JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

Vol. 23 No. 4
August, 1959

CONFERENCE ISSUE

JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

Vol. 23, No. 4 August, 1959

CONTENTS

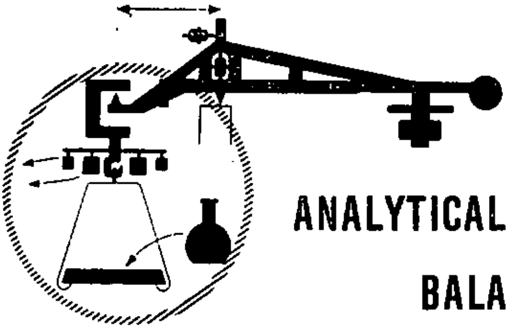
Published for the New Zealand Institute of Chemistry (Inc.), P.O. Box 250, Wellington, by

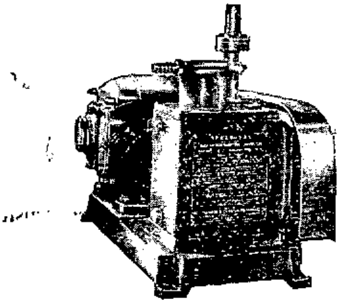
EDITORIAL SERVICES LIMITED
Ascot Chambers, 81 Ghuznee Street, Telephone 51-416.
C.P.O. Box 2721 Wellington, N.Z.

United Kingdom Advertising Representative
Walter Judd Ltd., 47 Gresham Street, London, E.C.2.

Edited by DR W. A. MCGILLIVRAY
Massey College Post Office, Palmerston North, N.Z.

Registrar, N.Z. Institute of Chemistry (Inc.)
D. J. Hogan, P.O. Box 1926, Christchurch, N.Z.





IT TAKES TEN YEARS TO MAKE A SCIENTIST

. . . and sometimes as long to find one. The nation desperately needs many more. We ourselves have none to spare. But we do, in fact, make scientists for others.

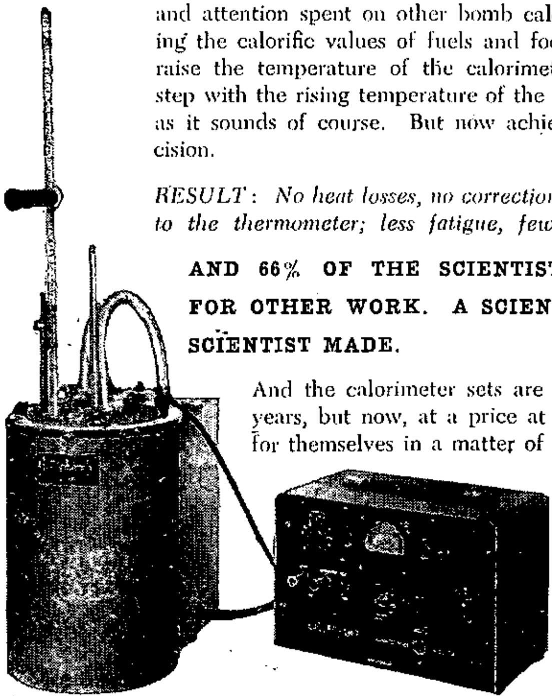
Our ADIABATIC BOMB CALORIMETER . . .

the first and only commercially available set of its kind, reduces by no less than 66% the time and attention spent on other bomb calorimeters in measuring the calorific values of fuels and foods. The trick is to raise the temperature of the calorimeter jacket exactly in step with the rising temperature of the bomb. Not as simple as it sounds of course. But now achieved, with high precision.

RESULT: No heat losses, no corrections, no tedious slavery to the thermometer; less fatigue, fewer sources of error.

AND 66% OF THE SCIENTIST'S TIME SAVED FOR OTHER WORK. A SCIENTIST SAVED IS A SCIENTIST MADE.

And the calorimeter sets are available, not in ten years, but now, at a price at which they will pay for themselves in a matter of months.



SEND FOR
TECHNICAL
SPECIFICATION
AND PRICES

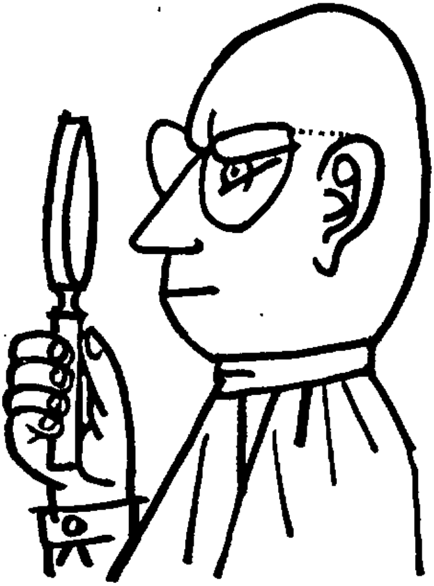
Gallenkamp SUPPLY THE WORLD'S LABORATORIES

Highest grade stainless steel – first-class workmanship – unequalled efficiency

A. GALLENKAMP & CO. LTD., Sun Street, London, E.C.2., England.
Cables: Gallenkamp, London.

APPOINTED AGENTS FOR NEW ZEALAND

GEO. W. WILTON & CO. LTD.
63 Shortland Street, Auckland, C.1.
156 Willis Street, Wellington.



JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

Vol. 23, No. 4 August, 1959

EDITORIAL

The Training of Chemical Technicians

Institute members have been pressing for some years now for the establishment of training courses for chemical technicians.

Part-time courses at technical schools, leading to "The New Zealand Certificate in Engineering", are already established in the main centres and the first group of successful students graduated last year. This course, of five years duration, requires some 6 to 8 hours study per week and candidates may enter after gaining a pass in the School Certificate examination. Employment in suitable engineering work is required so that candidates will gain experience in practical applications as well as in scientific principles of engineering.

Discussions held throughout the branches of the New Zealand Institute of Chemistry have shown that a scheme of this type for training chemical technicians would be welcomed by members and, following representations to the Department of Education, a meeting of interested bodies, including the N.Z.I.C., was convened by the Director of Education in August, 1957. This meeting laid down general principles for planning courses of instruction including the principle that the course should take three years, should occupy 8 hours per week, and should be available to candidates having School Certificate (irrespective of subjects passed).

Following this meeting, the Institute Examinations Committee, assisted by a sub-committee in Auckland, attempted to prepare a syllabus for this course. There had been many divergent views expressed throughout the branches of the Institute on the kind of courses required and on the standard which should be attained. Some expressed the view that the certifiicate (together with appropriate endorsements) should take the candidate virtually up to B.Sc. finals level. Others insisted that in their laboratories only routine workers were required and that a very modest standard of theoretical knowledge was all that was needed.

A syllabus was produced for a three year certificate which took the candidate up to a standard loosely described as "somewhat higher than University Stage I" standard in written chemistry, supported by elementary physics, mathematics and English. The emphasis throughout was placed on practical chemistry and laboratory skills, and practical examinations were required each year. Provision was made for an intermediate certificate to be taken by less able students after completing the first year's theoretical work together with three years' laboratory work. The difficulty which the Committee encountered was that the time required to get candidates to this standard in three years in both theory and practice proved to be greater than the 8 hours suggested by the meeting of August, 1957, and a course of 12 hours per week was stipulated, 6 hours being in the employer's time and 6 hours in the evenings. It was felt that asking for this additional time away from work was in line with trends in Great Britain where students at polytechnics are frequently allowed a whole day per week for instruction.

On presenting this scheme to the Education Department, the Institute learned that there might be difficulty in obtaining approval of an increased number of hours of day release and this proved to be the case when the meeting of August, 1957 was recalled in May, 1959. The representative of the Manufacturers' Federation said that many of their members would be happy to try such a scheme, but others felt that the time allowed off duty should be restricted to the usual 4 hours per week which is allowed to apprentices.

The following scheme was then proposed and agreed to by all present as an acceptable outline.

Year	*Hours* *Day Evening*	*Subjects*
1	4 + 4	Mathematics, Physics, Chemistry, English
2	4 + 4	Mathematics, Physics, Chemistry
3	4 + 4	Mathematics, Physics, Chemistry
4	4 + 4	* Advanced Chemistry
5	4 + 4	

*There should be an arrangement by which some students can cover the work of these two stages in one year by devoting extra time to their studies.

(a) A student who has passed School Certificate Mathematics and Physics, and University Entrance Chemistry, would be exempted from Year I on a subject for subject basis. Such a student could complete the course in three years if he took advantage of the provision for acceleration noted above.

(b) At the end of Year 2 an Intermediate certificate would be awarded and and final certificate after Year 5.

(c) It may be noted that the form of the course is such that options other than chemistry (e.g. applied physics, biology) could be introduced in Years 4 and 5 if that was ever thought desirable.

(d) An endorsement course could be studied for four hours per week of the student's own time, probably for one year, after the end of the certificate course.

If this scheme is implemented, and if the syllabus proposed by the Institute sub-committee is adopted, the New Zealand Certificate in Chemistry (if this be the title of the new certificate) should be equivalent in standard to the New Zealand Certificate in Engineering.

In view of the administrative steps to be taken before the new examinations can be established it seems unlikely that courses can begin before 1961.

A. L. ODELL,
Chemistry Department,
University of Auckland.

PHARMACY EDUCATION

Members may be interested in the following brief outline of a new full-time pharmacy training scheme which is to be introduced by the Education Department next year.

The Pharmacy Board of New Zealand expects shortly to cease registering indentures for pharmacy apprentices under the existing regulations. Thereafter to become a pharmacist will, in general, entail passing the qualifying examination set by the Pharmacy Board after completion of the second year of a two-year full-time course which it is anticipated will start in February, 1960, at the Central Technical College, Petone, and by serving subsequently a two-year apprenticeship term.

The first year, starting in 1960, is to be a course in basic sciences; the second year course opens in 1961 and covers professional subjects including pharmaceutics, forensic pharmacy, pharmaceutical chemistry, pharmacognosy, pharmacology and microbiology. The entrance standard is a University Entrance qualification. Bursaries and boarding allowances are available in certain cases.

This School of Pharmacy will be largely a self-contained unit within the Central Technical College and a Head of the School will be appointed shortly. Enquiries should, however, be made to the Principal of the Central Technical College, P.O. Box 177, Petone.

This course should not be confused with the University of Otago degree course leading to the degree of B.Pharm. This degree course which has been approved by the Senate of the University of New Zealand, will be available in the new quinquennium period 1960 to 1964. It is designed for the smaller numbers wishing higher training which will equip them for pharmaceutical manufacturing or for hospital dispensary work.

THE CONSTITUTION AND ABSOLUTE CONFIGURATION OF SOME DITERPENES

L. H. BRIGGS
Professor of Chemistry, University of Auckland.

(Based on address by the President delivered at Branch Meetings of the N.Z.I.C. during May and June.)

A large number of higher plants contain oils of aromatic smell which may be obtained by steam distillation. The distilled "essences", from which the term essential oil has been derived, have for many centuries been a source of international trade and indeed the early trade routes from East to West were mainly used for the export of spices, perfumes, etc.

The volatile compounds can be classified into three main groups:

(a) terpenes, hydrocarbons of the formula, $C_{10}H_{16}$
(b) sesquiterpenes, $C_{15}H_{24}$
(c) diterpenes, $C_{20}H_{32}$.

Oxygenated derivatives of all three classes also occur. The higher members of the family, triterpenes, $C_{30}H_{48}$, and polyterpenes also occur naturally. They are not volatile, however, but may be isolated in other ways. In general, most essential oils contain mixtures of terpenes, sesquiterpenes, and their derivatives, but relatively few contain diterpenes.

There is a peculiar geographical feature about the occurrence of diterpenes in essential oils and, so far, the only well characterized solid diterpenes have been found in oils from trees growing in countries bordering on the Pacific, *e.g.*, Tasmania, Japan, California and New Zealand. In contrast to the absence of diterpenes in essential oils from trees growing on the Australian continent, renowned for its wealth of *Eucalyptus* species rich in essential oils, most of the major timber trees of New Zealand possess essential oils containing diterpenes, often in large quantities. To date diterpenes have been shown to occur in the essential oils of *Agathis australis* (kauri), *Podocarpus totara* (totara), *P. spicatus* (matai), *P. ferrugineus* (miro), *P. hallii* (Hall's totara), *Dacrydium cupressinum* (rimu), *D. biforme* (yellow pine), *D. colensoi* (silver pine), *D. kirkii* (monoao), *Phyllocladus trichomanoides* (tanekaha), *P. alpinus* (mountain toatoa) and *P. glaucus* (toatoa).

It would appear that the geologically long separation of New Zealand from other land masses, estimated roughly as 60 to 70 million years, has been responsible for its unique flora and fauna thus leading to distinct differences in the composition of the essential oils of its flora.

With the exception of the Tasmanian relatives, *Dacrydium franklinii* (Huon pine) and *Phyllocladus rhomboidalis* (celery-leaf pine), and the Japanese trees, *Podocarpus macrophylla* and *Sciadopitys verticillata* (parasol pine), all the other trees containing diterpenes also occur commonly planted throughout New Zealand, *i.e.*, *Araucaria excelsa* (Norfolk Island pine), *Cupressus macrocarpa* (Monterey pine or macrocarpa) and *Cryptomeria japonica* (Japanese cedar).

It can thus be seen that the study of the diterpenes is one of particular interest to New Zealand chemists and contributions have been made by workers at Otago University, the Dominion Laboratory and the University of Auckland.

Seven well characterized crystalline diterpenes have been described in the literature (Simonsen and Barton, 1952), the only other well characterized diterpene being camphorene, a liquid hydrocarbon. Camphorene, from camphor oil, is probably an artefact formed by the polymerization of myrcene during the distillation. Diterpenes have also been described from two other New Zealand forest trees, *Libocedrus bidwillii* (pahautea) and *Podocarpus dacrydioides* (kahikatea), but these have not been substantiated by later workers (personal communication from Dr J. Murray).

The study of the crystalline diterpenes has been further simplified by the fact that podocarprene, from *Podocarpus macrophylla* and *Sciadopitys verticillata,* has been identified with kaurene from *Agathis australis,* while cryptomerene, from *Cryptomeria japonica,* has been identified with *iso*kaurene. In addition, the so-called γ-podocarprene, m.p. 197-199°, obtained by the action of alcoholic potash on podocarprene (kaurene) hydrochloride, has been shown to be the corresponding alcohol.

The remaining diterpenes whose constitution and absolute configuration are discussed below are phyllocladene, mirene, kuarene, rimuene and cupressene.

Constitution

PHYLLOCLADENE

We are indebted to Uota and the late Carl W. Brandt* for the earlier investigation of this diterpene and for the latter's proposed formula [1] which subsequent work has confirmed.

---

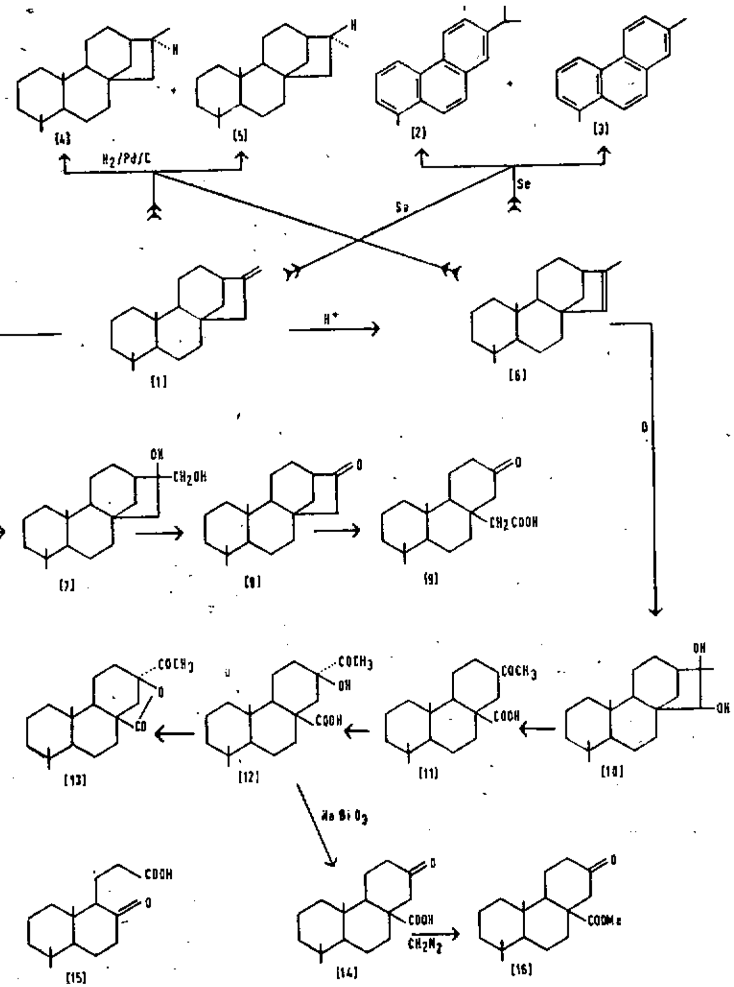
*I.C.I. Prizeman of the New Zealand Institute of Chemistry for his work on New Zealand plant products.

Selenium dehydrogenation yields both retene [2] and pimanthrene [3], fixing the position of 18 of the 20 carbon atoms. Catalytic hydrogenation gives isomeric α- and β-dihydrophyllocladenes, [4] and [5], showing that the diterpene is tetracyclic with one double bond. On heating with acids it is isomerized to *iso*phyllocladene [6] by a simple shift of the double bond since *iso*phyllocladene also gives a mixture of the same α- and β-dihydrophyllocladenes. It is interesting to note that α-dihydrophyllocladene is identical with iosene, a hydrocarbon obtained from European lignites. On the basis of these results and the nature of the oxidation products of both phyllocladene and *iso*phyllocladene shown in the following flow-sheet, Brandt (1952) proposed the formula [1] for phyllocladene, a modification of an earlier one by Uota.

Support for this formula was given by Bottomley, Cole and White (1955) by an intensive study of the infrared spectrum of the norketone [8] obtained from phyllocladene by oxidation. As an excellent example of the use of infrared spectra in structure elucidation they showed that the norketone contained a carbonyl group in a five-membered ring with one methylene group adjacent to the carbonyl group, a *gem*-dimethyl group and an angular methyl group between two six-membered rings.

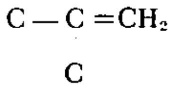
Further work in Auckland and by Dr R. Hodges in Glasgow (personal communication) has supported the Brandt formula although up till now there has been no direct chemical proof of the structure of rings A and B nor for the position of the angular methyl group which has been placed on C-12 on biogenetic grounds although its position on C-11 cannot be theoretically excluded. Many new compounds have been obtained but only those bearing on the configuration are described.

Oxidation of *iso*phyllocladene with permanganate yields a mixture of products including the glycol [10], the ketoacid [11] and the hydroxyketoacid [12]. The constitution of the last compound follows from the fact that it forms a γ-lactone [13] (infrared band at 1,761 cm^{-1}), and is oxidized by sodium bismuthate to the ketoacid [14]. It was previously considered by Brandt to have the formula [15]. Esterification of the ketoacid with diazomethane affords the ketoester [16], a key compound in determining the configuration (see below). The infrared spectrum of the ketoester indicates a carbonyl group in a six-membered ring (strong band at 1,721 cm^{-1}) while its behaviour to hydrolysis supports a sterically-hindered carboxyl group.



MIRENE

The infrared spectrum of this diterpene is almost identical with that of phyllocladene and only varies at some points in the intensity of the bands, evidence for its being isomeric with phyllocladene. On heating with glacial acetic acid it forms *iso*phyllocladene. As a tetracyclic diterpene with one double bond it forms dihydromirene different from either α- and β-dihydrophyllocladene or α- and β-dihydrokaurene (see below). Consistent with its having the group,

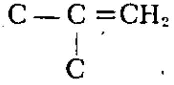


$$C-\underset{\displaystyle C}{C}=CH_2$$

it has a band in the infrared spectrum at 876 cm^{-1} and on oxidation forms a norketone similar to [8], with a similar spectrum.

KAURENE

The reactions and physical properties of this hydrocarbon also agree with its being isomeric with phyllocladene. Selenium dehydrogenation gives both retene and pimanthrene. Catalytic hydrogenation affords isomeric α- and β-dihydrokaurene. On heating with acids it is isomerized to *iso*kaurene which on hydrogenation also gives α-dihydrokaurene. This isomerization is analogous to that of phyllocladene into *iso*phyllocladene by an exocyclic-endocyclic double bond shift. Ozonization produces formaldehyde and a norketone, similar to [8], consistent with the presence of the grouping,

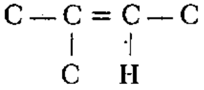


$$C-\underset{\underset{\displaystyle C}{|}}{C}=CH_2$$

The spectrum of the norketone is similar to that of phyllocladene norketone indicating a carbonyl group in a five-membered ring.

RIMUENE

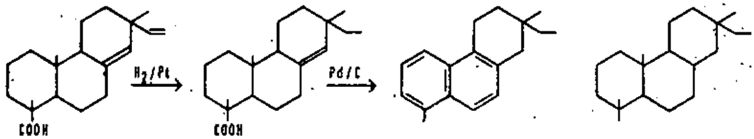
Selenium dehydrogenation of rimuene yields pimanthrene but no retene. Although *iso*phyllocladene is formed on digestion with formic acid rimuene is a tricyclic diterpene with two double bonds which, from infrared evidence, appear to be of the type,



$$C-\underset{\underset{\displaystyle C}{|}}{C}=\underset{\underset{\displaystyle H}{|}}{C}-C \qquad \text{and} \qquad C-CH=CH_2$$

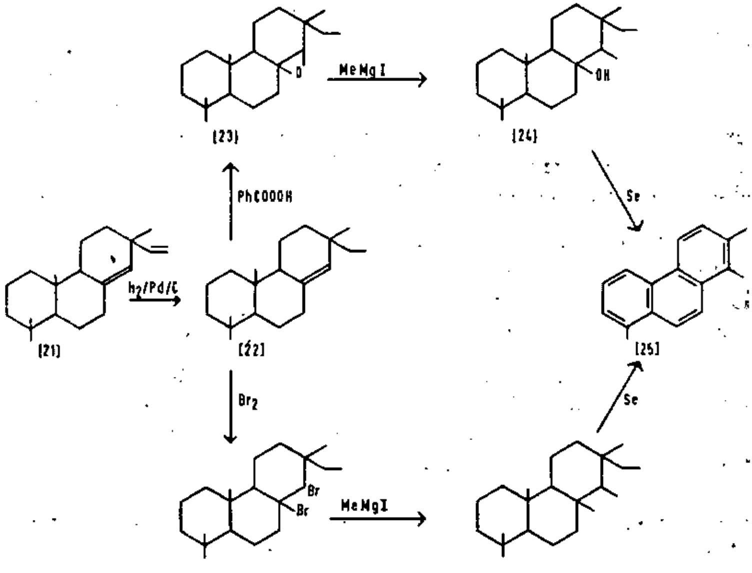
respectively. On catalytic hydrogenation dihydrorimuene is readily formed and, less easily, tetrahydrorimuene. The presence of the vinyl group is confirmed by the formation of formaldehyde on ozonolysis. On partial catalytic dehyrogenation of dihydrorimuene a naphthalene hydrocarbon [19] is obtained with physical properties identical with those of the compound derived from both of the isomeric dihydropimaric and dihydroisopimaric acids [18].

By application of the isoprene rule and incorporating the *gem*-dimethyl group, indicated by the infrared spectra, the carbon skeleton of rimuene may be written as [20]. There is obviously only one position for the vinyl group in the side chain,



[17] [18] [19] [20]

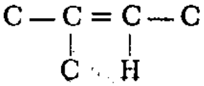
The remaining double bond has been shown to be in the 8 : 14-position in two ways. Peracid oxidation of dihydrorimuene [22] affords an epoxide [23] which, after treatment with methyl magnesium iodide and subsequent dehydrogenation with selenium, gave 1:2:8-trimethylphenanthrene [25]. The same compound could also be obtained by bromination of dihydrorimuene, treatment of the dibromo compound [26] with methyl magnesium iodide and dehydrogenation with selenium.



These facts support the structure [21] for rimuene which is obviously related to the stereoisomeric acids, pimaric, isopimaric and cryptopimaric acid [17].

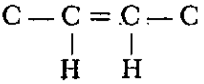
CUPRESSENE

Very little constitutional work has been carried out owing to the small amount available. It contains two double bonds of the type



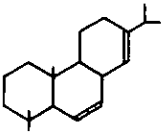
$$\begin{array}{ccccccc} C & - & C & = & C & - & C \\ & & | & & | & & \\ & & C & & H & & \end{array}$$

and



$$\begin{array}{ccccccc} C & - & C & = & C & - & C \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

from its infrared spectrum, and on catalytic hydrogenation it gives a saturated tetrahydro-derivative. Attempted dehydrogenation by heating with palladium charcoal gave, unexpectedly, *iso*-phyllocladene, despite the fact that it is stable to alcoholic sulphuric acid. The absence of an absorption peak in the ultraviolet spectrum indicates that conjugated double bonds are not present. On these and biogenetic grounds it has been assigned the provisional formula [28] although there are a number of alternative structures.



(28)

Configuration

In determining the configuration of the diterpenes we have drawn on the biogenetic schemes for the formation of diterpenes and their derivatives first suggested by Ruzicka (1953) and later elaborated by Wenkert (1955).

On the physical side we have utilized the new method of optical rotatory dispersion introduced and brilliantly exploited by Djerassi (1957). A brief outline of this method is given for the understanding of the following discussion.

Most optically active compounds show little change in the rotation with wave-length particularly between the sodium and mercury lines commonly used in measurements of rotation. With the introduction of a new instrument, a spectropolarimeter, where the polarimeter is coupled to a light source capable of being beamed at varying wavelengths as in an ultraviolet spectrophotometer, rotations may be measured over a wide range of wavelength. In compounds such as ketones where a chromophore is present, normally yielding an absorption peak in the ultraviolet region, and attached to an asymmetric environment there is a marked change in the rotation near the point of the normal absorption peak. This is shown in Fig. 1. The mirror image of the compound obviously has the reversed curve shown by the dotted line.

The characteristic increase in the rotation shown in the diagram is known as the Cotton effect. Those compounds whose rotation increases with decreasing wavelength are said to ex-

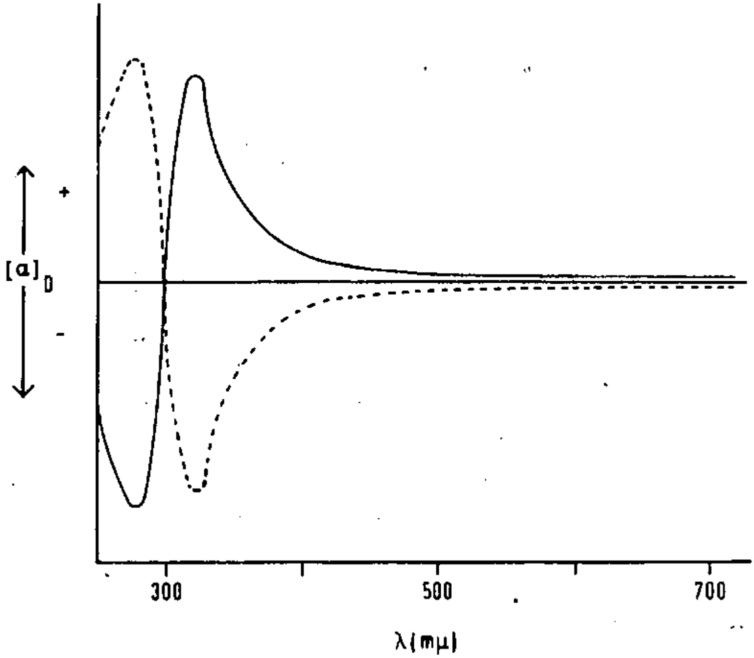


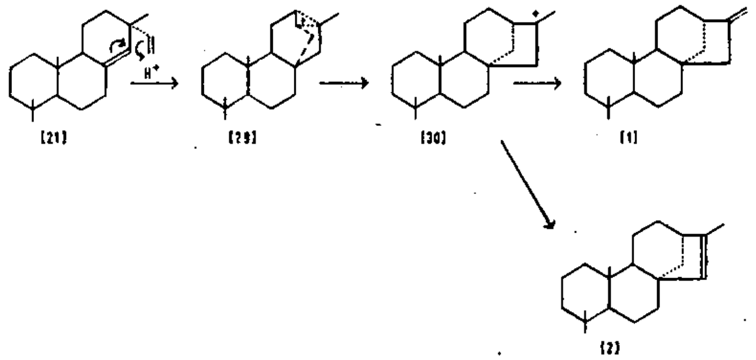
Fig. 1.

hibit a positive Cotton effect — their enantiomorphs exert a negative Cotton effect.

Mathematical treatment of the phenomenon and application to the absolute configuration of cyclic ketones has led to the formulation of the "octant" rule by Moffitt, Moscowitz, Woodward, Djerassi and Klyne (forthcoming publication) which enables the sign of the Cotton effect to be calculated.

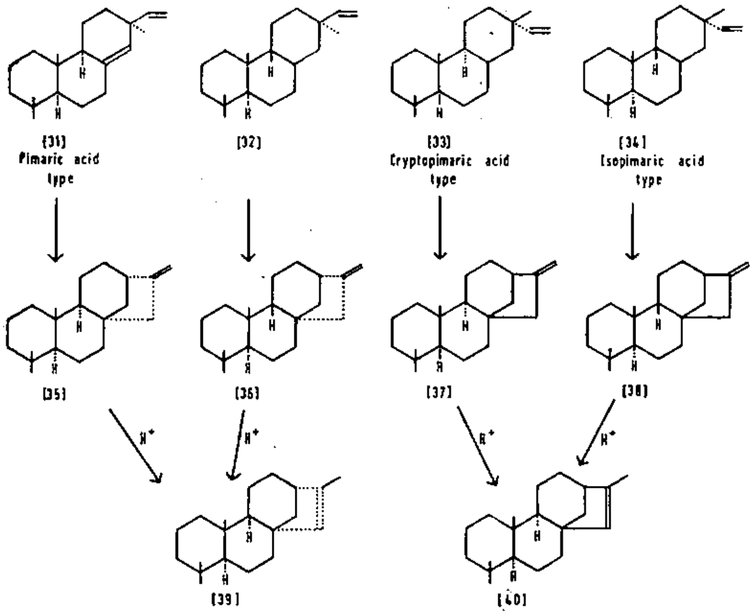
In agreement with the biogenetic schemes of Ruzicka and Wenkert we consider that the diterpenes are derived from a fundamental pimaradiene skeleton, formed initially perhaps from geranyl geraniol.

Rimuene is stable to prolonged heating with glacial acetic and mineral acids and hence must have a stable configuration, particularly at C-13. Specifically, however, with formic acid it is converted into *iso*phyllocladene, explained by the sequence: [21 to 1; 2]. The intermediate carbonium ion [30] can yield either phyllocladene [1] or *iso*phyllocladene [6] in biosyntheis (the two



diterpenes co-occur in *Araucaria excelsa* and *Phyllocladus trichomanoides*) but only the more stable *iso*phyllocladene on the above digestion with formic acid.

Three pimaradiene types of resin acids occur, pimaric, isopimaric and cryptopimaric acid. Although a final proof of the configuration at C-13 has not yet been given the available evidence supports the absolute configurations given. The formation of the tetracyclic diterpenes can then be represented.



In [36] and [38] ring B must be in a boat form and these represent relatively unstable forms while [35] and [37], with all chair rings, represent stable forms. In the further acid catalysed shift of the exocyclic double bond to the endocyclic position the less stable boat forms may pass over to the more stable all-chair form of *iso*-hydrocarbon. There is no change in configuration in passing from phyllocladene to *iso*phyllocladene since both isomers yield the same mixture of α- and β-dihydrophyllocladene on hydrogenation. Mirene, however, changes its configuration in passing to *iso*phyllocladene since it gives a different dihydroderivative on hydrogenation. Mechanics of the conversion of mirene into *iso*phyllocladene support the view that mirene differs only from phyllocladene in the configuration at C-13 and must be represented by the boat form of such a pair of isomers.

No such isomer of kaurene occurs, however, which, like kaurene itself, is also converted into *iso*kaurene by treatment with acids. Since kaurene and *iso*kaurene both yield the same dihydrokaurene it is assumed, therefore, that kaurene is the more stable isomer of a pair differing only at C-13.

Phyllocladene and kaurene, therefore, must be represented by the formulae [35] and [37]. The rotatory dispersion of the ketoester [16] derived from phyllocladene has a positive Cotton effect in agreement with the sign of the rotation predicted by Djerassi from the octant rule for the ketoester derived from [37] while the ketoester derived from [35] has a predicted negative Cotton effect. Phyllocladene must, therefore, be [37] and kaurene [35] and *iso*phyllocladene and *iso*kaurene [40] and [39] respectively. Further, rimuene must be [33] and mirene [38].

Approximate assessments of the Cotton effect of the rotatory dispersions of the norketones from phyllocladene [8], mirene, and kaurene are also in agreement with the observed results, positive, negative and positive, respectively.

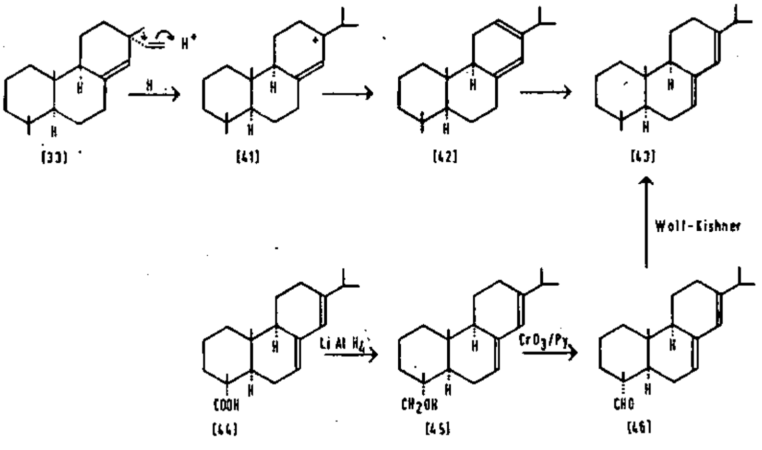
Cupressene is stable to alcoholic sulphuric acid and, on the above formulation, will have a stable configuration at C-13. Since it too may be isomerized to *iso*phyllocladene by heating with palladium charcoal it must have the same configuration at C-11, C-12 and C-13 as phyllocladene.

Final proof of the structure of phyllocladene, mirene and rimuene and the configuration of cupressene has now been afforded by the conversion of rimuene into abieta-7:9(14)-diene of known constitution and absolute configuration.

A mechanism, involving a Wagner-Meerwein transformation, has already been given for the transformation of rimuene into *iso*phyllocladene. Ruzicka (1953), however, has suggested an alternative biogenetic scheme for the conversion of diterpenes of the pimaradiene type into those of the levopimaric, *neo*abietic and abietic acid type. This was recently realized in the laboratory by Wenkert and Chamberlin (1959) by the conversion of both pimaric and isopimaric acid into abietic acid and now in the diterpene series.

When rimuene is heated with formic acid for 2 to 3 days the major product, besides *iso*phyllocladene, is an isomeric liquid hydrocarbon of the levopimaric acid type [42] but, on further digestion for 5 to 10 days, the major product is abieta-7:9(14)-diene [43], identified by comparison of its physical properties with a sample prepared from abietic acid [44] by conversion of the carboxyl group to a methyl group.

The isomerism and synthesis is illustrated by the sequence [33] to [46]. The levopimaric acid type of compound [42] is an intermediate in the reaction isomerizing to the more stable abietadiene type [43] on longer treatment.



Since the structure and absolute configuration of abietic acid is known (Klyne, 1953) and since rimuene, phyllocladene, mirene and cupressene can be isomerized to a common isomer, *iso*phyllocladene, the structures of rimuene, phyllocladene and mirene are confirmed. On the tentative formulation of cupressene [28], at least the configuration at C-11, C-12 and C-13 is confirmed.

On the above evidence and the scheme set out for the biogenesis of the diterpenes support is also given for the structure and absolute configuration of kaurene.

* * *

In drawing up this account of the diterpenes I wish to pay a tribute to the practical and theoretical contributions made by my colleagues and research students, including Drs B. F. Cain, R. C. Cambie, B. R. Davis, M. D. Sutherland, W. I. Taylor and J. K. Wilmshurst and R. W. Cawley and J. A. Loe.

LITERATURE CITED

BOTTOMLEY, W., COLE, A. R. H., and WHITE, D. E. (1955): *J. Chem. Soc., 1955* : 2,624.

BRANDT, C. W. (1952): *N.Z. J. Sci. Tech., 34B* : 46.

DJERASSI, C. (1957): *Bull. Soc. Chem., 1957* : 74.

KLYNE, W. (1953): *J. Chem. Soc., 1953* : 3,072.

RUZICKA, L. (1953): *Experientia, 9* : 357.

SIMONSEN, J. L., and BARTON, D. H. R. (1952): *The Terpenes,* Vol. 3, pp. 334-344. Cambridge University Press, London.

WENKERT, E. (1955): *Chem. and Ind., 1955* : 282.

WENKERT, E., and CHAMBERLIN, J. W. (1959): *J. Amer. Chem. Soc., 81* : 688.

ABSTRACTS OF PAPERS CONFERENCE, 1959

THE IMPACT OF ISOTOPES ON CHEMISTRY

J. F. DUNCAN

Chemistry Department, University of Melbourne, Victoria.

Since 1896, when Becquerel first discovered radioactivity, isotopes have had a profound effect on chemistry. They have been closely associated with developments in understanding the structure of the atom, the group displacement law, the mechanisms of chemical reactions, and the chemistry of several new or previously unobtainable elements; they have also directly led to the development of important new techniques in ultramicrochemistry. With these impressive contributions taking their place in history we may now assess the significance of the last sixty years of isotope chemistry in the following general terms.

Tracer work

The use of isotope tracers in all branches of science is now widespread. Perhaps the most important chemical contributions are in chemical analysis and in studying reaction mechanisms. Almost all elements can be assayed conveniently by isotopic methods either by mass spectrometry or by radiometry. Such techniques are often more convenient than conventional chemical methods, and are frequently more sensitive by three or four powers of ten (*e.g.*, 10^{-10}g, as is detectable in silicon semiconductors). Neither the analyst nor the reaction kineticist can properly regard himself as a master of his field nowadays unless he understands the several isotopic methods applicable to his interests. In studies of chemical reactions, for instance, isotope methods are currently revealing some unexpected features. Thus previously ignored self-exchange reactions can take place between the methyl groups of a single organic molecule, an observation which is closely related to current views of the structures of electron deficient carbonium ions.

Nuclear chemistry

Apart from work related to the differences in the chemical properties of isotopes (which is also of importance in reaction mechanistic studies) the other main field of study is concerned with differences in the nuclear properties of isotopes. Perhaps the synthesis of the transuranic elements is most important because to do this at all necessitated development of new microchemical techniques, and the existence of a second (actinide) rare earth series makes one ask why Pa, Th, and U should exhibit such stability in their higher valence states, and what the properties of element 104 will be. But there are other more recent developments which promise to contribute increasingly to chemical knowledge. Exploitation of these will, it seems, be the main contribution of isotope chemistry over the next decade. These methods, with typical applications, are summarized below.

Method	*Application*
Nuclear magnetic resonance.	Identification of the structure of gallium chloride as $Ga^+ [GaCl_3]^-$.
Neutron diffraction.	Hydrogen bonding structure of ice.
Recoil of radioactive atoms.	Binding energies of bismuth to lead oxides.
Electronic excitation during radioactive decay.	Ionization of electrons from any shell depends on the effective nuclear charge on the electron.

NATURALLY OCCURRING PEPTIDES AND THEIR BIOLOGICAL SIGNIFICANCE

R. L. M. SYNGE

The Rowett Research Institute, Bucksburn, Aberdeenshire, Scotland (at present working at Ruakura Animal Research Station, Hamilton, New Zealand).

An attempt will be made to survey in outline the natural occurrence of amino acid residues in compounds either of relatively low molecular weight (<10,000) or of relatively simple chemical composition. These include:

A number of acylated amino acid derivatives (many are significant as coenzymes or as detoxication products);
Toxic substances from bacteria and fungi;
Capsular and cell-wall components of bacteria;
Hormones;
Enzyme inhibitors;
Some physiologically interesting products of the enzymic splitting of proteins,

Finally the question will be discussed of the possible role of substances of this class in the biosynthesis of proteins; attention will be drawn to some recently discovered peptide-nucleotide compounds.

THE SCOPE OF NUCLEAR RESEARCH IN NEW ZEALAND

T. A. RAFTER

Nuclear Science Institute, Lower Hutt.

At a meeting of Cabinet on 3 June, 1958, approval was given for the establishment of a Nuclear Research Institute in New Zealand. This Institute is to be a branch of the Department of Scientific and Industrial Research and is to be administered by the Department in collaboration with the University of New Zealand. The Institute is to incorporate the existing D.S.I.R. Division of Nuclear Sciences.

The policy of the Institute is to be formulated by a Committee on Nuclear Sciences. This Committee is a Sub-Committee of the Council of D.S.I.R., on which are representatives of industry, the University, and D.S.I.R. Cabinet approved the expenditure of £240,000 on the first stage of development of the programme.

Dr W. M. Hamilton, addressing the Symposium on Nuclear Science in Wellington on 25 February, 1959, discussed the development of nuclear science in New Zealand, saying that approval had been given to enter into negotiations for the purchase of a 3 MeV Van de Graaff accelerator as part of the first stage of development, after which is visualized the installation of a 1 MW research reactor, probably of the swimming pool type.

The paper will discuss the scientific reasons leading up to these decisions, the problems that have to be faced in their implementation, and the scope of the facilities the Institute plans to offer.

RADIOCHEMICAL LABORATORY DESIGN

The University of Auckland Isotope Laboratory

D. R. LLEWELLYN and A. L. ODELL

Chemistry Department, University of Auckland.

The laboratory described in this paper is a teaching laboratory designed to train personnel in the handling of radioactive isotopes up to a level of ten curies. Areas of a radiochemical laboratory are often classified as red, if the activity of the isotopes handled in that area is between one millicurie and ten curies, blue, if it is between one microcurie and one millicurie, and white, for less than one microcurie. It was not considered desirable to divide the laboratory into three sections because this would involve considerable movement of students within the laboratory, with the corresponding difficulty in detecting faulty technique, and would also be wasteful of space. It was thus decided to design each laboratory bench so that it could be used, without appreciable restriction, for inactive work and yet be readily converted by a single operation into a blue area or, with only a slightly more elaborate procedure, to a red area.

Students should be trained to handle activities of ten curies with materials of much lower activity, and a multiplication factor was therefore introduced such that, for the purposes of health physics calculations, activity was always assumed to be 10^3 times the actual activity. This raises certain difficulties with monitoring equipment which must now have very high sensitivity.

GENERAL LAYOUT

The entrance lobby to the radioactive suite is divided into two parts. The first part, the decontamination area, contains two washbasins, two hot-air hand driers, two foot and hand monitors, and circulation space for twelve students. This part is separated from the remainder by a low bench which divides the hot area from the cold area and on which all personnel entering the laboratory can sit to put on overboots which are stored in lockers immediately above it. Just beyond the barrier in the hot area are numbered lockers for storing numbered laboratory coats, which are worn on all occasions. Leading off this lobby are the dispensing room, which is surrounded entirely by corridor, the counting rooms, a "special equipment" room, the dark room and the main laboratory. Figure 1 gives the general layout of the laboratory.

MAIN LABORATORY

The contamination of a laboratory and the ingestion hazard is much more easily controlled if the laboratory is scrupulously clean and there are no horizontal surfaces on which dust can collect. An attempt has been made to obviate such surfaces by bringing all services into the laboratory from above. Each bench has, immediately above it, a service box suspended from the ceiling and carrying gas, water, electricity, compressed air, drains for condenser water, and inlets to two 12 in. fan ducts which terminate 50 ft from the ground. The standard bench

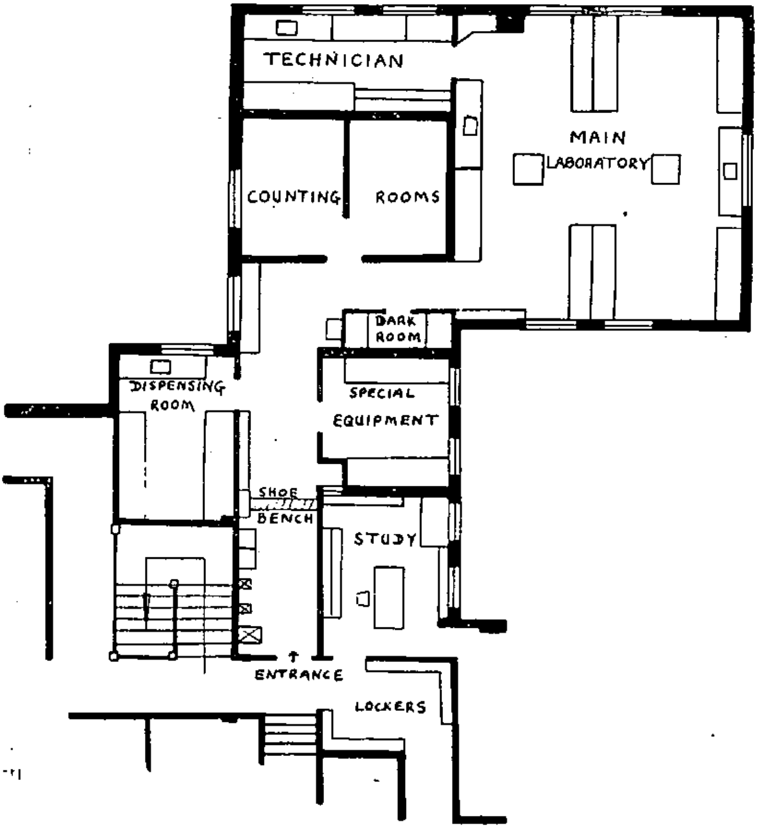


Fig. 1: General layout of laboratory.

module is shown in Fig. 2. It will be noticed that the bench top is supported by four tubular legs and that all laboratory furniture is suspended from this bench top and reaches to within only 12 in. of the floor, thus allowing for easy floor cleaning and polishing. For handling isotopes with moderate activity, a counterpoised glass screen, hinged on the edge of the service box, can be lowered to produce a fume cupboard with a sloping front which terminates 9 in. above the bench top. The fans in the service box produce a linear velocity of 200 ft/sec across the 9 in. gap. For work with the highest activity, total containment is necessary and this is obtained by fitting a glove box to the bench top and connecting it directly to the fan duct which must now contain an appropriate filter. Serious hazards may result

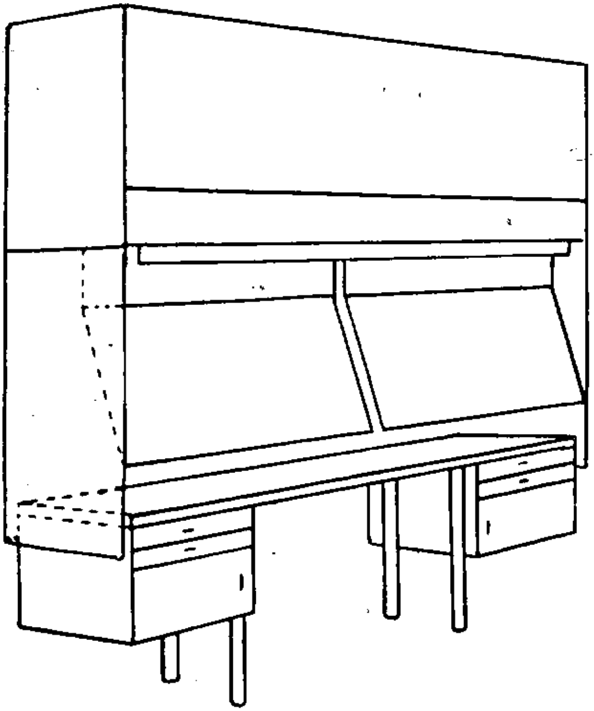


Fig. 2: Standard bench module.

if active material is inadvertently thrown down a sink. In this laboratory only two sinks are provided for washing up purposes and these are fitted with large polythene "hold up" bottles with built-in monitors so that active waste is readily detected and can be held until appropriate action is taken. Portable bench monitors are provided, one for each pair of students, and all apparatus is rinsed into storage jars and monitored before being washed in the sink.

COUNTING ROOM

The counting room contains no furniture. Three rails are attached to the walls on which counting racks, lead castles, tables, etc., can be hung as necessary. Fourteen inches from the ground is a duct carrying 230 V a.c. power with an outlet every 2 ft. Immediately above it, is a cable duct to carry wiring between any parts of the room. The oblique cover of this duct is arranged in 1 ft sections for easy removal. Similar rails are fitted at many points throughout the suite with a.c. power points below them.

DISPENSING ROOM

The dispensing room contains two of the 8 ft bench modules, for high activity work, and storage space for holding tanks in which isotopes can be stored until disposed of at sea or, for short lived isotopes, until the activity has fallen to a safe level.

RADIATION CHEMISTRY OF HYDROCARBON SYSTEMS

A. T. WILSON
Institute of Nuclear Sciences, Lower Hutt.

The effects of ionizing radiations on hydrocarbon systems will be discussed, with particular reference to possible useful applications. The olefin plus saturated hydrocarbon system, the saturated hydrocarbon system and the effect of temperature on the latter will be considered. The use of radiation to produce surface coatings will be described. The use of an electrical discharge to produce sheet-like macromolecules and the implications of this in the theory of chemical evolution will be discussed.

AN APPARATUS FOR LABELLING BY EXPOSURE TO TRITIUM GAS

A. L. ODELL, D. R. LLEWELLYN and G. R. WHITE
Chemistry Department, University of Auckland.

Since Wilzbach's discovery of the tritium labelling process by exposure to pure tritium gas (1) there have been several reports on this subject (2, 3, 4, 5, 6). Few details of the labelling apparatus have been given however and from those available (7, 5, 8) it appears that there is room for further development.

The apparatus needed for direct tritiation must be of unusual design and the important features of the apparatus described in this paper are as follows:

(1) Small quantities of tritium, less than 2 ml (5 curies) can be transferred almost quantitatively from one part of the apparatus to another without the use of an absorbant.

(2) Good pressure control can always be obtained and this is important if the tritum is recovered by absorption on heated uranium.

(3) Tritiation can be carried out at pressures above 1 atmosphere using reservoir H (Fig. 1). The efficiency of tritiation has been found to increase with pressure up to 100 mm (4) and it is intended to extend the investigation to higher pressures.

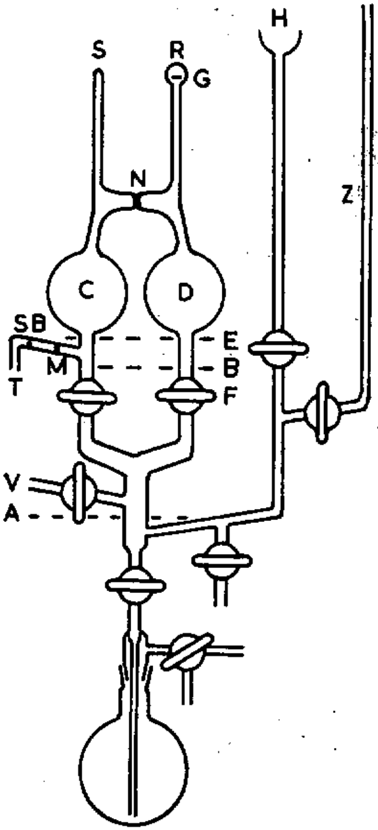


Fig. 1: Apparatus for labelling by exposure to tritium gas.

(4) Greased taps are never exposed to tritium, thereby eliminating the problem of handling and disposing of activated grease.

(5) All taps can be regreased while retaining the tritium in one or other of the limbs.

(6) By using the graduated side limb Z (Fig. 1) it is possible to determine the quantity of gas in the apparatus.

DETAILS OF APPARATUS

Refer Fig. 1 (M, N are porous discs of sintered ground glass [porosity 4] which will pass gases but not mercury). With the mercury level at A and the break seal vessel (5 ml) containing tritium (5 curies) attached at T, the apparatus is evacuated through V. The level is raised to B, the seal broken with steel ball SB and the tritium distributed in vessels C, D. (Less than

1 per cent. will be left in T). The level is then raised to E. By raising and lowering the level independently in both arms the tritium can be transferred to storage arm S or reaction arm R. S can be a simple glass vessel or can contain uranium powder heated by a tube furnace. The tritium can be trapped in S while the level in R is lowered through F to A and a new sample (in small boat G) placed in position. A liquid air trap is placed over R to prevent vapourization of volatile samples during pumping.

Literature Cited

(1) Wilzbach, K. E. (1957): *J. Amer. Chem. Soc.*, *79* : 1,013.
(2) Steinberg, D., Vaughan, M., Anfinsen, C. B., and Gorry, J. (1957): *Science*, *126* : 447.
(3) Rydberg, J., and Hanngren, A. (1958): *Acta. Chem. Scand.*, *12* : 332.
(4) Riesz, P., and Wilzbach, K. E. (1958): *J. Phys. Chem.*, *62* : 6.
(5) Dutton, H. J., Jones, E. P., Mason, L. H., and Mystrom, R. F. (1958): *Chem. and Ind.*, *36* : 1,176.
(6) Gordon, M. P., Intrieri, O. M., and Brown, G. B. (1958): *J. Amer. Chem. Soc.*, *80* : 5,161.
(7) Symposium on Tritium in Tracer Applications (1958): *Nucleonics*, *16* : 62.
(8) Swain, C. G., Kresge, J. (1958): *J. Amer. Chem. Soc.*, *80* : 5,281.

ELECTROMOTIVE FORCE STUDIES OF ELECTROLYTIC DISSOCIATION IN AQUEOUS CEROUS SULPHATE SOLUTIONS

J. M. AUSTIN and B. J. SHIRLAW
Chemistry Department, University of Canterbury, Christchurch.

From electromotive force measurements of the cell:

$$\begin{array}{c|lc|c} H_2\text{—Pt} & HCl & Ce_2(SO_4)_3 & AgCl\text{—}Ag \\ P_{H_2}=1\text{ atm.} & m_1 & m_2 & \end{array}$$

we have derived the thermodynamic dissociation constant in water at varying temperatures for the equilibrium system:

$$CeSO_4^+ \leftrightarrow Ce^{+3} + SO_4^=$$

The results agree reasonably well with those found from conductivity measurements on cerous sulphate solutions but differ considerably from those calculated from spectrophotometric studies of cerous sulphate solutions and measurements of cerous iodate solubilities in potassium nitrate and sulphate solutions. These different methods are compared with a view to finding the most reliable results for the above equilibrium system.

A NEW PHOSPHORUS SULPHIDE PHASE

G. A. RODLEY and C. J. WILKINS
Chemistry Department, University of Canterbury, Christchurch.

A new phosphorus sulphide phase may be obtained from melts of composition within the range P_4S_5 to $P_4S_{6\cdot 9}$. The X-ray powder pattern expands as the sulphur content of the melt falls. It is deduced that the phase is of variable composition. When red phosphorus is used as a reactant, addition of iodine is necessary to give a substantial yield of the new phase. Otherwise P_4S_7 is the chief product. The new sulphide is also formed from the reaction between hydrogen sulphide and phosphorus trichloride. It melts incongruently at 250° with separation of P_4S_7 and also decomposes below 200°. However, it persists for a few months at ordinary temperature. Extraction with carbon disulphide causes decomposition to P_4S_7 and P_4S_5.

Although the composition range of the newly identified phase includes P_4S_6, its existence would hardly explain the early reports of a sulphide of this stoicheiometric composition as the product from red phosphorus and sulphur. On the other hand the variable composition of the phase, its small temperature range of stability and its sensitivity to solvents and vacuum sublimination would have afforded the evidence considered by other investigators to weigh against the existence of any compound whatever in this composition region.

THE FLUORESCENCE OF A WEAK ACID

W. S. METCALF
University of Canterbury, Christchurch.

One might expect that the fluorescence of a weak acid whose conjugate base does not fluoresce would fall to one half in intensity at the pH at which half of the acid is converted to the base. This is so only if the rate of emission of fluorescence by the optically excited acid molecules is much faster than is the loss of a proton to give the nonfluorescent base. If the loss of a proton is the faster process, the fluorescence falls to one half in solutions which are much more acid, and where only a very small part of the acid has been converted to base.

The rate of emission of fluorescence is now a measurable quantity. Consequently it is possible, from a study of the effect of pH on the fluorescence of an acid-base system, to find upper or lower limits for the rate of loss of a proton from the acid, or in very favourable cases to measure this rate.

This paper describes such a study for the compound 9 methyl 10 morpholinyl-methyl anthracene whose basic form has a fluorescence intensity about 1 per cent. of that of the acid form.

ASSIMILATION OF CARBON FROM C^{14}-UREA BY LEAVES OF RYEGRASS AND RUSSIAN COMFREY

G. W. BUTLER and BERIS G. BUTLER
Plant Chemistry Division, Palmerston North.

Because there are a number of plants in which urease cannot be demonstrated, the possibility of alternative pathways for assimilation of urea is an interesting aspect of plant nitrogen metabolism. In this work the assimilation of 12.5 mM C^{14} – urea and ammonium C^{14} – bicarbonate was compared in ryegrass, which has moderate urease activity, and Russian comfrey (*Symphytum peregrinum*), in which urease activity cannot be detected by the usual methods.

With ryegrass the cut ends of leaves were dipped into the labelled solution; with comfrey discs were punched out and floated on the solution. Uptake and assimilation proceeded for periods of 1 to 16 hours in different experiments. Incorporation into the 80 per cent. ethanol-soluble fraction was then examined by paper chromatography, radioautography and "finger-printing".

It was found that carbon assimilation from urea proceeds quite rapidly in ryegrass leaves in the light. Strong labelling was always observed in sucrose, glutamic acid, glutamine, aspartic acid and alanine, and usually in two organic acid spots which are thought to be malate and carbamyl aspartate. The pattern was very similar to that seen for assimilation of C^{14} – bicarbonate, which proceeded at a somewhat faster rate than C^{14} – urea assimilation.

With Russian comfrey assimilation of urea in the light proceeded very slowly into sucrose and malate indicating that slight urease activity was present. In the dark the assimilation of urea by both species was very slight.

Thus in these experiments assimilation of carbon from urea appeared to proceed through urease action followed by carbon dioxide fixation and no evidence was obtained for alternative pathways.

THE METABOLISM OF CARBON DIOXIDE BY STREPTOCOCCUS BOVIS

D. E. WRIGHT
Plant Chemistry Division, D.S.I.R., Palmerston North.

Streptococcus bovis is a facultative anaerobe which is always present in the rumen. When grown in the presence of sucrose it will produce an extracellular polyglucosan, dextran, provided carbon dioxide is present in the growth flask.

The enzyme responsible for dextran synthesis, dextransucrase, synthesizes dextran according to the following equation:

$$\text{sucrose} \xrightarrow{\text{dextransucrase}} \text{dextran} + \text{fructose}$$

A study of its properties has shown that carbon dioxide does not affect its activity. The possibility that carbon dioxide influenced one of the metabolic pathways of sucrose fermentation was examined but no significant effect noted.

Growing *S. bovis* in the presence of labelled carbon dioxide has revealed the rapid assimilation of carbon dioxide by the bacteria. Extraction and hydrolysis of the bacterial cells has shown the presence of radioactivity mainly in aspartic acid with lesser amounts in glutamic acid, threonine, adenine, gaunine, uridylic acid and cytidylic acid.

The importance of carbon dioxide in dextran synthesis is considered to be due to the inability of *S. bovis* to utilize readily aspartic acid supplied in the growth medium. The significance of the growth factor requirements of *S. bovis*, the ability of Tween 80 to partially replace carbon dioxide, and similar effects of carbon dioxide with other bacteria will be discussed.

THE OXIDATION OF MALIC ACID BY MYCOBACTERIA

N. E. MORRISON
Travis Laboratory, Medical School, University of Otago, Dunedin.

Ultracentrifugation techniques have led to the separation of a particulate fraction from sonic extracts of *Mycobacterium smegmatis*, *M. stercoris* and *M. butyricum*. The particles sediment in the form of a gel containing yellow and red pigments and possess organized enzyme systems for the oxidation of L-malate and reduced diphosphopyridine nucleotide ($DPNH_2$); no addition of soluble cofactors is required. Succinate and fumarate are oxidized at 5 to 14 per cent. the rate of L-malate. The particles which contain 30 per cent. ethanol extractable lipids have not been found to oxidize other substrates. The product of L-malate oxidation has been identified chromatographically as oxalacetate and balance studies show the reaction is:

$$2 \text{ L-malate} + O_2 \rightarrow 2 \text{ oxalacetate} + 2\ H_2O$$

The properties of the L-malic oxidase system from *M. smegmatis* have been studied in detail. The optimum pH is 7.0 and the K_m, 5.2×10^{-3} M. The oxygen uptake is inhibited by quinacrine, dicoumarin and cyanide. Antimycin A is without effect. The L-malic oxidase system is stimulated by orthophosphate ions in non-phosphate buffers. The technique of plotting "difference spectra" in a double-beam recording spectrophotometer has shown the presence of cytochrome components which are readily reducible by L-malate and $DPNH_2$. The particles do not esterify orthophosphate with adenosine-5′-diphosphate in the presence of a hexokinase acceptor system during the oxidation of L-malate or $DPNH_2$.

There is no significant inhibition of L-malic oxidase following dialysis or treatment of the particles with finely divided charcoal. The carriers involved in the transport to oxygen are thus firmly bound to the particles. Attempts to detect bound pyridine nucleotides by chromatographic, chemical, enzymic or fluorometric methods have been completely nugatory. It is thus conceivable that the "cytochrome-linked malic dehydrogenase" functions without the participation of bound pyridine nucleotide.

The preparation of a phenol blue-linked malic dehydrogenase has been achieved by heat treatment of the particles. The preparation, still in a sedimentable state, does not consume oxygen in the presence of L-malate or significantly oxidize added $DPNH_2$. The properties of the phenol blue-linked malic dehydrogenase will be discussed.

PARTIAL STRUCTURE OF THE "BEAKER TEST" SUBSTANCE

D. W. RUSSELL
Plant Chemistry Division, D.S.I.R., Palmerston North.

In recent years certain antibiotics of fungal origin have been characterized as heteromeric peptides containing α-hydroxyacids alternating in a cyclic structure with α-aminoacids. Chemical studies of facial eczema toxicity by E. P. White at Ruakura have led to the isolation of a similar compound, from the fungus *Sporidesmium bakeri,* which is responsible for the "beaker test" for facial eczema toxicity. The observations of White on the structure of this compound, BTS, have now been confirmed and extended.

BTS is a white, crystalline, optically active substance, m.p. 260° (subl.). It is very soluble in glacial acetic acid and in chloroform, but only slightly soluble in other common organic solvents and water. Elementary analysis (R. L. M. Synge, personal communication) is consistent with the empirical formula $C_{16}H_{28}O_4N_2$. The infra-red spectrum is closely similar to that of amidomycin, which possesses a cyclic molecule composed of alternate valyl (-Val-) and α-hydro*iso*valeryl (-Vol-) residues. Vigorous acid hydrolysis liberates valine and leucine, together with a third ninhydrin-positive substance X.

Mild alkaline hydrolysis degrades BTS with the formation of two acidic compounds, α- and β-sporidesmolic acids (SA). These are readily separable by extraction with chloroform, in which α-SA is almost insoluble, whereas β-SA is very soluble.

β-SA is a white crystalline solid, m.p. 164°, neutralization equivalent 332. It is optically active, contains nitrogen but possesses no free amino group. Partial acid hydrolysis liberates X, leucine and valine in that order, together with an ether-soluble acid tentatively identified by paper chromatography as α-hydroxy*iso*valeric acid. Acid hydrolysis of X liberates further quantities of leucine and valine, although hydrolysis apparently does not proceed to completion. On the basis of these findings the structure H.Vol.Val.Leu.OH is proposed for β-SA and H.Val.Leu.OH for X. The dipeptide sequence could not be confirmed by the FDNB method of F. Sanger. These and other observations on the structure of BTS will be discussed, together with further structural work on both α- and β-sporidesmolic acids.

ELECTROPHORESIS OF THE COPPER COMPLEXES OF GLYCINE, GLYCYLGLYCINE AND DIGLYCYGLYCINE

P. R. CARNEGIE and R. L. M. SYNGE
Ruakura Animal Research Station, Hamilton and Rowett Research Institute, Scotland.

The copper complexes of glycine, glycylglycine and diglycylglycine were prepared by saturation with copper phosphate at pH 9.18. Their electrophoretic mobilities were determined by paper electrophoresis at the same pH and compared with the mobilities of glycine, glyclyglycine and diglycylglycine determined under the same conditions. The anionic mobility of the copper complex of the dipeptide was much less than the mobility of the free dipeptide. On the other hand, the anionic mobility of the copper complex of the tripepetide was only slightly less than the mobility of the free tripeptide. A clear separation of the copper complexes of the dipeptide and the tripeptide was thus achieved. The results were compared with those to be expected from the data of Dobbie, Kermack and Lees (1955). The method may prove generally useful for separating dipeptides from higher peptides.

Literature Cited

Dobbie, Hazel; Kermack, W. O.; Lees, H. (1955): *Biochem. J.*, 59 : 240, 246, 257.

EXTRACTION OF PLANT MATERIALS

R. GARDNER

Dr R. Gardner & Partners Ltd., 41 Dowling Street, Dunedin.

This is a general treatment of the subject of extraction by means of solvents from vegetable drugs and similar materials.

Aspects dealt with include application of the two-film theory to extraction, effect of comminution, relationship between solvent volume and quantity of extract, use of maceration methods, technique of percolation and an approach to a quantitative theory of percolation.

CHEMICAL AND BIOCHEMICAL ASPECTS OF SELENIUM

I. M. CAIRNEY, F. B. COUSINS and C. DRAKE

(Abstracts of the three papers in this session are not yet available but will be cyclostyled and distributed at Conference.)

ACID AND BASE STRENGTHS AT HIGH TEMPERATURES

A. J. ELLIS

Dominion Laboratory, D.S.I.R., Wellington.

There have been very few conductance measurements on electrolytes above 100° C since the pioneer experiments of Noyes early this century. In the present paper a design is given for a high-temperature cell which has been used to measure, by standard conductance techniques, the variation with temperature of weak acid and base strengths.

The results presented include K_a values for acetic, propionic, butyric and benzoic acids up to 250° C. From these it has been possible to obtain an improved general equation to predict the dissociation of weak acids at high temperatures. The derived thermodynamic functions ΔS, ΔH, ΔC_p and $\delta \Delta C_p / \delta T$ of dissociation are presented.

The factors contributing to the variation in acid and base strength with changes of temperature and pressure are discussed and the concept of acidity and pH in water solutions at high temperature is examined from the point of view of geological processes.

GEOCHEMISTRY OF HOT CHLORIDE-WATER UNDERLYING THERMAL AREAS

S. H. WILSON

Institute of Nuclear Sciences, D.S.I.R., Wellington.

The investigations at Wairakei have shown that the discharges of the bores come from a body of water of temperature about 260° C, and chloride content 1,500 p.p.m. Early in the chemical work it was surmised from the constancy of the ratios Cl/F, Cl/B and Cl/As that the body of water was of constant composition. Later work has shown, now that the upper layers of altered water have gone, that the water is of remarkably constant composition, as regards chloride content and the further ratios, Cl/CO_2, Cl/S, Cl/NH_4, Na/K and Na/Li. Statistical examination of the analyses has shown that the chloride content has altered little in five years. Slight variations in chloride content seem to be due to loss of heat as steam or by conduction from the original water, or to some dilution with cold water.

It seems probable that the water has obtained many of its constituents from magmatic steam. However, from the high Cl/CO_2 ratio, from the low nitrogen content and from the sulphur isotope evidence, it seems that the water has lost about 90 per cent. of its original gas content together with corresponding amounts of steam. The conclusion is that the origin of the water can not be directly under Wairakei but that the water must have travelled laterally from its origin losing gas and steam on the way.

Other thermal areas here and abroad seem to be maintained by hot chloride water. If water samples from springs only are available, one can use only the ratios, Cl/F, Cl/B, Cl/As, Cl/Br, and Br/I. The evidence is that ratios characteristic of each area are constant in that area and much different from those of other areas. However, the results from bores at Waiotapu are difficult to interpret and indicate that there is more than one body of hot chloride water.

It does not seem that magmatic steam can be the sole source of the heat in the mixture of ground water and magmatic steam. The heat of cooling and solidification of igneous rocks cannot be neglected. The hypothesis is put forward that there has been a long preliminary period, say 20,000 years, in which both magmatic constituents and conducted heat have soaked out from a plutonic mass and this is followed by a shorter period, say 2,000 years, of hot spring activity.

ULTRA-VIOLET ABSORPTION SPECTRA OF SULPHUR-OXY ANIONS IN NATURAL WATERS

R. M. GOLDING
Dominion Laboratory, D.S.I.R., Wellington.

Most of the sulphur-oxy anions have a characteristic ultraviolet absorption spectrum and a survey of these spectra is given. Particular mention is made of the polythionates and their separation by chromotography on Dowex 1X-2 resin which gives an accurate method for their analysis. The complex equilibria

$$SO_2 \leftrightarrow HSO_3^- \leftrightarrow SO_3^{2-} \leftrightarrow HS_2O_5^- \leftrightarrow S_2O_5^{2-}$$

is discussed in the light of the spectral results. Finally the complex nature of sulphur in geothermal waters is discussed and the need is indicated for greater care in analysing sulphur anions in natural waters.

CYCLITOLS FROM TANEKAHA

S. K. ADHIKARI, R. A. BELL and W. E. HARVEY
Victoria University of Wellington.

The heartwood of tanekaha (*Phyllocladus trichomanoides*) is rich in cyclitols, which can be readily obtained from the wood by extraction with acetone and water. Fractionation of the water soluble extract by crystallization, partition chromatography, and electrophoresis has shown that it consists mainly of sequoyitol and pinitol, together with smaller amounts of *myo*-inositol, *d*-inositol, and arabinose. Methods for the separation of complex mixtures of cyclitols and sugars will be briefly discussed.

THE WATER SOLUBLE POLYSACCHARIDES OF PINUS RADIATA

D. J. BRASCH
Dominion Laboratory, D.S.I.R., Wellington.

Two polysaccharides have been isolated from the water soluble carbohydrates of New Zealand grown *Pinus radiata,* an arabogalactan and galacto-gluco-mannan. Studies on the arabogalactan show it to have a highly branched structure, the branching occurring mainly at position 1, 3 and 6 of *D*—galactopyranose residues. All of the arabinose units are present as *L*—arabinofuranose end groups.

Preliminary experiments on the galacto-gluco-mannan are also reported.

THE PARTIAL STRUCTURE OF DACRYDOL, A POLYHYDROXY DITERPENE

P. K. GRANT
Dominion Laboratory, D.S.I.R., Wellington.

The chemistry of a new polyhydroxylated diterpene will be discussed. This diterpenoid tetrol, for which the name "dacrydol" is proposed, has been isolated from the heartwood extractives of *Dacrydium colensoi* (silver pine), and a partial structure for its chemical constitution will be proposed. Points of unusual chemical behaviour and the stereochemistry of dacrydol as related to other diterpenes will be discussed.

THE NEED IN NEW ZEALAND FOR A CHEMICAL INDUSTRY BASED ON COAL

J. I. GRAHAM
formerly Professor of Coal Mining (Research), University of Otago, *now retired*

New Zealand could produce from coal many commodities at present imported at considerable cost in overseas funds, *e.g.*, tar, bitumen, creosote, phthallic anhydride, pentachlorophenol, nitrogen compounds and various raw materials for the plastics industry and liquid fuels.

The complete conversion of coal into oil is very attractive but this does not yet appear to be economic, although tests by I.C.I. have shown that by high pressure hydrogenation Stockton coal can produce more oil per ton than most other coals tested. Further research on both complete and partial hydrogenation of these coals is most desirable. The production of liquid fuels from synthesis gas is more applicable to low rank coals cf. use of brown coal, Yallourn, Australia.

Carbonization of 500 tons of Buller coal per day would give the 9,000 tons of tar required by the Ministry of Works and other concerns above that now produced by gas undertakings. Plant which will give either metallurgical coke or smokeless domestic fuel to suit market demands is desirable. The most suitable site for coke ovens and other chemical works is Ngakawau, near Westport, where, with the present mining equipment, high quality coal could be made available at 45s. per ton or less.

Production of ammonia from hydrogen obtained by thermal decomposition of coal, coke, or gaseous hydrocarbons is now a well established economic process even though oxygen and nitrogen have to be liquified on a tonnage basis. Unfortunately the annual consumption of nitrogenous fertilizers in New Zealand, although increasing, is at present only about 3,500 tons nitrogen because of the widespread use of clover. Nevertheless, bearing in mind the possibility of supplying some of the underdeveloped countries of Asia, the erection of plant to yield 10,000 tons of ammonia from hydrogen derived from coke-oven gas should be an economic proposition. From this nitric acid, ammonium nitrate or urea could be made according to market requirements. The severe shortage of potash in New Zealand makes the extraction of this either from glauconite, or other mineral, from seaweed or from sea water by the Norduco process a matter of urgency. Nitric acid would be required in quantity and an increased output of ammonia would be necessary.

An integral part of the new industry should be the generation of cheap electricity at a coal-fired station using Charleston lignite and other coals high in sulphur, recovery of the latter from flue gases helping to reduce cost of generation and the quantity of imported sulphur.

There is need for an extended programme of research, both technical and fundamental, on New Zealand coals.

METALLURGICAL COKE FROM NEW ZEALAND COAL

W. G. HUGHSON
Dominion Laboratory, D.S.I.R., Wellington.

The great upsurge in the manufacture of steel in most industrial countries has focussed attention on the manufacture of suitable metallurgical coke and this in turn has led us to consider what coals are available for the purpose. It has fallen to the lot of the chemist to be responsible for analysing coals and cokes. He must study the effect of the various coal constituents on the final carbonized product and must know what elements are deleterious to metals and steels in subsequent processes. This paper gives a brief history of coke making in New Zealand up to the present time.

Availability of reserves are examined with a view to selecting the coals which are suitable, either alone or in a blend, for the manufacture of a suitable metallurgical coke. The main characteristics of the coals are volatile matter, ash, sulphur, phosphorus, and coking properties. In the resultant coke we must consider moisture, size grading, hardness, grindability, reactivity, combustibility and quantity and composition of ash. Knowing the requirements of a suitable coke from world experience, our reserves can be examined to determine the quantity of suitable coal available. It is then really a matter for the economist to examine the demand for coke in New Zealand, the prospects for overseas sales, the optimum size of plant and if and where the plant should be erected. Alternatively, an agreed mix (or individual coals) might be sold overseas for treatment in existing plant.

COAL IN THE NUCLEAR AGE

W. B. WATSON
School of Mines and Metallurgy, Otago University.

This review attempts to determine the correct role for coal, in the world and in New Zealand, in an age moving towards increasing utilization of nuclear power. World power requirements are expected to increase at a rate of 3½ per cent. per year, and if this increased demand is provided by oil and coal, world reserves will be exhausted in 54 and 111 years respectively. An additional source of power is required, and nuclear power is the only practical alternative.

At present rates of production, world coal reserves are adequate for 1,275 years and oil reserves for 154 years. If oil production continues to increase at a rate of 7½ per cent. per year, oil reserves will be exhausted in 35 years. Over 50 per cent. of oil production is used for transport and small-power units, and the demand will increase with increasing use of automobile and air transport, and dieselization of railways and shipping. Nuclear generated electricity can be used for railways and nuclear power may have limited direct application to railways and shipping. For all transport, nuclear power has the problems of minimum economic unit size, weight of screening, and possible widespread contamination in the event of a fault or accident, and it is unlikely to replace completely the internal combustion engine.

Possible ways of safeguarding future oil supplies for transport are to:

(1) Limit oil production and restrict its use to transport;
(2) Increase percentage recovery;
(3) Convert natural gas to oil;
(4) Recover oil from oil shale;
(5) Convert coal to oil.

There are economic disadvantages to all these methods at the present time, but in the near future both oil shale and coal will have to be exploited for oil production; coal with its larger reserves has the greater potential. The oil-from-coal industry dates back to 1850 but in comparison with natural oil it has usually been economic only in special circumstances, *e.g.*, in Hitler Germany and now in South Africa where, for obvious reasons, coal is the cheapest in the world. Further research on the process is required to reduce the capital cost and minimum economic size of plant, and permit the exploitation of relatively small blocks of coal.

In New Zealand, immediate increases in power demands will be provided by further development of hydro-electricity and possibly by gas from the complete gasification of sub-bituminous coal, and long-term increases by the introduction of nuclear power. The percentage of power requirements provided by coal is steadily declining but existing markets and possible industrial development should ensure the continued prosperity of the Waikato and Southland coalfields.

The Grey and Buller coalfields have difficulties due to the poor transport facilities to markets and production is tending to decline. The Grey coalfield provides the coking coal for the country's gasworks but reserves are limited and their rapid exhaustion by exporting coal does not appear to be in the best interests of the country. Various schemes have been advocated for the location of industry on the Buller coalfield but most schemes require only a small consumption of coal. The only effective solution to the declining prosperity of the Buller, and one which would utilize the natural coal resources of the country is the introduction of an oil-from-coal industry. This should be an economic proposition in the near future and ultimately a necessity.

CHEMICAL COMPOSITION OF FRUITS IN RELATION TO BITTER PIT OF APPLES

H. O. ASKEW

Cawthron Institute, Nelson.

Bitter-pit is a world-wide storage affliction of a number of, but not all, varieties of apple, which appears to be due to physiological causes. To date very little work has been done on the chemical composition of fruit in relation to this defect.

As a preliminary to further work the changes in dry matter, mineral, nitrogen, and sugars content of apples of Cox's Orange variety have been examined. Beyond the expected changes in mineral and nitrogen contents there occur variations in the proportions of the several elements calcium, magnesium, potassium, sodium, and phosphorus during development and approach to maturity of the fruits. This could be important in relation to the storage quality at harvest. Turning to the sugars, glucose remains relatively constant throughout growth, but sucrose and fructose increase rapidly and are at high levels at maturity of the fruit. The level of sugars has been found to vary with size of the fruit at harvest. Moreover the amounts of sugars, and the proportions between them, vary in different parts of the apple. Incidence of bitter-pit is definitely related to size and sugar content of the fruit. It is probably related also to the amounts and proportions of the minerals in the fruit. Pitted tissue differs considerably in chemical composition from healthy tissue.

Analyses are also available for varieties of apple other than Cox's Orange to see if there is any relationship between chemical composition and susceptibility to bitter-pit. Companion leaf samples to those of the fruit have also been analysed.

Some workers have suggested that the level of calcium, and its proportion to other elements in the tissue is important, low calcium being associated with incidence of pitting. To explore further this suggestion, Cox's Orange trees have been sprayed with solutions of acetates of calcium, magnesium, potassium, and sodium. Use of the calcium salt has given very promising reductions in incidence of bitter-pit. On the other hand the other compounds have increased the amount of pitting. Some progress towards commercial control of this serious disease therefore appears possible.

The chemical data already obtained show interesting correlations between a number of the constituents estimated and the severity of incidence of the ailment. It does not seem to be too much to claim that it may prove possible to offer advice to growers as to the best time to pick their fruit, and to offer a prediction of the likelihood or not of bitter-pit appearing in a particular season's fruit.

This paper is a brief account of a large amount of analytical and field work carried out by a team at the Cawthron Institute.

COLORIMETRIC ESTIMATION OF PROTEIN IN MILK BY DYE-BINDING CAPACITY WITH AMIDO BLACK OR ORANGE G

R. M. DOLBY
The Dairy Research Institute (N.Z.), Palmerston North.

Acid and basic dyes (Orange G and Safranine) were used by Fraenkel-Conrat and Cooper (1944) to determine basic and acidic groups in proteins. Schober and Hetzel (1956) applied this principle to estimate protein in milk using Amido Black 10 B. Diluted milk and dye solution, buffered to pH 2.8, were mixed and centrifuged. The unprecipitated dye was measured in a spectrophotometer.

The method was improved by Steinsholt (1957a, b) and by Raadsveld (1957, 1958). The last two workers reported that in 95 per cent. of milk samples, deviation from Kjeldahl protein was less than 0.1 per cent. The method was considerably more accurate than formol titration.

Udy (1956) used Orange G in a similar way to estimate protein in flour and in milk. His method was further developed by Ashworth and Seals (1957) and by Treece, Gilmore and Fechheimer (1958, 1959). The latter works claimed that, disregarding NPN, the dye method was as accurate as the Kjeldahl method and took less than one-fourth the time.

The methods of the above workers were adopted by the present writer as follows:

Dye Solutions

Amido Black 10 B (Merck's "for electrophoresis") 0.6165 g/l. in 0.3 M citric acid.

Orange G (B.D.H. S.S.) 1 g/l. in 0.3 M citric acid.

Method

Dilute 5 ml milk with water to 100 ml. Add 5 ml of the diluted milk to 10 ml of dye solution in a centrifuge tube and shake. After 10 minutes, centrifuge at 2,500 rev/min for 5 minutes. Dilute 3 ml of the supernatant to 100 ml and read optical density at 615 mμ for Amido Black or at 480 mμ for Orange G. Run a blank with water instead of milk and record difference in density between blank and sample.

Data will be presented on the effect of ratio of dye to protein, purity of dye, correlation between the two methods (Amido Black and Orange G) and of each method with the Kjeldahl method for protein in milk of individual cows. The effect of difference in dye-binding capacity between casein and lactalbumin will also be considered.

Literature Cited

ASHWORTH, U. S. and SEALS, R. (1958): *J. Dairy Sci., 41* : 227.
FRAENKEL-CONRAT, H. and COOPER, M. (1944): *J. Biol. Chem., 451* : 239.
RAADSVELD, C. W. (1957): *Off. Org. K. ned. Zuivelbd., 49* : 823.
RAADSVELD, C. W. (1958): *Off. Org. K. ned. Zuivelbd., 50* : 146.
SCHOBER, R. and HETZEL, H. F. (1956): *Milchwiss, 11* : 123.
STEINSHOLT, K. (1957a): *Meieriposten, 46* : 259.
STEINSHOLT, K. (1956b): *Meieriposten, 46* : 901.
TREECE, J. M. , GILMORE, L. O. and FECHHEIMER, N. S. (1958): *J. Dairy Sci., 41* : 727.
TREECE, J. M., GILMORE, L. O. and FECHHEIMER, N. S. (1959): *J. Dairy Sci., 42* : 367.
UDY, D. C. (1956): *Nature* [Lond.], *178* : 314.

HEATING REACTIONS IN WET WOOL

H. P. ROTHBAUM

Dominion Laboratory, D.S.I.R., Wellington.

When wet wool is baled, the temperature of the bales can rise up to 75° C. It has been shown that this heating is due to thermophilic bacteria whose maximum growth temperature is about 76° C. The heat output of the bacteria has been measured and found to be considerably greater than the value reported in the literature.

Wool in equilibrium with air over 80 per cent. relative humidity may also show some heating due to mould growth. The simplest effective way of preventing such heating is to dry wool to a moisture content corresponding to a humidity below 60 per cent.

Apart from biological heating it has been found that wet wool can be directly oxidized by air or oxygen and this reaction is sufficiently exothermic to heat slipe wool from 80 to 100° C under near adiabatic conditions. It has been shown that the rate of this reaction depends on the water content and fibre length of the wool and up to 50 per cent. of the weight of wool has been lost by oxidation at 100° C in oxygen. The products are carbon dioxide and a residue whose appearance differs completely from wool, but whose chemical analysis and amino acid composition (determined by paper chromatography) is close to that of ordinary wool. The only significant change is oxidation of cystine to other sulphur containing amino acids and this agrees with the usual assumption that most oxidizing agents preferentially oxidize cystine (12 per cent. of the wool). However, no mechanism can yet be suggested for this unusual, drastic, direct low temperature oxidation of a major portion of the wool.

OFFICIAL NOTICE

A General Meeting of members of the New Zealand Institute of Chemistry (Inc.) will be held in the Chemistry Lecture Theatre, Otago University, at 4.30 p.m., on Thursday, 27 August, 1959.

AGENDA

(1) Apologies, welcome, etc.
(2) Confirmation of the Minutes of the last General Meeting held at the Hamilton Girls' High School on 27 August, 1958.
(3) Presidential remarks.
(4) Institute Prizes for 1959.
(5) Officers for the coming year.
(6) Annual Report for the year ending 31 August, 1959.
(7) Balance Sheet for the eighteen month period ended 30 April, 1959.
(8) General.

W. E. Harvey,
Hon. General Secretary.

CONFERENCE PROGRAMME

Tuesday, 25 August

Evening

7.30 Enrolments, Allan Hall, University of Otago.
8.00 Opening of Conference and Supper, Allan Hall.

Wednesday, 26 August

Morning

9.00 Late enrolments, Chemistry Dept., University of Otago.
9.30 The Impact of Isotopes on Chemistry. J. F. Duncan, Guest Lecturer.
10.30 Morning Tea.
11.00 The Design of the Isotope Laboratory at the University of Auckland. (D. R. Llewellyn and A. L. Odell).
11.30 The Radiation Chemistry of Hydrocarbon Systems. (A. T. Wilson)
12.00 Tritium labelling and Tritium counting. (A. L. Odell, D. R. Llewellyn and G. R. White).

Afternoon (A Series)

2.30 Electromotive Force Studies of Electrolytic Dissociation in Aqueous Cerous Sulphate Solutions. (J. M. Austin and B. J. Shirlaw)
3.00 A New Phosphorus Sulphide Phase. (G. A. Rodley and C. J. Wilkins)
3.30 The Fluorescence of a Weak Acid. (W. S. Metcalf)

Afternoon (B Series)

2.30 Assimilation of Carbon from C^{14}-Urea by Leaves of Ryegrass and Russian Comfrey. (G. W. Butler and Beris G. Butler)
3.00 Metabolism of Carbon Dioxide by *Streptococcus bovis*. (D. E. Wright)
3.30 The Oxidation of Malic Acid by Mycobacteria. (N. E. Morrison)
4.00 Afternoon Tea.
4.30 Easterfield Lecture. (A. D. Campbell)

Evening

8.00 Chairman's Address, Chairman N.Z. Section R.I.C. (G. M. Moir) 'The Biochemistry of Cheese'. Film and supper.

Thursday, 27 August

Morning

9.15 Naturally Occurring Peptides and their Biological Significance. R. L. M. Synge, Guest Lecturer.
10.15 Morning Tea.

A Series

10.45 Chemical and Biochemical Aspects of Selenium. (Papers by I. M. Cairney, F. B. Cousins, C. Drake).

B Series

10.45 Partial Structure of the "Beaker Test" Substance. (D. W. Russell)
11.15 Electrophoresis of the Copper Complexes of Glycine, Glycylglycine and Diglycylglycine. (P. R. Carnegie and R. L. M. Synge)
11.45 Extraction of Plant Materials. (R. Gardner)

Afternoon (A Series)

2.30 Acid and Base Strengths at High Temperatures. (A. J. Ellis)
3.00 Geochemistry of Hot Chloride-Water Underlying Thermal Areas. (S. H. Wilson)
3.30 Ultra-Violet Absorption Spectra of Sulphur-Oxy Anions in Natural Waters. (R. M. Golding)

Afternoon (B Series)

2.30 Cyclitols from Tanekaha. (S. K. Adhikari, R. A. Bell and W. E. Harvey)
3.00 Water Soluble Polysaccharides of *Pinus radiata*. (D. J. Brasch)
3.30 The Partial Structure of Dacrydiol, a Polyhydroxy Diterpene. (P. K. Grant)
4.00 Afternoon Tea.
4.30 Annual General Meeting, N.Z.I.C., Chemistry Lecture Theatre.

Evening

8.00 Annual Meeting, N.Z. Section R.I.C., Chemistry Lecture Hall. Discussion Groups.

Friday, 28 August

Morning

9.30 The Scope of Nuclear Research in New Zealand. T. A. Rafter, Guest Lecturer.
10.30 Morning Tea.

A Series

11.00 The Need in New Zealand for a Chemical Industry Based on Coal. (J. I. Graham)
11.30 Metallurgical Coke from New Zealand Coal. (W. G. Hughson)
12.00 Coal in the Nuclear Age. (W. B. Watson)

B Series

11.00 Chemical Composition of Fruits in Relation to Bitter Pit in Apples. (H. O. Askew)
11.30 Colorimetric Estimation of Protein in Milk by Dye Binding Capacity with Amido Black or Orange G. (R. M. Dolby)
12.00 Heating Reactions in Wet Wool. (H. P. Rothbaum)

Afternoon

Visits (*see* Notice Board).

CHAIRMAN'S ADDRESS

On Wednesday evening an address will be given by Dr C. M. Moir, Chairman of the N.Z. Section of the R.I.C. Dr Moir is Dairy Chemist in the Agriculture Department's Wallaceville Dairy Laboratory and the subject chosen is "The Biochemistry of Cheese". This will deal mainly with Cheddar cheese and there will probably be a short film to show the cheese-making process. Some samples of this and other types of cheese now made in New Zealand may also be available for gastronomic analysis at supper-time.

EASTERFIELD MEDAL — 1959

The Easterfield Medal for 1959 has been awarded to Dr A. D. Campbell, Lecturer in Chemistry, University of Otago. A graduate of Otago, Dr Campbell was first appointed to the staff of the Chemistry Department in 1948. Since 1951 he has been in charge of the Micro-chemical Laboratory which serves a large number of laboratories throughout New Zealand. Dr Campbell spent 1954 at the Glasgow University as Corday-Morgan Commonwealth Research Fellow. In 1955 he was awarded the Morcom Green, Edwards Prize. Dr Campbell will deliver the Easterfield Address at the forthcoming Conference.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE FOR 18 MONTHS ENDED 30 APRIL, 1959

1957	INCOME			
	Administration Expenses			
250	Salary Registrar		375 0 0	
111	Travelling Expenses		344 17 4	
36	Printing and Stationery		88 16 2	
37	Honorarium Secretary		84 0 0	
60	Branch Expenses Allowance		90 0 0	
26	Postage and Sundries		77 16 10	
12	Audit Fee		15 15 0	
7	Depreciation		8 13 0	
539				1084 18 4
	Chemistry in Action			69 0 6
	Journal Expenses			
364	Printing Costs		649 7 8	
27	Postage		40 1 2	
21	Editor's Honorarium		52 10 0	
412	Total Expenses		741 18 10	
287	*less* Advertising	269 12 11		
30	Subs.	52 7 6		
			322 0 5	
95	Total Cost to Institute			419 18 5
42	Provision for Taxation			17 4 6
34	Conference Surplus Transferred to Overseas Visitors Fund			—
23	Examination Committee Expenses			19 18 0
313	Excess of Income Transferred			—
1046				£1,610 19 9

1957	EXPENDITURE		
	Subscriptions	1220 4 10	
	Proportion Compounded Subscriptions	2 3 9	
962			1222 8 7
	Interest		
	Post Office Savings Bank	8 2 11	
	National Savings	31 3 5	
26			39 6 4
25	Examination Committee Fees		34 10 0
	Conference Surplus	12 5	
	less R.I.C. Share	2 5	
33			10 0
	Excess of Expenditure Over Income for the Year Transferred to Accumulated Funds		314 4 10
1046			£1,610 19 9

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT 30 APRIL, 1959

1957	LIABILITIES	£	s.	d.	£	s.	d.
	Sundry Creditors	59	13	11			
363	Provision for Taxation	24	12	6			
					84	6	5
59	Subscriptions Paid in Advance				77	3	0
	Provision for Printing	150	0	0			
	Provision for Essay Prize	30	0	0			
–	Provision for Overseas Visitors Travelling	75	0	0			
255					255	0	0
	Accumulated Funds						
	Balance 1.11.57	1600	4	9			
	less Transfer to Trust Fund		—				
	less Excess of Expenditure Over Income	314	4	10			
1600	Balance 30.4.59				1285	19	11
1091	Trust Fund				1143	11	2
30	Compounded Subscriptions				27	13	3
26	I.C.I. Prize					—	
3424					£2,873	13	9

1957	ASSETS	£	s.	d.	£	s.	d.
	Cash Balances						
	Bank of New Zealand	140	3	11			
	Petty Cash	1	0	6			
	Post Office Savings Bank	214	11	5			
1027					355	15	10
625	National Savings Account				656	3	9
	Subscriptions in Arrears	656	18	0			
	less Provision for Overdue Subscriptions	50	0	0			
497					606	18	0
139	Sundry Debtors — I.C.I. Prize				26	5	0
	Office Equipment at Cost	66	3	0			
	less Depreciation	6	3	0			
17					60	0	0
	Addressograph Plates						
	Balance 1.11.57	8	0	0			
	less Depreciation	3	0	0			
8					5	0	0
	Trust Fund Investments						
	Post Office Savings Bank	613	11	2			
	Hutt County Council Debentures	500	0	0			
	Amount Receivable	30	0	0			
1091					1143	11	2
20	Advance 1959 Conference				20	0	0
3424					£2,873	13	9

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

TRUST FUND FOR THE PERIOD ENDED 30 APRIL, 1959

1957				By Balance 1.11.1957	1091	7	1
To Balance Carried Down	1143	11	2	Interest on Deposit	22	4	1
				Interest on Debentures	30	0	0
	£1,143	11	2		£1,143	11	2

AUDITORS' CERTIFICATE

We have audited the books of the New Zealand Institute of Chemistry (Inc.) for the period ended 30 April, 1959, and have compared them with the vouchers produced to us, and with the above balance sheet, and accompanying statements. We have verified the various cash balances, and certify that, in our opinion, the balance sheet shows the true position of the Institute.

Wellington, N.Z.
12 June, 1959.

DYMOCK, MacSHANE & SCLANDERS
Auditors

Correspondence

RECRUITMENT OF CHEMISTS AND TEACHERS

SIR,

In the April issue (*J. N.Z. Inst. Chem.*, 23 : 46) I have read of the good work being done by Professor D. R. Llewellyn and others in conducting Auckland sixth-form students over laboratories in an attempt to broaden their education and to induce them to take up chemistry as a profession.

This is indeed commendable as too often in New Zealand one who is teaching chemistry feels that the subject unfortunately becomes rather abstract because it is impossible to visit great chemical engineering works.

But on the other hand I am afraid that such visits will do little to induce sixth-form pupils to take up chemistry as a profession because by that time, in nearly all cases, their professional future is planned by reason of the subjects they have elected to take for their University Entrance and Scholarship years. The best one could hope for in these circumstances is to divert some who had chosen allied professions such as engineering to the profession of chemistry. This would give no real increase in the supply of available scientists. Perhaps some students might be diverted from medicine, which would of course be a definite gain, as it would seem that at present this profession, by reason of its glamour and monetary opportunities, obtains too many of our best intellects.

The suggestion I would make then, is to take all the top fourth forms of the schools on these conducted tours and glamourize chemistry and the sciences generally, and stress that if they wish to enter the profession of chemistry, etc., they must choose the hard path to School Certificate and study, in Forms 5 and 6, mathematics, chemistry and physics. Then there might be real purpose in the conducted tours of sixth-form students.

In conclusion may I make a plea for emphasis on the need for teachers of mathematics and science? It is seldom that a New Zealander attains the stature of Rutherford, and indeed perhaps his greatest contribution to society was as a teacher and an inspirer of others. A dedicated scientist could become a teacher during term time, and, in the 12 weeks or so which a generous society insists on its pedagogues accepting as holidays, he could devote himself without let or hindrance to his research. Perhaps in thirty years' time he would get just as much satisfaction and joy on meeting one of his old students, a complex of molecules, as he would when he recalled, say the time he was able to elucidate the structure of a complex protein molecule!

C. C. WERRY,
Head of Science Department,
Dannevirke High School.

25 May, 1959.

[Professional bodies such as our Institute must assume increasing responsibility for ensuring an adequate supply of future scientists. The suggestion in this letter that Branches, in arranging visits and lectures for sixth formers, are leaving their approach too late, merits very careful consideration. Large numbers at the fourth form level would constitute a problem but this would not be insurmountable since we could as suggested above, restrict ourselves to the brighter pupils who were already considering, or might be persuaded to consider, proceeding to some type of university degree or similar academic qualification.—Ed.]

A VISIT TO PLANT CHEMISTRY DIVISION

Each year the Manawatu Branch arranges for local post-primary school pupils to visit places of chemical interest in the district. The Editor was impressed with the comments of some of the pupils after a recent visit of this type and at his request the following brief account of the visit was supplied by one of the pupils. It is clear that far from being "blinded with science" the pupils gained some impressions of real value and that visits of this sort may well influence the future careers of some of them.

"On 17 June a party of over one hundred pupils from Palmerston North post-primary schools visited the laboratories of the Plant Chemistry Division. These visits to places of chemical interest in the district are arranged each year by the Manawatu Branch of the New Zealand Institute of Chemistry and are always looked forward to. Fifth-formers are taken to an industrial establishment and sixth-formers to one or more of the research laboratories. It must be admitted that as fifth-formers our interest is perhaps a little too much on the excellent supper that we know will conclude the evening, but in the sixth-form we are starting to think about future employment and we were all keen to see what chemistry really had to offer.

"The evening was a most enjoyable one. To begin with we learnt from the Director, Dr A. T. Johns, something about the Division and the work done there; then we were shown round the laboratories and the different workers explained in more details just what they were doing. The displays included protein separations using the electrophoresis apparatus and the ultracentrifuge; various types of chromatography; isotope work and radiation counting; apparatus for large-scale extraction of plant materials; and the fistulated cows and the apparatus used in bloat research.

"With all of this crowded into one brief evening it is difficult to sort out all our impressions. I think what impressed us most was the obvious keeness of the chemists and also of the technicians for their work. As Professor Walker wrote in "Chemistry in Action" last year, they really made us feel that in chemistry they had found a job which was also their hobby. A second point which struck some of us was the contact which the chemists had with the living organisms. At school we tend to regard chemistry as a "dead" science and to think that if we want the added interest of dealing with the sort of reactions that go on in animals and plants, we must turn to careers like medicine, veterinary science, agriculture, etc. Our visit to the Plant Chemistry Laboratory made it clear that we must reconsider our ideas and that chemistry can provide the varied interests for which many of us are looking in the scientific career we choose. We are very grateful to the Institute of Chemistry for providing this opportunity for us to see what modern chemistry is really like."

LIST OF MEMBERS

The first list of amendments to the 1958 List of Members will be published in the near future. Would members whose entries are incorrect or incomplete advise the Registrar immediately.

Registrar, N.Z.I.C., P.O. Box 1926, Christchurch.

BRANCH NEWS AND NOTES

MANAWATU BRANCH

¶ The June meeting of the Branch was addressed by the President, Professor L. H. Briggs. Professor Briggs spoke on his recent work on the constitution and absolute configuration of some diterpenes.

¶ During June a group of over one hundred sixth-form pupils from local schools visited the laboratories of the Plant Chemistry Division. A larger group of fifth-formers were shown over the laboratories and the manufacturing and packaging plants of Glaxo Laboratories (N.Z.) Ltd. As in previous years these visits were most successful, the interest of the children amply repaying the effort involved in the organization.

WELLINGTON BRANCH

¶ Dr R. L. M. Synge addressed the June meeting of the Branch on the "Use of Molecular Sieve Effects for Separating Large Molecules".

¶ I. R. C. McDonald will shortly visit overseas research centres connected with wood chemistry.

¶ Congratulations to T. A. Rafter, formerly Director of the Division of Nuclear Sciences, D.S.I.R., on his appointment as Director of the recently established Institute of Nuclear Sciences.

CANTERBURY BRANCH

¶ H. McD. Rankin has transferred from Ballins Breweries, Christchurch, to N.Z. Breweries Ltd., Wellington.

¶ Miss Sally Page, Chemistry Department, University of Canterbury, has been awarded an 1851 Exhibition Scholarship which she will take up at University College, London. Miss Page leaves in August.

¶ Professor J. Packer leaves this month on Refresher Leave. He will be visiting Great Britain and will also be spending a short time in the United States in transit.

¶ Continuing the Canterbury Branch policy of providing special lectures for interested upper-sixth form chemistry students, an address on "High Polymers" was given recently by J. Vaughan of the Chemistry Department. There was again a large and appreciative audience. The lecture was followed by the colour film, "The World that Nature Forgot".

OTAGO BRANCH

¶ Our congratulations are extended to Dr Muriel E. Bell of Nutrition Research who has been granted an Honorary Fellowship of the Royal Australian College of Physicians.

¶ Dr F. G. Soper addressed the April meeting on the subject "Some Random Observations". Views on university teaching methods and universities in general arising from the speaker's recent trip overseas were expressed. At this meeting the Inglis Memorial Prize and the New Zealand Institute of Chemistry Prize were presented to R. C. Cunninghame and I. L. Weatherall respectively.

¶ Early in May Professor L. H. Briggs visited Dunedin. The branch arranged a dinner in his honour followed by a meeting where he spoke on "The Constitution and Absolute Configuration of the Diterpenes". Branch members enjoyed this visit of the 1959 Dominion President.

¶ The usual May meeting was held later in the month when the branch chairman, J. W. McChesney, delivered an address on "Some Aspects of Education, with Particular Reference to the Teaching of Science". Some interesting views were stated on the place and purpose of technical schools in New Zealand.

COUNCIL MINUTES

ABRIDGED MINUTES OF A MEETING OF THE COUNCIL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.) HELD IN THE CONFERENCE ROOM, D.S.I.R., WELLINGTON, ON WEDNESDAY, 6TH MAY, 1959.

PRESENT

Professor L. H. Briggs (President, in the Chair), E. W. Hullett (Vice-President), Dr A. L. Odell (Auckland), Dr E. P. White (Waikato), Dr W. A. McGillivray (Manawatu), J. R. Beck (Wellington), D. J. Hogan (Canterbury, Registrar), Dr A. J. Ellis (Otago proxy) and Dr W. E. Harvey (General Secretary). An apology for absence was received from Dr A. D. Campbell (Otago delegate).

CONFERENCE, 1959

Dr A. J. Ellis reported on the arrangements in hand for the Combined Conference in Dunedin. Dr R. L. M. Synge, Dr J. F. Duncan and T. A. Rafter have accepted invitations to deliver special lectures. The R.I.C. Chairman's Address on the "Biochemistry of Cheese" will be delivered by Dr G. M. Moir.

FUTURE CONFERENCES

The New Zealand Science Congress will be held in Wellington early in 1960 and Branches were asked to express an opinion as to whether the N.Z.I.C. should fully support the larger Congress and not hold its own Conference in 1960.

AWARD OF L.A.C.

The Examinations Committee reported that the following have completed the requirements for the L.A.C. and Certificates were awarded accordingly.

MIDDLETON, B. W., Wallaceville Animal Research Station.
BAARSLAG, Miss M., Southdown Freezing Works, Penrose.
BIERINGS, F. J., N.Z. Refrigerating Co., Islington (accredited).

LECTURE BY PRESIDENT

RESOLVED (Vice-President/Canterbury) That the Editor be asked to publish the Presidential Address which the President has delivered to various Branches.

SALARIES SURVEY

The Salary Survey has been completed by G. S. Lambert and A. G. Frieberg.

RESOLVED (Chair) That the Salary Survey be received and that it be published in the *Journal* subject to editorial supervision.

RESOLVED (Waikato/Manawatu) That G. S. Lambert and A. G. Frieberg be warmly thanked for their work in carrying out the Salary Survey.

STANDARDS COUNCIL REPRESENTATIVE

RESOLVED (Auckland/Otago) That the Minister be requested to reappoint G. A. Lawrence as the Institute representative on the Standards Council.

INSTITUTE PRIZES

Assessors were appointed to consider the entries for the Institute prizes.

INVESTMENTS

The Secretary reported that the Trustees had agreed to the investment of £500 of the Trust Fund monies.

TECHNICIAN TRAINING

The Secretary reported that the Superintendent of Technical Education would shortly call a meeting of interested persons to discuss the Institute's proposals for the training of technicians.

RESOLVED (Wellington/Vice-President) That Dr A. L. Odell, J. W. McChesney and Dr W. E. Harvey be appointed to represent the Institute. (This meeting was held on 26 May, and agreement was reached on all essential points.)

SUBSCRIPTION RATES FOR FELLOWS

The Canterbury Delegate presented a statement dealing with fellowship of the Institute. RESOLVED (Manawatu/Canterbury) That the Canterbury Branch statement be referred to Branches for consideration before the next meeting.

INSTITUTE RECORDS

RESOLVED (Auckland/Manawatu) That Dr W. E. Harvey and W. G. Hughson be empowered to sort through the Institute records and destroy documents of no further value.

JOURNAL

L. J. Rollo, who was present for part of the meeting at the invitation of Council, explained the new arrangements for the production of the *Journal*. It is now absolutely essential that copy be in the hands of the printers on the required date. If this is not the case delays of several weeks are inevitable as the printer's time schedule is very tight.

CAREERS IN CHEMISTRY BOOKLET

Consideration of this matter was deferred until the next meeting.

UNIONS

At the invitation of Council, J. K. Johannesson of Wellington was present during the discussion on Union matters. After a very full discussion it was RESOLVED (Auckland/Canterbury) that Council requests Dr W. E. Harvey to consult with the Wellington Branch of the Institute and other professional bodies with a view to forming a Union of Professional Chemists as soon as they see fit. Council recommends that the minimum qualification for membership should be the same as that for the associateship of the Institute, and further that the closest possible ties be maintained between the N.Z.I.C. and the proposed Union. If substantial departures from these principles should prove to be necessary, Dr W. E. Harvey was instructed to call an extraordinary meeting of Council if possible, or in any case to obtain the approval of the President before taking any action.

MEMBERSHIP

Election of Associates

The following were elected to the associateship:

FOSTER, PETER KINNEAR, Dominion Laboratory, Wellington.
FRANCIS, GRAEME CECIL, Standard Vacuum Oil Co., Wellington.
GOLDING, RAYMOND MARSHALL, Dominion Laboratory, Wellington.
WEIR, ALAN JAMES, Horowhenua College, Levin.
WILKS, CLYDE BANNISTER, Lever Bros. Ltd., Petone.

Leave

The following were granted leave with remission of subscriptions: J. M. Austin (1 Year), B. R. Davis (2 Years), W. E. Dasent (1 Year), P. P. Williams (2 Years), M. P. Williams (2 Years), W. H. West (2 Years).

Compounded Subscriptions

L. P. Symes was exempted from payment of further subscriptions, having passed the age of 65 years.

Resignations

Registrations were accepted with regret from the following:
R. C. Bell, J. Melville, W. G. Whittlestone.

DRAFT BALANCE SHEET

L. J. Rollo presented a draft Balance Sheet for the 18-month financial period ended 30 April, 1959. This Balance Sheet has yet to be audited but after brief discussion it was RESOLVED that the usual transfer of monies of the Trust Fund be not made in the financial year under discussion.

RETIRING REGISTRAR

Council expressed to L. J. Rollo its appreciation for the efficient service he had rendered to the Institute during the period in which he was Registrar.

FUTURE CONFERENCES

A letter was received from the Secretary of the N.Z. Section, R.I.C., referring to Council's decision that future Conferences should be held under the name of the N.Z.I.C. alone. At the request of the R.I.C., Council appointed a sub-committee consisting of the Vice-President, the General Secretary and the Wellington delegate to discuss this matter and related topics with representatives of the R.I.C.

A.N.Z.A.A.S. COUNCIL

A letter from the General Secretary of A.N.Z.A.A.S. invites Council to nominate delegates to attend the general Council meeting of A.N.Z.A.A.S. to be held in Perth, Western Australia in August, 1959.

RESOLVED (Canterbury/Auckland) that the Standing Committee be given power to nominate delegates to the A.N.Z.A.A.S. Council meeting.

> NOTE: The General Secretary of the N.Z.I.C. would like to hear of any Associates or Fellows who will be attending the A.N.Z.A.A.S. meeting.

UNESCO

A letter was received from the Secretary of the National Commission for UNESCO's Technical Sub-Committee on Science inviting the Institute to nominate one further person to present the Institute (J. A. D. Nash represents the Institute at the present time). After discussion it was agreed to write pointing out that as there were already four members of the Institute on the Technical Sub-Committee, Council considered that it would be more desirable to appoint further members who were not chemists.

W. E. HARVEY,
Hon. General Secretary.

BOOK REVIEWS

AIR POLLUTION CONTROL, by W. L. Faith. Published by John Wiley & Sons, Inc., New York, 1959. 259 pp. *Price,* 8.50 dollars.

Atmospheric pollution is becoming of increasing importance because of the rapid increase in the size and number of cities, because of the increase in range and complexity of the chemical products manufactured and utilized, and because of the discharge into the atmosphere of radioactive gases and dusts from factories and from exploding bombs. The appearance of a book gathering together the relevant information is therefore both timely and welcome. The author has presented a carefully written and eminently readable account of the subject. To the chemist the chapters on sources and composition of atmospheric pollutants, on methods of sampling and of testing for them, and on methods for alleviation and legal control of the nuisance, will be of direct interest. For the reviewer it was news to learn that "photochemical smog" can be caused by a sunlight-induced reaction of oxides of nitrogen with hydrocarbon residues from the combustion of old fuels.

The book can be read with interest and profit by all chemists; but to the public health, works, and boiler-house chemists, in particular, it brings information of vital importance in readily accessible form. The format and the printing are up to the publishers' usual high standard.

F.H.McD.

CAHIERS DE SYNTHESE ORGANIQUE, VOL. V, by J. Mathieu and A. Allais. Published by Masson et Cie, Paris, 1959. 394 pp. *Price,* 7,800 Fr.

This fifth volume of a very valuable series is equally as good as those which have gone before. It covers sections 12—Loss of a functional carbon—and 13—Cleavage of carbon chains and opening of carbocyclic rings. The organization of the work is on a self evident pattern so that very little French is required to understand it. The printing and production are first-rate.

S.G.B.

CHEMICAL CONSTITUTION, by J. A. A. Ketelaar. Published by Elsevier Company, New York, 1958. 447 pp.

In comparison with the enormous advances in chemistry that have been achieved experimentally and technically, the theoretical background—the mechanism of chemical processes and an understanding of chemical properties—has attracted little attention. Professor Ketelaar's book is a detailed quantitative study of the present state of knowledge of the interactions between atoms and molecules, which determine all phenomena in chemistry. Liberal use has been made of wave-mechanics and this will necessarily limit the appeal of this book to those chemists with an above average mathematical background.

This is the second edition in English to be published and is a high quality production. It has been completely rewritten and the very extensive tables and references brought up to date.

R.C.L.

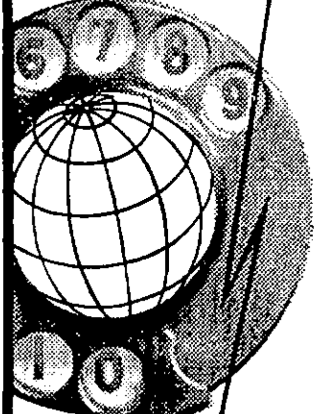
CONFERENCE NOTES

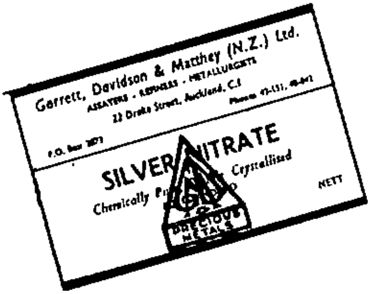
CONFERENCE NOTES

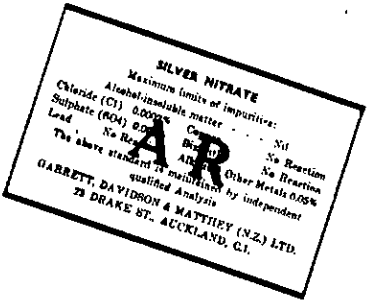
CONFERENCE NOTES

CONFERENCE NOTES

CONFERENCE NOTES


6
7
8
9
1
0


Garrett, Davidson & Matthey (N.Z.) Ltd.
ASSAYERS · REFINERS · METALLURGISTS
22 Drake Street, Auckland, C.1
P.O. Box 2073
SILVER NITRATE
Chemically Pure Crystallised
NETT
PRECIOUS METALS


SILVER NITRATE
AR
GARRETT, DAVIDSON & MATTHEY (N.Z.) LTD.
22 DRAKE ST., AUCKLAND, C.1.