949. Reinhold Publishing Corporation. (Through Technical Books Ltd., Wellington). £5.

The first edition of this book appeared in 1928 and has received wide recognition as a standard reference work on tin production and utilisation. This new edition, while following the same general plan as its predecessor, has been expanded to include many new discoveries, processes, techniques and applications that have appeared in the tin industry in the last twenty years.

The subjects covered in the book include a review of the occurrence, mining and dressing of tin ores, the production and refining of the metal, industrial applications such as plating, tinplate, hot-dipped coatings, foil, collapsible tubes and alloys, reclamation of secondary tin, physical and chemical properties of the metal, constitutional thermal equilibrium diagrams and analytical methods.

During World War II. the fall of the chief tin-producing areas of the world into the hands of the enemy resulted in strenuous efforts in the allied countries to conserve and reclaim tin in every way. Among the resulting developments described by the author may be mentioned electrolytic refining, electrolytic tinplate, non-electrolytic methods of plating, conservation of tin in alloys and substitute solders, improvements in the reclamation of secondary tin and the detinning of tinplate scrap.

Throughout the book it is evident that the author has made a very exhaustive search of all phases of the literature on tin. At times one feels that, in his eagerness to include all available data, he has not considered sufficiently whether the matter as presented can be of any possible use. For instance, the greater part of the forty pages devoted to lists of compositions of industrial alloys serves no other purpose than to show that a great many alloys containing a proportion of tin have been made. Such minor defects, however, detract little from the value of the wealth of information carefully collected and compiled that will make this treatise a valuable reference work on any phase of the study of tin.

—G.S.L.

B. D. H.

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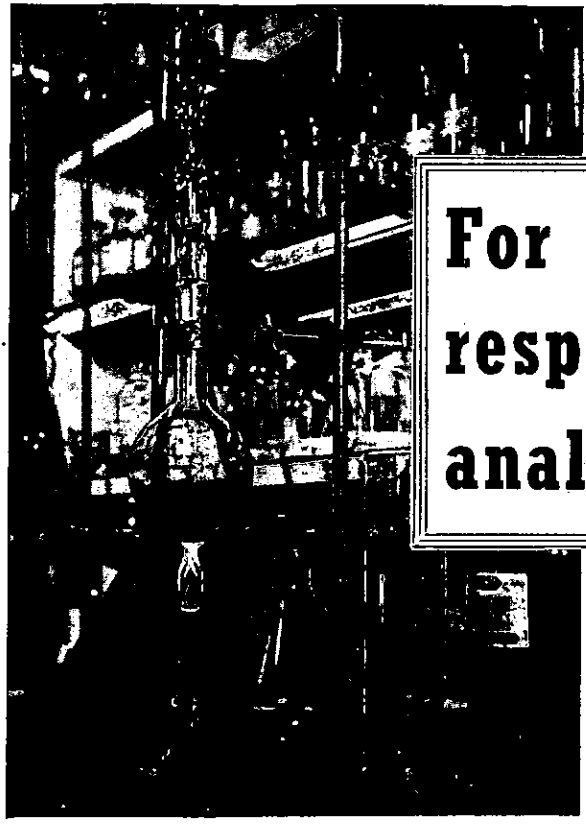

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Sir William Perkin

founded the modern synthetic dyestuffs industry. He began his chemical career as an assistant at the Royal College of Chemistry, but his first great discovery was actually made in his spare time in a rough laboratory at home when he was no more than eighteen. This took place in 1856, when Perkin was trying to prepare quinine artificially. He failed to produce synthetic quinine, but by oxidizing crude aniline with potassium dichromate obtained a dark solid which turned out to be a good purple dye. It was, in fact "mauve" the first of the great family of aniline dyes. Perkin took out a patent for the manufacturing process and, in 1857, set up a factory near Harrow. This was the beginning of the aniline dye industry, which has since become of key importance to the civilized world.

Born in London in 1838, Perkin was educated at the City of London School before proceeding to the Royal College of Chemistry. As well as discovering "aniline purple" he also invented a process for manufacturing alizarin (the red dye of madder root). Achieving financial independence as a result of his discoveries, he was able to devote his attention to pure chemical research. He was President of the Chemical Society in 1883 and of the Society of Chemical Industry in 1884. He was knighted in 1906, the jubilee of his discovery of the first aniline dye.