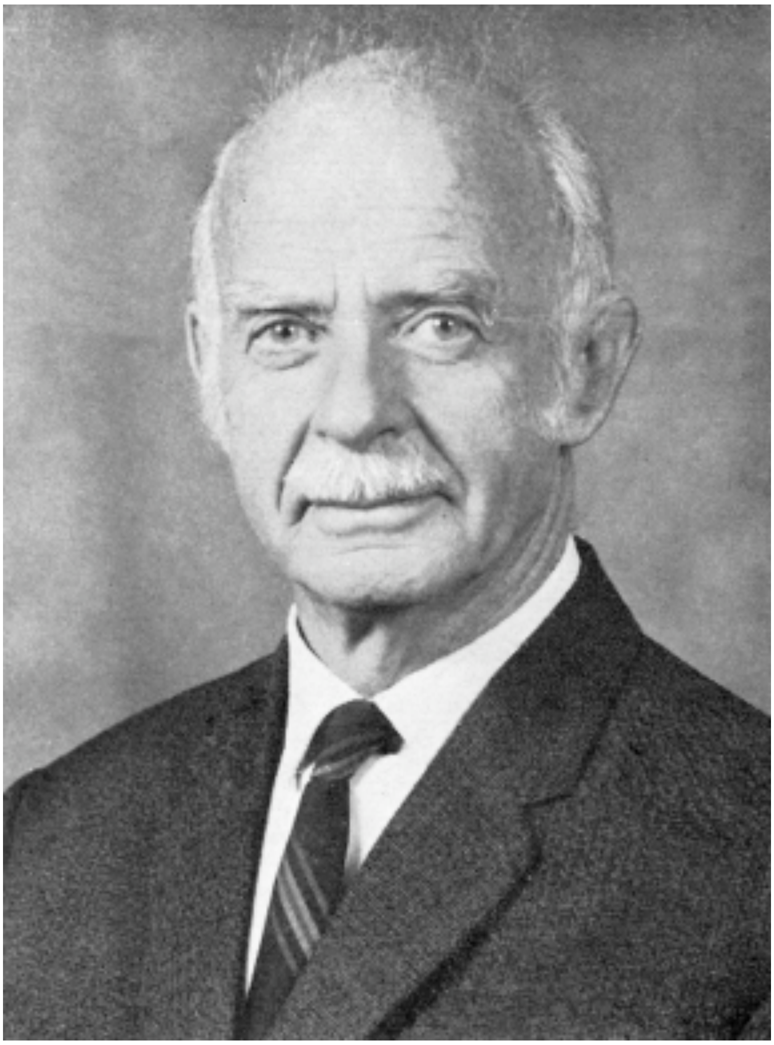
Liversidge Research Lecture

No. 6
1946

PLANT PRODUCTS OF NEW ZEALAND

LINDSAY H. BRIGGS

The Royal Society of New South Wales



Lindsay Heathcote Briggs

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LINDSAY HEATHCOTE BRIGGS 1905-1975

Lindsay Heathcote Briggs was born on 3 January 1905 in Hastings, New Zealand. His secondary education was at Hastings District High School where he was Dux in 1919 and 1920, and was awarded a Senior National Scholarship in 1919; from 1921 to 1923 he attended Auckland Grammar School where he won a Williamson Scholarship in 1922 and a University Entrance Scholarship in 1923. He then studied science at Auckland University, winning a Sir George Grey Scholarship in 1926, and graduated M.Sc. with Honours in 1928 while holding a Duffus Lubecki Research Scholarship. In 1929 he was awarded a New Zealand National Research Scholarship, but he relinquished this to take up a Sir James Gunson Scholarship for research in Dairy Science at Massey Agricultural College. In 1931 he proceeded to Oxford where he worked under Professor (later Sir) Robert Robinson; he was awarded an Oxford Exhibition Scholarship of the British Association for the Advancement of Science, and in 1933 he graduated D.Phil. with a thesis entitled "The Molecular Structure of Strychnine". In 1933 he was appointed as Lecturer in Chemistry at Auckland University where he undertook a study of the phytochemistry of the New Zealand flora. His plant chemistry was broadly based, ranging over studies of essential oils, diterpenes, flavonoids, lignans, anthraquinones, alkaloids, depsipeptides and fungal metabolites. An important part of his work, that won him international recognition, was his research on the structures of the *Solanum* steroidal alkaloids. In 1939 he was promoted to Senior Lecturer, and in 1941 he was awarded D.Sc. by the University of New Zealand. He was promoted to Associate Professor in 1948 and to Professor of Chemistry in 1956. Upon retirement in 1970, he became Professor Emeritus.

For about a year (1942-1943) during the Second World War he was seconded to the New Zealand Government for secret work on the development of nitrogen mustard gases, and for the organization of the training of civilian gas-identification officers. On several occasions he was Acting-Head of the Chemistry Department; he was Dean of the Faculty of Science for the period 1955-1957, and served on many University committees. During periods of study leave he was Commonwealth Visiting Fellow at the University of Aberdeen (1961-62), and Visiting Professor with a Fulbright-Hays award at the University of North Carolina, Chapel Hill in 1968-69; during that year he was also the Robert A. Welch Foundation Lecturer at the University of Texas.

Lindsay Briggs was very active in affairs of The New Zealand Institute of Chemistry (NZIC), The Royal Society of New Zealand, and the Auckland Institute and Museum. He was President of the Royal Society of New Zealand in 1956, and President of the NZIC in 1959. His other extramural activities included membership or leadership of several committees concerned with secondary education, and medical research.

Honours and Awards

1936	Fellow, New Zealand Institute of Chemistry (FNZIC)
1942	Fellow, Royal Society of New Zealand
1943	Hector Medal, Royal Society of New Zealand

1946 Liversidge Research Lecture, Royal Society of New South Wales

1949 ICI Medal (the first awarded), NZIC

1952 Coronation Medal for services to the community

1956 Fellow, Australian and New Zealand Association for the Advancement of Science

1965 Honorary Life Member, Auckland Institute and Museum

1970 Honorary Fellow, NZIC

Biographical Source

Cambie, R.C., 'Lindsay Heathcote Briggs 1905-1975, M.Sc., D.Phil., D.Sc., F.R.S.N.Z., F.A.N.Z.A.A.S.', *Proc. Roy. Soc. New Zealand*, 1974-5, **103**, 100-110.

Scientific Publications of L.H. Briggs

A list of the 166 scientific papers of L.H. Briggs is given as an appendix to the biographical memoir cited above under Biographical Source.

Liversidge Research Lecture No. 6, 1946

PLANT PRODUCTS OF NEW ZEALAND*

LINDSAY H. BRIGGS
Department of Chemistry, University of Aukland, New Zealand

I should first like to express my appreciation of the honour in being invited by the Royal Society of New South Wales to deliver the Liversidge Research Lectures, for 1946. This I take not so much as a personal honour but an opportunity of describing on behalf of numerous investigators some of the pioneering work done on plant products in New Zealand. I think the term pioneering is deserved as in most cases the investigators themselves have tramped over the hills and mountains in search of their plants or trees and often carried the material home on their backs. When dealing with essential oils where several hundred pounds of leaves are required, this has meant a great deal of sheer physical effort.

In the terms of the Liversidge Bequest it is suggested that lecturers should indicate the future field of research rather than give a mere review. As it is impossible, however, to indicate further lines of development without stating what has been done, I propose including a review of work already done on the plant products of New Zealand, with suggestions as to future work; where possible some correlation with the chemistry of the flora of New South Wales will be given.

There is no question that the flora of New Zealand is unique and one of the most remarkable known. Despite the small area of New Zealand, it constitutes one of the distinct botanical regions of the world, equal in importance to regions of much vaster area. No less than 75% of the 1,800 species occur endemic to the country, and the peculiar geography of New Zealand has allowed for the existence of manifold types, tropical to sub-antarctic, sea-level to alpine, desert to rain-forest types. Just as New Zealand offers great scope for the botanist, it offers an almost unrivalled field to the chemist interested in the various constituents found in plants.

So far only a very small number of plants have been chemically studied, and they have yielded diverse types of products, essential oils, alkaloids, colouring matters and dye-stuffs, steroids, tannins, etc. It must be emphasised at the outset that a great deal of this work has been done from purely scientific motives leaving the commercial development, if any, to future investigators.

Several of these investigations have arisen from the discovery of chemical substances of various types in related species abroad and from their economic and medicinal use by the Maoris and early settlers. Elsdon Best, an eminent authority on Maori history, has pointed out that plants were used by the Maoris for medicinal purposes only after the arrival of the pakeha. Before this, the Maori considered his ailments were the punishment of the gods for his transgressions and his fatalist nature did not allow of any appeal to medicine to ease his pain or ward off death.

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* Two Liversidge Research Lectures delivered before the Royal Society of N.S.W., August 12th and 13th, 1946. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1946, **80**, 151-177.

A list of plants used in the native pharmacopoeia is given by Taylor (1867), the medicinal properties of some New Zealand plants by Baker (1886), while Goldie (1904) gives a further comprehensive account of the diseases and remedies of the Maori. A later list of definitely poisonous plants and other possibly medicinal plants was compiled by Aston (1918*a*, 1919*a*, 1923*b*), while additional notes on the chemistry of the flora have been recorded by Gardner (1923, 1924*a*).

In the intervening twenty years since the last summary, a considerable amount of work has been done on the chemistry of New Zealand plants by workers in the universities and government research institutions, and it is the object of the lecturer to summarise the important contributions made in this period. It will be more convenient, perhaps, to discuss them according to the chemical type of compound contained in them rather than from a systematic botanical point of view.

Essential Oils

FILICES

Recent work has provided further examples of the occurrence of volatile oils in this large class of sub-kingdom.

Paesia scaberula, "Scented Fern"

This fern, which is common on waste-land frequently after a burn, gives a volatile oil only during its fresh growth. An examination of the oil on a small scale (Briggs and Sutherland, 1946) has shown the presence of the paraffin, heptacosane, $C_{27}H_{56}$, while sesquiterpenes are probably also present.

Asplenium lamprophyllum*

The freshly broken stalks give an immediate odour of oil of wintergreen which has been confirmed chemically (Briggs and Taylor, 1946). The methyl salicylate occurs in the free state and not bound as its glycoside, monotropitoside (Klein, 1932, p. 821). The closely related species, *A. bulbiferum*,* is free from this constituent, the detection of whose characteristic odour may thus be used for the identification.

PINACEAE*

Agathis australis, "Kauri"

This is one of the most magnificent trees grown, but so much demand has been made for its timber that it is now very scarce except in reserves. The fresh gum and particularly the fossil gum is extremely valuable in the paint and lacquer industry, and gum to the value of over £23,000,000 has already been exported. The essential oil of the leaves of this one endemic species has been examined by Hosking (1928, 1930), who isolated α-pinene, camphene, limonene, citronellal, cineole, borneol, bornyl acetate, cadinene and the diterpene, kaurene. Kaurene is probably related to isophyllocladene which may be regarded as the basic diterpene.

Kauri gum has also been analysed by Hosking (1929), who isolated α-pinene, dipentene and fenchyl alcohol from the steam volatile portion. The presence of glucose, galactose and arabinose was indicated in the gum fraction, while the resin fraction yielded two resin acids and large quantities of neutral kauro-resin, regarded as a diterpenoid oxide. The resin acids will be discussed later.

Libocedrus bidwillii.

From the investigationa of Goudie (1923*a*), Birrell (1932) and Hassall, Slater and co-workers (1946), the oil has been shown to contain α- and β-pinene, limonene, a new terpene ketone and a non-diterpenoid hydrocarbon, $C_{16}H_{32-34}$.

TAXACEAE*

Species of the *Podocarpus* * genus comprise a large section of the milling timber in New Zealand, the main members of which have been examined for essential oils, the constituents being recorded in Table 1.

TABLE I.

P.spicatus. [1] "Matai"	*P. ferrugineus* [2] "Miro"	*P. totara.* [3] "Totara“	*P. dacrydioides.*[4] "Kahikatea"	*P. hallii.* [5]
α-Pinene	α-Pinene	α-Pinene	α-Pinene	
β-Pinene		β-Pinene	β-Pinene	
Limonene	Limonene	Terpene alcohol		
Herabolene ?	Cineole			
Cadinene	Cadinene	Cadinene	Sesquiterpene	
Sesquiterpene ketone		Sesquiterpene alcohol	Sesquiterpene alcohol	
Podocarprene	Mirene	Totarene	Diterpenes?	Phyllocladene
Liquid diterpene		Rimuene		

[1] Butler and Holloway, 1939.

[2] Hosking and Short, 1928; Hosking, 1930.

[3] Aitken, 1929; Beath, 1933.

[4] Aitken, 1929; Hunter, 1932.

[5] Briggs, 1940.

The most characteristic feature is the occurrence of diterpenes throughout, often in high yield, each species giving a different isomer. *P. hallii* has been classified as a variety of *P. totara*, but the isolation of a distinct diterpene would support its status as a true species. The genus *Podocarpus* extends to Australia, Africa and Malay and further research is warranted even from a phytochemical point of view. No species from New South Wales has yet been investigated.

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* An asterisk placed after the family, genus or species name indicates that the same family, genus or species respectively is also recorded in New South Wales.

Dacrydium Species

Members of this genus also comprise a large section of the forest trees of New Zealand, and as a further example of the unique botany of this country this genus also includes the world's smallest pine, *D. laxifolium*, sometimes only three inches high at mature growth. The essential oils examined are listed in Table II.

TABLE II

D. kirkii [1]	*D. cupressinum* [2] "Rimu"	*D. biforme* [3]	*D. colensoi.* [4]
α-Pinene	β-Pinene	Terpene	Terpene ?
Myrcene			
Limonene			
Carvone			
Bornyl acetate			
Cadinene	Sesquiterpene	Cadinene	Sesquiterpenes
Sesquiterpene alcohol, $C_{15}H_{25}OH$			
Phyllocladene	Rimuene	Phyllocladene	Phyllocladene
Six other unidentified constituents in small amount	Diterpene		

[1] Briggs and Taylor, 1946. [2] McDowall and Finlay, 1925; Carrie, 1932.
[3] Goudie, 1923*b*; Aitken, 1928*a*. [4] Blackie, 1929, 1930.

The separation of 14 different constituents in the oil of *D. kirkii* using an efficient fractionating column would suggest that a similar reinvestigation of other species would likewise show a much larger number of constituents and add to our knowledge of phytochemistry.

By extracting the woods of *Dacrydium* species, Hosking and Brandt (1934, 1935, 1936*a*, *b, c*) have obtained a very interesting series of related oxygenated diterpenes which will be discussed later.

Phyllocladus Species

Phyllocladus alpinus

The diterpene phyllocladene is the main constituent of this oil which has not yet been thoroughly investigated (Briggs, 1937*a, b*; Brandt, 1938).

Phyllocladus trichomanoides, "Tanekaha"

Numerous constituents have been found in this oil, including α-pinene, myrcene, limonene, cadinene, copaene, cadinol, phyllocladene and isophyllocladene (Briggs and Sutherland, 1946). The remaining species, *P. glaucus*, also yields an oil which has yet to be investigated.

Although the genus *Phyllocladus* extends to Tasmania, no member has been listed from New South Wales.

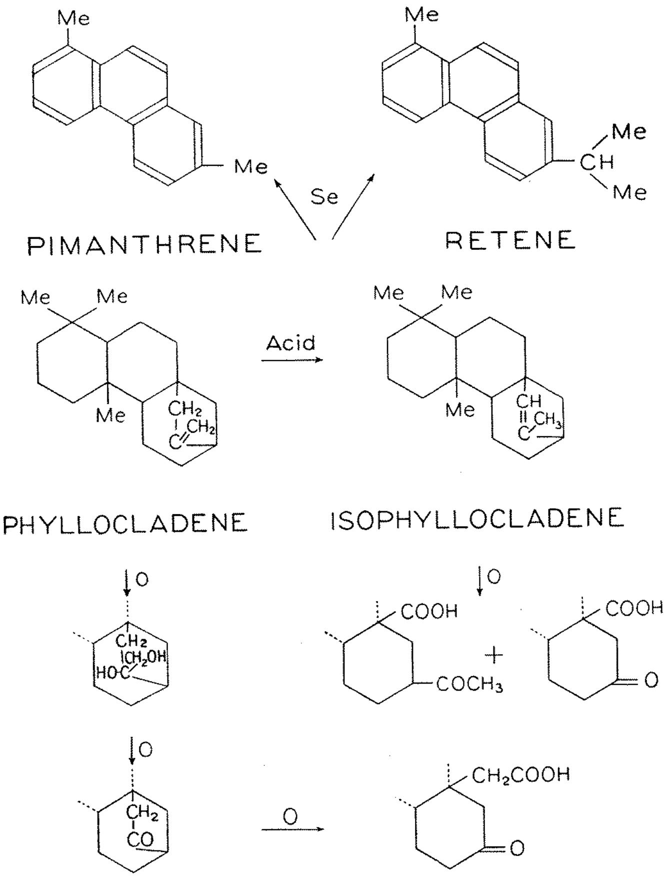


FIGURE 1

The main characteristic of the essential oils of the Pinaceae and Taxaceae so far described is the presence of diterpenes, which have already been reviewed by Briggs (1937*c*). The basic compound appears to be isophyllocladene, into which a number of the others appear to be isomerised (see also Briggs and Sutherland, 1942). There are eight possible stereoisomers as well as optical isomers of the tetracyclic isophyllocladene and phyllocladene and a number of the isomeric diterpenes so far described may differ only as stereoisomerides. More diterpenes have been described from the New Zealand flora than from any other source.

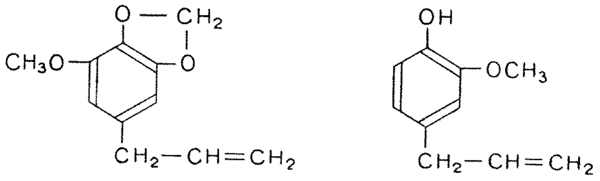
Nishida and Uota (1935, 1936) suggested formulae for phyllocladene and isophyllocladene based on the dehydrogenation to a supposedly new phenanthrene hydrocarbon, "scianthrene", regarded as 1-isopropyl-7-methylphenanthrene. A synthesis of the latter by Orcutt and Bogert (1941), however, indicated the incorrectness of this view. Brandt (1938), on the other hand, obtained both pimanthrene and retene on selenium dehydrogenation and proposed alternative partial formulae for these isomers. The criticism by the author (1941*b*), however, that they did not obey the isoprene rule, is invalid and the correctness of these formulae now appears to be confirmed by later unpublished work of Brandt (1946). (See Fig. 1.)

The occurrence of diterpenes in essential oils has been used by Holloway (1938) for a suggested revision of the botanical classification of the families containing them.

PIPERACEAE*

Macropiper excelsum

The one New Zealand representative has been shown (Briggs, 1941*a*) to contain myristicin as its major constituent as well as other unidentified constituents and further work is in progress. The use of this plant as a "painkiller" for toothache and the isolation of myristicin is interesting in view of the relation of the latter to eugenol, the major constituent of oil of cloves, which is used for the same purpose.



MYRISTICIN EUGENOL

FIGURE 2

MAGNOLIACEAE*

Drimys colorata,* "Horopito"

Melville and Levi (1932) identified in this oil β-pinene, limonene, terpene alcohols, sesquiterpenes and a solid sesquiterpene alcohol. No constituent of the essential oil had the hot taste characteristic of this species.

PITTOSPORACEAE*

Pittosporum eugenioides*

The interesting feature of this oil (Murray, 1946) is that the major constituent (70%) appears to be *n*-nonane. The other constituents are as yet unidentified. The fruit of species from the Philippine Islands, e.g. *P. resinifolium* and possibly *P. pentrandrum,* also contain the paraffin, heptane (Bacon, 1909).

RUTACEAE*

Phebalium nudum*

This sweetly scented shrub contains an essential oil investigated by Radcliffe and Short (1928) and found to contain citronellal, citral, cinnamic acid, a phenol, camphene, limonene, a sesquiterpene and a sesquiterpene alcohol.

Melicope ternata*

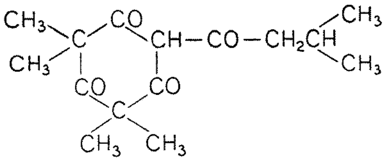
This is one of the most pleasant smelling trees of the flora, but the oil was obtained by Radcliffe (1929) on too small a scale to be investigated in detail.

MYRTACEAE*

*Leptospermum scoparium**, "Manuka"

The constituents of the oil of this species, which also extends to Tasmania and Australia, are highly oxygenated. Besides the terpene hydrocarbons α-pinene, eudesmene and aromadendrene there occur citronellal, citronellol, citral, geraniol, cineole, the phloroglucinol derivative, leptospermone, and acetic, isovaleric and cinnamic acids (Gardner, 1924b, 1925; Short, 1926).

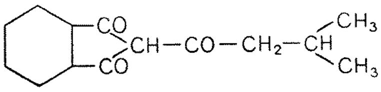
Manuka is probably the most widespread tree or shrub of the flora and its essential oil is probably the most valuable, although it has not yet been used commercially. The oil is very pleasant smelling and could well be used as a cheap perfume for soaps, etc. The unusual constituent leptospermone has been shown (Briggs, Penfold and Short, 1938; Briggs, Hassall and Short, 1945) to have the following constitution:



LEPTOSPERMONE

FIGURE 3

and like the closely related constituents from male fern, a well-known anthelmintic, it, too, has anthelmintic properties. It is also closely related to synthetic 1: 3-indandiones, such as "valone ", with high insecticidal properties (Kilgore, Ford and Wolfe, 1942), and tests on the insecticidal properties of leptospermone have shown it to have a good synergistic effect but inferior to valone (Kerr, 1946).



VALONE

FIGURE 4

Leptospermum ericoides*

This species is not as common as *L. scoparium.* Short and Johnson (1923) have reported the following constituents in the oil, α- and β-pinene, citral, α-terpineol, terpinyl acetate, tasmanol and aromadendrene.

Metrosideros Species*

A survey of the oils from species of this genus *(Metrosideros scandens, M. parkinsonii, M. diffusa, M. colensoi, M. excelsa, M. collina, M. umbellata, M. robusta, M. perforata)* has been made by Gardner (1931). The oils fall into two classes, (*a*) oils containing mainly sesquiterpenes and sesquiterpene alcohols, (*b*) oils containing, in addition to sesquiterpenes and sesquiterpene alcohols, notable proportions of terpenes and terpene alcohols mainly as esters. The terpenes found were α- and β-pinene and dipentene, the ester citronellyl acetate. The sesquiterpene yields cadinene hydrochloride, but attempts to dehydrogenate it to cadalene were unsuccessful, only azulene being isolated. It would appear, therefore, that a mixture of sesquiterpenes is present.

Myrtus bullata*

A preliminary examination of the oil of this species by Brandt (1946) has revealed the presence of phenols and a crystalline benzoate, $C_{12}H_{12}O_2$ m.p. 68°.

MYOPORACEAE*

Myoporum laetum*, "Ngaio"

The oil from this tree is unique in that there is a complete absence of normal terpene compounds. Besides a solid paraffin, $C_{32-34}H_{66-70}$, 86% of the oil consists of an unusual constituent, ngaione, $C_{15}H_{22}O_3$. Following the original investigations by McDowall (1925, 1927, 1928), Brandt and co-workers (1946) have shown it to have the partial formulae

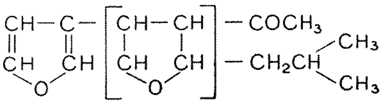


FIGURE 5

The leaves are toxic to sheep and the essential oil has similar toxic properties (Cunningham and Hopkirk, 1945). The Australian species *Myoporum deserti,* "Dogwood Poison Bush", also has poisonous properties, and an examination of this tree would be of interest.

RUBIACEAE*

Coprosma foetidissima*

The disgustingly foetid odour of this plant has been shown by Sutherland (1946) to be due to traces of methyl mercaptan.

COMPOSITAE*

Olearia paniculata*

McLean and Slater (1945) have isolated from the essential oil, β-pinene, limonene, two sesquiterpenes and a diterpene oxide, olearyl oxide, $C_{20}H_{34}O$. The most unusual feature of this oil is the occurrence of a diterpene derivative. Diterpenes are rare in essential oils and occur typically only in the Pinaceae and Taxaceae. The presence of such a constituent in a species of the flowering order Compositae might indicate a more widespread distribution than at present recognised.

Olearia ilicifolia*

This gives a small yield of oil containing a paraffin alcohol and other constituents still under investigation (Murray, 1946).

CORIARIACEAE

Coriaria ruscifolia, C. thymifolia and C. angustissima

Although non-volatile, it is convenient to consider a toxic compound from these species in this section.

From the leaves and seeds of these three species Easterfield and Aston (1901) isolated an extremely poisonous substance, tutin, $C_{15}H_{18}O_6$ closely related to coriamyrtin, $C_{15}H_{18}O_5$ (from the European species, *C. myrtifolia*), picrotoxinin, $C_{15}H_{18}O_6$ and picrotin, $C_{15}H_{18}O_7$ (from members of the tropical family Menispermaceae*) and iso- and hyenanchin, $C_{15}H_{18}O_7$ (from the African species *Hyenanche globosa*). Japanese workers (Kinoshita, 1930, 1931; Kariyone and Sato, 1930, 1931) regard tutin as identical with "coriarine" from *Coriaria japonica,* since no depression of melting point occurs on admixture and the crystalline forms are identical. Although Slater (1943) regards tutin as different from "coriarine" from differences in the melting point of the acetate and dihydro derivative, the evidence is unconvincing. Little constitutional work has yet been done on tutin, but from its similarity to coriamyrtin and picrotoxinin both chemically and pharmacologically, it would appear that it is not glucosidic as suggested by Easterfield and Aston but an oxygenated lactone of the sesquiterpene series. Since the lethal dose for cats is 1 mg. per kg. body-weight, while 1 mg. causes nausea, vomiting and incapacity for work for 24 hours in a healthy full-grown man, further work could add considerably to our knowledge of the relation of chemical constitution to physiological activity.

It is of interest to record in this connection that Sutherland (1946) has traced the cause of poisoned honey to this source. Sporadic outbreaks of food poisoning occur in New Zealand which may be traced to the use of honey from certain areas. Suspecting tutin as a possible cause, Sutherland was able to isolate from the poisonous honey in 0.01% yield a new compound, mellitoxin, $C_{15}H_{18}O_7$ obviously related to tutin and of the same order of toxicity. Examination of various parts of the plant of *Coriaria ruscifolia* failed to detect this compound. However, by extraction of the "honey dew", produced on the leaves at certain seasons by the Passion Vine hopper, *Scolypopa australis*, the same substance was isolated. It is obviously an oxidation product of tutin produced by the insect. Like tutin, it is an unsaturated, hydroxylated lactone probably derived from a sesquiterpene.

The same insect, as well as the native longhorn beetle, *Aemona hirta*, is also responsible for the formation on *Leptospermum scoparium* of a manna, a complex sugar giving only glucose on hydrolysis (Worley, 1928, 1929).

In my opinion a great field still lies ahead in terpene chemistry. Physical methods of analysis such as mass-spectra and infra-red spectroscopy have yet to be applied as general methods. These, however, depend mainly on the constants of known compounds and so far very few terpene compounds have been obtained in a really pure state. Their separation has previously depended on fractional distillation and only in the past few years has any attempt been made to use efficient fractionating apparatus, up to 100 theoretical plates, and most of the work already done on the analysis of essential oils would bear repetition with modern equipment. Fractionation alone is not the whole solution owing to polymerisation and condensation that occurs during the long period of distillation essential in modern practice. It seems obvious from the literature also that, where so-called pure fractions give poor yields of derivatives, these in many cases are mixtures, possibly azeotropes. The use of high-boiling, water-soluble polyhydric alcohols in the formation of azeotropes from which the alcohols may then be removed by solution in water has been used to great advantage in the separation of different types of hydrocarbons in petroleum (Mair, Glasgow, Jr., and Rossini, 1941) and these or similar methods have yet to be applied to the separation of essential oil constituents.

A great deal of knowledge is still required of the chemistry of the terpene compounds themselves. The constitution of a large number of compounds still requires elucidation and those of the diterpenes particularly remain essentially a New Zealand problem. Synthetic work has lagged behind the constitutional side and as an example it may be pointed out that the most common terpene constituent, α-pinene, was only synthesised a few years ago by Komppa.

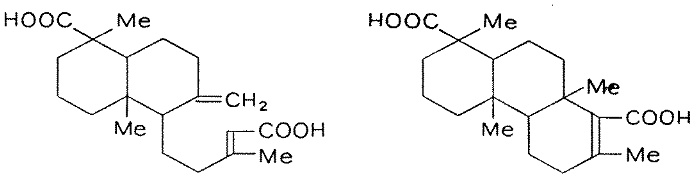
Comparatively little has been done in the synthetic field using terpene constituents as raw materials, α-pinene being one of the cheapest of chemicals. Just as aliphatic chemistry has been reborn in America and elsewhere in the rise of the petroleum industry, so I suggest that terpene chemistry should be reborn. Most of the terpenes have an initial advantage in being optically active and by the introduction of hetero atoms, oxygen, nitrogen, sulphur, etc., a wide diversity of products could be obtained and exploited.

Resin Acids and Resinols

PINACEAE

Agathis australis, "Kauri"

Kauri gum has been analysed by Hosking (1929) and among other terpene constituents and resenes (compounds of unknown structure but probably diterpenoid ethers since they give retene on dehydrogenation) a resin acid, agathic dicarboxylic acid, has been isolated. Further investigations by Ruzicka, Hosking and co-workers (1929, 1930, 1931, 1932, 1938, 1941) have indicated the following probable structures for it and its isomeric acid obtained by treatment with acids.

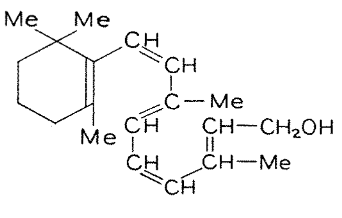


AGATHIC ACID

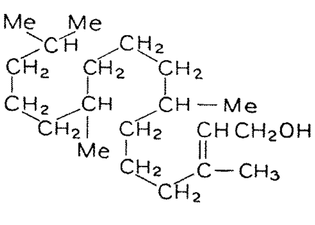
ISOAGATHIC ACID

FIGURE 6

These acids differ in their carbon skeleton from the abietic acid type, but have the same carbon skeleton as vitamin A and phytol, the alcoholic component of chlorophyll and vitamins E and K.



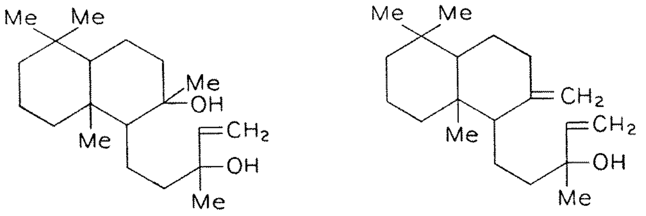
VITAMIN A



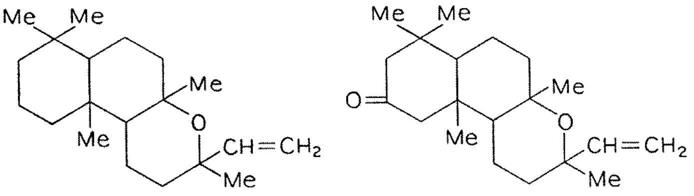
PHYTOL

FIGURE 7

Similar compounds occur in the wood of *Dacrydium* species investigated by Hosking and Brandt (1934, 1935, 1936*a,b,c*) which in turn are related to sclareol, a ditertiary alcohol from the oil of *Salvia sclarea* (Janot, 1930, 1931, 1932). The occurrence of these diterpenoid compounds in such widely differing plant families, Taxaceae and Labiatae respectively, is worthy of note, while recently a compound of the same type, olearyl oxide, has been isolated by McLean and Slater (1945) from the oil of *Olearia paniculata,* a member of the Compositae. The first three substances represent the diterpene analogues of terpin hydrate, α-terpineol and cineole.



SCLAREOL   MANOOL (Ex D. BIFORME)



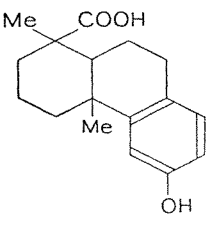
MANOYL OXIDE (Ex D. COLENSOI)   3-KETOMANOYL OXIDE (Ex D. COLENSOI)

FIGURE 8

That olearyl oxide is related is indicated by the fact that it is dehydrogenated by selenium to agathalene (1:2:5-trimethylnaphthalene), the aromatic hydrocarbon common to compounds of this series.

A further trihydroxy diterpene oxide from *D. colensoi* apparently belongs to a different series since it yields pimanthrene on selenium dehydrogenation.

From the heartshakes of *Podocarpus dacrydioides,* "kahikatea", and *Dacrydium cupressinum,* "rimu", a resin acid has been isolated by Easterfield and Aston (1903) and identified by Easterfield (1910) as podocarpic acid. Its constitution has been established by Short and co-workers (1933, 1935, 1936, 1938) and Campbell and Todd (1942) as -

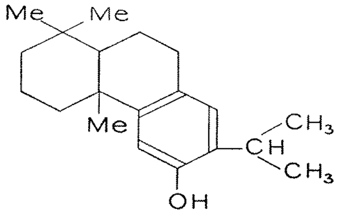


PODOCARPIC ACID

FIGURE 9

which is thus related to abietic acid. As a phenol it has shown some promise as an antioxidant in fats (Brooker, 1946).

The oleo-resin of *Podocarpus ferrugineus,* "miro", gives rise to ferruginol (Easterfield, 1910), the constitution of which has been established by Brandt and Neubauer (1939) and Campbell and Todd (1940, 1942). It is closely related to hinokiol, $C_{20}H_{30}O_2$, from *Chamaecyparis obtusa* (Yoshiki and Ishiguro, 1933; Keimatsu and Ishiguro, 1935; Huzii and Tikamori, 1939) since both give the same phenol on dehydrogenation.



FERRUGINOL

FIGURE 10

The constitutions of other diterpene acids from this tree (Brandt and Neubauer, 1940) still await elucidation.

The "bloom" of freshly cut totara timber, "*Podocarpus totara* ", consists essentially of totarol, $C_{20}H_{30}O$, first isolated by Easterfield (1910; see also Easterfield and McDowell, 1915). Short and Stromberg (1937) have shown it to be a tricyclic secondary alcohol with three double bonds. Dehydrogenation with selenium affords 7-hydroxy-1-methylphenanthrene, but additional work still leaves the constitution doubtful.

There is considerable scope in this field not only on the degradative and synthetic side but in the use of these compounds, especially podocarpic acid with a preformed "aromatic ring", for the preparation of useful therapeutics. As an example, Fieser and Campbell (1939) have by simple reactions transformed abietic acid, one of the cheapest of organic chemicals, into compounds of high physiological activity.

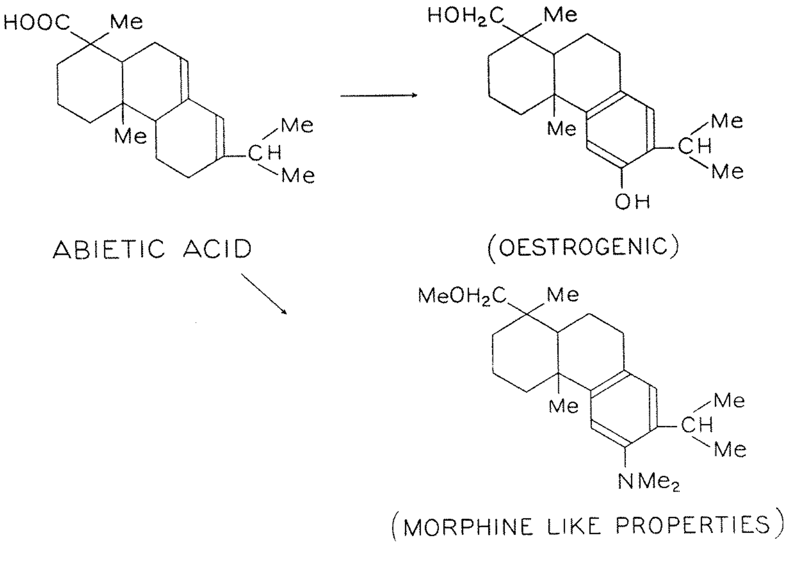
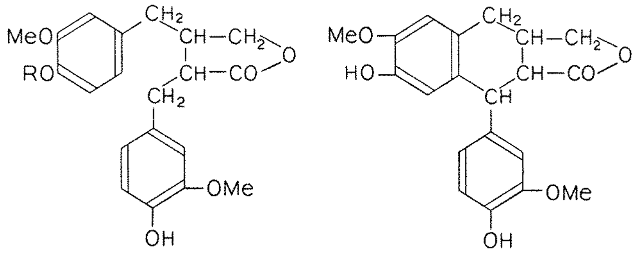


FIGURE 11.

The heart-shakes of *Podocarpus spicatus,* "matai", however, contain two resinols or lignanes of a different type, matairesinol and conidendrin. The former was first isolated by Easterfield and Bee (1910), the latter by Haworth, Richardson and Sheldrick (1935) and Briggs and Peak (1936). Their constitutions have been established by degradation (Haworth and Richardson, 1935; Briggs, Peak and Woolloxall, 1935) and by synthesis by Haworth and co-workers in a brilliant series of investigations in this field. The monomethyl ether of matairesinol occurs as a glucoside in the seeds of the burdock, *Arctium lappa* (Shinoda and Kawagoe, 1929). It may be not without interest that a potent antibiotic has also been isolated from the same source.

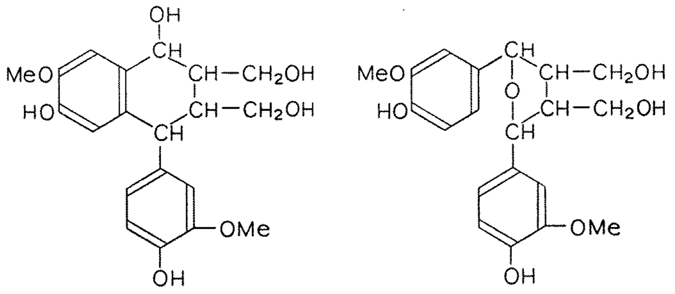


MATAIRESINOL (R= H)
ARCTIGENIN (R=Me)

CONIDENDRIN

FIGURE 12

In the heart-shakes *of Olea cunninghamii,* "maire", a lignane of similar type occurs, isoolivil, isomeric with the olivil obtained from the European olive (Briggs and Frieberg, 1937).

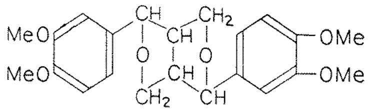


ISOOLIVIL

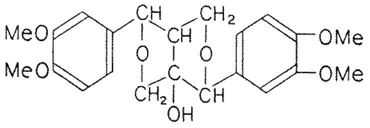
OLIVIL

FIGURE 13

Two representatives of this class have been isolated in Australia, eudesmin from the kinos of *Eucalyptus hemiphloia* (Robinson and Smith, 1915) and gmelinol from the wood of "colonial beech", *Gmelina leichhardtii* (Smith, 1913; Birch and Lions, 1938; Harradence and Lions, 1940). The constitution of eudesmin has been established, while gmelinol is probably its hydroxy derivative.



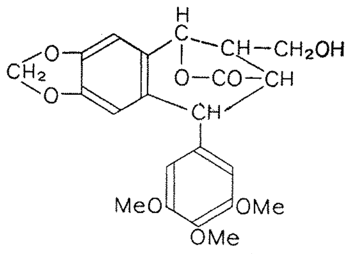
EUDESMIN



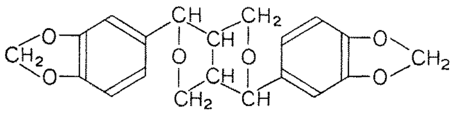
GMELINOL

FIGURE 14

The whole series of lignanes has been reviewed by Haworth (1936, 1942), some of which have interesting properties. Podophyllotoxin has a strong purgative action while α-sesamin and its diastereoisomer, l-asarinin, have a synergistic effect towards pyrethrum extracts as insecticides (Haller, McGovran, Goodhue and Sullivan, 1942).



PODOPHYLLOTOXIN



SESAMIN

FIGURE 15

Matairesinol, isoolivil and their simple derivatives, however, have no such synergistic action.

Alkaloids

LYCOPODIACEAE *

*Lycopodium species**

Some of the New Zealand endemic species are under investigation by Manske in extension of his previous work on the alkaloids of this genus (for a summary see Manske, 1944).

GRAMINEAE *

Lolium perenne, L. temulentum, L. multiflorum, Festuca arundinacea, Setaria* lutescens.*

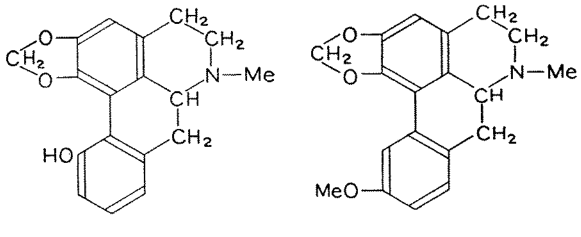
During the autumn of 1939 a serious outbreak of facial eczema occurred in New Zealand. In a search for a probable cause the fodder of the animals was investigated and a series of new alkaloids, the main members being named perloline and perlolidine, were discovered in the above grasses, all introduced species - but only at periods of flush of growth (Grimmett and Melville, 1943; Grimmett and Waters, 1943; Reifer and Bathurst, 1943; Bathurst, Reifer and Clare, 1943; Cunningham and Clare, 1943; Shorland, White and Grimmett, 1943; Shorland, 1943). This is one of the few records of an alkaloid occurring in the large order of Gramineae. When fed to animals, however, perloline failed to produce facial eczema (for further details see Clare, 1944).

From the investigations by White and Reifer (1945) it would appear that perloline is a harmine derivative, $C_{40}H_{34}0_7N_4$, containing four methoxy groups, an alcoholic group, four tertiary nitrogen atoms only two of which are basic. Oxidation of perloline yields perlolidine, $C_{25}H_{18}O_2N_4$, the other isolated base, both of which are very strongly fluorescent.

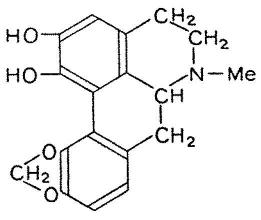
MONIMIACEAE *

Laurelia novae-zealandiae, "Putakea"

The bark of this tree, which grows abundantly in swampy forests, contains three most important alkaloids, pukateine, laureline and laurepukine. The constitutions of the first two alkaloids, first isolated by Aston (1901, 1909, 1010) have been elucidated by Barger, Girardet and Schlittler (1931, 1932) and confirmed by synthesis.



PUKATEINE LAURELINE



LAUREPUKINE(?)

FIGURE 16

The constitution of laurepukine still awaits final confirmation by degradation and synthesis.

A preliminary report on the pharmacology of pukateine was made by Malcolm (1909) and a detailed examination by Fogg (1935), who found that it possessed strong analgesic properties, similar to morphine but without its after effects.

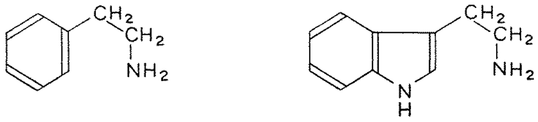
New South Wales has members of this tribe in the genera *Daphnandra, Aetherosperma* and *Doryphora,* from each of which alkaloids have already been isolated. *Daphnandra micrantha,* first investigated by Bancroft (1886), has been shown by Pyman (1914) to contain three alkaloids, daphnandrine, $C_{36}H_{38}O_6N_2$, micranthine, $C_{36}H_{32}O_6N_2$, and daphnoline, $C_{34}H_{34}O_6N_2$, of still unknown structure. On phytochemical grounds it would suggest that they are constituted similarly to the alkaloids of pukatea but with two molecules condensed together through possible ether linkages.

Other New Zealand species of the Monimiaceae are under investigation.

LEGUMINOSAE *

In a comprehensive study on endemic and introduced species of this family White (1946) has examined over 210 species and varieties. It is only necessary here, however, to discuss those endemic to New Zealand or Australia. Of the 14 examined which are endemic to New Zealand all were alkaloid-free, viz. *Carmichaelia australis, C. compacta, C. flagelliformis, C. gracilis, C. grandiflora, C. odorata, C. prona, C. subulata, C. williamsii, Chordospartium stevensoni, Clianthus puniceus, Corallospartium crassicaule, Notospartium carmichaelia, N. glabrescens.*

The following species occurring in New South Wales were also found to be alkaloid free: *Goodia lotifolia, Daviesia latifolia, D. corymbosa, Dillwynia cinerascens, Jacksonia scoparia, Oxylobium ellipticum, Swainsona galegifolia, Kennedya prostrata, K. rubicunda, Cassia artemesioides, C. sophera.*



β-PHENYLETHYLAMINE TRYPTAMINE

FIGURE 17

Twenty-eight Australian species of *Acacia* growing in New Zealand were examined, but high concentrations of an alkaloid, identified as β-phenylethylamine, were found only in a section of the genus with uninerval phyllodes and flowers in racemes, viz. *Acacia hakeoides, A. linifolia, A. linifolia* var. *prominens, A. lunata, A. pravissima, A. suaveolens, A. cultriformis, A. podalyriaefolia.* The same base with other alkaloidal material was isolated from *A. longifolia* and *A. floribunda.* Other species gave indications by odour of the presence of basic material, viz. *A. acinacea, A. baileyana, A. decurrens, A. decurrens* var. *dealbata, A. decurrens* var. mollis, *A. drummondii, A. elata, A. falcata, A. leprosa, A. linearis, A. melanoxylon, A. pycnantha, A. retinoides, A. saligna, A. stricta, A. verticillata, A. vestita,* as well as *Albizzia julibrissin* and *A. lophantha.*

From *Acacia floribunda* and *A. pruinosa* tryptamine was isolated in addition to β-phenylethylamine, which has only previously been found in traces in plants, mainly parasites and fungi, while tryptamine has not previously been found naturally in plants or animals. The occurrence of these bases is of considerable interest in the biogenesis of alkaloids (Robinson, 1936) and in their synthesis under physiological conditions (Hahn and Schales, 1935; Schöpf and Bayerle, 1934); however it is remarkable that more complicated alkaloids are absent in these species.

SOPHOREAE *

The alkaloids of the seeds of three of the five listed endemic species have been examined in detail.

Sophora microphylla

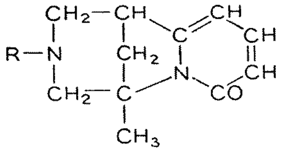
The seeds contain mainly methylcytisine and matrine, a little cytisine and two further new alkaloids in minute amounts (Briggs and Ricketts, 1937).

Sophora tetraptera

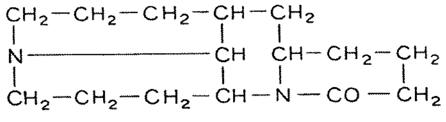
The alkaloids here are mainly matrine, a little methylcystine and one of the new bases from *S. microphylla,* again in minute amount (Briggs and Taylor, 1938).

Sophora chathamica

This species from the Chatham Islands has been differentiated from *S. microphylla* on the slender evidence of slight changes of the juvenile form. The alkaloids from the seeds are identical with those of S. *microphylla,* which would suggest identity (Briggs and Russell, 1942*a*).



CYTISINE (R=H)
METHYLCYTISINE (R=Me)



MATRINE (?)

FIGURE 18

The new alkaloid occurring in *S. microphylla, S. tetraptera* and *S. chathamica* (?) also occurs in much larger quantity in the Hawaiian species, *S. chrysophylla,* and has been named sophochrysine (Briggs and Russell, 1942*b*).

The constitutions of cytisine and methylcytisine have already been elucidated, a provisional structure of matrine has been suggested (Henry, 1942), but the empirical formula of sophochrysine is still uncertain.

Recently an investigation has been made (Briggs, and Mangan, 1946) on the seeds of an undescribed but possibly new species growing at Anawhata, near Auckland. The major alkaloid has been identified as methylcytisine with some cytisine. The presence of only a very small amount of matrine indicates a sharp difference from those endemic species already examined and would thus support the establishment of a new species.

CORYNOCARPACEAE

Corynocarpus laevigata, "Karaka"

The kernels of the berries of this coastal tree were cooked and thus used by the Maoris for food. The raw material, however, contains a poisonous glucoside, karakin $C_{20}H_{30}O_{19}N_4$ which is destroyed in the cooking process. It was first isolated by Skey (1871) and later investigated by Aston and Easterfield (1901, 1903), Carrie (1934) and Carter (1943).

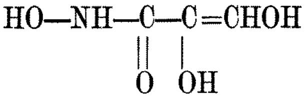
On hydrolysis different products are obtained with various reagents. According to Carter the initial hydrolysis proceeds according to the following equation:

$$C_{20}H_{30}O_{19}N_4 + 3H_2O \text{ ------} \rangle \; 2\,C_3H_5O_4N \; + \; 2\,C_7H_{13}O_7N$$

Karakin Hiptagenic acid Sugar derivative

forming hiptagenic acid and a sugar derivative. The former compound is also obtained as a hydrolytic product of hiptagin, a similar glucoside from the bark of the tree, *Hiptage madablota* (Gorter, 1920). The sugar derivative loses carbon dioxide on boiling to form an aminohexose, hydrolysed further with alkali to a hexose, from which glucosazone was isolated.

Hiptagenic acid according to Gorter has the constitution



$$\mathrm{HO{-}NH{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{OH}{|}}{C}{=}CHOH}$$

while Carter regards it as

$$\mathrm{HO\text{-}N{=}CH\text{-}CH(OH)\text{-}COOH}$$

The final solution of the constitution of these unique compounds still awaits further experiment.

SOLANACEAE *

*Solanum aviculare**

The fruit of this shrub, which occurs both in New Zealand and New South Wales, was first investigated by Levi (1930), who isolated a glycosidic alkaloid, thought to be new but identified later by Bell and Briggs (1942) as solasonine occurring in *S. sodomaeum* and *S. xanthocarpum**. Based on degradative studies by Oddo and co-workers, Rockelmeyer and Briggs, Newbold and Stace (1942; see this paper for references) the following formula was suggested by Briggs *et al.* (1942).

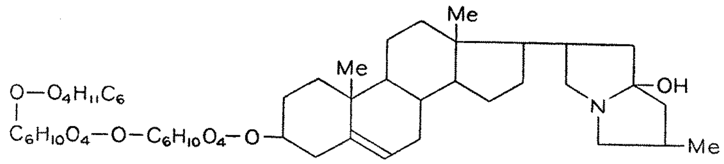
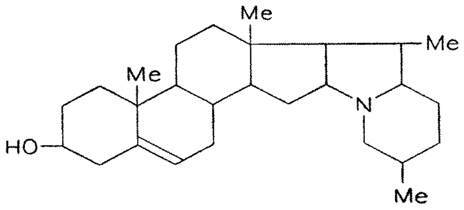


FIGURE 19

It differs only as the carbinol amine of solanine, from *S. tuberosum,* for which a similar structure had been proposed. It contains the cholesterol carbon skeleton and it was assumed that the basic portion was joined to the ring structure by only one point of attachment from the isolation of Diels' hydrocarbon on selenium dehydrogenation. Recently, however, Prelog and Szpilfogel (1942) have identified, through synthesis, the basic dehydrogenation product of solanidine as 2-ethyl-5-methylpyridine, and to accommodate this fact they proposed a modified structure for solanidine.

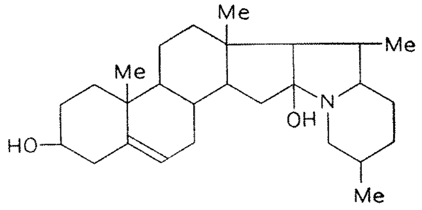


SOLANIDINE

FIGURE 20

A comparison of the rotations of solanidine and its derivatives with those of similar derivatives of cholesterol (Prelog and Szpilfogel, 1944) has shown that the two compounds are directly related stereochemically, and this constitution of solanidine has now been confirmed by Uhle and Jacobs (1945) through the partial synthesis of dihydrosolanidine from sarsasapogenin of known constitution.

Dehydrogenation of solasodine gives a basic portion whose picrate has the same melting point as that of 2-ethyl-5-methylpyridine (Rochelmeyer, 1937) indicating their identity. Solasodine, therefore, probably has the same skeleton as solanidine, but the hydroxyl group has now been attached to C16, thus obviating the formation of a nine-membered ring for the *chano* compounds on the previous formulation.



SOLASODINE

FIGURE 21

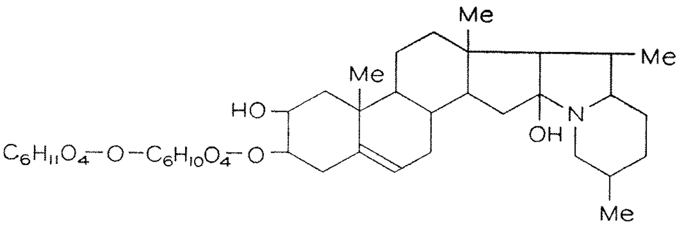
Experiments on the interconversion of solanidine and solasodine are in progress.

Solanum auriculatum

The alkaloid of the fruit of this introduced species, now naturalised in various parts of New Zealand, was first considered to be identical with solasonine (Anderson and Briggs, 1937) but later shown to be a new alkaloid, solauricine, but extremely closely related to solasonine (Bell, Briggs and Carroll, 1942; Briggs and Carroll, 1942).

Solanum marginatum

From the fruit of this introduced species, but now naturalised in the Marlborough Sounds, a new alkaloid, solmargine [*sic*, the correct spelling is solamargine], has been isolated. Experiments to date in the author's laboratory (Briggs, Harvey and Odell, 1946) have shown it to be a rhamno-glucoside of the following probable constitution:



SOLMARGINE

FIGURE 22 [Ed., the correct spelling is solamargine]

The structure of the veratrine alkaloids, obtained from a genus far removed from the Solanaceae, and whose relationship to the *Solanum* alkaloids was suspected, has now been proved experimentally by the formation of 1:2-cyclopentenophenanthrene (but no Diels' hydrocarbon) and 2-ethyl-5-methylpyridine on selenium dehydrogenation of rubijervine (Jacobs and Craig, 1945).

Over two dozen species of *Solanum* in New South Wales are open to investigation, while the pharmacology of these alkaloids has yet only been poorly investigated. Since they are steroid alkaloids, specific tests characteristic of the other various types of steroids should be carried out.

COMPOSITAE *

Senecio kirkii*

Of the 30 species found in New Zealand one, *S. lautus*, extends to Australia, while the rest are all endemic.

Manske (1944) has recently surveyed the alkaloids from this genus, the largest genus of the Compositae, if not of flowering plants generally, containing probably at least 1,000 species. It would appear that each species elaborates a different alkaloid or a different series of alkaloids and Manske has shown that species can be differentiated by their alkaloidal content where there is practically no difference in their morphological characters. The pioneering work of Baker and Smith correlating the chemistry of the essential oils and the morphological characters of the genus *Eucalyptus* thus has its analogies in the alkaloid field.

Work has now been commenced on the alkaloids of the New Zealand species and from *S. kirkii a* new crystalline base senkirkine, $C_{18}H_{25}O_6N$, m.p. 197-198° (picrate, m.p. 226-226.5°) has been obtained (Briggs, Mangan and Russell, 1946).

Eighteen species are listed for New South Wales, none of which has yet been examined chemically.

Brachyglottis repanda

This shrub or small tree belongs to a genus of two or possibly even one closely allied to *Senecio* and endemic to New Zealand. The plant is poisonous to stock causing "staggers". The leaves definitely contain an alkaloid in small yield, possibly allied to the *Senecio* alkaloids but it has not yet been fully investigated.

Colouring Matters

TAXACEAE *

Podocarpu spicatus*, "Matai"

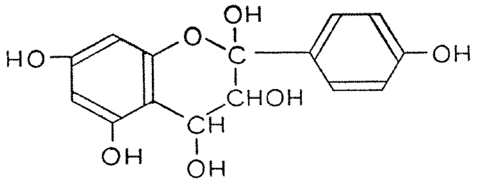
In working up the mother liquors of matairesinol and conidendrin, three colouring matters have been isolated, the flavonol, quercetin, and two new coloured compounds A and B of still unknown structure.

The absorption spectrum of A, which is isomeric but not identical with rhamnazin, does not correspond to that of a flavonol (Briggs, 1946).

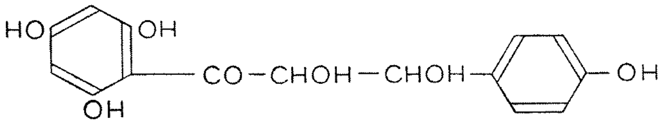
VERBENACEAE *

Vitex littoralis*, "Puriri"

Two colouring matters were isolated from the wood of this tree by Perkin (1898), which, after hydrolysis, yielded the aglycones vitexin and homovitexin. Vitexin has also been isolated as its glucoside by Barger (1906) from *Saponaria officinalis*. Degradative work by Perkin (1900), Barger and Péteri (1939) has directly related it to apigenin of known structure and alternative formulae have been proposed.

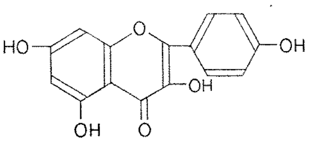


(REDUCED FLAVONONE TYPE)



(REDUCED CHALKONE TYPE)

FIGURE 23



APIGENIN

FIGURE 24

The absorption spectrum of vitexin should throw considerable light on its constitution.

RUBIACEAE *

This family is one of the largest and best defined families in the plant kingdom, containing more than 450 genera and 5,500 species.

*Coprosma Species**

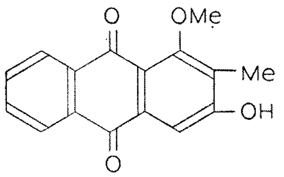
The inner bark of numerous species was extensively used by the Maoris for colouring their flax fibre (Te Rangihiroa, 1911). During the Great War of 1914-1918, when synthetic khaki dyes were difficult to obtain, Aston (1917, 1918b, c, 1919b, 1923a) investigated species of this genus for dyestuffs and showed that a number were suitable for the purpose. From *C. australis* he isolated two pigments which were not, however, identified nor characterised.

He has also shown that differences are exhibited by many species in the colour of the bark and that given on addition of sodium hydroxide solution, whence it would appear that a diversity of coloured compounds is present in this genus.

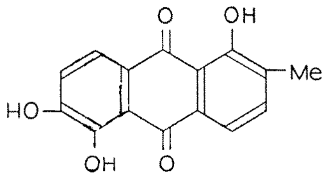
This work has now been continued and a series of anthraquinone colouring matters has been obtained (Briggs, Craw, Dacre, Nicholls and Ronaldson, 1946).

C. australis

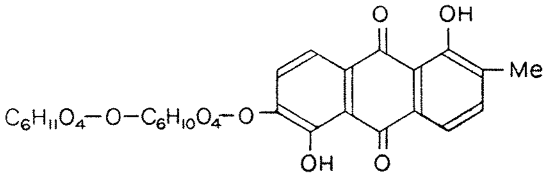
The two compounds isolated by Aston have been identified as rubiadin methyl ether and morindone. In addition two more compounds have been obtained by chromatographic adsorption, morindin, the rhamno-glucoside of morindone, and another, yet unidentified. As morindone is a powerful dyestuff giving a wide variety of colours with different mordants and the colouring matters are present to the phenomenal extent of 24% of the dry weight of the bark of this tree, it should form a valuable raw material for the home-dyer.



RUBIADIN METHYL ETHER



MORINDONE

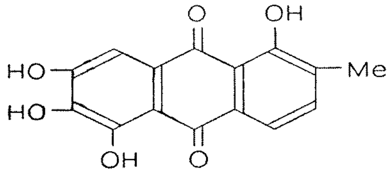


MORINDIN

FIGURE 25

C. areolata

By chromatographic adsorption two colouring matters have been isolated, rubiadin methyl ether and a new pigment, areolatin, for which the following provisional formula is proposed.



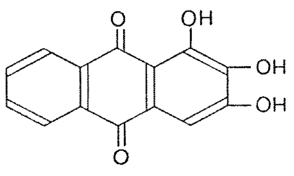
AREOLATIN

FIGURE 26

Areolatin is also an excellent dyestuff and again the yield of colouring matters from the bark is phenomenally high (18% of the dry weight).

C. lucida.

Eight colouring matters have been isolated, apparently different from those already isolated, of which one has been identified as anthragallol, the first record of its occurrence in nature.



ANTHRAGALLOL

FIGURE 27

C. rubra

Chromatographic adsorption indicates the presence of three coloured compounds, one of which has been identified as rubiadin methyl ether.

The glycoside asperuloside, first isolated from *Asperula odorata* and also from the leaves of *C. lucida, C. robusta* and C. *repens* (Hérissey, 1933) is widely distributed in the bark as well and has now been identified in that of *C. lucida*, *C. robusta, C. repens* and *C. arborea.* Asperuloside, $C_{18}H_{22}O_{11},H_2O$, which is colourless, on hydrolysis yields a greenish-black insoluble compound, possibly an hydroxylated naphthaquinone derivative.

It is hoped to make a comprehensive survey of these colouring matters not only from their intrinsic chemical interest but also from a systemic point of view in the elucidation of the problem of hybridisation which occurs commonly among species of this genus (Allan, 1930).

Tannins

A number of other trees, shrubs and plants were also used by the Maoris for dyeing. Usually the fibres were soaked in extracts of the bark containing tannin and then in ferruginous springs so that a black colour, in reality an ink, was produced. Some of these have been examined for tannin content, and although high in some cases they do not compete with normal sources from *Acacia* species. Quantities of the bark of *Phyllocladus trichomanoides* were formerly exported for tanning purposes, mostly to France for glove leather. The following list is given by Aston:

	%
Phyllocladus trichomanoides	29
P. glauca	29
Weinmannia racemosa	19-23
W. sylicola	10-13
Nothofagus fusca	9-16
N. solandri	13
Metrosideros lucida	9
M. robsta	11
Elaeocarpus dentata	6-10
E . hookerianus	4-10
Dacrydium cupressinum	10
Podocarpus ferrugineus	7
Fuchsia excorticata	3-4
Eugenia maire	17
Coriaria ruscifolia	2-16

In addition Aston points out that the following species of lichens grow in New Zealand which are used commercially for dyeing in Scotland and Ireland in the preparation of Harris, Lewis, Donegal and Shetland homespun materials, viz. *Parmelia caperata, P. saxatelis, P. parietina, P. perlata, P. conspersa, Lecanora tartarea, Cetraria islandica, Gyrophora cylindrica, Ochrolechia parella* and *Teloschistes flavicans.*

Saponins

Owing to the relative ease with which sarsasapogenin may be transformed into the sex hormones which are only available in minute amounts from other natural sources such as urine, a search has been made for further sources of steroid saponins. In what is probably the most extensive report yet made on natural products Marker, Wagner, Ulshafer, Wittbecker, Goldsmith and Ruof (1943) have described a summary of their investigations of over 300 species, from which known saponins were isolated in addition to 14 new ones whose structures were elucidated. Many of the species belonged to the Agavaceae, which in New Zealand is represented by the familiar cabbage tree, *Cordyline australis,* three other species of the same genus and the common flax, *Phormium tenax*. The roots of these plants are therefore worthy of investigation for the same purpose.

During investigations on the saponins of *Pomaderris elliptica,* "Gum Diggers' Soap", and two introduced species, *Zantedeschia aethiopica,* "arum lily", and *Arum maculatum,* which are still incomplete, a survey of the literature revealed a phytochemical fact apparently not generally recognised. Two main types of saponins exist, one of steroid and the other of triterpenoid acid structure. From those whose structure has been investigated in some detail it would appear that the steroid type occurs only in the monocotyledon class of the Angiospermae, while the triterpenoid type are restricted to the dicotyledons.

A saponin, perhaps identical with the glycoside pittosporin, occurs in the leaves of *Pittosporum corrifolium*, *P. crassifolium, P. eugenioides* and *P. huttonianum.* The same compound has also been found to occur in species whose habitat lies outside New Zealand (Klein, 1933, p. 1135).

Fibres

Phormium tenax, "Flax"

Besides its possible use as a source of saponins the New Zealand flax is one of our most important plants from another economic point of view. The fibre is of very high quality, and although production fluctuates, up to 1939 over 180,000 tons, to the value of nearly £10,000,000, have been exported.

Analyses have been made by various workers (Hutton, 1869; Church, 1873 Aitken, 1928; McIlroy, 1944), while a preliminary study has been made on the hemicellulose portion by McIlroy, Holmes and Mauger (1945). From this it would appear that the hemicellulose is constituted of a main chain containing nine or ten xylo-pyranose residues united by 1:4-β-linkages, terminated at the reducing end by a complex, highly branched acid nucleus containing d-glucuronic acid as one component.

Sea-Weeds

Some of the New Zealand species have been investigated for their iodine, potassium and other mineral content. During the recent war, when supplies of agar-agar were cut off from Japan, a search was made in New Zealand for species suitable for the purpose. Due to the efforts of Miss Moore, two species, *Pterocladia lucida* and *P. capillacea,* were found suitable and collections were arranged over the coastal areas of the North Island. In three years nearly 250 tons were collected and processed. The agar-agar obtained is of excellent quality and has approximately twice the gelation strength of the Japanese product (Moore, 1944, 1946).

As yet no attempt has been made to exploit New Zealand sea-weeds for the manufacture of sea-weed rayon, the fundamental constituent of which is alginic acid (Speakman, 1945). A recent survey of *Macrocystis* shows that the Cook Strait area alone could provide an annual harvest of about 4,000 tons of dry kelp at an estimated cost of £10 per ton (Melville, 1946).

Antibiotics

Although the first examples of antibiotics were discovered in the lower plant forms, there are now numerous references to their occurrence in the higher forms. With its wealth of endemic species New Zealand offers wide scope for further investigation along these lines.

In conclusion, for my part of the work carried out on the plant products of New Zealand I should like to express my sincere thanks to a willing band of co-workers who, over the years, have helped to elucidate some of Nature's secrets and have found joy in doing so. I am also greatly indebted to the Royal Society of New Zealand, the Chemical Society, London, the Australian and New Zealand Association for the Advancement of Science, the Research Council of the Department of Scientific and Industrial Research, New Zealand, for research grants, and Imperial Chemical Industries for gifts of chemicals.

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