CHEMISTRY IN NEW ZEALAND

JOURNAL OF
THE NEW ZEALAND
INSTITUTE
OF CHEMISTRY

CONFERENCE ABSTRACTS

Vol. 32, No. 4, August, 1968

SHELL OIL NEW ZEALAND LIMITED

Staff appointments

At the end of this year Shell will be offering employment to men (or women) with degrees in Chemistry, Civil or Mechanical Engineering, Agricultural Science and Commerce. There may be also a few opportunities for graduates in other subjects, e.g. Economics, Law or Arts.

POSITIONS AVAILABLE

Most of the graduates will initially be stationed in Wellington.
Each man is appointed as soon as possible to a position best suited to his qualifications, talents and interests and he is asked to follow a planned programme to enable him to use all his knowledge and ability at an early opportunity. The work is accepted as qualifying for corporate membership of professional Institutions or Societies.

Chemists will begin in the Central Laboratory on product development and testing, technical service, and the supervision of quality control, and may also be employed in chemicals marketing.

Engineers are responsible for design,development, construction and maintenance of oil storage facilities, processing plants, buildings, pipelines and road tankers.

Agricultural Science graduates are appointed to the Shell farm trade organisation, acting as specialist advisers on the marketing, development and application of chemicals for agricultural purposes.

Commerce graduates are employed primarily in finance, where the responsibilities include quarterly accounts, treasury, taxation, credit, investment, audit, payroll, costing, budgets and management accounting.

Data Processing with a Systems 360 60 IBM computer also offers a field for graduates with the necessary aptitudes for systems analysis, programming, operational research, etc.

ADVANCEMENT

As well as specialising initially in work for which he is qualified the graduate will be trained to take a comprehensive view of Shell activities generally.

The Shell group of companies, which is international in character, scope and shareholding, is engaged in New Zealand and throughout the world in two industries, petroleum and chemicals. Both are growing in volume and complexity and show ample prospect of development in the future.

Shell Oil New Zealand Limited is staffed by New Zealanders, of whom the most able may be eligible for promotion to senior positions overseas. With individual recognition, supervision and guidance each graduate is encouraged to progress towards the most senior position he is capable of filling. His own efforts towards self development may be aided in several ways, including overseas training for the most promising men.

SALARIES

Young graduates have a special salary scale and it is Shell's policy to offer salaries and conditions of employment (including retirement benefits) at least comparable to those offered by other large firms.

VACATION EMPLOYMENT

A few vacation jobs will also be available in Wellington next summer for students now in their second to last year of a degree course in Engineering, Commerce or Chemistry. No unusual obligations are imposed but preference will be given to men seriously interested in the eventual prospect of a Shell career.

ENQUIRIES

More detailed information is available in the booklet "A guide to graduate employment with Shell Oil New Zealand Limited" Copies of this booklet are available from the University.

Interviews can be arranged to suit any students who may be interested.

Enquiries may be addressed to:
The Staff Manager, Shell Oil New Zealand Limited,
Shell House, The Terrace, PO Box 2091, Wellington. Telephone 45-060.

or Shell House, Albert Street, PO Box 1084, Auckland. Telephone 32-240

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CHEMISTRY IN NEW ZEALAND

Journal of
The New Zealand
Institute of Chemistry

Vol. 32, No. 4, August, 1968

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

Contents

Editor: Miss J. Mattingley, B.Sc., A.N.Z.I.C.
P.O. Box 250, Wellington.

Advertising Manager:
Miss W. Jeune, B.Sc., A.N.Z.I.C.

Printed by David F. Jones Ltd., 108 Tory Street, Wellington.

Cover Photo: Recent aerial view of Auckland looking south. The University Chemistry Department (centre), Auckland Technical Institute (right of centre), School of Engineering (left), Auckland Hospital (top left), Student Union (foreground). —Auckland Star photo.

Distribution. The Registrar:
D. J. Hogan, B.Sc., A.N.Z.I.C.
P.O. Box 1926, Christchurch.

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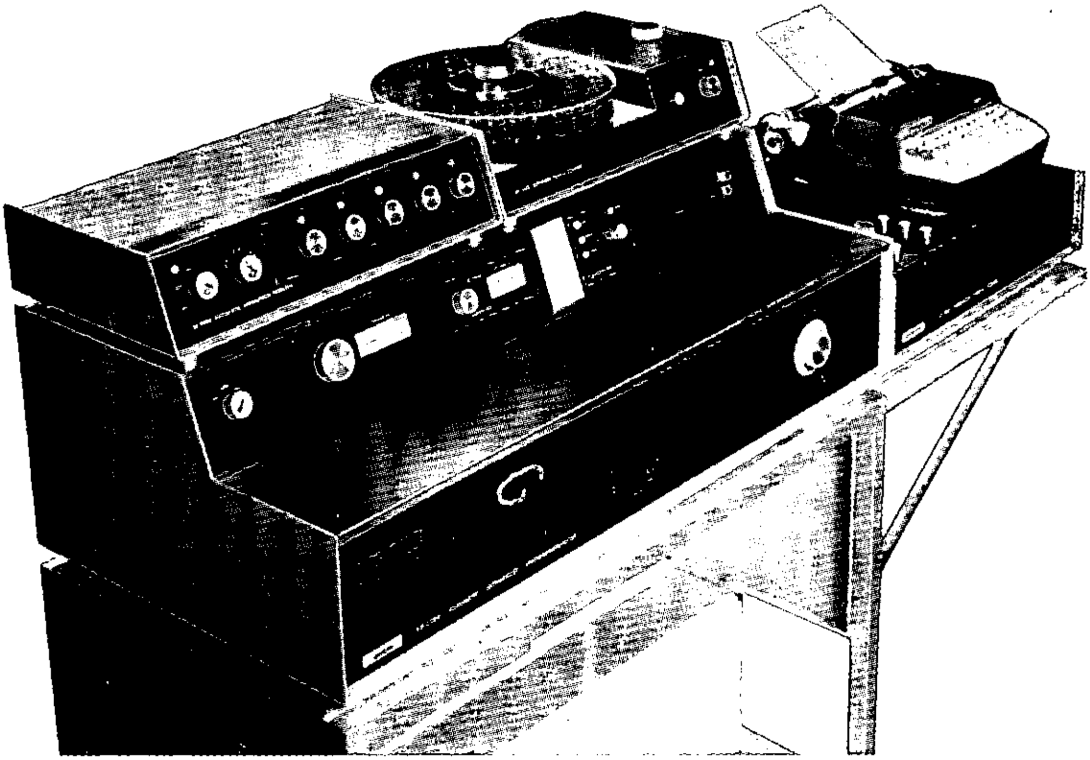
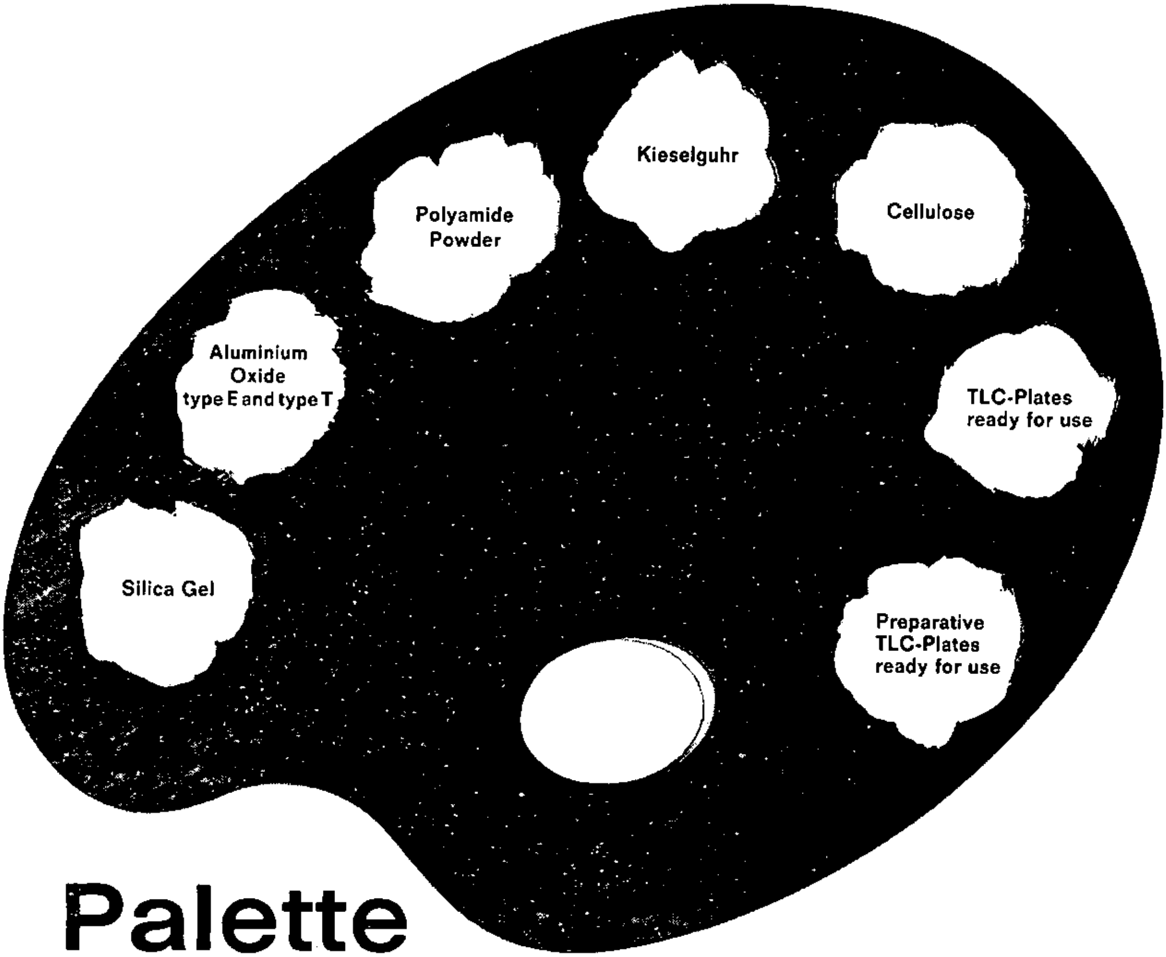
The Journal of the N.Z. Institute of Chemistry has an audit circulation Certificate of New Zealand Advertisers.

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CHEMOTAXONOMY OF THE NEW ZEALAND PODOCARPACEAE

R. C. Cambie and R. J. Weston
Chemistry Department, The University of Auckland

Principles of Plant Taxonomy[1]

Plant taxonomy is a science which includes the identification, nomenclature, and classification of plants. The identification of a plant is the process by which it is determined to be identical with or similar to an already known plant. Nomenclature is concerned with the determination of the correct name of a known plant according to an accepted nomenclatural system. Classification is the placing of a plant in categories (taxa) according to a plan or sequence and in conformity with the nomenclatural system. Every species is classified as a member of a particular genus, every genus belongs to a particular family, the family to an order, the order to a class, and the class to a division.

The theory of evolution postulates that plants now living are descendants of ancestral types, from which it follows that there are genetical relationships among the living plants. The principles of modern plant classification recognize that these relationships exist and these principles have been formulated in an attempt to bring together related plant groups in so far as knowledge of them permits. This knowledge, assembled for the purpose of arriving at a satisfactory classification, is drawn from all available sources among which are those phases of science which deal with plant morphology, anatomy, cytology, genetics, paleobotany, phytogeography, ecology and biochemistry. However, the differences between plants, or their similarities, are measurable to a large extent by their morphological characters. A morphological character is one inherent in, or manifested by, a structural component of the plant. In general, it is concerned with the organography of the plant and with characters that are usually discernible with the aid of no more than a good hand lens. The recognition by taxonomists of the significance of the related sciences listed above has resulted in an expansion of the concept as to what is a morphological character. For example, in the extreme viewpoint some taxonomists now consider the number of chromosomes to represent as significant a morphological character as that provided by the number of stamens. The value of a morphological character is measured by its constancy; the more constant the character, the greater the reliability that can be placed upon it.

Morphological criteria can be divided into two main classes, vegetative characters and reproductive characters.

The use of vegetative characters, that is the roots, stems, leaves, buds and habit of growth, as taxonomic criteria is limited for two basic reasons. Firstly, the total number of vegetative characters is few compared with the number of species of vascular plants, and secondly, it is often found that these characters are not particularly constant.

Reproductive characters include *inter alia* the inflorescences (arrangements of the flowers on the floral axis), sepals, petals, stamens, carpels, ovary position, flower types, distribution of sexes, fruits and seeds. The number of these characters and the number of components of these organs are many times greater than that available from vegetative characters. For this reason the number of mathematical combinations of reproductive characters is infinitely greater and normally exceeds the number of species to be differentiated. In addition to being more abundant, reproductive characters in general are more constant than vegetative characters.

Principles of Chemotaxonomy[2,3,4]

Early in the development of natural products chemistry many botanists and chemists considered that it might be possible to characterize and classify plants on the basis of their chemical constituents. Interest in the relationship between plant constituents and plant classification long remained insignificant, mainly because the number of natural products of known structure was small and the knowledge of their distribution was very scanty. In recent years however, with growing knowledge of the structure of natural products, there has been a renewed interest in "chemotaxonomy" and its potentialities are becoming more obvious.

The evolution of plants depends on a combination of internal and external factors such as mutation, recombination of genetic differences, geographical isolation and natural selection. During evolution it may happen that unrelated groups of plants give rise to morphologically similar ones. Such a process is called "convergence". Conversely, related plants may give rise to very dissimilar descendents ("divergence"). Such phenomena can cause considerable taxonomic difficulties, and it is in such cases and those where morphological characters are not constant that the chemist might best be able to assist botanists in solving their problems. For example, it is very improbable that a morphological convergence would be accompanied by "chemical convergence". The chemical examination of such critical groups of plants is therefore of considerable interest. Chemical contributions to the classification of plants are based on their chemical constituents, that is, on their "molecular characteristics". These characteristics are genetically controlled and have the advantage over morphological ones in that they can be described very exactly in terms of definite structural and configurational chemical formulae. The method of "chemotaxonomy" is thus simple in principle and consists of the investigation of the distribution of chemical compounds, or groups of biosynthetically related compounds, in series of related or supposedly related plants.

Taxonomically, the most valuable substances are those which are not involved in the primary metabolic processes and which do not have any special task to fulfil. Compounds in this category are those which in the past have been regarded as unimportant and which are, in their biological environment, relatively stable by-products often denoted by the term "secondary constituents". Following the principle that taxonomically important substances should preferably be sought in old, less specialized organs in which seasonal variations are unimportant, the heartwood constituents of plants have so far received the most attention from chemotaxonomists. The heartwood of a plant is entirely dead and serves essentially mechanical purposes only. However, chemical constituents generally vary considerably from one organ to another and for this reason it is preferable that investigations should be made on all of the individual parts of a plant.

At present it is beyond the capacity of a chemist to differentiate between large taxonomic categories such as divisions, classes and orders as does the botanist. However, the virtue of the chemical method is that it is completely independent of classical biological methods and thus can be used in certain cases to check the botanist's conclusions and point out problems not normally apparent. Conifers constitute an isolated and ancient group of plants, some of whose genera are suitable for comparative chemical investigations and whose classification is not clear. The family Podocarpaceae of the order Coniferales is represented in New Zealand by a number of endemic species and thus provides an interesting field for chemotaxonomic studies.

The Order Coniferales[5]

Classification: The division Spermatophyta (the vascular, seed-bearing plants) can be divided into five classes,

1. Angiospermae
subclasses:

Monocotyledoneae (one seed-leaf) Dicotyledoneae	flowering plants (angiosperms)
2. Conopsida 3. Ephedropsida 4. Gnetopsida 5. Cyadopsida	gymnosperms

The angiosperms are characterized by
- (i) the presence of flowers;
- (ii) the enclosure of the seeds in fruits formed by development of the pistil of the flower;

whereas the gymnosperms are characterized by
- (i) the absence of flowers, the pollen and seeds being produced usually in cones;
- (ii) the absence of a closed pistil, the seeds being naked on a specialized leaf or a scale of the cone.

The Conopsida, or cone-bearing plants, are divided into three orders[6], Ginkgoales, Taxales, and Coniferales.
The structure of the orders Ginkgoales and Taxales is shown in Table I. Included is the number of species (in brackets) within each genus. The order Ginkgoales has only one species *Ginkgo biloba,* the maidenhair tree.

TABLE I

Order	Ginkgoales	Taxales
Family	Ginkgoaceae	Taxaceae (Yew family)
Genera	*Ginkgo* [1]	*Amentotaxus* [4] *Austrotaxus* [1] *Pseudotaxus* [1] *Taxus* [8] *Torreya* [6]

The order Coniferales has six families which are not large compared with families of angiosperms. Species of the Coniferales occur throughout the world and are the dominant lumber trees of temperate regions. The families and genera of the order are shown in Table II.

The Podocarpaceae[6,7]

This family contains approximately 150 evergreen shrubs or trees and embraces seven genera (see Table II). *Acmople,* a genus allied to *Podocarpus* and *Dacrydium* but differing chiefly in its seed-characters, has limited distribution, its natural habitat being New Caledonia and the Fiji Islands, although fossil evidence indicates that *Acmopyle* formerly had a wider distribution in S.E. Asia, Australasia and South America. *Dacrydium* species, which are also allied to *Podocarpus,* are chiefly natives of New Zealand but occur also in Malaysia, Indo-China, Thailand, New Guinea, Australia, Tasmania, New Caledonia

TABLE II

Order Coniferales

Families	Araucariaceae	Cephalotaxaceae	Podocarpaceae	Pinaceae	Taxodiaceae	Cupressaceae
Genera	*Agathis*	*Cephalotaxus*	*Acmopyle* [3]	*Abies*	*Athrotaxis*	*Actinostrobus*
	Araucaria		*Dacrydium* [21]	*Cathaya*	*Cryptomeria*	*Austrocedrus*
			Microcachrys [1]	*Cedrus*	*Cunninghamia*	*Callitris*
			Microstrobos [2]	*Keteleeria*	*Glyptostrobus*	*Calocedrus*
			Phyllocladus [6]	*Larix*	*Metasequoia*	*Chamaecyparis*
			Podocarpus [113]	*Picea*	*Sciadopitys*	*Cupressocyparis*
			Saxegothaea [1]	*Pinus*	*Sequoia*	*Cupressus*
				Pseudolarix	*Sequoiadendron*	*Diselma*
				Pseudotsuga	*Taiwania*	*Fitzroya*
				Tsuga	*Taxodium*	*Fokienia*
						Juniperus
						Libocedrus
						Neocallitropsis
						Papuacedrus
						Pilgerodendron
						Tetraclinis
						Thuja
						Thujopsis
						Widdringtonia

and Chile. They frequently yield a resinous exudation from the wood. *Microcachrys,* a monotypic genus, and *Microstrobos,* with only two species, contain shrubs which are natives of Tasmania and New South Wales and are normally found only at alpine elevations. *Phyllocladus* species, which can be recognised by their flattened leaf-life branchlets (phylloclades) and the small hard seeds borne at the edges of them, are natives of Tasmania, New Zealand, the Phillipines and Borneo. *Podocarpus,* which is by far the most dominant genus of the family, contains both trees and shrubs which are largely confined to the mountain forests of warm temperate to tropical countries of the southern hemisphere. Minor variations in leaf and seed structures have led to the division of *Podocarpus* into eight sub-genera as follows (number of species in brackets);

i Dacrycarpus [10] found in S.E. Asia, East Indies, S. Pacific Is. to New Zealand.
ii Microcarpus [1] found in New Caledonia.
iii Nageia [6] S.E. Asia, E. Indies, Phillipines to New Guinea.
iv Afrocarpus [6] Africa.
v Polypodiopsis [5] S. America, S. Pacific Is., New Guinea, New Caledonia, Fiji.
vi Sundacarpus [1] N. Australia, Indonesia, Phillipines.
vii Stachycarpus [10] Central and S. America to New Zealand, Australia, New Caledonia.
viii Eupodocarpus [74] Central and S. America, Africa, Asia, Australasia, S. Pacific Is.

Eupodocarpus is divided into four subsections[7]; A (Africa), B (Asia, S. Pacific, Australia), C (Central and S. America) and D (Chile, S.W. Pacific).

The seventeen species of the family which are endemic to New Zealand are distributed among three genera, *viz. Podocarpus* [7 species], *Dacrydium* [7], and *Phyllocladus* [3].

The New Zealand species attributed to the *Podocarpus* and *Dacrydium* genera present some difficulties in classification. *D. cupressinum* is the only New Zealand species of Florin's group B[8] of the *Dacrydium* genus, which includes *D. araucarioides, D. balanse,* and *D. lycopodioides* of New Caledonia, *D. novo-guineese* of New Guinea, *D. beccarii* of Malaysia, and *D. elatum* of the Phillipines, Malaysia and Fiji. Florin's groupings were based on leaf morphology. Details of chromosome morphology indicate a close relationship between Florin's group B and the section Dacrycarpus of *Podocarpus,* which includes only *P. dacrydioides* in New Zealand. These two groups, together with *D. taxoides* all have $2n = 20$ metacentric chromosomes.[9] Doyle[10] and Quinn[11] have shown that the embryology of *D. cupressinum* and presumably that of other members of Florin's group B is more similar to that of section Dacrycarpus of *Podocarpus* than to that of other species of *Dacrydium* or *Podocarpus.* The wood[12,13] contains abundant axial parenchyma and sparse tangential pitting in the latewood, which separate it anatomically from all other New Zealand species of *Dacrydium* and place it closest to *P. dacrydioides* in *Podocarpus.*

However, *D. cupressinum* possesses morphological features distinct from *Podocarpus.* For example, the mature ovule of *D. cupressinum* is erect and possesses an epimateum which is reduced to a basal sheath. In *Podocarpus* species the epimateum entirely covers the ovule and is fused to the integument, while in *P. dacrydioides* the carpidium (subtending bract) is fused to the epimateum—conditions not found in *D. cupressinum*[14,15]. Although the pollen of most podocarps has two or three well-defined bladders, in *D. cupressinum* pollen the bladders are usually small or rudimentary[16]. In addition they have coarse external thickening, a feature which amongst the other Neew Zealand species is found only in *D. bidwillii* and *D. biforme.*

Chemistry of the Podocarpaceae[17]

The New Zealand species of the Podocarpaceae have been the subject of considerable investigation by natural products chemists centred mainly at the Universities of Auckland and Otago and at the Chemistry Division of the D.S.I.R. Early studies were principally concerned with examination of essential oils which are, in general, a rich source of diterpene hydrocarbons such as phyllocladene(1),* kaurene(2), rimuene(3), and hibaene (cupressene; 4). The determination of the structures and investigation of the chemistry of these compounds has been a major topic of research in a number of laboratories both in New Zealand and overseas. More recent studies have been concerned with a systematic examination of the heartwood constituents of the *Podocarpus* and *Dacrydium* species. In addition, the leaves have been surveyed for the presence of alkaloids, leucoanthocyanins, triterpenoids, saponins,[18] diterpene hydrocarbons,[19] n-alkanes,[20] biflavonoids[21] and a *p*-diphenol oxidase.[22] The results up until 1965 are summarised in a phytochemical register by Brooker, Cambie, and James[17].

HEARTWOOD CONSTITUENTS

With the exception of *Phyllocladus,* the heartwood extractives of most other New Zealand species of the family have been investigated and have usually been found to contain oxygenated diterpenoids. As pointed out by Brandt and Thomas[23] these compounds fall into two distinct groups, *viz.*

(a) phenolic tricyclic diterpenoids such as ferruginol (5), totarol (6, $R = Me$) and podocarpic acid (7, $R = H$), which appear to be characteristic of *Podocarpus*

(b) non-phenolic bicyclic diterpenoids such as manool (8, $R = Me$) and torulosol (8, $R = CH_2OH$) which appear to be characteristic of *Dacrydium.*

A noteworthy exception is *D. cupressinum* whose heartwood constituents show little affinity to those of other *Dacrydium* species; they are of the phenolic diterpenoid type found in *Podocarpus* (see Tables III and IV)[24]. Since anatomical features of the wood also place it closer to *Podocarpus* (*vide supra*) this has led to the suggestion that the species might be better placed in the latter genus[2,23].

The phenolic diterpenoids of the New Zealand *Podocarpus* heartwoods are summarised in Table III. Of these trees *P. spicatus* is aberrant in that its heartwood contains a series of non-terpenic substances, *viz.* the lignans matairesinol (14), conidendrin (15) and seco-isolariciresinol (16), and the flavonoids quercetin (17, $R = OH$), kaempferol (17, $R = H$), taxifolin (18, $R = OH$), aromadendrin (18, $R = H$), genistein (19) and podospicatin (20). Only one other *Podocarpus* species whose heartwood has been examined chemically is devoid of diterpenoids, this being *P. gracilior,* an East African tree investigated by Bevan and Taylor[32].

The four New Zealand trees in the subsection Eupodocarpus are distinguished from the remainder in that their heartwoods contain totarol as the major diterpenoid constituent. This compound has also been isolated however, from the exotic species *P. mannii*[33] (Stachycarpus), *P. milanjianus*[32] (Eupodocarpus), *P. nagi*[34] (Nageia), and *P. macrophyllus*[34] (Eupodocarpus).

An interesting aspect of the chemistry of the totarol-containing species is that most contain the dimeric compounds podototarin (13, $R_1 = R_2 = H$) or macrophyllic acid (21)[35]. The linkage of such bisditerpenoids is formed between the C-atoms in the *ortho*-position to the phenolic group, and podototarin has been synthesized from totarol both by chemical means and by the action of enzymes from the fungus *Polyporus versicolor* and from the leaves of gymnosperms. The biosynthesis of such bisditerpenoids can thus be assumed to involve an oxidation of the phenolic group by the action of a phenol-dehydrogenating enzyme (*p*-diphenol oxidase) as has been proposed for the formation of lignin from coniferyl alcohol[36]. The oxygen radical produced can then become stabilized by the union of the mesomeric *ortho*-radicals.

Only the bled resin constituents of *P. ferrugineus* have been reported[28-30]. However, current investigations[37] show that, like the resin, the heartwood contains ferruginol (5) as the major diterpenoid.

The heartwood diterpenoids from the New Zealand *Dacrydium* species are given in

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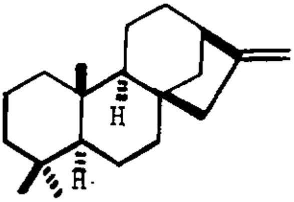
*NOTE—Figures in parenthesis, e.g. (1) refer to list of structures.



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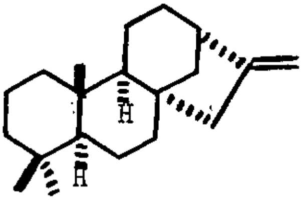

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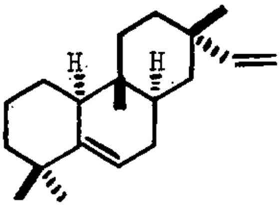

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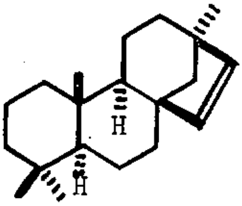

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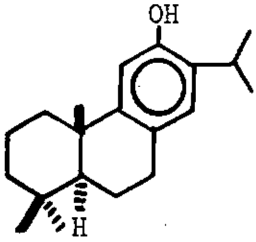

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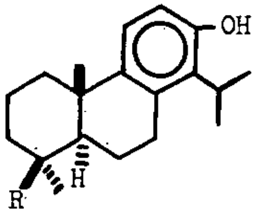

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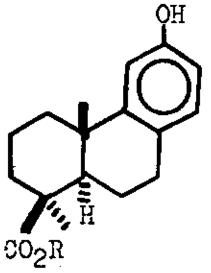

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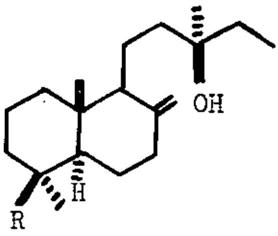

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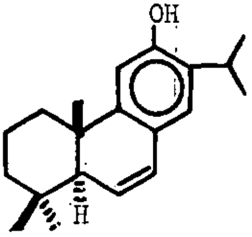

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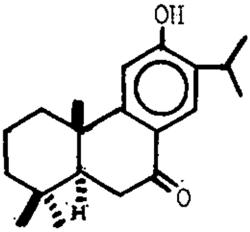

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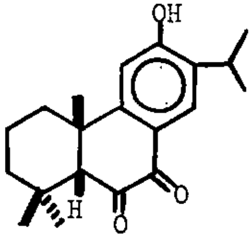

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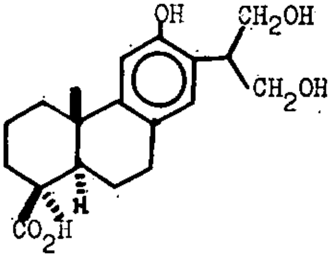

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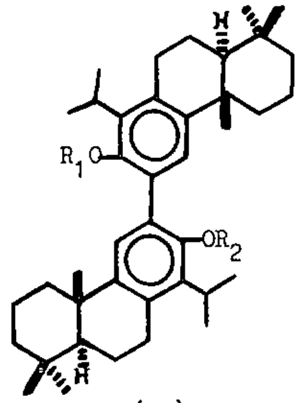

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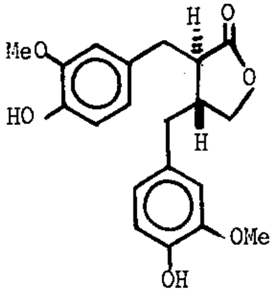

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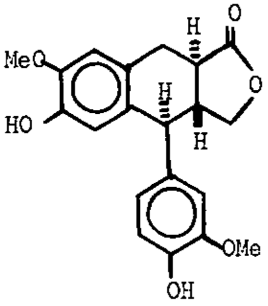

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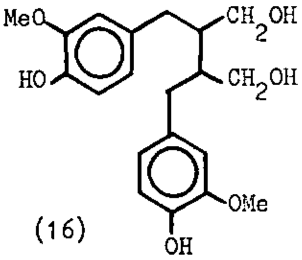

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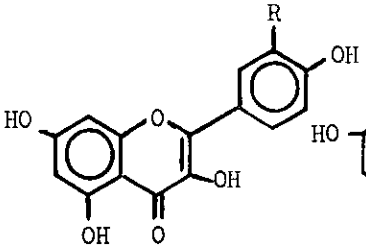

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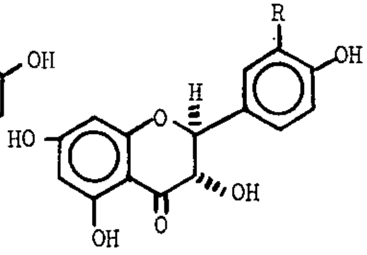

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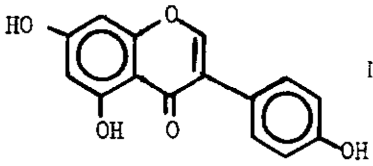

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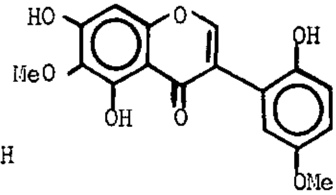

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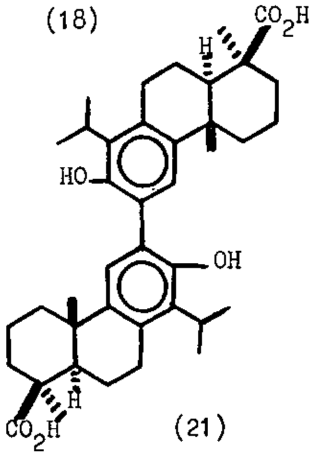

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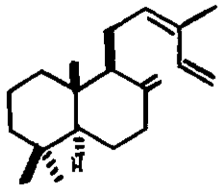

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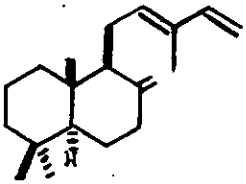

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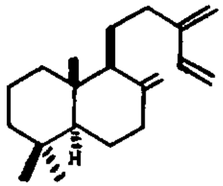

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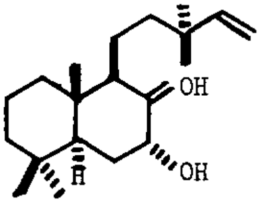

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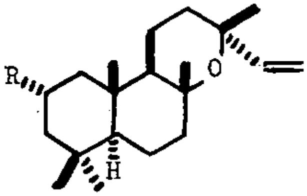

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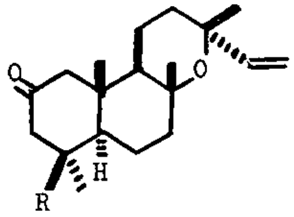

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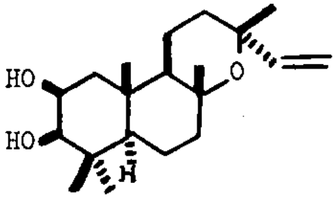

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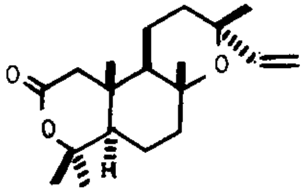

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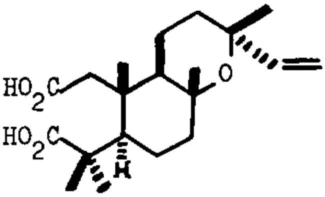

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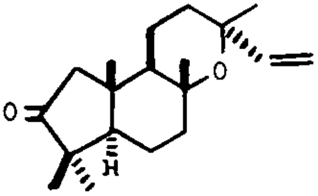

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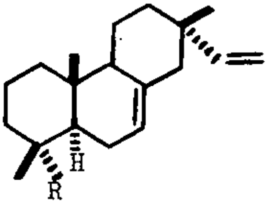

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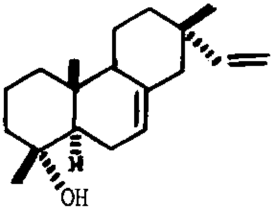

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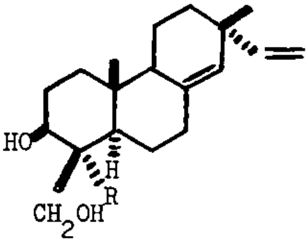

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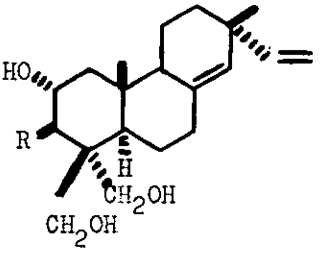

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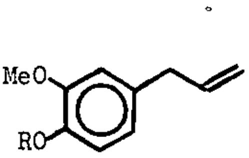

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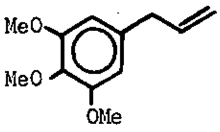

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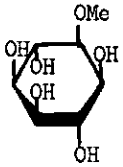

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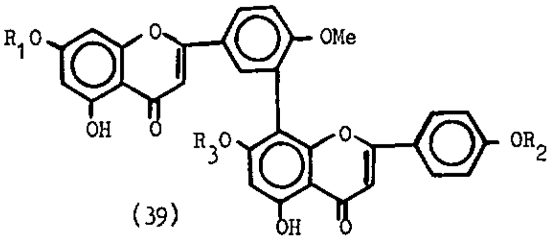

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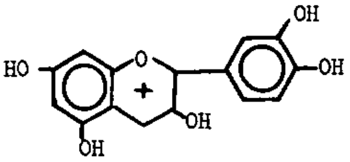

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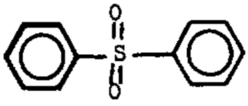

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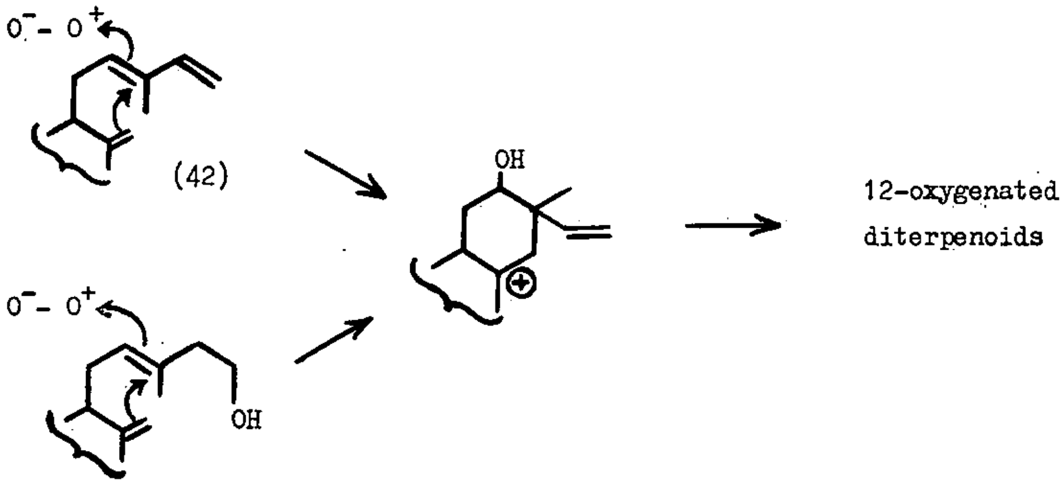

(42)

(43)

Table IV. With the exception of *D. laxifolium* the remaining species have been extensively investigated. Hosking and Brandt[38] isolated manool (8, R = Me) and an acid, subsequently identified as isopimaric acid (32, $R = CO_2H$)[39], from the heartwood of *D. biforme*. More recently Carman and Grant[40] isolated the hydrocarbon biformene from the same source and characterised it as the alkene formed from the dehydration of manool. Following the synthesis and separation of the three possible dehydration products of manool, Carman and Dennis[41] showed that natural biformene was a mixture of *cis*- and *trans*-biformene (22, 23) with a trace of sclarene (24). In addition to manool and biformene, Cambie and Mander[42] isolated the further diterpenoid constituents isopimaradienol (32, $R = CH_2OH$), isopimaradienal (32, R = CHO), 2-oxomanoyl oxide (27, R = Me), and detected the presence of manoyl oxide (26, R = H), torulosol (8, $R = CH_2OH$) and torulosal (8, R = CHO) by gas-liquid chromatography. Another hydrocarbon, isopimaradiene (32, R = Me), has been isolated by Enzell and

TABLE III
Phenolic Diterpenoid Constituents of New Zealand *Podocarpus* Heartwoods

Section and Species	Ferruginol (5)	6,7-Dehydroferruginol (9)	Sugiol (10)	Xanthoperol (11)	Podocarpic acid (7, R = H)	Methyl podocarpate (7, R = Me)	Pododacric acid (12)	Totarol (6, R = Me)	19-Hydroxytotarol (6, R = CH_2OH)	19-Oxototarol (6, R = CHO)	19-Carboxytotarol (6, R = CO_2H)	Podototarin (13, R_1 = R_2 = H)	Podototarin monoacetate (13, R_1 = H, R_2 = Ac)	Refs.
Sect. Dacrycarpus														
P. dacrydioides A. Rich.	+	+	+	+	+	+	+							25
Sect. Eupodocarpus														
P. acutifolius Kirk					+			+				+		26
P. hallii Kirk			+		+			+	+	+	+			27
P. nivalis Hook					+	+		+				+	+	26
P. totara G. Benn.			+		+	+	+	+	+			+		28
Sect. Stachycarpus														
P. ferrugineus G. Benn.*	+	+	+											29, 30
P. spicatus R. Br.														31

* Only the constituents of the bled resin of this tree have been reported.

Thomas[43], while a further oxygenated diterpenoid is still under investigation[44].

Brandt[45], and more recently Grant and his co-workers[46], examined the heartwood of *D. bidwillii* and found manool (8, R = Me), isopimaradiene (32, R = Me), and isopimaradienal (32, R = CHO) as the major components. Minor diterpenoids were identified as isopimaradienol (32, R = CH_2OH), isopimaric acid (32, R = CO_2H) and torulosol (8, R = CH_2OH), while a new nor-diterpene was characterised as 18-nor-isopimaradien-4α-ol (33).

Three oxido-diterpenes, manoyl oxide (26, R = H), 2-oxomanoyl oxide (27, R = Me) and what was considered to be a trihydroxymanoyl oxide, $C_{20}H_{32}O_4$, m.p. 208°, were isolated from the heartwood of *D. colensoi* by Hosking and Brandt[47]. From the same source, Grant[48] isolated a tetrol "dacrydol" which he later showed to be a mixture. He also obtained an unusual ring A nor-diterpenoid, colensenone (31)[49,50]. In a recent series of papers, Grant and his co-workers[51-53] have reported the isolation of four manoyl oxide derivatives and four sandaracopimaradiene derivatives. The oxido-diterpenoids were shown to be 2α-hydroxymanoyl oxide (26, R = OH), 2-oxo-3-oxamanoyl oxide (29), 2,3-dicarboxy-2,3-secomanoyl oxide (30) and 19-hydroxy-2-oxomanoyl oxide (27, R = CH_2OH). The diol, 3β,19-dihydroxysandaracopimaradiene (34, R = Me) was also isolated. "Dacrydol" was shown to consist of three compounds each possessing a novel *geminal* hydroxymethyl group, which were identified as 2α,3β,18,19-tetrahydroxysandaracopimaradiene (35, R = OH), 2α,18,19-trihydroxysandaracopimaradiene (35, R = H) and 3β,18,19-trihydroxysandaracopimaradiene (34, R = CH_2OH).

Hosking[54] examined the heartwood of *D. kirkii* and showed that the major constituent of the neutral extract was manool. An acid also present in the heartwood was subsequently identified as isopimaric acid (32, R = CO_2H)[39]. The heartwood extractives of *D. kirkii* have recently been reinvestigated in

TABLE IV — Diterpenoid Constituents of New Zealand *Dacrydium* Heartwoods

Species	Biformenes (22, 23) and Sclarene (24)	Manool (8, R = Me)	Torulosol (8, R = CH_2OH)	Torulosal (8, R = CHO)	7α-Hydroxymanool (25)	Manoyl oxide (26, R = H)	2-Oxomanoyl oxide (27, R = Me)	2α-Hydroxymanoyl oxide (26, R = OH)	2β,3β-Dihydroxymanoyl oxide (28)	2-Oxo-3-oxamanoyl oxide (29)	2,3-Dicarboxy-2,3-secomanoyl oxide (30)	19-Hydroxy-2-oxomanoyl oxide (27, R = CH_2OH)	Colensenone (31)	Isopimaradiene (32, R = Me)	Isopimaradienol (32, R = CH_2OH)	Isopimaradienal (32, R = CHO)	Isopimaric acid (32, R = CO_2H)	18-Norisopimaradien-4-ol (33)	3β,19-Dihydroxysandaracopimaradiene (34, R = Me)	2α,3β,18,19-Tetrahydroxysandaracopimaradiene (35, R = OH)	2α,18,19-Trihydroxysandaracopimaradiene (35, R = H)	3β,18,19-Trihydroxysandaracopimaradiene (34, R = CH_2OH)	Podocarpic acid (7, R = H)	Totarol (6, R = Me)	Ferruginol (5)	Δ^6-Dehydroferruginol (9)	Sugiol (10)	References
D. biforme Pilger	x	x	x	x		x	x							x	x	x	x											30, 38-43
D. bidwillii Hook. f. ...		x	x												x	x	x	x										45, 46
D. colensoi Hook.						x	x	x		x	x	x	x						x	x	x	x						47-53
D. cupressinum Lamb. ...																							x	x	x	x	x	24
D. intermedium Kirk. ...		x																										55
D. kirkii F. Muell.	x	x	x		x	x			x					x	x		x		x									54-56
D. laxfolium Hook. f. ...																												54, 55

conjoint work at the Universities of Auckland[55] and Otago[56]. Identified in the extracts were the *cis-* and *trans-*biformenes (22, 23), sclarene (24), manool (8, R = Me), torulosol (8, R = CH_2OH), manoyl oxide (26, R = H), isopimaradiene (32, R = Me), isopimaradienol (32, R = CH_2OH), 3β,19-dihydroxysandaracopimaradiene (34, R = Me) and two new diterpenoids whose structures have been determined as 7α-hydroxymanool (25) and 2β,3β-dihydroxymanoyl oxide (28). Other constituents are still under investigation.

As is the case for the *Podocarpus* genus, anomalies are also found in the heartwood constituents of the *Dacrydium* genus. The Tasmanian species *D. franklini* differs from its New Zealand relatives just as distinctly as does *P. spicatus* from the other *Podocarpus* species since it is apparently lacking in higher terpenic compounds. The steam volatile oil from the heartwood of *D. franklini* contains eugenol (36, R = H), eugenol methyl ether (36, R = Me), elemicin (37) and several other phenolic compounds[2].† This apparently anomalous chemistry of *D. franklini* is reflected in its cytology. The number of chromosomes possessed by thirteen of the twenty-one *Dacrydium* species is known. Of these thirteen, eight possess 2n = 20 chromosomes, *D. kirkii* possesses 2n = 22, *D. biforme* possesses 2n = 24, and *D. franklini, D. intermedium,* and *D. laxifolium* possess 2n = 30 chromosomes.

Hosking[54] noted that, unlike other members of the *Dacrydium* genus, an extract of *D. intermedium* heartwood yielded considerably more acidic material than neutral material, the latter being characterised by the presence of a small quantity of a volatile oil with an odour reminiscent of eugenol methyl ether (36, R = Me). Recently, in addition to manool, we have isolated two and detected a further two phenolic compounds from the heartwood of *D. intermedium* which have been shown to be lignans[55]. Lignans are dimeric compounds formed by the oxidative coupling of phenols related to eugenol. Although this is the first report of the occurrence of lignans in the heartwood of a species of the *Dacrydium* genus, lignans have been isolated from *Podocarpus spicatus* (Podocarpaceae)[31], and a number of species (e.g. *Thuja plicata, Chamaecyparis* and *Juniperus* species) of the family Cupressaceae[57], *Taiwania cryptomerioides*[57] (Taxodiaceae) and from several species of genera in the Pinaceae[58]. Hence the occurrence of these compounds in the heartwood of a conifer is not unexpected.

The occurrence of manool in the heartwood of *D. intermedium* is a necessary and sufficient criterion to classify this species with the remaining six endemic New Zealand *Dacrydium* species. The isolation of lignans from the heartwood of *D. intermedium* is important, however, with regard to the taxonomy of this species within the *Dacrydium* genus. It was indicated earlier that *D. intermedium* is cytologically similar to *D. franklini* and *D. laxifolium* and now it has been shown to be chemically similar to *D. franklini*. It will therefore be of considerable taxonomic interest to find whether or not the heartwood of *D. laxifolium* also contains lignans or lignan precursors. Unfortunately, this species is one of the smallest conifers known, mature specimens sometimes being found which are no more than three inches high and wide. Some difficulty may therefore be experienced in collecting sufficient heartwood for examination.

Only one heartwood of the three New Zealand *Phyllocladus* species has been examined chemically. This is of *P. trichomanoides* which was found by Harvey and his co-workers[59] to contain the cyclitols sequoyitol, pinitol, myoinositol, (+)-inositol, 1-0-methylmucoinositol (38) and the pentose, arabinose. The bled resin of this species contains diterpenoid acids, as yet unidentified[60].

BARK CONSTITUENTS

The barks of only a few of the New Zealand species of the family Podocarpaceae

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†See also the recent paper: K. H. Baggaley, H. Erdtman, N. J. McLean, T. Norin and G. Eriksson, *Acta Chem. Scand.*, 1967, *21*, 2247.

have been investigated. In general, the bark constituents of those examined systematically (*viz. D. biforme*[42], *D. cupressinum*[61] and *Phyllocladus glaucus*[62]) appear to be unexceptional in that the major diterpenoid constituents of the first two are the same as those (i.e. manool and totarol) from the corresponding heartwood.

LEAF CONSTITUENTS

Leaves are usually more easy to collect than other parts of a plant and thus the leaves of members of the Podocarpaceae have been investigated in some detail. Most of the essential oils from the New Zealand species have been examined at some time and the majority found to contain monoterpenes and/or sesquiterpenes. A number of the latter compounds are still unidentified and considerable scope exists for a re-examination of the monoterpenoid and sesquiterpenoid constituents by modern methods utilizing gas-liquid chromatography and mass spectrometry. Some progress towards this objective has been made by workers at the University of Auckland[63].

In a comprehensive gas-liquid chromatographic survey for the occurrence of diterpene hydrocarbons in the essential oils from the leaves of conifers, Cambie and co-workers[19] noted that, without exception, all New Zealand species contained this type of compound. From 32 members of the family only the four exotic species *Podocarpus falcatus, P. gracilior, P. salignus* and *P. usambarensis* were found to be devoid of diterpene hydrocarbons. However, no clear pattern of characteristic constituents emerged for the different genera or sub-genera and it was concluded that the diterpene hydrocarbons were of limited taxonomic value. A comparable survey[20] of the n-alkanes from the surface wax of the leaves was more encouraging since it was found that *Podocarpus* species have mainly n—C_{29} and n—C_{31} compounds while *Phyllocladus* species have n—C_{33} and n—C_{35} as the dominant alkanes. Furthermore, the amount of alkane material in the *Dacrydium* species is low compared with that present in the *Podocarpus* species. Of the eight *Dacrydium* species examined, *D. cupressinum, D. franklini,* and *D. laxifolium* have similar distribution patterns which are different from those of the remaining species. It is therefore noteworthy that these three species also differ from the remaining species in their heartwood constituents.

Following the isolation of the bisditerpenoids podototarin (13, $R_1 = R_2 = H$) and macrophyllic acid (21) from the heartwood of *P. totara* and *P. macrophyllus* respectively, Cambie and Bocks[22] carried out a survey of the leaf extracts of gymnosperms for the presence of an enzyme capable of oxidative coupling. *p*-Diphenol oxidase activity was observed in the leaf extracts of all New Zealand species except *P. dacrydioides, P. ferrugineus, P. hallii* and *D. cupressinum.* In a further survey Cambie and James[21] examined the leaf extracts of gymnosperms for the presence of biflavonoids. They found that all species contained biflavonoids with C—C linkages between the moieties. Compounds such as bilobetin (39, $R_1 = R_2 = R_3 = H$), ginkgetin (39, $R_1 = Me$, $R_2 = R_3 = H$) and kayaflavone (39, $R_1 = H$, $R_2 = R_3 = Me$) with one, two, and three methoxy groups respectively, were the most common. While the presence of biflavonoids in the leaves seems to be diagnostic for species of the Podocarpaceae, little correlation was observed with the presence of a *p*-diphenol oxidase. This would indicate that the method of testing for the oxidase was too insensitive since it has been suggested[64] that biflavonoids are probably produced in the plant by the oxidative coupling of flavonoid precursors.

In an earlier survey[18] the leaves and other parts of the New Zealand conifers were examined by means of simple test-tube reactions for the presence of alkaloids, leucoanthocyanins, saponins, and triterpenes. No member of the Podocarpaceae was found to contain alkaloids, saponins or triterpenes but all contained leucoanthocyanins. The anthocyanidins derived from these compounds by acid hydrolysis were identified for each species by paper chromatography, cyanidin (40) being the predominant product. In most cases the bark appeared to be the richest source of the leucoanthocyanins and only *P. dacrydioides* was unusual in that it was the only tree to contain a leucopelargonidin.

Biosynthetic Relationships

The elucidation of the structures and configurations of naturally occurring organic compounds paves the way to an understanding of their biosynthesis which is a matter of fundamental systematic importance. Relationships exist between the "biosynthetic complexity" of a substance and its taxonomic significance. Many organic compounds, even those of quite complex nature, may be formed by relatively simple biosynthetic processes. Different plants sometimes contain substances which, although belonging to different chemical classes, appear to be biosynthetically analogous. Such plants probably contain similar enzyme systems, and the compounds which they produce may therefore indicate that a relationship exists between the relevant plants.

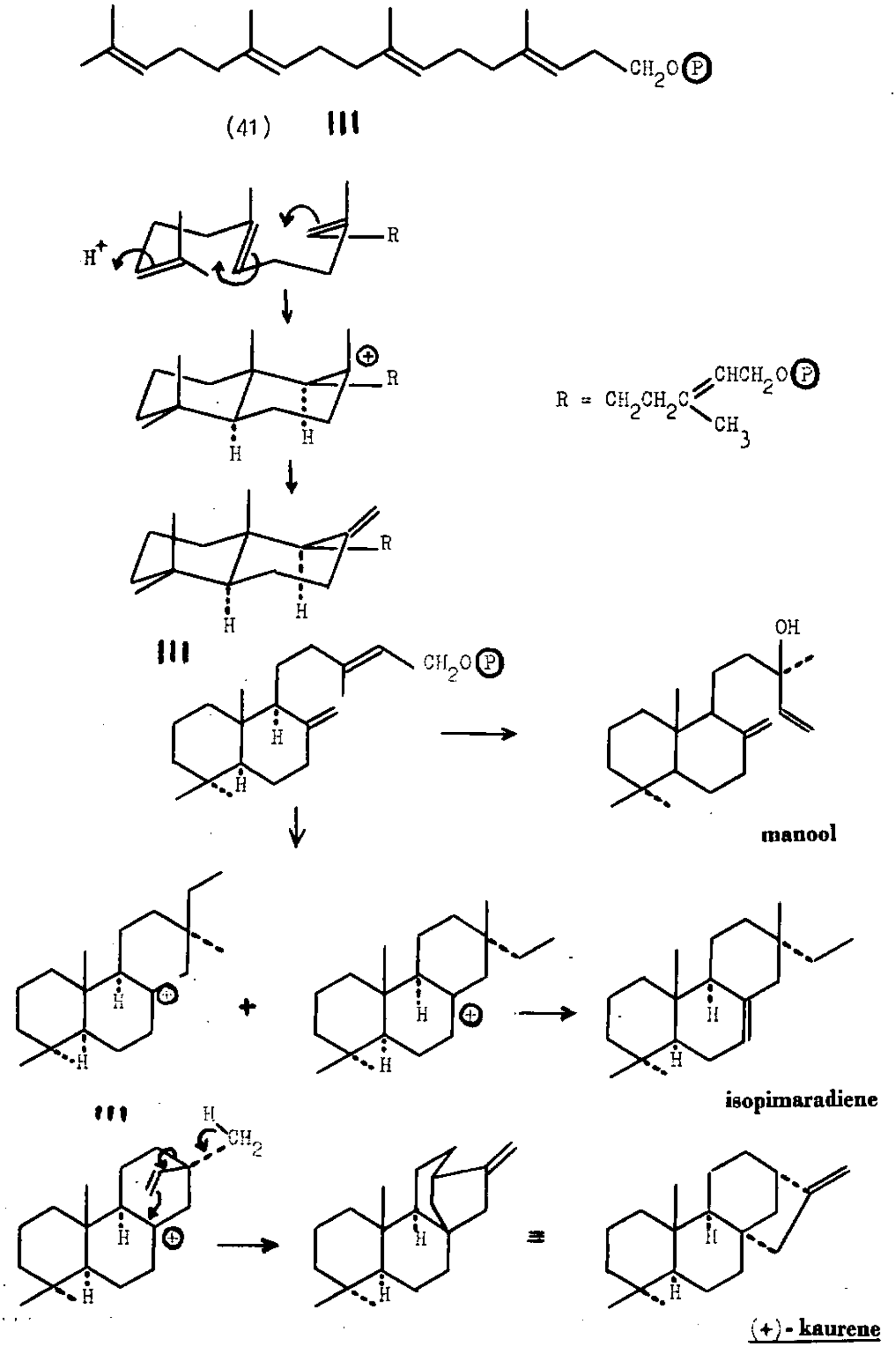
The biosynthesis of diterpenoids is now well established and a number of reviews on this topic have been published[65]. Excluding those with a phenolic ring C, three basic types of diterpenoid are encountered in the New Zealand Podocarpaceae—those possessing a labdane skeleton, an isopimarane skeleton, or a kaurane skeleton. The three types are biosynthesized from geranylgeranyl pyrophosphate (41) which can be arranged on an enzyme such that an acid-catalysed cyclization followed by loss of a proton gives 15-hydroxylabda-8(17),13-diene. The resulting structure has a two-chair conformation and the typical *trans*-anti-*trans* stereochemistry which is that possessed by most but not all diterpenoids. The subsequent rearrangements of 15-hydroxylabda-8(17),13-diene pyrophosphate to give the above three types are shown in Fig. I.

The formation of the aromatic diterpenoids has been assumed to arise from manool type compounds by proton-initiated cyclization and dehydrogenation. The occurrence of numerous 12-oxygenated aromatic diterpenoids has led ApSimon and Edwards[66] to suggest that the cyclization may take place from the diene (42) or triene (43) by initiation with oxygen as shown in Fig. 2. Biosynthetically, podocarpic acid (7, R = H) has suffered the loss of an isopropyl group, but more remarkable structurally is totarol and its derivatives which do not obey the Isoprene Rule[65]. Two suggestions have been made to account for their formation from an isoprenoid precursor[67,68].

Conclusion

The heartwoods of sufficient of the New Zealand conifers of the Podocarpaceae have now been examined in order to observe an emerging pattern of diterpenoid constituents. From a consideration of previous chemical studies and of morphological features it has even been possible to predict with some confidence the type of compound and in some cases particular compounds to be expected in the heartwoods of species which have been examined in more recent work. As detailed above however, some unexpected results have been obtained. Perhaps the most striking of these is the recent isolation of diphenyl sulphone (44) from the heartwood of *D. intermedium* and of sulphonic acids from that of *D. kirkii*[55]. Sulphur-containing compounds are not common constituents of plants and this is apparently the first isolation of such compounds from a heartwood. Their function and biosynthesis pose an interesting problem.

While some attempt has been made to study the chemistry of heartwoods and leaves of New Zealand species, considerable work is still required on these and other organs of the plants before it will be possible to claim that a reasonably satisfactory chemical description of a single species has been obtained. This is especially so in the light of the much greater number of established botanical facts for each species.


CH2O(P)
H+
R
R = CH2CH2C(=CHCH2O(P))CH3
H
OH
manool
isopimaradiene
CH2
(+)-kaurene

(41)

REFERENCES

[1] G. H. Lawrence, "Taxonomy of Vascular Plants", (MacMillan), New York, 1951.

[2] H. Erdtman, in "Chemical Plant Taxonomy", Ed. T. Swain (Academic), London, 1963. pp. 89-125.

[3] H. Erdtman, in "Perspectives in Organic Chemistry", Ed. A. R. Todd (Interscience), New York, 1956, 453.

[4] "Comparative Phytochemistry", Ed. T. Swain (Academic), New York, 1966.

[5] L. Benson, "Plant Classification", (Heath), Boston, 1957, p.2.

[6] W. Dallimore, A. B. Jackson and S. G. Harrison, "A Handbook of Coniferae and Ginkgoaceae", (Edward Arnold), London, 4th Edit., 1966.

[7] H. H. Allen, "Flora of New Zealand", Vol. I, (R. E. Owen), Wellington, 1961, p. 104; J. T. Buchholz and N. E. Gray, *J. Arnold Arbor.* (Harvard Univ.), 1948, *29,* 49.

[8] R. Florin, *Svenska Vet-Akad., Handl.* Stockholm, 1931, Pt. 3, 10.

[9] J. B. Hair, "Pacific Basin Biogeography. A Symposium", Ed. J. L. Gressitt (Bishop Museum Press), Honolulu, 1963, 401.

[10] J. Doyle, *Scien. Proc. Roy. Dub. Soc.,* 1954, *26,* 347.

[11] C. J. Quinn, Ph.D. Thesis, Univ. of Auckland, 1966.

[12] H. R. Orman and J. S. Reid, *N.Z.J. For.,* 1946, *5,* 215.

[13] R. N. Patel, *N.Z.J. Bot.,* 1967, *5,* 171.

[14] H. H. Allan, ref. 7, p. 105.

[15] E. W. Sinnott, *Ann. Bot.,* 1913, *27,* 39.

[16] L. M. Cranwell, *N.Z.J. Sci. Tech.,* 1940,*22,* 1.

[17] S. G. Brooker, R. C. Cambie, and M. A. James, *Trans. Roy. Soc. N.Z.* (General), 1966, *1,* 205.

[18] B. F. Cain, S. Scannell, and R. C. Cambie, *N.Z.J. Sci.,* 1961, *4,* 3.

[19] R. T. Aplin, R. C. Cambie, and P. S. Rutledge, *Phytochemistry,* 1963, *2,* 205; R. T. Aplin and R. C. Cambie, *N.Z.J. Sci.,* 1964, *7,* 258.

[20] J. Borges del Castillo, C. J. W. Brooks, R. C. Cambie, G. Eglinton, R. J. Hamilton and P. Pellitt, *Phytochemistry,* 1967, *6,* 391.

[21] R. C. Cambie and M. A. James, *N.Z.J. Sci.,* 1967, *10,* 918.

[22] R. C. Cambie and S. M. Bocks, *Phytochemistry,* 1966, *5,* 391.

[23] C. W. Brandt and B. R. Thomas, *Nature,* 1952, *170,* 1018.

[24] C. W. Brandt and B. R. Thomas, *N.Z.J. Sci. Tech.,* 1951, *33B,* 30.

[25] L. H. Briggs, R. C. Cambie, R. N. Seelye and A. D. Warth, *Tetrahedron,* 1959, *7,* 270; A. R. Cashmore, M.Sc. Thesis, 1963, and Ph.D. Thesis, 1966, Univ. of Auckland.

[26] C. R. Bennett and R. C. Cambie, *Phytochemistry,* 1967, *6,* 883.

[27] R. C. Cambie, W. R. J. Simpson, and L. D. Colebrook, *Tetrahedron,* 1963, *19,* 209.

[28] R. C. Cambie and L. N. Mander, *Tetrahedron,* 1962, *18,* 465.

[29] C. W. Brandt and L. G. Neubauer, *J. Chem. Soc.,* 1939, 1031; 1940, 683.

[30] L. H. Briggs and R. C. Cambie, *Tetrahedron,* 1960, *8,* 356; J. B. Bredenberg, *Acta Chem. Scand.,* 1957, *11,* 932.

[31] L. H. Briggs, R. C. Cambie and J. L. Hoare, *Tetrahedron,* 1959, *7,* 262 and references therein.

[32] C. W. Bevan and D. A. H. Taylor, *J. Chem. Soc.,* 1963, 6050.

[33] D. A. H. Taylor, *J. Chem. Soc.,* 1963, 1553.

[34] Private communication from T. Takahashi, Govt. Forest Experiment Station, Tokyo.

[35] S. M. Bocks, R. C. Cambie, and T. Takahashi, *Tetrahedron,* 1963, *19,* 1109.

[36] K. Freudenberg, *Fortschr. Chem. Org. Naturstoffe,* 1962, *20,* 41; K. Freudenberg and H. Geiger, *Chem. Ber.,* 1963, *96,* 1265 and refs. therein.

[37] R. C. Cambie and R. J. Madden, unpublished results.

[38] J. R. Hosking and C. W. Brandt, *Chem. Ber.,* 1935, *68B,* 1311; *N.Z.J. Sci. Tech.,* 1936, *17,* 750; J. R. Hosking, *Chem. Ber.,* 1936, *69B,* 780.

[39] A. Brossi and O. Jeger, *Helv. Chim. Acta,* 1950, *33,* 722.

[40] R. M. Carman and P. K. Grant, *J. Chem. Soc.,* 1961, 2187.

[41] R. M. Carman and N. Dennis, *Aust. J. Chem.,* 1967, *20,* 157.

[42] R. C. Cambie and L. N. Mander, *N.Z. J. Sci.,* 1964, *7,* 188.

[43] C. R. Enzell and B. R. Thomas, *Tetrahedron Letters,* 1964, No. 8, 391.

[44] R. J. Weston, unpublished results.

[45] C. W. Brandt, *N.Z. J. Sci. Tech.,* 1951, *33B,* 141.

[46] P. K. Grant, C. Huntrakul, and D. R. Sheppard, *Aust. J. Chem.,* 1967, *20,* 969.

[47] J. R. Hosking and C. W. Brandt, *Chem. Ber.,* 1934, *67B,* 1173; 1935, *68B,* 37, 286; *N.Z. J. Sci. Tech.,* 1936, *17,* 750.

[48] P. K. Grant, *J. N.Z. Inst. Chem.,* 1959, *23,* 121.

[49] R. M. Carman and P. K. Grant, *J. Chem. Soc.,* 1962, 3740.

[50] P. K. Grant and N. R. Hill, *Aust. J. Chem.,* 1964, *17,* 66.

[51] P. K. Grant, N. R. Hill, and M. H. Munro, *J. Chem. Soc.,* 1965, 3846.

[52] P. K. Grant and M. H. Munro, *Tetrahedron,* 1965, *21,* 3599; *Tetrahedron Letters,* 1965, No. 42, 3729.

[53] R. E. Corbett, P. K. Grant, M. J. McGrath, and M. H. Munro, *Tetrahedron Letters,* 1966, No. 27, 3173.

[54] J. R. Hosking, *N.Z. J. Sci. Tech.,* 1937, *33B,* 206.

[55] R. C. Cambie and R. J. Weston, unpublished results.

[56] P. K. Grant and co-workers, unpublished results.

[57] H. Erdtman and T. Norin, in *Fortschr. Chem. Org. Naturstoffe*, 1966, *24*, 257.

[58] W. M. Hearon and W. S. MacGregor, *Chem. Rev.*, 1955, *55*, 958.

[59] S. K. Adhikari, R. A. Bell, and W. E. Harvey, *J. Chem. Soc.*, 1962, 2829.

[60] R. C. Cambie, unpublished results.

[61] R. C. Cambie and B. F. Cain, *N.Z. J. Sci.*, 1960, *3*, 121.

[62] E. G. Brooker, *N.Z. J. Sci.*, 1959, *2*, 212.

[63] M. Kingsford, Ph.D. Thesis, Univ. of Auckland, 1963; J. P. Bartley, M.Sc. Thesis, Univ. of Auckland, 1966.

[64] W. Baker and W. D. Ollis in "Recent Developments in the Chemistry of Natural Phenolic Compounds", Ed. W. D. Ollis, (Pergamon Press), Oxford, 1961, p. 152.

[65] L. Ruzicka, *Experientia*, 1953, *9*, 357; *Proc. Chem. Soc.*, 1959, 341; *Pure and Appl. Chem.*, 1963, *6*, 493; J. B. Hendrickson and J. H. Richards, "Biosynthesis of Steroids, Terpenes, and Acetogenins", (Benjennin), New York, 1964.

[66] J. W. ApSimon and O. E. Edwards, *Canad. J. Chem.*, 1961, *39*, 2543.

[67] E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, 1958, *80*, 211.

[68] A. W. Johnson, T. J. King, and R. J. Martin, *J. Chem. Soc.*, 1961, 4420.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY

(INCORPORATED)

NOTICE OF MEETING

ANNUAL GENERAL MEETING

to be held on

Wednesday, August 21st, 1968
at 8.30 p.m.

in the Chemistry Department of the
University of Auckland.

Agenda: Apologies
Minutes of Last A.G.M.
Chairman's Remarks
Adoption of Annual Report and Balance Sheet
General.

W. E. Harvey, General Secretary.

PERCY REGINALD PARR

1899 — November 1967

An Appreciation . . .

> "FROM various sources there has been compiled a list of persons in New Zealand who earn a livelihood by chemistry . . . The number is 139 . . . including 52 who are teachers . . .".

The Profession of Chemistry in New Zealand — Wright, *N.Z. Jour. Sci. & Tech.* Vol X, No. 1, May 1928, p. 62.

This may seem an odd start to an obituary, but Percy Reginald Parr, who died last November, was one of the other 87 and I understand was the first chemistry graduate of Auckland University College to enter industry as a chemist.

He was one of the University Scholarship winners in 1917 and took pride in later years in his part in the establishing of the Auckland Grammar School tradition. He didn't tell you of his success in the Scholarship examination but one of his friends recently produced his marks with a note that he topped the list in one subject, was second in chemistry and over-all fourth in New Zealand. His academic record at the University was very much what one would expect from this. He graduated M.Sc. with Honours in 1922.

He started work with W. & R. Fletcher (N.Z.) Ltd. in 1923 and spent the whole of his working life with them. After a month with H. W. Lawrence at the laboratory in Johnsonville, he was on his own. At that time he did all the work for three freezing works and for the N.Z. Cattlecake and Oil Company in a basement with windows on a level with a cinder roadway.

The early industrial chemist in New Zealand had literally to be a jack of all trades and a master of one. If you couldn't solder, hard as well as soft, you had no water-baths or ovens. If you couldn't wind a muffle for an electric furnace you waited months for a new one—and in the meantime devised some alternative method that needed no ignition. If you wanted equipment in a hurry you built it if it was "one off", or otherwise designed something that a works carpenter or plumber could turn out—and usually showed them how!

If the works ran out of nitrite because the all-wise purchasing department had ordered nitrate, the lab turned out nitrite by the hundredweight until stocks were replenished. Always, if it couldn't be bought or if the price was uneconomical, the lab was called on to fill the gap.

In the rush of day to day routines, investigating complaints and checking or developing new processes, there was the insistence on meticulous standards. More than one of his assistants was surprised to hear the quiet inquiry "How long is it since you checked your work on . . ." whatever might have been on hand at the moment. Out of the oven would come something—"Check this and show me the result." He spoke firmly but I cannot call to mind any occasion on which he ever spoke harshly. If anything was astray, everything was checked by two people, both of whom knew a lot more when it was all over.

There is no doubt whatever that he was the complete master of his chosen profession but it was always clear that his skill at improvisation went beyond his mastery of chemistry.

As a man he was of very great breadth of vision and his interests were as wide. This is natural in one who originated from pioneer stock. The family moved from the East Tamaki area because of troubles with the Maoris and took up land at Glen Eden in 1851. They were orchardists. Life in a family of this kind explains his talent for improvisation. He had many tales of achievement—a whole row of apple trees, too valuable to lose, transplanted without losing a crop; a blackberry hedge the fruit from which labelled "berries" fetched top price in the markets at the start of the boysenberry craze!

He could tell you the number of wells in the Westfield industrial area. He could state the acreage, the average annual rainfall, the amount of water pumped from each well—all to disprove the existence of any underground stream.

He could discuss music with you, particularly church music as he was at one time the deputy organist at the Church of the Holy Sepulchre at the top of Khyber Pass.

If you wanted to shoot rabbits he could tell you accurately within minutes the times they would appear to feed in the country round his home.

If you had a problem with a tidal mudflat at your door he could advise you about it and the *Spartina townsendii* at Westfield has grown from what he personally planted there.

He knew his New Zealand trees and could quote that the largest tree, timberwise, ever to be milled was a kauri from somewhere down Thames way. This produced sufficient timber for some fantastic number of average size state houses—35 I think it was! At the other end of the scale he had for many years a lawn of native grasses, principally *Microlena* sp.

He would discuss books and literature—"Cautionary Tales" or Shaw as well as classics. He reminded me rather more than a year ago that I had introduced him to Kipling's "Proofs of Holy Writ" and was interested that I was glad he had lent me a copy of "Salambo".

These notes do not mark the limits of his interest and accomplishment for people ranked very high in his concern. Often their problems were his, particularly in depression days. As a landlord he accepted responsibility for feeding five tenants, and told them that only when they had some work need they pay some rent.

Most of you who read this never met Percy Parr, let alone knew him, yet if you are a member of the N.Z. Institute of Chemistry you owe him something because he was one of its founders. He was a prime mover in the Auckland Chemical Society and one of those with sufficient vision to realise the wisdom of establishing a national organisation. It has been common talk that his was the deciding vote which ensured the establishment of the Institute.

I can't tell you how many papers he had published. I don't know the lectures he delivered. When he was Chairman of the Auckland Branch and which year he was President are other matters beyond my ken, though the records will tell you.

Here was a man who never sought the limelight. When there was work to be done he was there. When the credit was being distributed he was mostly somewhere else doing some other job out of sight. Mostly he was giving. What immortality a man may achieve, he has. So many things stand firmer because of his efforts. I think all of us are in his debt.

Eric Pain.

NEW FACILITIES FOR RESEARCH

New Zealand Fertiliser Manufacturers' Research Association

J. Rogers, M.Sc., Ph.D., F.N.Z.I.C.

Director, New Zealand Fertiliser Manufacturers' Research Association

In the past eighteen months important developments have occurred at the Otara Research Station of the New Zealand Fertiliser Manufacturers' Research Association (F.M.R.A.), and with the N.Z.I.C. Conference being held at Auckland in August, an outline of these changes involving staff, equipment and buildings is timely. The setting of F.M.R.A's laboratories, 12 miles south of Auckland on the motorway—20 minutes' drive from the city, is the 'star-shaped' building with tower and flag-pole almost in the centre of Figure 1. Five thousand feet of space in this building, which is shared with the Auckland office of the New Zealand Geological Survey, and eight acres of surrounding land are leased from the D.S.I.R. which purchased the property in 1948.

The Otara Research Station was originally built, using bricks and tiles brought from Europe as ship's ballast, by the Dilworth Trust in 1917 as a farm school for the sons of men lost in the Merchant Navy during the 1914-18 war. Of distinctive architecture, the building is a landmark in a community which has grown in six years from about 500 to over 30,000 people. Clydemore Primary School and Bairds Intermediate School are close at hand. Otara College—now in its third year—is several hundred yards away. The M.T.I. (Manukau Technical Institute) is now building half a mile down the road.

At the 10th Conference of the Fertiliser Industry in November 1966, Mr. R. A. Warburton, M.B.E., B.Sc., Chairman of F.M.R.A., opened the J. K. Dixon Memorial Wing which had been altered to provide laboratory space for physical chemistry and staff offices. Dr. Dixon, a former President of the New Zealand Institute of Chemistry and director of Soil Bureau, had represented D.S.I.R. on F.M.R.A's Management Committee from its inception in 1950. Mr. Warburton referred to Dr. Dixon's distinguished

Fig. 1

Fig. 2

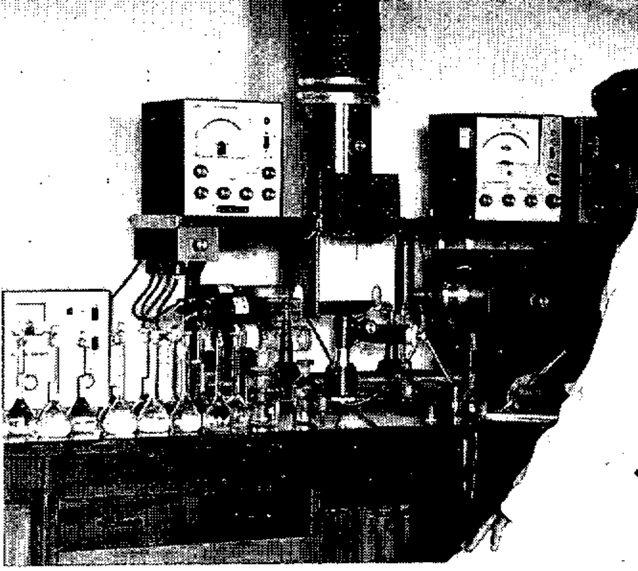


Fig. 3

contributions to soil chemistry in New Zealand—so excellently summarised by A. J. Metson in the September 1966 issue of New Zealand Agricultural Science.

Figure 2 shows X-ray diffraction and fluorescence equipment recently installed in the physical chemistry laboratory in the J. K. Dixon wing. Manufactured by General Electric, U.S.A., this X-ray spectrometer is of advanced design and the first of its kind in New Zealand, and possibly Australasia. The arrival of these units at Otara just before Christmas was a highlight in the first year of a current triennium of development for which the fertiliser industry doubled its contribution to F.M.R.A. in the year ending 30th June 1968. For the next two years this grant will increase again to treble, so that from 1968-69 F.M.R.A's income from industry and government will be more than $100,000. Plans are presently being prepared for a chemical engineering building which may be under construction by August—another step in implementing the policy of emphasis on research into fertiliser manufacture.

Dr. J. B. Macaskill, a new member of F.M.R.A. staff, recently graduated Ph.D. (Otago), is shown working with the X-ray equipment. In a staff of 15, seven are graduates and another, Mr. John Rouse, recently passed the Associateship examination of the N.Z.I.C. with merit.

Since 1963 much research at Otara has been devoted to ways of using the 150 million tons of iron/aluminium phosphates which cover the apatite on Christmas Island. One research finding which is being developed is that the availability to pasture plants of the phosphate in the iron/aluminium phosphate minerals crandallite, millisite and barrandite is markedly increased by heating them at 500°C. This heat treatment also destroys the ordered arrangement of the atoms in these minerals. Their X-ray diffractograms no longer are sharp characteristic peaks, but only a broad curve. The Christmas Island Phosphate Commissioners have generously recognised F.M.R.A's work on ways to use this important mineral resource, jointly owned by New Zealand and Australia, by a substantial donation to the cost of this new equipment.

By arrangement with the British Phosphate Commissioners a sample, which is representative of each shipment of phosphate rock coming to New Zealand from Christmas Island, is taken by special equipment on the loading cantilever at Christmas Island. Immediately the shipment reaches its unloading port in New Zealand the sample is forwarded to Otara. In less than two hours, grinding, pressing and analysis for phosphorus, iron and aluminium by X-ray fluorescence can be completed. The results possibly reach the fertiliser

(continued on page 134)

INSTITUTE OF CHEMISTRY

CONFERENCE 1968

PAPERS in the Biochemistry, Geochemistry and Mineral Resources, Liaison, Chemical Engineering, and Student Papers sessions are outlined below. Readers are reminded that notes on all aspects of Conference were given in the previous issue. The full programme and final timetable details will be available to delegates on registration.

ABSTRACTS

(Please take these with you to Conference)

BIOCHEMISTRY

ELECTRON MICROSCOPY AND THE ELUCIDATION OF MEMBRANE STRUCTURE

S. BULLIVANT
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University of Auckland

THE "unit membrane" theory of the structure of membranes regarded all membranes as bi-molecular lipid layers with proteins on their surfaces. Differences between membranes were supposed to reside largely in the protein layers. Recently developed techniques of electron microscopy, especially negative staining and freeze-etching, allow a view of the plane of the membrane rather than its cross section. A constant feature of membranes seen by these techniques is an array of particles which appears to be within the membrane and indeed to form it. In some cases these particles can be correlated with biochemical subunits; a particular example is the quantasome of the chloroplast. It appears that in many cases the "unit membrane" theory is an over-simplification and that membranes are composed of arrays of biochemically active lipid-protein subunits.

MECHANISMS OF IONIC ACCUMULATION ACROSS MEMBRANES

P. M. WIGGINS
Department of Cell Biology,
University of Auckland

ALMOST all living cells have the ability to maintain a high internal concentration of potassium and a low internal concentration of sodium. This they contrive to do in the face of steep concentration gradients of both ions, the external solution bathing the cells containing relatively high sodium and low potassium concentrations.

These ionic gradients could be maintained either by active transport processes on the cell membrane, or by selective accumulation of potassium and exclusion of sodium by the cell as a whole. Evidence for both points of view will be discussed.

BIOCHEMICAL ASPECTS OF TRANSPORT ACROSS MICROBIAL MEMBRANES

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THE permeases, or transport carriers, were until recently merely hypothetical proteins invented by biochemists to account for the puzzling phenomenon of membrane transport. Yet one by one permeases are being isolated, characterised and even in one case, crystallised. A permease, defined by its ability to catalyse transport across an intact cell membrane, cannot be directly assayed when the membrane is no longer present. All procedures for monitoring the isolation of permeases therefore make use of ancillary features of the transport process—in most cases the ability of the isolated molecule to bind its substrate. Recent work in this field is briefly reviewed. In many instances the assumption that specific inducible transport systems exist allows a ready explanation of the experimental data. As an example, the rate of oxidation of fatty acids and triglycerides by spores of *Penicillium roqueforti* is discussed.

BIOCHEMICAL PROPERTIES OF THE ERYTHROCYTE MEMBRANE

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THE lack of any internal cell structures and the membrane localisation of virtually all the cell lipids make the erythrocyte a popular choice for the study of membrane properties. Membrane protein characterisation is as yet incomplete, but the presence of a structural protein having a tendency to aggregate and some helical configuration is evident.

With regard to lipid-protein interactions, most of the polar groups can be removed from the phospholipids without destroying gross membrane structure.

Each species has a characteristic erythrocyte phospholipid distribution, but considerable interspecies variation exists. Fatty acid constituents, however, are considerably influenced by diet. In addition to direct exchange of cholesterol and some phospholipids with plasma counterparts, the circulating erythrocyte can take up and esterify plasma monoacyl phospholipids.

DISTRIBUTION OF H+ ACROSS THE CELL MEMBRANE

DR. D. S. CAMPION
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THE central role of the hydrogen ion (H^+) in metabolic processes makes accurate measurement of intracellular pH(pH_{ICF}) and determination of the factors controlling the transcellular membrane distribution of H^+ of considerable interest. Using double-barrelled pH-sensitive, glass micro-electrodes we have made simultaneous measurements in rats of pH_{ICF} and membrane potential (E_m). Rat extracellular fluid pH is 7.4; muscle cell pH measured by electrode is 6.0 and simultaneous E_m is —90 mV (negative inside); liver cell pH is 6.95 and E_m is —25 to —28 mV. This demonstrates that in these tissues the H^+ is in electrochemical equilibrium across the cell membrane according to the Nernst equation:

$$E_m = RT/F \ \ln H^+_{ICF}/H^+_{ECF}$$
$$= 61.5\ (pH_{ECF} - pH_{ICF}) \text{ at } 38°C.$$

Manipulation of muscle E_m resulted in very rapid adjustment of pH_{ICF} so that electrochemical equilibrium was always maintained. This demonstration of extreme mobility of H^+ across the membrane suggests that water in the cell membrane may be in a structured state and that H^+ may be "moving" by the phenomenon of protonic conduction as observed by Eigen.

THE MECHANISM OF ACTION OF INSULIN

J. G. T. SNEYD
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INSULIN is well known to stimulate the transport of glucose into muscle and adipose tissue. Recently it has become clear that not all the biological effects of insulin can be explained on this basis. Evidence will be presented that the actions of insulin on lipolysis and glycogen synthesis in adipose tissue and on glucose output by the liver are mediated by a fall in the tissue level of cyclic 3′5′ AMP. Glucose transport does not appear to be controlled by cyclic 3′5′ AMP.

PATTERNS OF GROWTH HORMONE RELEASE AND ITS PERIPHERAL ACTION

D. J. SCOTT
Radioisotope Unit, Auckland Hospital

HUMAN growth hormone is a polypeptide of 187 amino acids and molecular weight of 21,500. After synthesis and storage in the acidophil cells of the pituitary gland it is released into the blood under the influence of a small, polypeptide releasing factor arising from a specific area in the hypothalamic region of the brain stem. This area senses changing levels of blood glucose and amino acids and integrates these with neural stimuli set up by stress and exrcise.

The fluctuating pattern of plasma growth hormone levels consists of slowly rising peaks prior to meals and troughs during and after meals. Sharp peaks associated with stress and exercise are superimposed.

The peripheral action of the hormone is concerned with stimulating protein synthesis. An obvious aspect is the impulse to cartilage formation at the epiphyseal plates at the ends of long bones, resulting in linear growth.

STEROIDAL HORMONES IN PREGNANCY

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University of Auckland

THE biosynthesis, catabolism and function of the steroid hormones in human pregnancy involve complex interrelationships between foetus, placenta and mother. These interrelationships are as yet only partly understood. Although the production of all steroid hormones is influenced by pregnancy, the most striking change is the tremendous increase in the production of progesterone (up to 10 times non-pregnancy rate) and oestrogens (for oestriol, up to 1,000 times non-pregnancy rate). The biosynthesis of progesterone takes place in the placenta, probably from maternal cholesterol. Oxygen biosynthesis involves the foeto-placental unit, precursors from the foetus being further metabolised by the placenta to yield oestrogens. The significance of the high levels of progesterone and the oestrogens in pregnancy is not clear; pregnancies with abnormally low production of oestrogen or both oestrogen and progesterone can follow an apparently normal course.

GEOCHEMISTRY AND MINERAL RESOURCES

THE CHEMISTRY OF ORE BODIES

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Chemistry Division, D.S.I.R.

MINERAL exploration philosophy and the evaluation of mineral prospects and deposits are strongly influenced by one's theory of origin of the deposits involved. General theories of origin of some types of deposits are reviewed and the influence of conflicting genetic theories on exploration programmes are pointed out. Element and rock type associations recur in many ore deposits, e.g. tin with granites, arsenic with gold, platinum and nickel with ultra-basic rocks, and although not always well understood, are used successfully in many exploration programmes.

The genetic details of hydrothermal deposits are, in general, poorly known and the application of chemical studies at elevated temperatures and pressures to clarify the mechanisms of transportation and deposition of heavy metals in hydrothermal systems is briefly reviewed. The hydrothermal chemistry of gold-silver deposits associaed with Tertiary volcanic rocks is examined, and a genetic parallel is drawn between the Taupo Volcanic Zone, the Coromandel Peninsula, and areas in central Nevada, U.S.A., that are currently experiencing an exploration and development boom.

GEOCHEMICAL PROSPECTING

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THE geochemical prospecting method involves the detection and interpretation of unusual concentrations of elements associated with a particular type of mineralization. An outline is given of its role as an important exploration technique in comparison with geophysical methods.

The types of element anomalies that are found about particular mineral deposits are briefly reviewed. In particular situations collection and analysis of rock, soil, stream waters or stream sediments for the mineralized element or an associated "path-finder" element are undertaken. The methods used for chemical analysis must be capable of handling hundreds of samples in a few days. Geochemical prospecting usually is based on the secondary dispersion of elements which occurs during the weathering of rock and associated minerals. Interpretation of results requires some knowledge of the chemistry of solution, transport, and precipitation processes for the elements in ground waters, streams, soils and sediments. Methods of examination are used which amplify the differences which occur in samples because of their proximity to mineralization.

Regional geochemical surveys based on the analysis of stream silts have proved to be an efficient and economic means of examining large areas (10^2-10^3 square miles) for potential mineralization. Detailed examination of a mineralized locality on the other hand is often based on a survey of element concentrations in a particular soil horizon.

To illustrate the principles and applications of geochemical prospecting, examples are given from New Zealand projects.

BIOGEOCHEMICAL PROSPECTING FOR URANIUM IN NEW ZEALAND

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Massey University of Manawatu

THE uptake of uranium by the flora of the Buller Gorge Region of New Zealand has been investigated with a view to carrying out biogeochemical prospecting in the area.

Uranium was determined fluorimetrically and the total activity of samples of plant ash and soils (presumably radium + thorium + uranium) was determined with a low-background α-counter.

Two species of trees (*Weinmannia racemosa* and *Nothofagus fusca*) and two shrubs (*Coprosma australis* and *Quintinia acutifolia*) had concentrations of uranium in the leaves which correlated well with the soil levels. It is hoped to use this fact for biogeochemical prospecting for several elements simultaneously by spectrochemical analysis of the plant ash in addition to the fluorimetric determinations of uranium.

The discovery that certain elements such as beryllium and molybdenum, which are found in association with uranium, are also accumulated in some species of plants leads to the possibility of using these elements as 'pathfinders' for uranium.

THE MICROBIAL LEACHING OF COPPER ORES

R. M. ALLEN
Department of Chemical Engineering,
University of Canterbury

A COPPER extraction plant has been designed in the Department of Chemical Engineering at the University of Canterbury based on microbial research in the U.S.A. and New Zealand on the rate of bacterial attack on copper sulphide ores. Such a microbial leaching process substantially reduces the capital investment required, enabling the copper from the relatively small deposits occurring in this country to be economically recovered.

PAPER FILLER CLAYS

I. R. C. McDONALD
Chemistry Division, D.S.I.R.

THE successful utilisation of a mineral deposit often involves an investigation of industrial problems far removed from the more obvious aspects of mineral chemistry. This is well illustrated by experiences with New Zealand clays used as fillers in writing paper.

Writing papers commonly contain up to 10 percent of a kaolinite-type filler-clay. The abrasive properties of these fillers influences the subsequent cutting properties of papers prepared with the fillers, but there is little quantitative data relating clay abrasion to paper cutting properties. Methods have been developed to relate cutting properties to the increasing load on the cutting knife caused by abrasion of the cutting edge. The successful development of laboratory tests is an essential prerequisite to any attempt to beneficiate the clay and thus gain its acceptance in industry, since it is not practicable to carry out experimental work with the output of a factory cutting writing paper on a commercial scale.

LIAISON BETWEEN GOVERNMENT, INDUSTRY AND TERTIARY EDUCATION

RESEARCH ORGANIZATIONS

W. A. McGILLIVRAY
Director, New Zealand Dairy Research Institute, Palmerston North

RESEARCH organizations, jointly financed by industry and Government, occupy an important place in the New Zealand scientific scene. In their main function of carrying out research and development work, both short-term or applied and long-term or fundamental, and in their other responsibilities they are often in the position of helping to define for their respective industries the need for high quality professional staff and the type of graduate they require; and they should be able to feed back to the universities information about the scientific and technological requirements of the country.

It is suggested that while the quality of the New Zealand graduate is as high as anywhere else in the world, the direction of his training is seldom consciously related to the needs of New Zealand industry; the New Zealand universities have failed to develop a national character in keeping with our agricultural economy and, as a consequence, have tended to train our best students for export rather than for service in our export-earning primary industries.

INDUSTRY

DAN A. WATKINS
Managing Director, Ivon Watkins-Dow Limited, New Plymouth

IT is one of the contradictions of living that in a world reticulated with unprecedented forms of communication we should have to discuss liaison amongst tertiary educational institutions, government and industry—or to be precise, the need for improving it. In a country as literate as ours communication, with its connotation of "common participation", should be a fact of life in our relations.

As a representative of industry I will try to tell you the changing attitude of industry, in particular the manufacturing section, to what we believe has developed into competition between the universities, government organizations and industry for the country's top brains. I will also stress the need for a greater understanding of industry's requirements by those responsible for tertiary education.

Maybe it is industry's fault if a graduate leaves a university with the impression that by going into industry he has started on "a straight run to the grave" as one researcher put it; or that the undergraduate, unable to face the thought of a continuous rat race, finds it difficult to believe that industry can be "a community of people working together for a common end with mutual support and mutual respect, and no place for a rat!"

I believe that liaison is basically a question of attitudes, and I hope to explain how these can change or be changed to our mutual benefit.

THE TECHNICAL INSTITUTES

R. A. KEIR
Auckland Technical Institute

IN the modern technological society, education and training are two sides of the same coin. Because they reach into every aspect of commercial and industrial activity at all levels, the technical institutes have a vital role in the economy of a developing country like New Zealand. Their work in vocational training should complement that of the universities and the two should flow in parallel to ensure that the university trained scientists are provided with the increasing numbers of technologists and sub-professional supporting personnel that the successful development of their research and planning requires.

The accelerating demands for craft and sub-professional training will require many more technical institutes and it seems reasonable to expect that many of our provincial towns will need these facilities during the next decade. This demand is characteristic in many countries; Britain has 39 universities and more than 600 technical colleges; U.S.A. is building many more junior and community colleges the courses in which closely resemble some of those in our own technical institutes; Australia is developing colleges of technology providing part-time courses leading to degrees and diplomas in a wide range of technologies outside those in the universities. Such a development in New Zealand may assist in producing professionally qualified people with the more practical type of approach which some industries may require. This type of development should be encouraged rather than resisted by our universities because experience shows that benefits derive for all in the end.

Greater opportunities are required for one or two-year full-time courses in technical institutes to prepare adolescents for careers in applied science. Prolonged adherence to the traditional British system of craft apprenticeship may impede the development of a flexible work force. The advantage of the American type of vocational training is that it provides a reservoir in times of underemployment which can supply the increased need for skills when the demands come. The trade schools and community colleges fill up when jobs are scarce and empty out when work is plentiful. A reduction in apprenticeship such as is taking place in the building industry at present leaves an irreplaceable gap in manpower.

Technician training in applied science has supplied an urgent need but much more should be done. There is a growing demand for post certificate courses in Applied Chemistry and Food Technology which could be met by providing part-time courses in technical institutes leading to diplomas in these fields. If the N.Z. Institute of Chemistry supports these, they will be in good company because the leading professional institutions in the world have never opposed developments of this kind.

UNIVERSITY

H. N. PARTON
University of Otago

New Zealand is a late entrant into fields of tertiary education other than those regarded as appropriate to the universities and to teachers' colleges. However, the agricultural colleges have long ago developed a distinctive form of technical-cum-university training which makes a major contribution to our principal industry—agriculture. We cannot yet envisage development of other industries to match agriculture, and consequently our demand for any particular type of technical skill is likely to remain small for a long time. In some fields graduate training will be most economic if carried out overseas, while numbers at the technician level in these fields may justify courses in our own technical institutes. In others, the demand for graduates and technicians may fall short of justifying separate university and technical institute courses, but may call rather for co-operation in the sharing of the time of specially qualified staff for training both groups, and even of equipment and laboratory space. Technical institute staffs should have access to research facilities within universities.

Universities are criticised here and elsewhere on the grounds that the fields into which university teachers lead their students bear little relation to the problems of industry and the government services. A university is a teaching and research institution, concerned with undergraduate and graduate instruction. It has two products, graduates and scholarship (usually termed research in the sciences). Its claim on the public purse must be primarily based on the community's need for these two products. Direct service to industry can only be a marginal activity and must never be the basis of university financing. The fields in which university research supervisors choose to train their apprentice researchers must remain a matter of free choice. Those who choose unwisely will soon discover their unwisdom.

CHEMICAL ENGINEERING

THE FUEL CELL

P. L. SPEDDING
Department of Chemical and Materials Engineering, University of Auckland

The basic principles of direct electricity generation by means of the fuel cell are presented with emphasis on the thermodynamic and mass transfer phenomena involved. Various types of fuel cells are described in some detail with emphasis on the more practical varieties. Typical operating data are outlined together with the various factors which limit cell output and operating life. Attention is directed to various areas where research could well help in overcoming the problems which at present are limiting cell performance and whose solution would lead to wider application of the fuel cell. Some of the practical uses to which the fuel cell has been put are detailed.

THE RECOVERY OF FLUORIDE FROM SUPERPHOSPHATE MANUFACTURE

W. E. RUSSELL
The N.Z. Farmers' Fertilizer Co. Ltd., Auckland

In the manufacture of superphosphate from phosphate rock and sulphuric acid a small proportion of silicon tetrafluoride is evolved as part of a gaseous by-product. In general, these fluoride-containing gases have been regarded as a nuisance and water scrubbing and subsequent neutralisation have been required in certain cases to prevent atmospheric and stream pollution.

The fluoride, however, represents a potentially valuable recoverable material. This paper describes the design and operation of a small process for the economical recovery of a substantial part of the evolved fluoride in the form of a commercial 15% strength hydrofluosilicic acid. This material is finding increasing acceptance overseas as a fluoridating agent for public water supplies and the major part of the production from this plant is utilised for this purpose.

THE EVALUATION OF KRAFT BLACK LIQUOR EVAPORATOR PERFORMANCE

W. J. BELL
N.Z. Forest Products Ltd., Tokoroa

The evaporation of waste liquor from the Kraft pulping process is a very necessary step in the recovery of waste chemicals. The waste liquor, commonly known as black liquor in the pulping industry, is evaporated from 13 percent solids content to 45 percent solids content by means of multiple effect, long tube, vertical evaporators.

This paper describes the development of a method to evaluate the performance of these units. The application of heat transfer theory, development of testing methods, correlation of basic data and layout of a digital computer programme are described.

AUTOMATIC CONTROL IN THE PROCESS INDUSTRIES

R. M. ALLEN

*Department of Chemical Engineering,
University of Canterbury*

Automatic control of industrial processes is a part of modern technology at all levels from the thermostat to the process control computer. A number of basic techniques using pneumatic instrumentation are available to handle many types of control problems and recommendations can be made on their use and adjustment. At present, the scale of most industrial processing plants in New Zealand favours the use of control equipment of this type. rather than direct digital computer control.

STUDENT PAPERS

There will be a second session on Friday afternoon in addition to the one on Thursday morning in the programme. The speakers will be present Ph.D. students in chemistry or biochemistry. The following University nominations have been received at the time of printing.

Auckland

MR. W. A. DENNY
"STEROID SYNTHESIS FROM DITERPENE PRECURSORS"

Massey

MR. W. D. SUTTON
"SEQUENCE STUDIES WITH BACTERIOPHAGE DEOXYRIBONUCLEIC ACID"

Victoria

MR. D. F. COOK
"CO-ORDINATION COMPOUNDS OF SOME CYCLIC TETRA-AMINES"

MR. T. W. JORDAN
"INSECT MICROSOMAL OXIDATIONS"

Otago
To be selected

Canterbury
To be selected

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT 30th APRIL, 1968

1967 $		$	$
	CURRENT LIABILITIES		
75	Sundry creditors	158.60	
228	Subscriptions received in advance	267.30	
400	Royal Institute of Chemistry Funds held in Trust	400.00	
(703)	*Total Current Liabilities*		825.90
	SPECIAL FUNDS		
14	Compounded subscriptions	4.44	
150	Education fund	150.00	
—	Overseas visitors travelling fund	300.00	
(164)			454.44
	TRUST FUND		
	Balance 30.4.67	2,580.37	
	Plus Interest credited	2.20	
2,580	*Balance 30.4.68*		2,582.57
	ACCUMULATED FUNDS		
	Balance as at 30.4.67	1,930.83	
	Excess of Income over Expenditure for year	2,291.71	
1,931		4,222.54	
	Less Overseas Visitors Fund Appropriation	400.00	
	Balance 30.4.68		3,822.54
$5,378			$7,685.45

1967 $			$	$
	CURRENT ASSETS			
20	Petty Cash Funds		16.94	
879	Bank of New Zealand		2,837.35	
	Subscriptions in arrears	615.71		
	Less Provision for overdue subscriptions	100.00		
381			515.71	
232	Sundry Debtors		221.45	
236	Publications on hand		357.43	
—	Advance—Conference		80.00	
(1,748)	*Total Current Assets*			4,028.88
	TRUST FUND INVESTMENTS, AT COST			
80	Post Office Savings Bank		82.57	
1,000	Hutt County Council Redemption Loan		1,000.00	
1,500	Lyttelton Harbour Board Stock		1,500.00	
(2,580)				2,582.57
	GENERAL FUND INVESTMENT			
1,000	North Canterbury Hospital Board Stock			1.000.00
	FIXED ASSETS, AT COST			
	Office Equipment	241.90		
	Less Depreciation	169.90		
48			72.00	
	Addressograph Plates	62.35		
	Less Depreciation	60.35		
2			2.00	
(50)	*Total Fixed Assets*			74.00
$5,378				$7,685.45

AUDITOR'S REPORT

I have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended 30th April, 1968, and have received all the information and explanations I have required. In my opinion, according to the best of my information and the explanations given to me as shown by the books of account, the Balance Sheet, Income and Expenditure Account, and Trust Fund Account are properly drawn up so as to give a true and fair view of the state of the Institute's affairs as at 30th April, 1968.

Christchurch, 20th June, 1968.

J. W. SHANAHAN, Auditor.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30th APRIL, 1968

EXPENDITURE

1967 $		$	$
	Administration Expenses		
907	Printing, Stationery, Postages, Tolls, etc.	868.44	
334	Travelling Expenses	625.13	
520	Salary Registrar	560.00	
411	Branch Expense Allowances ...	440.00	
150	Honoraria (*Less* proportion charged to Journal)	210.00	
59	General Expenses	106.39	
84	Audit Fees	80.00	
12	Depreciation	18.00	
(2,477)			2,907.96
2,718	Cost of Journal (including proportion of Editor's Honorarium $90)	3,159.12	
1,546	*Less* Revenue from Advertising	1,963.30	
(1,172)			1,195.82
22	Chemistry in Action—net cost ...		—
	Examination Expenses	60.00	
82	*Less* Examinees' Fees Received ...	60.00	
			—
—	Chemistry Essay Prize		50.00
71	Overseas Visitors Travelling Fund over spent		—
208	Excess of Income over Expenditure for year		2,291.71
$4,032			$6,445.49

INCOME

1967 $		$	$
3,736	Subscriptions—Annual	6,148.37	
10	Proportion Compound Subscriptions	10.16	
(3,746)			6,159.03
	Interest Received		
32	Bank of New Zealand	45.98	
181	Local Body Stock	180.64	
(213)			226.62
72	Surplus, Distribution of Publications		59.84
$4,032			$6,445.49

OVERSEAS VISITORS TRAVELLING FUND

1967		$
612	Travelling Expenses Paid during year	100.00
—	Balance	300.00
$612		$400.00

1967		$
296	Balance to 30.4.67	—
72	Received from General Fund	400.00
214	Donations	—
30	Conference Surplus Credited to Fund	—
$612		$400.00

(continued from page 125)

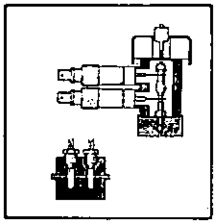
manufacturers before unloading is completed. One aim of this service is to provide a better basis for making superphosphate from blends of Christmas Island phosphate rock with Nauru and Florida phosphates. Figure 3 shows Mr. John Rouse making calibration analyses for iron and aluminium with the AA-4 Techtron Atomic Absorption Spectrometer installed at Otara in August 1967.

Another project for which the X-ray equipment is providing valuable information is a study of phosphorite dredged at 1,200 feet from the sea floor on the Chatham Rise. X-ray diffractograms show clearly the different minerals—apatite, calcite, quartz, feldspar, glauconite—and the proportions in which they are present in the pebble, sand, silt and clay fractions. This work is being done on a contract basis for a United States mining company in co-operation with the Department of Mineral Technology, University of Otago. The products from research on the beneficiation of the apatite in this material are being analysed at Otara and tests made of their suitability for superphosphate and phosphoric acid production.

This co-operative project illustrates F.M.R.A's policy of working with university and government research groups as well as the member companies in order to serve the fertiliser industry more effectively.

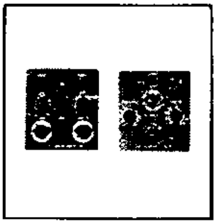
MODULINE—the time-tested G.C. concept that has been copied, but never equalled

DETECTORS



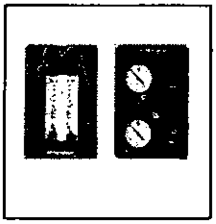
New ionization detectors for highest sensitivity and linearity at all operating temperatures up to 400°C. A universal detector base allows rapid interchange of FID, phosphorus, H^3 and Ni^{63} E.C. detectors. The new T.C. detector features WX filaments and decreased cell volume for high stability and sensitivity.

PROGRAMMERS



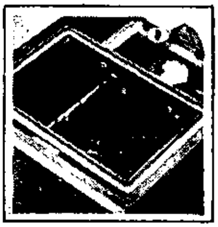
Choose from the unique fully automatic Matrix with step programming, the automatic linear, or the all-new linear programmer or isothermal proportional controller. For unequalled accuracy, performance, and operational flexibility, each programmer is a plug-in module—all solid state with no batteries or tubes.

FLOW CONTROL



Dual/differential flow controllers for each column provide precise control, and maximum versatility and ease of operation. You can choose either the rotameter or pressure gauge type. Panel-mounted needle valves provide convenient, precise control of the separate H$_2$ and air flow to each ionization detector.

COLUMN OVEN



Moduline gives you the largest column oven available in a bench-type G.C. With over 1000 in^3 of readily accessible, usable space, it easily accommodates preparative, capillary, and analytical columns, either metal or glass. And it still has ample room for a variety of valves.

varian aerograph

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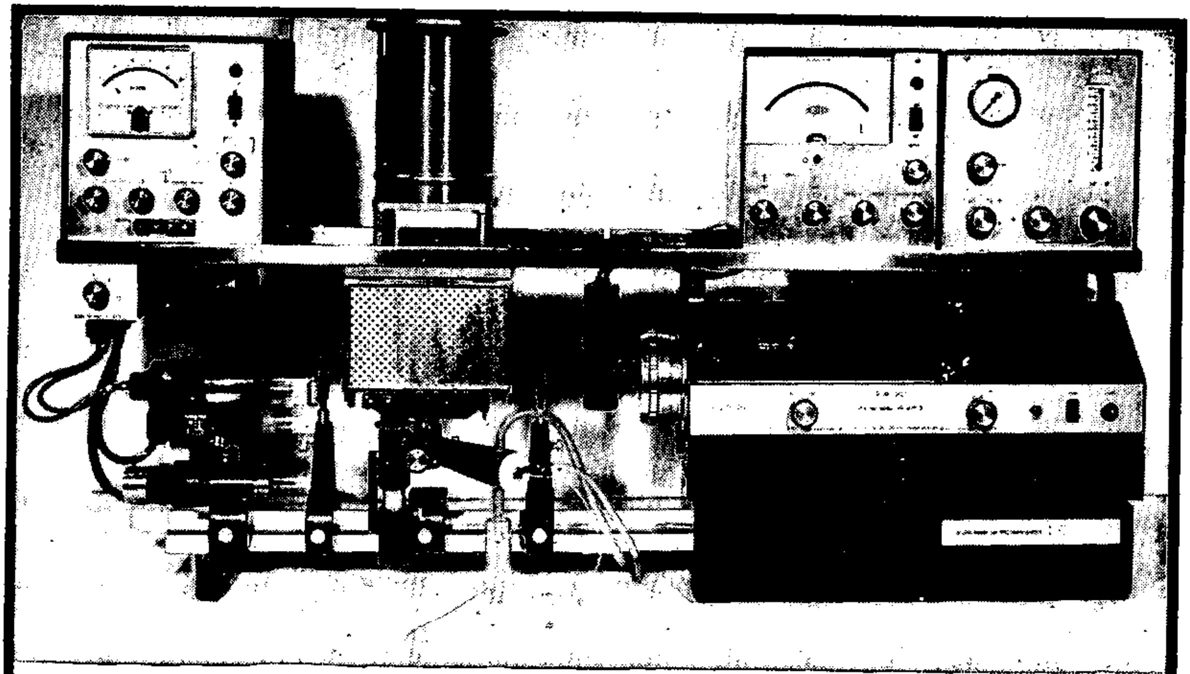

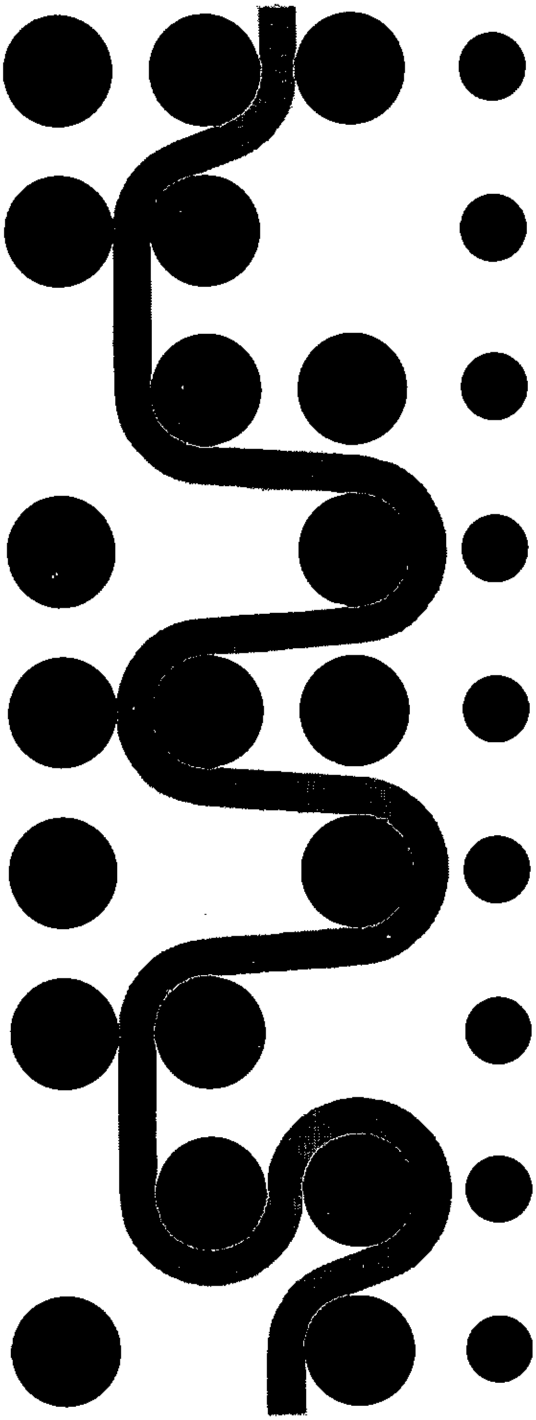

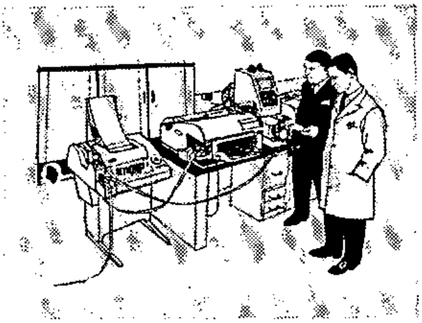

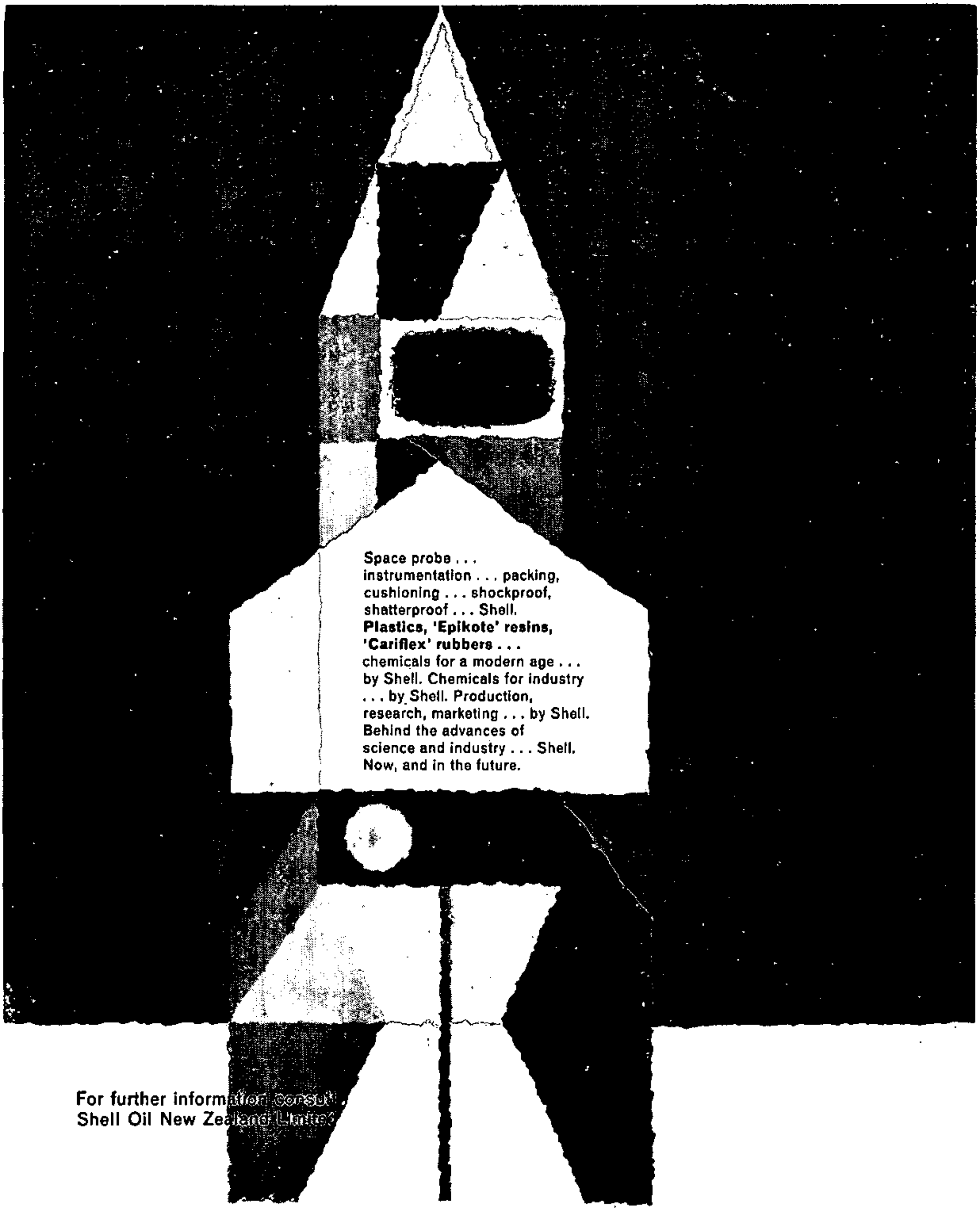

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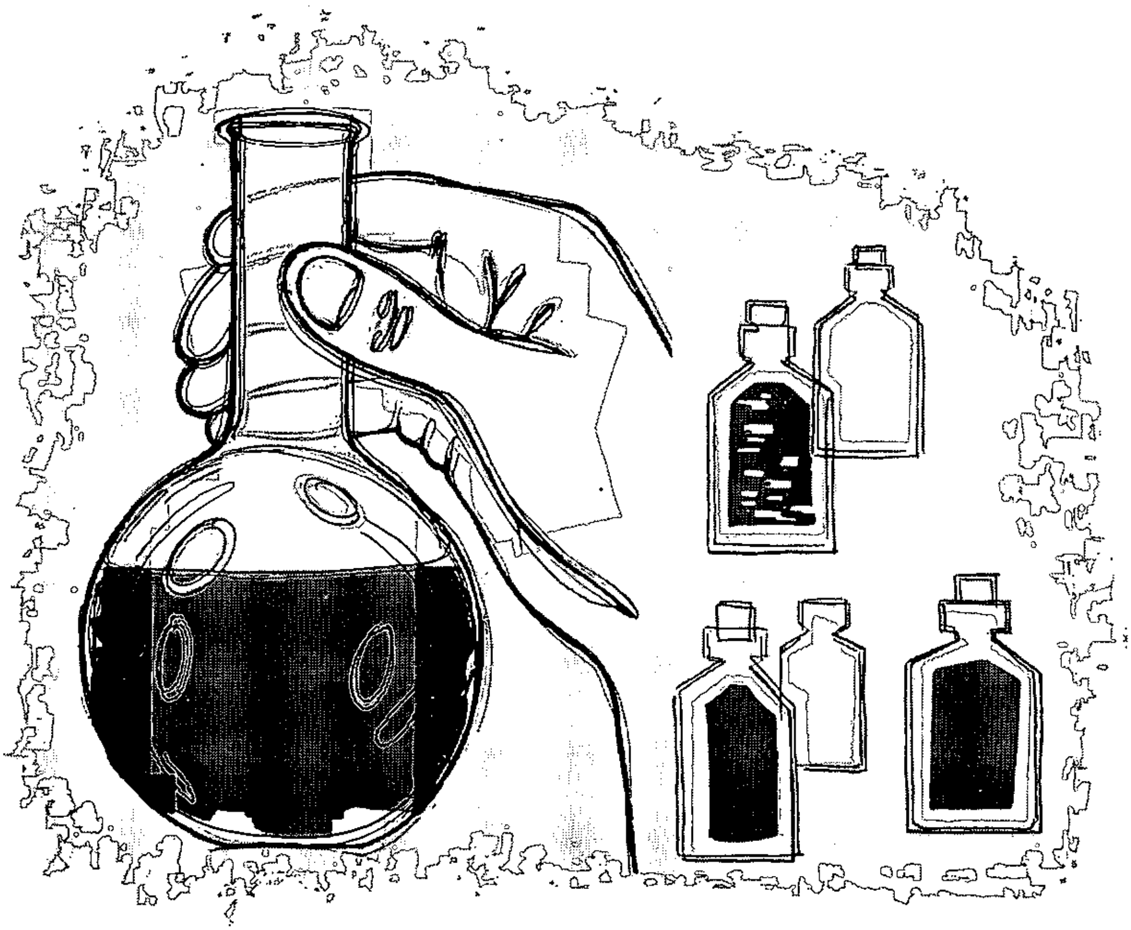


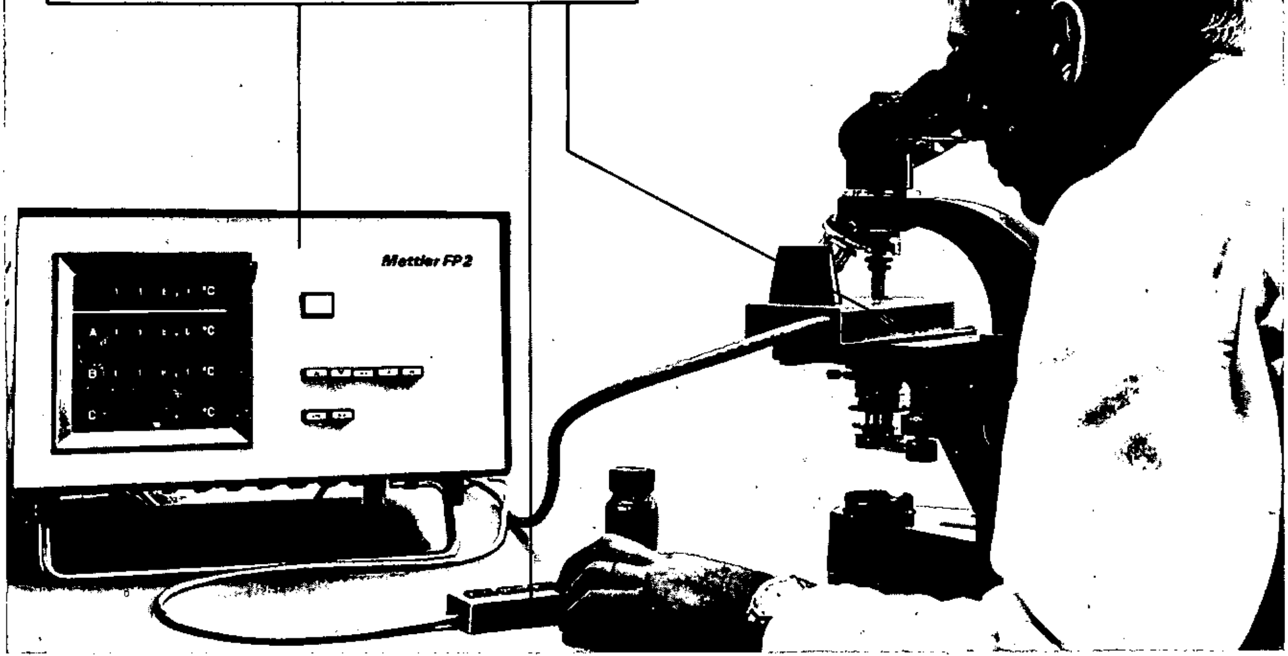
Mettler makes microthermal investigations without disturbance possible.

The researcher

retains first, by simply pressing a button, the temperature at the moment, where characteristic changes occur to the micro sample during the heating process. All routine manipulations, such as control of the temperature, thermometer reading and recording of the results are eliminated.

The Mettler FP2

consists of three elements: Micro hot stage, electronic control unit and push button station for the fixation of the temperature values. The following features guarantee that one can rely on the analytical data supplied by the METTLER FP2.



The temperature field of uniform pattern of the micro hot stage is heating up the sample regularly. Fully automatic temperature control allows three heating rates. The exact measuring of the sample temperature is guaranteed by a platinum resistance thermometer, embedded in the heating plate and in direct contact with the sample. Thanks to digital result storage, three independent temperature values can by stored with an accuracy of 0.1 °C.

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