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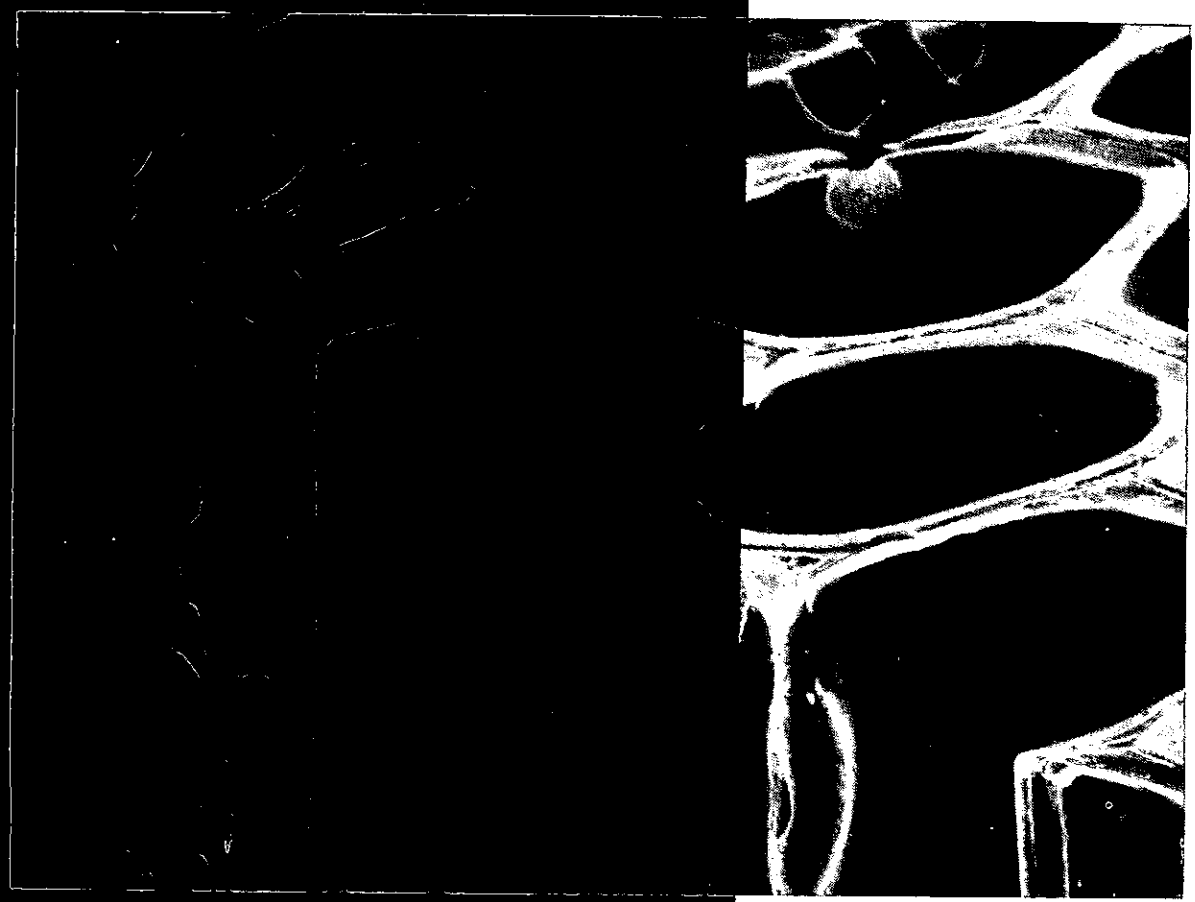

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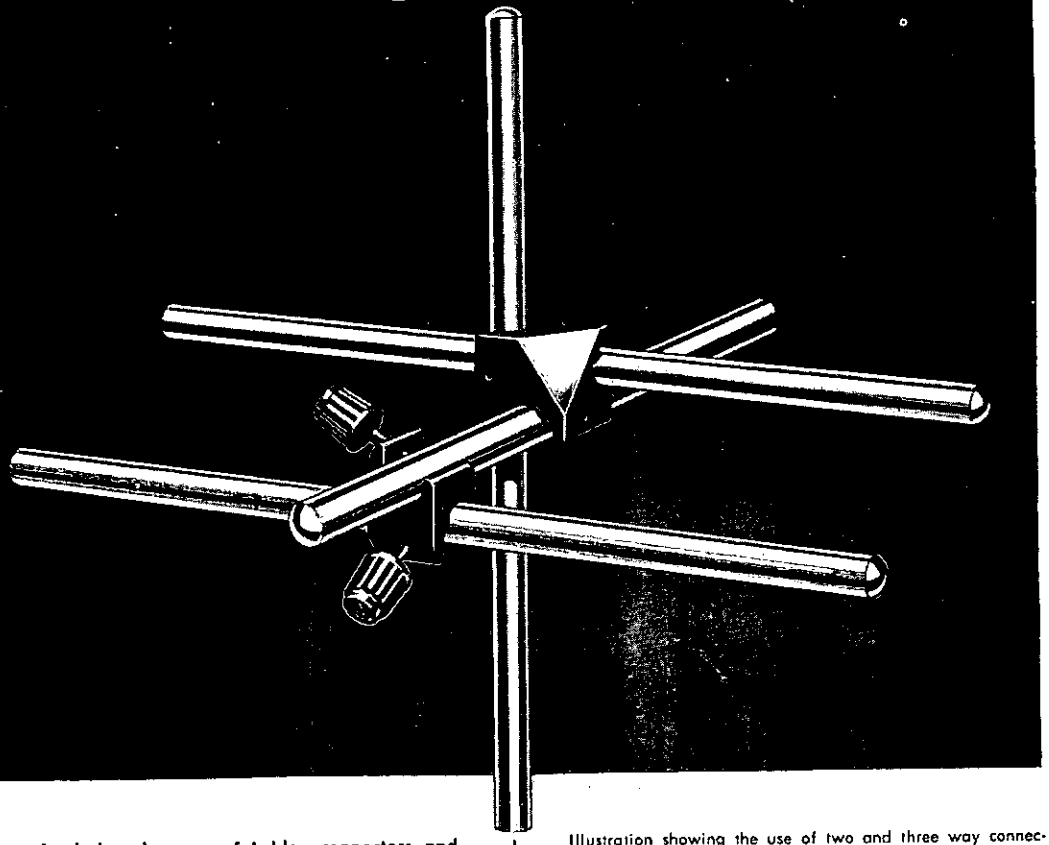

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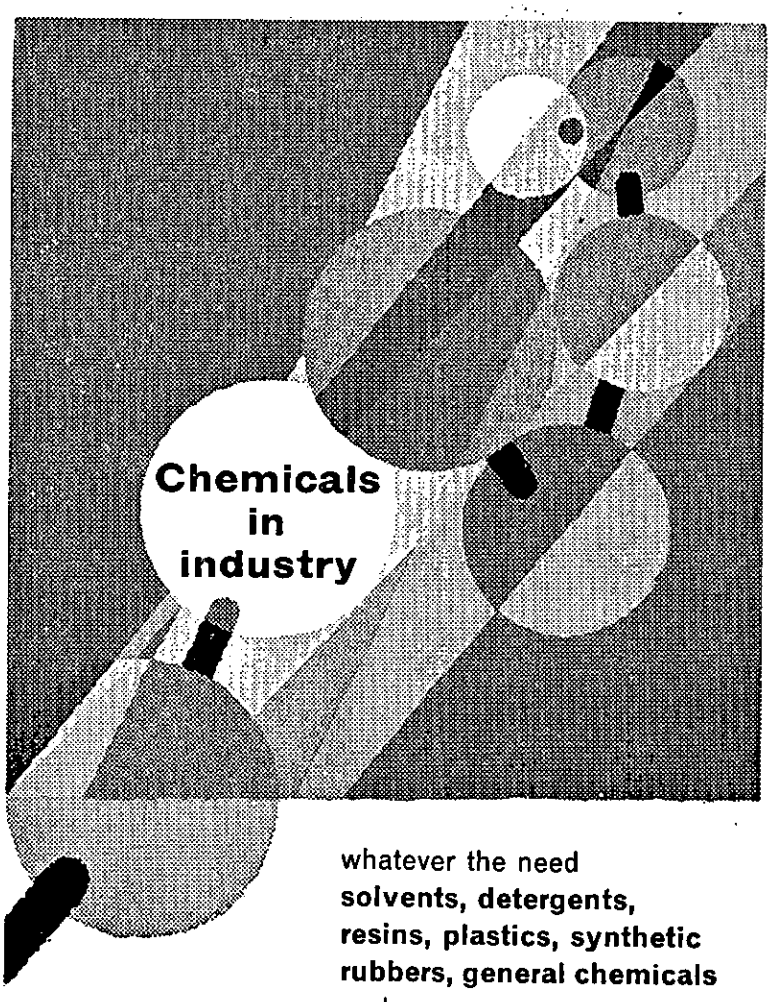

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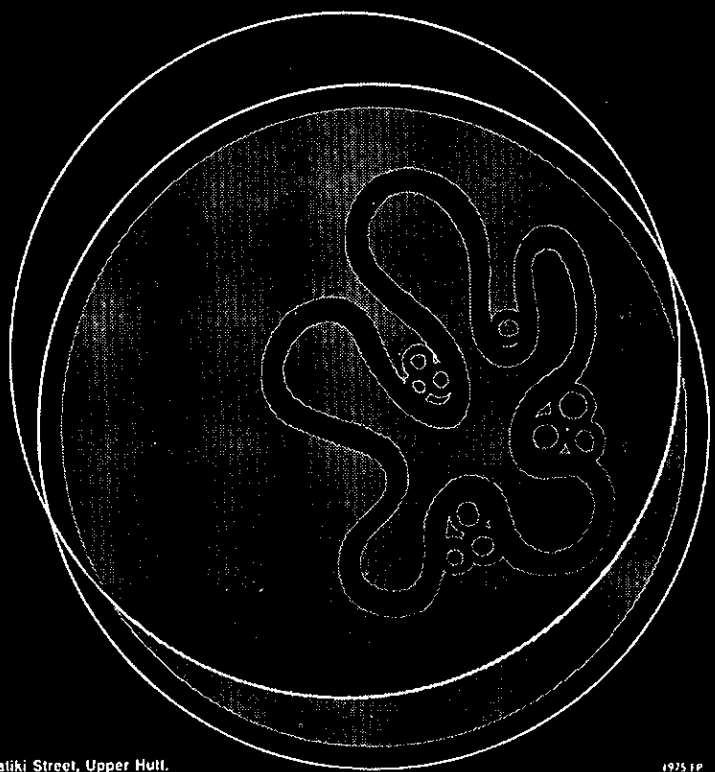

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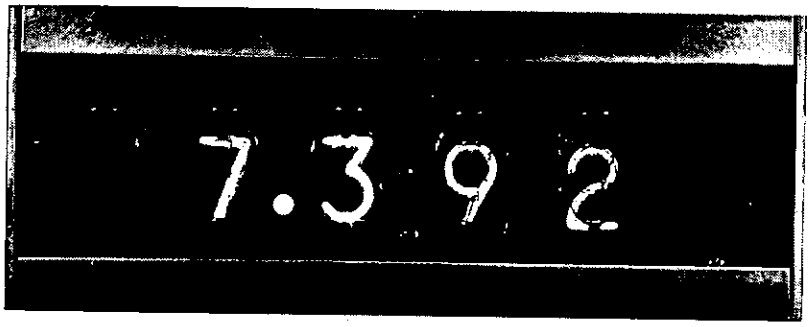

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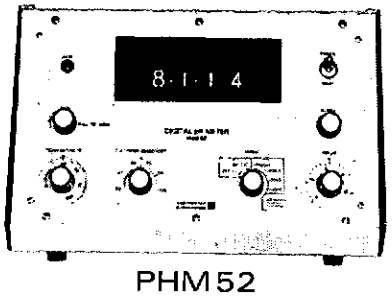

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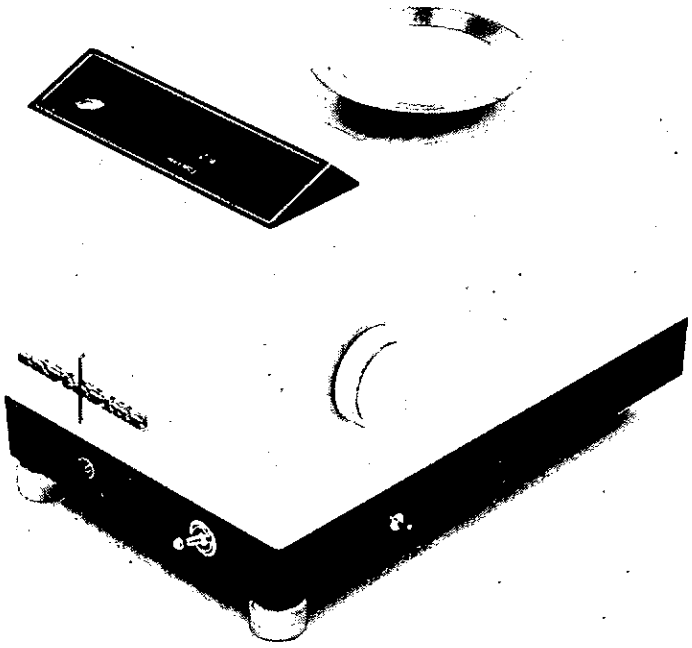

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THE PROBLEM OF LIGNIN

A short review of lignin chemistry

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Chemistry Division, Department of Scientific and Industrial Research,
Petone, New Zealand

Introduction

In 1969 about 50 billion tons of lignin were removed from wood in the production of wood pulp.* A similar quantity of hemicellulose was unavoidably lost at the same time. A high proportion of this 100 billion tons of organic raw material was burnt in recovery boilers. A very little of it would have been utilized in road-sealing, as a tanning agent, or as a low-grade fertilizer; still less of it would have been utilized in the low-yield production of vanillin, methanol, ethanol, acetic acid, and other specific chemicals. In addition, a small, significant proportion in dilute solution would not have been recovered in any form and would have constituted the major effluent problem associated with the pulp and paper industry.

In New Zealand in 1969 the pulp and paper industry produced some 300,000 tons of chemical pulp[1b] at a yield of around 46 percent. At the same time it therefore extracted and burnt about 160,000 tons of lignin and 160,000 tons of hemicellulose. The energy return from this combustion would more or less have equalled that required for the waste liquor evaporation, the cooking digesters, and the pulp drying of the pulping process.[2] Thus, in a limited sense, the burning and recovery of the energy so liberated must be considered a form of lignin utilization. But although an alternative power supply might cost as much as $30 per ton of pulp,[2] it is important to consider the pulping process as a whole before equating this figure with the value of lignin and hemicellulose used as a fuel. Most of the expensive pulp bleaching stages of paper making are only necessary because of the discolouration that accompanies industrial delignification. Indeed, the greater part of the entire pulping process has only been developed because of our inability to make strong, colour-fast papers from lignified fibres. On this basis lignin must be considered to appear on the debit side of the pulp and paper balance sheet.

The low financial returns received from the colossal amounts of lignin which are removed annually by pulping provide more than adequate economic reasons for studying lignin and wood chemistry with a view to lignin utilization. The singular lack of success of man's efforts to utilize lignin as an isolated product, and his limited ability to utilize it in the form of paper (as in groundwood, newsprint etc.), have been related to his lack of understanding of lignin at the molecular level. Consideration of the current role of lignin in industry thus serves as an introduction and gives some perspective to this review of lignin structure and chemistry.

Lignin Preparations and their Isolation

Lignin is an amorphous substance which comprises 25-30 percent of the organic material in a tree. In the main it has resisted chemical understanding because it is so intractably bound up with the other wood polymers that it has probably never been isolated in a pure, unchanged form. The same may perhaps be said of other naturally occurring polymers like cellulose, but the changes or the impurities that are associated with the isolation of these other polymers are small compared with those associated with the isola-

* Calculated from pulp production figures in reference 1a.

tion of lignin. Broadly, lignin preparations may be isolated by selective extraction or as the residue remaining after dissolving the carbohydrates. Both methods of preparation produce two classes of product: those which in their isolation have undergone only slight chemical changes but which have been obtained in such low yields as to be non-representative of wood lignin as a whole; and those which have been obtained in high yields but which are probably so chemically altered as to be almost unrecognizable as lignin. Both types of preparation often contain appreciable amounts of impurities, particularly carbohydrates.

In the tree, lignin is almost white or pale cream in colour. The degree of chemical change which occurs when it is isolated is crudely, but usefully, measured by its colour. All of the high yield isolated lignins are darkly coloured whereas the low yield lignins are generally pale and may be almost white (table).* The high yield lignin from the pulp mill, for example, is dissolved to give a solution known as *black* liquor. The lignin that can be isolated from black liquor bears only a distant relationship to the lignin of the original trees and although extensively studied, it has contributed little to the elucidation of lignin structure.

Since isolated lignins all have different properties, their methods of isolation must always be specified. The table lists some of the more commonly isolated lignins, their methods of isolation and some of their properties. Note, for example, that methanol lignin has undergone some methylation and that dioxan/HCl lignin has been partially chlorinated. Of the preparations listed in the table only artificial DHP lignin, milled-wood lignin and natural lignin may be considered suitable for most scientific investigations. Natural lignin—referring in this review to lignin as it exists in the tree—has been called variously "native", "pseudo", or "proto-", lignin. Freudenberg prefers to call it just 'lignin'. To avoid confusion the word 'lignin' is here used in its general sense—so that where the origin of the lignin being discussed is important it will be specified.

* See p. 13.

Lignin in the Plant Kingdom

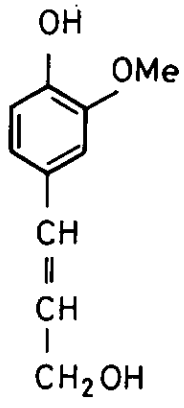
A botanist would recognize lignin as a substance with special staining characteristics which encrusts the walls, and particularly the middle lamellae, of cells of vascular plants. It is generally accepted that true lignin is absent from the non-vascular, more primitive plants, although a substance closely resembling lignin is found in a number of mosses.

The question of the occurrence, or non-occurrence, of lignin in members of the plant kingdom must depend upon the definition of lignin. Many phenolic plant materials which are not lignin will give positive results with tests which are normally regarded as being specific for lignin. The presence in lignified plants of lignins having a wide range of molecular weights further confuses the situation. Probably the best definition that can be made of lignin includes a general description of its properties, the most significant of which are: its aromatic content; its methoxyl content; its oxidation to Hibbert's ketones and the aromatic aldehydes syringaldehyde (XIII), vanillin (XII), and p-hydroxybenzaldehyde (XI); its reaction with thioglycolic acid; and its elemental composition based on a C_9 phenylpropanoid skeleton. These and other properties are discussed below.

The vascular plants are the largest of those which grow on land. The presence of lignin in their supporting and conducting tissues is said to have enabled them to develop large, upright forms. This plant reinforcement and rigidity is usually thought of as the prime function of lignin in the plant. It has also been suggested that lignification is a form of excretion by which the higher plants can eliminate unwanted substances.

Lignin Biosynthesis

Tracer and enzyme studies on the formation of lignin in plants suggest the hypothetical sequence: carbohydrates → shikimic acid



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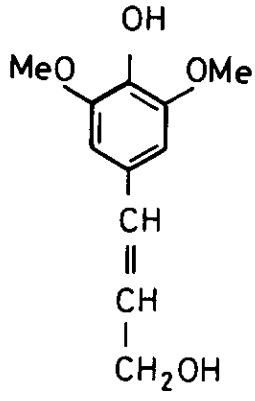

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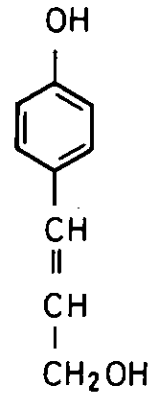

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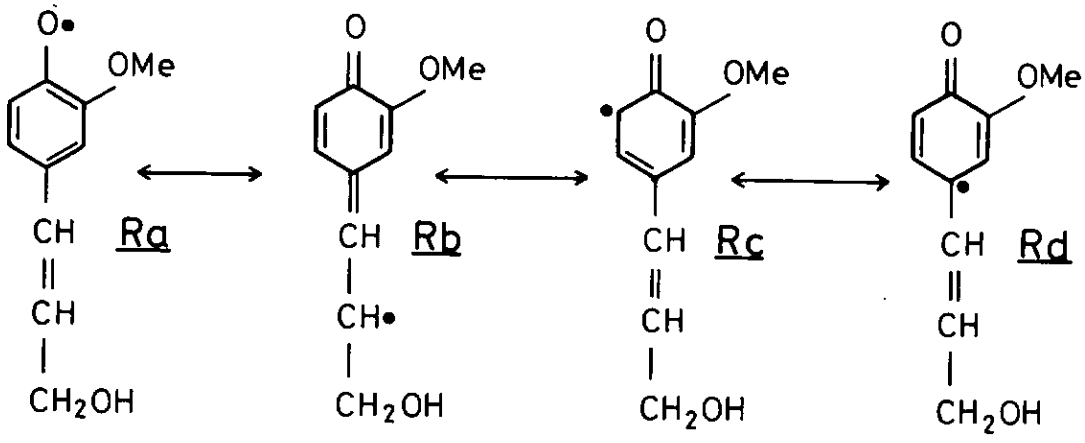


(IVa) (IVb) (IVc) (IVd)

→ phenylalanine → cinnamic acid derivatives → cinnamyl alcohols → lignin. Freudenberg and others have extensively studied this last step, the polymerization of cinnamyl alcohol derivatives, notably coniferyl alcohol, and have built up a coherent picture of what natural lignin is and how it is linked in the plant.

Following the work of Freudenberg, lignin is now generally considered to be a polymer derived from coniferyl alcohol (I), sinapyl alcohol (II) and *p*-coumaryl alcohol (III) by enzymatic dehydrogenation. In the laboratory the dehydrogenation of coniferyl alcohol alone, which gives rise to a dehydrogenation polymer known as artificial DHP lignin, has been most studied. This compound is dehydrogenated by peroxidases or laccases in aqueous solution to form a free radical (IVa-d). Evidence for the existence of this intermediate comes mainly from product analysis, although a weak unresolved e.s.r. signal has been observed during the dehydrogenation.[3] The distribution of the electron density of this coniferyl radical is represented by the four main canonical forms (IVa-d). Polymerization of the coniferyl radical can thus be thought of as proceeding through these positions of high electron density.

Less rigorously, the tendency has been to describe the dimers, or dilignols which are the first products in the polymerization of coniferyl alcohol, in terms of direct combinations of the canonical forms: Ra Ra, Ra R_b, R_a R_c . . . etc. Thus of the thirty or more dilignols and derivatives which have been isolated by interrupting the polymerization at a nearly stage, the three major products correspond to the combinations Ra R_b (*V*, stabilized by addition of water to give *VI* in about 15 percent yield); R_b R_b (VII to give (VIII), DL-pinoresinol, by further condensation, 15 percent yield); R_b R_c (*IX* to give (*X*) dehydrodiconiferyl alcohol, 15 percent yield).

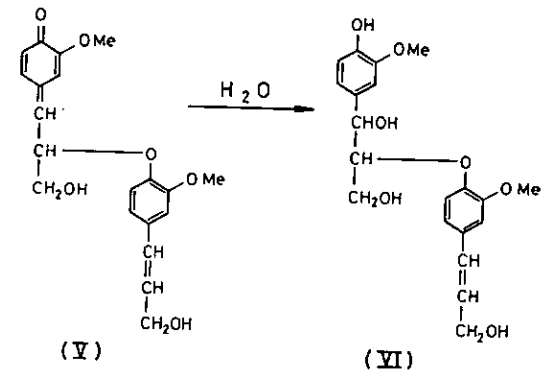
The remaining dilignols, including some with diphenyl linkages, have been isolated mainly in yields of about 1 percent. Trilignols resulting from combination of the coniferyl radical as given by R_b with (*VI*), (*VIII*), and (*X*) have also been isolated. Continuation of this type of polymerization eventually results in precipitation of artificial DHP lignin. This substance is a mixture of polylignols having a mean molecular weight in excess of 800[4a].

The ability of the coniferyl radical to polymerize through a number of different positions can thus give rise to a very complicated non-uniform polymer. Add to this the possibility of further extensive condensations and the presence in nature of the other two coumaryl alcohols (*II*) and (*III*), and it can be seen that lignin is potentially a very complex material containing a variety of functional groups and covering a wide range of molecular weights.

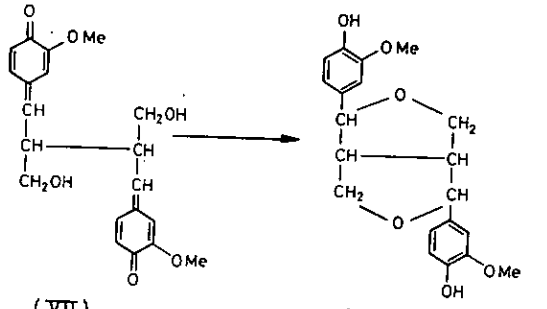
Lignin Chemistry and Properties

Although it seems that we cannot represent lignin by a single structural formula, nevertheless a lot of very useful information can be derived from a knowledge of its statistical composition and properties. The latter have been derived from studies of synthetic dilignols as well as from studies involving isolated lignins.

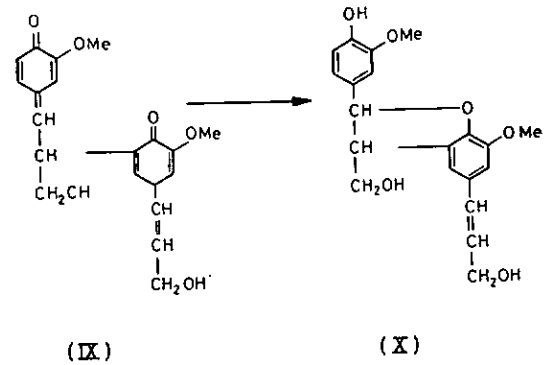
When calculated on the phenylpropane C_9 basis, average spruce lignin has a composition $C_9H_{7.15}O_2(H_2O)_{0.4}(OCH_3)_{0.92}$. A synthetic conifer lignin produced from a mixture of about 80 parts coniferyl alcohol, 14 parts of *p*-coumaryl alcohol, and 6 parts of sinapyl alcohol also has this composition. The composition ($C_9H_{9.08}O_2(OCH_3)_{0.92}$) of the mixture of alcohols from which it was derived thus differs from the lignin composition by having about 2 H atoms more and 0.4 molecules of water less. One of these hydrogen atoms would have been lost in the dehydrogenation, the other presumably is lost in secondary condensations. Addition of water to quinone methides in the polymer would



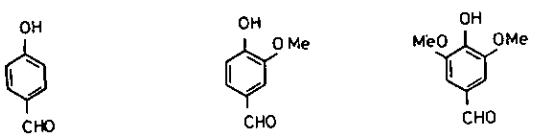
(V) (VI)



(VII) (VIII)



(IX) (X)



(XI) (XII) (XIII)

account for the presence of 0.4 molecules of water in the formula.

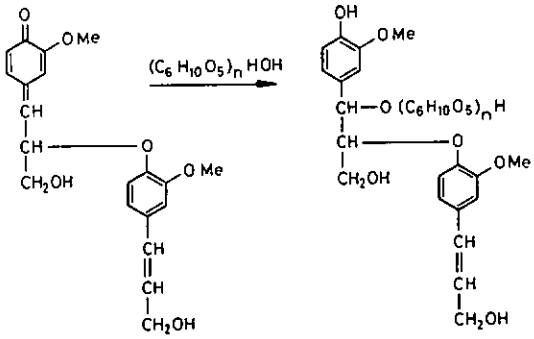
Hardwood lignins, which give together with some *p*-hydroxy benzaldehyde (XI), vanillin (XII) and syringaldehyde (XIII) in approximately equal quantities upon alkaline nitrobenzene oxidation, are derived from a coumaryl alcohol mixture containing about equal quantities of coniferyl alcohol and sinapyl alcohol. Lignins of lower plants, which give more *p*-hydroxybenzaldehyde on alkaline nitrobenzene oxidation, are derived from a coumaryl alcohol mixture richer in *p*-coumaryl alcohol. The range represented by hardwood, softwood and lycopod lignins also shows the decrease in methoxyl content that one would expect from a consideration of their precursors. Thus beech lignin contains about 1.4 OCH_3 groups per C_9 lignin unit; spruce lignin contains about 0.9 OCH_3 groups per C_9 lignin unit; and lycopod lignin contains about 0.7 OCH_3 groups per C_9 lignin unit. Hence a preparation derived from sphagnum moss which had a methoxyl content well outside this range (only 0.25 per C_9 unit) should probably not be accredited the title 'lignin'. In cases like this the methoxyl content of lignin obviously has a diagnostic value. It is traditionally determined by reaction of the methoxyl group with hydroiodic acid, n.m.r. rarely being applicable to lignin preparations because of their insolubility.

The complete list of functional groups in lignin is probably a very long one, and no doubt at present includes a number of condensed groups not actually present in natural lignin. More comprehensive reviewers[4, 5, 6, 7] have included much information derived from studies on more or less highly degraded lignins whose interpretation is either obscure, or related more to a particular industrial process than to lignin chemistry. This they were in some measure bound to do, because it is doubtful if all of the salient features of lignin chemistry have yet emerged. Nevertheless, once the biosynthesis of lignin has been explained, the chemistry of lignin can be usefully discussed under only three more head-

ings: quinone methides; benzyl alcohols and benzylaryl ethers; and hydroxyl groups, particularly phenolics.

1. Quinone methides

Although, as we have seen, quinone methides are formed during the dehydrogenation of coniferyl alcohol, very few are thought to be present in final polymer. Studies on the yellowing of wood by light suggests that, in freshly cut *Pinus radiata*, 1 lignin unit in 120 is in the quinone methide form. This 0.8 percent of quinone methides appears to be sufficient to bring about the complete destruction of the lignin by light absorption.[8] The transient quinone methides formed during the dehydrogenation are, however, responsible for many of the important links in the final lignin polymer. As they are formed they readily combine with carbohydrate hydroxyl groups to give lignin-carbohydrate bonds (e.g. IVa + IVb → V → XIV), with water to give benzyl alcohols, or with phenols to give benzyl aryl ether linkages within the lignin.



(V) (XIV)

The lignin-carbohydrate bonds, which must be broken for the lignin to be removed as in pulping, are thus primarily benzyl ether links. Where the benzyl ethers have *p*-hydroxy substituents, as in the dilignol derivative (XIV), they are hydrolyzed by acid at about the same rate as sucrose, but in lignin proper they will often be greatly stabilized by etherification of the *p*-phenolic hydroxyl group during the further progress of lignification.

2. Benzyl alcohols and benzyl aryl ethers

The other two products of addition to quinone methides, the benzyl alcohols and the benzyl aryl ethers, are jointly responsible for the characteristic lignin reaction with thioglycolic acid.[10] They are also very important for other reactions of lignin. The benzyl alcoholic groups complicate attempts to degrade lignin by hydrolysis with acids, for benzyl carbonium ions are generated which condense with other phenolic rings in the lignin. Similar condensations also occur with hot alkali owing to reformation of *p*-quinone methides. Both processes lead to more highly condensed structures that form bakelite-like resins from the amorphous lignin. This undesirable condensation is partially overcome in pulping by the addition of sulphite or bisulphite ions which sulphonate the benzyl alcoholic groups, thereby increasing the water solubility of the lignin.

The benzyl aryl ethers occur in lignin at the rate of about 0.1 per C_9 unit. They provide what are probably the weakest bonds between lignin units. When they have free phenolic *p*-hydroxyl substituents they may be split by lukewarm water; when they have etherified substituents they may be hydrolyzed by water at higher temperatures or by methanol containing 0.5 percent HCl at room temperature. Like the benzyl alcohols, they are readily sulphonated during pulping.

3. Hydroxyl groups

The other lignin functional group that has an important role in lignin chemistry is the phenolic hydroxyl. About one lignin unit in three is thought to contain this group. Thus for many purposes lignin may be regarded as a polyphenol which undergoes many of the typical phenolic reactions. It ionizes and discolours instantly in alkali, it may be acetylated or methylated by mild reagents, and it can also function as an efficient free radical scavenger in such reactions as the yellowing of wood by light[8, 9]. The remainder of the hydroxyl groups is aliphatic (about 1 per C_9 lignin unit), con-

sisting of primary and secondary alcohols in the ratio of about 1:3. These and the phenolic hydroxyls and, perhaps, the lignin carbonyl groups (less than 0.2 per C_9 unit) may play a major role in the hydrogen bonding and hydrophilic properties of lignin. They may thus have an important function in the production of paper from lignified fibres.

To sum up, lignin is formed in the tree by the free radical polymerization of *p*-coumaryl alcohols, giving transiently quinone methides, and ultimately an amorphous polymer linked within itself and to the cell carbohydrates by a variety of bonds, most important of which seem to be benzyl ethers. The polymer is thought to contain a wide range of functional groups, of which by far the most important chemically are the benzyl alcohols and the phenols.

Conclusion

The picture of lignin which is presented here and which is currently adhered to by most lignin chemists (and it must be admitted that there are still a few dissentors) is not a wholly satisfying one to the chemist. Unlike the amino acid units of proteins, the various units in lignin are not set together on a template by genetic information. The sequence of the individual units in lignin is said to be entirely random. Moreover, unaltered units of the lignin polymer cannot be obtained by degradation as can simple amino acids by hydrolysis of proteins. Thus there is inevitably a measure of hypothesis and speculation built into any one person's idea of lignin. That this speculation is considerably less than it was even 10 years ago must be largely due to the convincing work of Freudenberg and co-

PRINCIPAL LIGNIN PREPARATIONS

Type	*Method of Isolation*	*Yield (%) (Approx.)*	*Colour*	*Other Characteristics*
1. Natural	Not isolated	100	almost white	Insoluble, grafted onto carbohydrates, OMe content (softwood) 15-16%.
2. Artificial DHP	Prepared synthetically from coniferyl alcohol	—	cream	Soluble in aqueous organic solvents. Contains 16.8% OMe. Molecular weight above 800.
Carbohydrate Extraction Methods:				
3. Klason	Extraction with cold (72%) hot (100°c) (3%) H_2SO_4	90	black	Insoluble, charred materials.
4. Hydrochloric Acid	Carbohydrates removed with cold 40% HCl	90	brown	Drastically chemically changed. Highly inter- and intra-mole-cularly condensed.
5. Cuproxam	Alternate boiling with 2% H_2SO_4 and extraction with ammoniacal CuO	90	yellow-brown	Contain some carbohydrates.
Lignin Extraction Methods:				
6. Methanol	Extraction with MeOH/HCl at 90° for 80 hours	25	buff	OMe content (softwood) 21.5%.
7. Dioxan	Extraction with dioxan/ conc. HCl	60	light brown	Partially chlorinated.
8. Soluble	Extraction with cold acetone or methanol	1	cream	Low molecular weight, high phenolic hydroxyl content.
9. Milled Wood	Ground in ball mill in presence of toluene. Lignin extracted with cold aq. dioxan	25	buff	Molecular weight 8,000-11,000, probably a little lower than natural.

workers. However, it is important to realise that although Freudenberg's free radical mechanism for lignin biosynthesis has gained wide acceptance, it has still not been shown to be unequivocally correct. To date no one has knowingly observed the coniferyl or related radicals; nor shown that such radicals are definitely intermediates in lignin biosynthesis; nor explained, for example, how they can polymerize in so many different ways, presumably by diffusion, and yet not be quenched by the atmospheric oxygen which must be present in the tree and which is so fatal to other unhindered phenoxy radicals. Until this sort of fundamental question is answered, our understanding of lignin chemistry and structure, which depends to a large degree upon an understanding of lignin biosynthesis, will at the best be only a highly probable guess.

From the point of view of lignin utilization the absolute structure of lignin is not so important. An understanding of the mechanisms of lignin reactions will probably contribute more to our ability to use lignin than will a total synthesis.

It seems likely that in the long run we will be able to overcome the lignin utilization problem by dispensing with the current pulping processes and by learning how to make strong, light-fast lignified papers. To do this we must understand how and why paper has its strength, we must be able to block groups with undesirable reactions, and we must be able to persuade the lignin molecule to enter into bonding that will contribute to the formation of a strong paper. The more academic questions of lignin evolution, function, biodegradation, etc., will all have their part to play, but our current knowledge of lignin is such that we must now be able to apply basic chemical principles to wood or any lignified material and thereby predict and control their use and behaviour.

BIBLIOGRAPHY

'Lignin Structure and Reactions', *Advances in Chemistry* Series of American Chemical Society **59**, (R. F. Gould, ed.), Washington, D.C., (1966).

'Lignin—A Natural Polymeric Product of Phenol Oxidation' by J. M. Harkin in *Oxidative Coupling of Phenols*, ed. W. I. Taylor and A. R. Battersby, Marcel Dekker Inc.; New York, (1967).

Constitution and Biosynthesis of Lignin by K. Freudenberg and A. C. Neish, Springer-Verlag, New York, (1968).

REFERENCES

1. *Pulp and Paper International, Review No.* 1970 (a) pp. 30-208 (b) p. 162.
2. Rydholm, Sven A., *Pulping Processes*, Interscience Publishers, New York (1965), pp. 776-777.
3. Freudenberg, K., Chen, C. L., Harkin, J. M., Nimz, H. and Renner, H., *Chem. Commun.*, (1965), 224.
4. Brauns, F. E. and Brauns, D. A., *The Chemistry of Lignin*. Supplement Volume, Academic, New York, (1960), (a) p. 696.
5. Brauns, F. E., *The Chemistry of Lignin*, Academic, New York, (1952).
6. Pearl, I. A. et al.,
   Annual Reviews of Lignin Chemistry in
   Tappi (1969), **52**, 575.
   Forest Prod. J. (1967), **17**, 23
   (1965), **15**, 379
   (1964), **14**, 435
   (1963), **13**, 373
   (1962), **12**, 141
   (1961), **11**, 85.
   (1960), **10**, 91
   (1959), **9**, 85
7. Pearl, I. A., *The Chemistry of Lignin*, E. Arnold Ed., London (1967).
8. Leary, Gordon, Preprints 5th International Pulp Bleaching Conference, Atlanta (1970).
9. Leary, Gordon, *Tappi* (1968), **51**, 257.

ESR STUDIES OF SOME ORGANIC RADICALS

By B. M. Peake
Chemistry Department, Canterbury University, Christchurch
(Winning paper in the Student Paper Competition, NZIC Conference, 1969)

Electron Spin Resonance (ESR) is a technique which forms a branch of the subject in chemistry known as Magnetic Resonance Spectroscopy. This is concerned with the observation of transitions that have been induced by the absorption of electromagnetic radiation in the presence of an external magnetic field. In ESR these transitions are between states of different electron spin, while in Nuclear Magnetic Resonance (NMR) the transitions arise from different nuclear spin states. So let us consider these electron spin states in more detail.

A single electron has an inherent magnetic moment, μ, given by

$$\mu = -g\beta S$$

where g is the Lande g factor
β is the Bohr magneton for an electron
S is the spin angular momentum of the electron.

Application of an external magnetic field, H, to this single electron will lead to an interaction with the magnetic moment such that it aligns itself either parallel or antiparallel with the magnetic field. These two situations are designated by the symbols $1 - \frac{1}{2} >$ and $1 + \frac{1}{2} >$ respectively. In the absence of the magnetic field they have the same energy, i.e. they are said to be degenerate, but in the presence of a field they lose this degeneracy and the energy level diagram for this situation is shown in Figure 1. The difference in energy between the two states is given by the quantity $g\beta H$ and transitions between the two states can be induced by the application of an oscillating magnetic field, H_1, perpendicular to the external field H and with a frequency ν such that

$$h\nu = g\beta H.$$

This equation is known as the Resonance condition and upon substitution of values for h, g, β and a value for H of 3,500 Gauss we obtain a value of about 10,000 Mc/s which is in the microwave region of the electromagnetic spectrum. Hence ESR, although essentially a magnetic resonance technique, is also considered a branch of microwave spectroscopy. In practice, the frequency, ν, of the oscillating field H_1 is normally kept constant and the external field H varied until the resonance condition is satisfied.

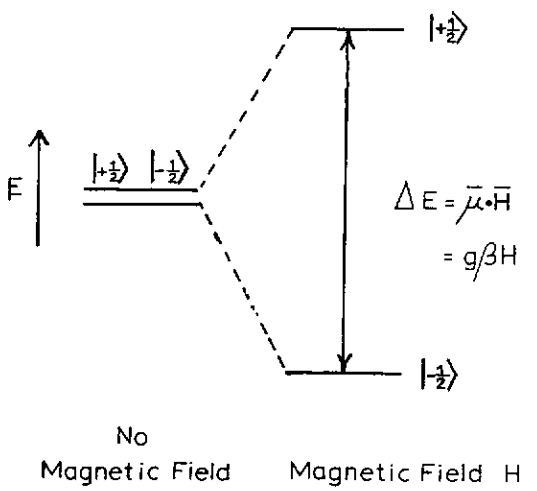


Fig. 1

As well as this interaction with the external field known as Zeeman interaction, the electron magnetic moment also interacts with the magnetic moment of nearby nuclei and this is known as Hyperfine interaction. It causes each electron spin state to be split up into a number of further states each of different energy. This gives rise to many more transitions and it is a scanning of the complete range of possible transitions that is known as an ESR spectrum. The Hyperfine interaction in a spectrum may be described by a series of Hyperfine Coupling Constants which are

essentially values of distances between groups of lines in a spectrum (analogous to the J coupling constants obtained from NMR spectra).

As far as organic compounds are concerned, all bonding orbitals are normally doubly occupied and there is no net electron magnetic moment. Thus we cannot observe ESR transitions in these compounds as they stand. However, if we add an electron to give an anion radical, or remove one to give a cation radical, then the compounds have an electron magnetic moment and thus now give an ESR spectrum. Such species are said to be paramagnetic and this technique is alternatively known as Electron Paramagnetic Resonance, or EPR. If certain atoms in these radical ions have identical hyperfine coupling constants, they are said to be equivalent and usually occupy symmetrically equivalent positions in the molecule. It may be shown that the interaction of an unpaired electron with n equivalent nuclei of nuclear spin I will give $2nI + 1$ lines spaced a constant distant apart and whose relative intensities, in the case where $I = \frac{1}{2}$, are proportional to the coefficients in the binomial expansion of $(1 + x)^n$.

To make all these points clearer let us consider the specific case of the naphthalene radical anion (figure 2). Naphthalene as it stands will give no ESR signals as it has no unpaired electrons. However, if it is reacted with an alkali metal in an ethereal solvent then the radical anion is formed and ESR signals are obtained from it. Considering only Zeeman interaction we get a single line (2a), the position of which is given by the resonance condition. Hyperfine interaction of the electron with the four equivalent protons in the 1,4,5,8 positions will cause this single line to be split into five lines equally spaced apart and with intensities in the ratio 1:4:6:4:1 (2b). Similarly, interaction with the other four protons in the 2,3,6,7 positions splits each of these five lines into another five with the same intensity distribution but with a different spacing (2c). If the theoretical spectrum is compared with the spectrum that is actually observed (2d) for this species, we can see that there is almost perfect agreement. It should be pointed out that the instrumentation of an ESR spectrometer is such that the first derivative is recorded rather than the absorption curve. In practice, we prepare the radical, obtain its ESR spectrum, and then feed trial values for the hyperfine coupling constants into a computer program written to simulate ESR spectra. These trial values are then adjusted until a good agreement between the calculated and observed spectra is found.

Once having obtained the hyperfine coupling constants for a given species from its ESR spectrum, then what can we do with them? There is a large amount of information that can be obtained from them including: (1) it may be shown that, to a first approximation, the hyperfine coupling constant for an atom is proportional to the density of the unpaired electron at this atom. We can express this as

$$A = Q\rho$$

where A is the hyperfine coupling constant
Q is a constant known as McConnell's Constant
ρ is the unpaired electron density.

Thus knowing Q and A, we can calculate ρ. We can also obtain ρ from Molecular Orbital (MO) calculations and so using ρ parameters determined from ESR spectra, we can check the MO calculations on a given compound; (2) the values of hyperfine coupling constants are markedly dependent on the geometry of a molecule and so from a knowledge of them we can obtain certain angles and conformational information.

Having given a brief introduction to ESR and its applications to organic radical ions, I now wish to consider the particular compounds that I have been studying with ESR. These are a series of peri-substituted naphthalenes. Of these, the two compounds I wish to discuss are hexahydropyrene and dipleiadane, and in particular, their radical

SUCCESSOR TO THE
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Newsletter

THE ROYAL SOCIETY OF NEW ZEALAND

No. 10 SUMMER 1970

RUTHERFORD CENTENARY

The centenary of Lord Rutherford's birth occurs on 30 August, 1971, and the Royal Society of London Rutherford Lectures will be given in New Zealand by his grandson Professor P. Fowler.

An approach by the Society to Government for a special stamp to commemorate Lord Rutherford's birth has been unsuccessful.

COOK BICENTENARY SCHOLARSHIP

In recognition of the assistance given to the Cook Bicentenary Expedition by the governments of Tonga and of the Cook Islands a scholarship was offered to one person from each country for practical training in New Zealand for one year.

Mr. Otenili Tuipulotu from Tonga has been at Flock House studying animal husbandry since the beginning of September, and a varied programme has been arranged for him in other parts of New Zealand through the co-operation of the Department of Agriculture.

Miss Jean Dashwood has been nominated by the Cook Islands Government for training in Education but will not take up this scholarship until 1971.

OTAGO BRANCH CENTENARY BOOKLET

Because of enlargement of the historical section the publications date may be a little later than previously announced.

RESEARCH GRANTS

Members are reminded that some research funds are available from the Hutton Fund, the Mappin Trust and the Skinner Fund. Rules are printed in Proceedings 97 pp. 97-99, 101-102 and 104-105.

HONOURS

Dr. W. M. Hamilton, F.R.S.N.Z., and Dr. F. B. Shorland, F.R.S.N.Z., have been awarded the New Zealand Association of Scientists' medal for outstanding service to science.

CALENDAR OF MEETINGS

Information on national and international scientific meetings to be held in New Zealand between April, 1971, and April, 1972, should be sent before 15 February, 1971, to Dr. E. B. Kidson, 13 Charlotte Street, Nelson.

AGRICULTURAL SCIENCE

Agricultural Science Conference Week. 23-27 August, 1971, at Lincoln College.

Those taking part include the Soil Science Society, Hydrological Society, Farm Management Society, Soil Conservators Association, N.Z. Institute of Agricultural Science.

INTERNATIONAL UNION FOR QUATERNARY RESEARCH (INQUA)

The IXth INQUA Congress is to be held in Christchurch from 2-10 December, 1973. This will be the second time the congress has been held outside Europe. The 1973 Congress is being organised by a committee under the chairmanship of Prof. Maxwell Gage, with Prof. Jane M. Soons as secretary.

INQUA seeks to bring together those working on all aspects of the Quaternary — from tectonics to human pre-history, and so its scope is far wider than can be covered by any one scientific discipline. Accordingly, each country belonging to INQUA sets up a National Committee for Quaternary Research. In New Zealand it has been set up by the Royal Society, the present chairman being Dr. R. P. Suggate and the secretary Mr. C. G. Vucetich.

INQUA attempts to stimulate co-operation on particular topics through the organisation of commissions and subcommissions, some for regional purposes, other concerned with world-wide problems. New Zealand has representatives on several of these groups, and in addition Prof. Soons is a Vice-President of INQUA. The principal commissions of interest to New Zealand are those concerned with Quaternary Stratigraphy (with sub-commission on on stratigraphy nomnclature and the lower boundary of the Pleistocene), Tephrochronology, Neotectonics, Shorelines and Quaternary Biology. The first circular will be sent out early next year.

NUTRITION SOCIETY

The Nutrition Society will hold its Annual Meeting in conjunction with the Fourth Asia/Oceania Congress of Endocrinologists at Auckland University 31 January to 6 February, 1971.

SOCIETY FOR SOCIAL RESPONSIBILITY IN SCIENCE

After numerous discussions it seems that *at present* there is no need for formation of such a society in New Zealand. The intentions of such a society are already to a certain extent carried out by the Royal Society. It regularly sets up committees to investigate and report on controversial issues. The reports are published. Recent examples are The Omega System, Oil Pollution, Fallout from French Nuclear Tests. Currently a committee is investigating the evidence for the relationship of coronary heart disease to animal fats (of direct concern to our dairy industry); a committee is studying the use and control of pesticides and herbicides in N.Z., and the adequacy of control, monitoring, research, etc.; a committee on problems of the environment is being set up in response to a request from the International Council of Scientific Unions.

The Member Bodies' Committee considers that each member body should keep a watching brief on the activities which involve its own scientific discipline; that this should be the concern of each member of a Member Body.

The subject of Social Responsibility will be placed automatically on each agenda of M.B.C. meetings. Any person or Member Body may request that a particular problem be included for discussion.

It is intended to keep open the question of the need for a separate Society for Social Responsibility in Science. The need may arise later.

EDITORIAL

Associate Editors in botany and geology are still needed.

XII NEW ZEALAND SCIENCE CONGRESS

This will be held in Palmerston North early February, 1972. It is being organised by Manawatu Branch.

INTERNATIONAL MEETINGS

The following delegates attended international meetings during 1970:—

SCAR	Oslo	17-22 August	R. D. Adams (R. W. Willett)
IMU	Nice	1-10 September	J. A. Kalman
ICSU	Madrid	23-29 September	G. W. Markham
SCIPB	Rome	28 September to 2 October	G. A. Knox J. A. R. Miles
IUBS	Washington	4-9 October	G. W. Butler

OBITUARY

We record with regret the death of Sir Charles Cotton, F.R.S.N.Z., Professor Emeritus of Victoria University, on 29 June, 1970. Sir Charles was Associate Editor of the Society's Transactions for many years until his death.

ROYAL ASTRONOMICAL SOCIETY

The Royal Astronomical Society is celebrating its Fiftieth Jubilee on 21-22 November. There will be a public exhibition at the Carter Observatory.

ROYAL SOCIETY OF NEW ZEALAND — CHANGE IN FORM OF TRANSACTIONS

The last Annual Meeting of Fellows decided to discontinue the present system of issuing separate papers in several series or sections (at present Biological Sciences, Earth Sciences and General). Instead, the Society will produce its regular publication in the form of a single, quarterly journal containing papers of acceptable quality in all its disciplines. This new serial publication will be known as the *Journal of the Royal Society of New Zealand,* and will begin with Volume *1*. Biographically, a new title is necessary. The *Transactions* have already had a complicated history—Volume *18* (1886) was also described as Volume *1* of a "New Series". Volumes *41-57* had "New Issue" on their title pages. From Volume *58,* the term "Quarterly Issue" was used. Since 1961 the divisions of the *Transactions* have been known both as "Sections" and "Series". The new *Journal* will be, in effect, a continuation of, or successor to, the *Transactions.* It is intended, therefore, to conclude the present system with the completion of Volume *12* (Biological Sciences), Volume *8* (Earth Sciences) and Volume 2 (General) about the end of this year. The new quarterly *Journal* will start in 1971.

The change in method of publication will provide an opportunity to change the format to the international size B5, 250 x 176 mm.

The subscription will be $10.00 to members and $18.00 to non-members of the Society.

The Society's annual *Proceedings* will be continued in the same form as at present, continuing the volume numbering which was begun with the first issue of *Transactions and Proceedings* in 1869.

D.F.J. LTD.

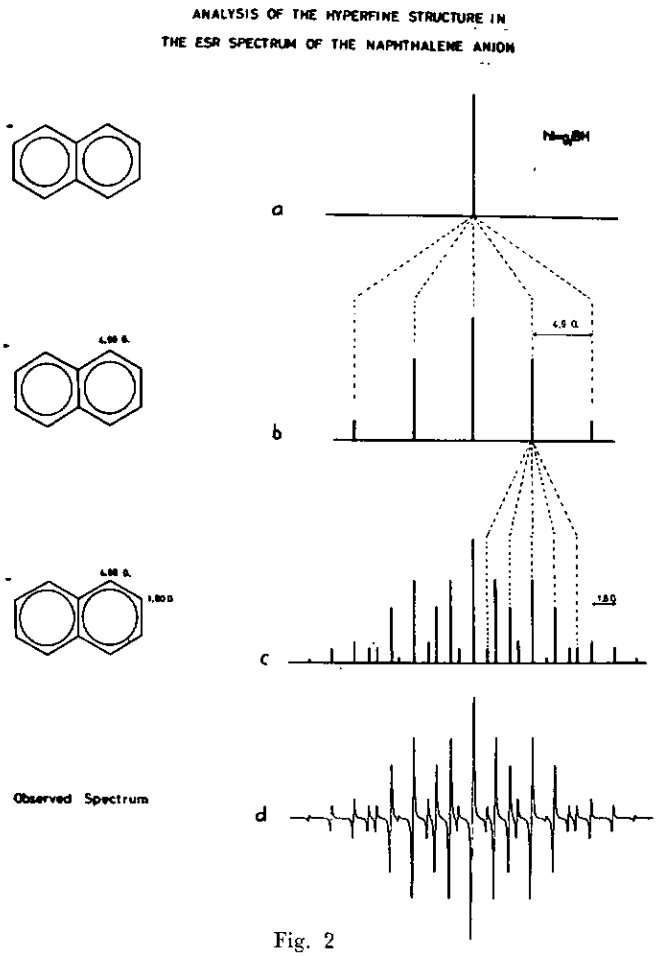
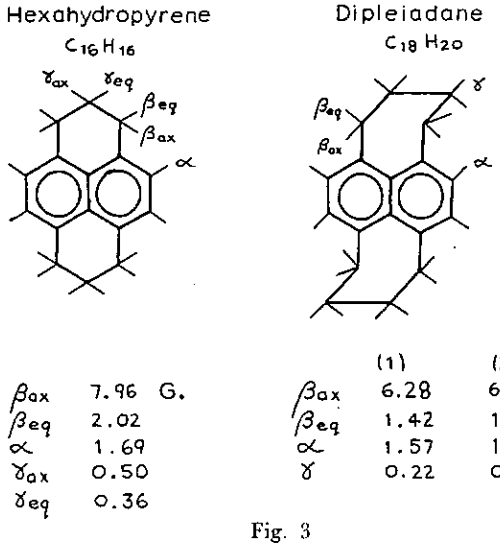


Fig. 2



			(1)	(2)
β_{ax}	7.96 G.	β_{ax}	6.28	6.16
β_{eq}	2.02	β_{eq}	1.42	1.57
α	1.69	α	1.57	1.57
γ_{ax}	0.50	γ	0.22	0.22
γ_{eq}	0.36			

Fig. 3

anions shown in Figure 3. The former of these was obtained commercially while the later was synthesised by Mr. D. Leonard to whom I am very grateful for the gift of a small sample.

The interest in these two radical anions from an ESR point of view lay in: (a) the effect of the aliphatic substituents on the coupling constants of the aromatic protons compared with the anion radical of the unsubstituted naphthalene anion radical; (b) the extent of transfer of unpaired spin density from the aromatic ring system into the aliphatic side chains; (c) what conformational information could be obtained from spectra of the two species. The hexahydropyrene anion had been studied previously, but its ESR spectrum had been analyzed in terms of a single γ coupling constant; if one examines molecular models of the compound it would appear that the four γ protons may be divided into two sets which are in two different geometric environments—thus one would predict two γ coupling constants for these protons rather than the one previously observed. So we prepared the radical anion by reduction of the parent compound with potassium in 1.2-dimethoxyethane and obtained the ESR spectrum at —95°c shown in Figure 4. This was identical in all respects with that which had been reported before and so provided us with a check on our methods of preparation and ESR instrumentation. We attempted to synthesise this spectrum using the coupling constants previously reported and obtained a spectrum that agreed in position but not in intensity of lines with the observed one.However, using the set of coupling constants given in Figure 3 we obtained a theoretical spectrum which is in perfect agreement (Figure 4).

Further consideration of molecular models indicated that hexahydropyrene could exist in either chair or boat forms. We could not resolve the spectrum at —95°C into the sum of spectra of two such species, but from a temperature dependence study we observed drastic changes in the spectrum as we raised

EPR SPECTRUM OF HEXAHYDROPYRENE ANION IN 1,2 DIMETHOXYETHANE WITH K⁺ AS COUNTER-ION

FIGURE I(a) Experimental TEMP.= -95°C

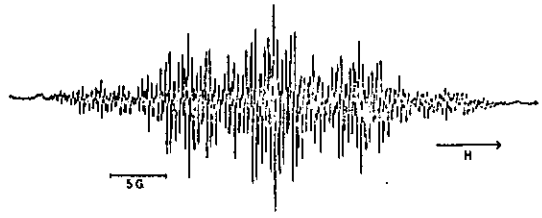


FIGURE I(b) Computer Simulated (Linewidth is 0.1 G.)

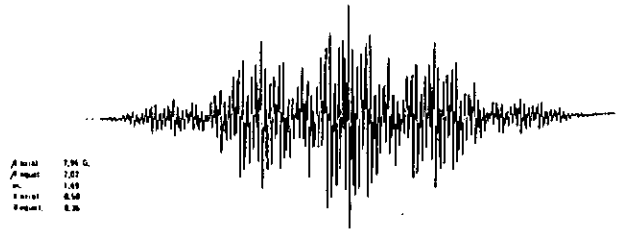
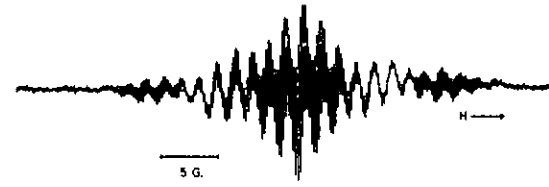


Fig. 4

EPR SPECTRUM OF DIPLEIADANE ANION IN 1,2-DIMETHOXYETHANE WITH K⁺ AS COUNTER-ION

Experimental TEMP.=-95°C



Computer Simulated (Linewidth is 0.1 G.)

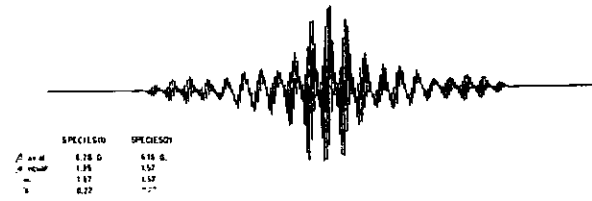


Fig. 5

the temperature. Certain lines became very broad due to a phenomenom known as the Linewidth Alternation effect and this could be analyzed in terms of interconversion between the two forms. From the ESR spectrum at +23°c we calculated the rate of interconversion at this temperature to be $\sim 10^8 sec^{-1}$. Also at this temperature only one γ proton coupling constant of value 0.41 Gauss was observed, and this may be reconciled with our seeing the average (0.43 Gauss) of the two values we had observed at —95°c.

We next considered the anion radical of dipleiadane. This compound is very similar to hexahydropyrene in that it may exist in two forms, but it would appear from molecular models that the introduction of another methylene group into the aliphatic ring leads to considerably more strain in this part of the molecule. Thus we hoped to obtain from ESR spectra of the dipleiadane anion, evidence of two forms and if possible, an estimate of the extent of distortion in the molecule.

The radical anion was prepared again by reduction with potassium in 1,2-dimethoxyethane and was the usual olive green colour which is characteristic of substituted naphthalene radical ions. However, this time it was only stable for 6-8 hours compared with days in the case of the hexahydropyrene anion which was our first indication that the molecule may be rather strained. We obtained the ESR spectrum at —95°c shown in Figure 5. This has a number of interesting features of which the most notable is the lack of resolution on either side of the central group of lines. We tried to simulate this spectrum using only one set of coupling constants and found that it was not possible to obtain this feature. So we considered the possibility of there being two species present at this temperature with slighly dierent β_{ax} and β_{eq} coupling constants. Using the two sets given in Figure 3 we obtained the theoretical spectrum shown in Figure 5 and one can see that it is in quite good agreement. We assigned the two species to the boat and chair forms

of dipleiadane, although it is not possible to assign either set of constants to any one form. It is also not possible to estimate the extent of distortion other than to say that the reason why the two β coupling constants should be different in one form compared with the other is that the distortions are probably different in each form.

Confirmation of the presence of chair and boat forms of dipleiadane at −95°c was obtained from the temperature dependence of the ESR spectrum. A very similar spectrum to that obtained for hexahydropyrene anion at +23°c was obtained for the dipleiadane anion at +55°c. If one assumes that thermal energy is responsible for this interconversion, then one may conclude from this that the activation energy for interconversion in the later case is higher than in the former. This was a further indication that there was more steric hindrance in the dipleiadane molecule than in hexahydropyrene. Unfortunately the unstable nature of the dipleiadane anion at high temperatures gave rise to a very poor signal to noise ratio. in spectra, and so it was not possible to get an absolute value for this activation energy.

Having obtained the hyperfine coupling constants for these two species, we then considered what we could do with them: obviously we had obtained information concerning the geometry and conformation of these molecules, so we then tried to relate these constants to unpaired spin densities calculated from MO theory. So far we have considered only Huckel theory and thus we have been restricted to the π-electron system of the naphthalene ring and we have not been able to take into account the aliphatic substituents. By altering the Coulomb integrals for the 1,4,5,8 positions to allow for the inductive effect of these later groups, and using a value of $Q = -25.5$ Gauss, we obtained good agreement between observed and calculated spin densities for the aromatic protons in the 2,3,6,7 positions.

This is as far as has been reached in this project. In the future we plan to study the ESR spectra of these radicals in more polar solvents such as 2-methyltetrahydrofuran and diethylether where we would expect to get ion pairing effects. We also plan to undertake some more sophisticated MO calculations using Extended Huckel and Self Consistent Field theory.

I wish to thank my supervisor Dr. R. F. C. Claridge for many hours of help and discussion and Dr. T. Seed for the use of his ESR spectrometer.

LIST OF FIGURES

ICI PRIZE 1970

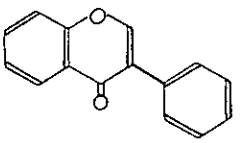
The ICI prizewinner for 1970 was Dr. E. C. Wong. Dr. Wong was Chairman of the Manawatu Branch 1969-70, and is now Manawatu delegate to Council. *Studies on Flavanoid Biosynthesis* is a short account of the work for which he was awarded the prize.

STUDIES ON FLAVONOID BIOSYNTHESIS

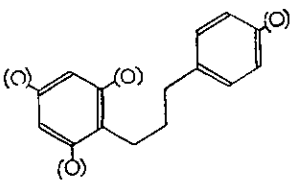
E. Wong

Applied Biochemistry Division, D.S.I.R., Palmerston North

My interest in the flavonoids came first via the isoflavones, oestrogenic compounds having the cyclic nucleus shown in (I). These compounds occur in pasture legumes and may cause infertility in grazing animals. Structurally and biogenetically they are closely related to the flavonoid compounds, which are derivatives of 1,3-diphenylpropane (II). Many classes of phenolic natural products are included within the flavonoids, differing structurally one from another in the state of oxidation of the central three carbon atom fragment (Fig. 1). The biosynthesis of isoflavones is thus but a special case of the much broader problem of flavonoid biosynthesis.



(I) *Isoflavone skeleton*



(II) *Flavonoid skeleton, $C_6C_3C_6$*

When I commenced these studies in 1962, it was known that the $C_6C_3C_6$ skeleton common to the flavonoids comes from both of the two known routes to aromatic compounds, viz. the acetate and shikimic acid pathways. Further, it was believed that chalcones pro-

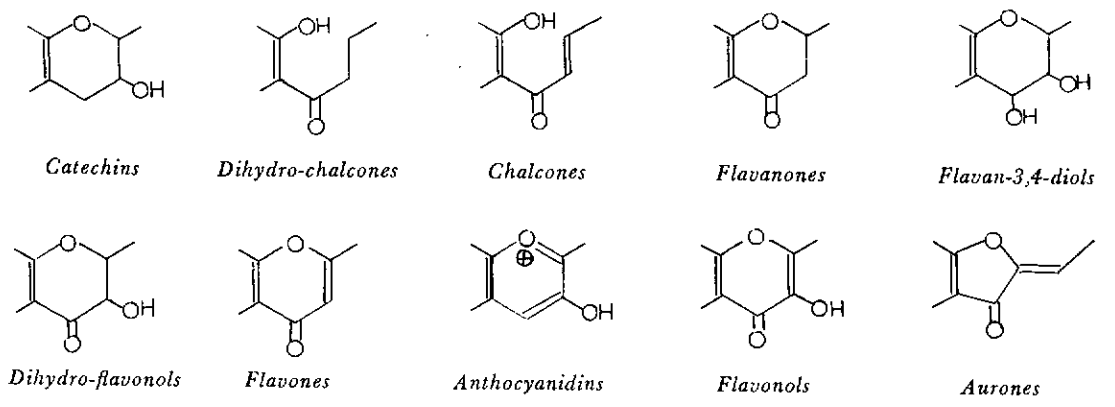


Fig. 1. Partial skeletal structures for the flavonoid classes.

bably represent the primary flavonoid product. By means of feeding experiments using radioactive precursors, it has since been shown[1,2] that chalcones are converted into many other classes of flavonoids, including isoflavones. Similar *in vivo* tracer studies[3] and chemico-genetical studies[4] have revealed other biogenetic relationships subsequent to the chalcone stage. The biogenetic interrelationships of the different classes of flavonoids based on such studies can be summarised in Fig. 2.

The scheme shown above indicated only broad biogenetic relationships. To learn more about the details of the pathway and the mechanisms involved in the various transformations, biochemical studies at the enzymic level were initiated. In 1966, an enzyme catalysing the isomerisation of chalcones (e.g. III) to flavonones (e.g. IV) was isolated,[5] and the properties of this isomerase have since been studied in some detail.[6] Since the majority of flavonoids contain a central heterocyclic ring, it seemed reasonable to believe that flavanones represent the primary heterocyclic intermediate to other flavonoid types. The isomerase enzyme would thus seem to be occupying a key position in the biosynthetic pathway. Further experiments however revealed that flavanones and chalcones are biochemically interconvertible and this raised the question whether both chalcone and flavanone are necessarily involved

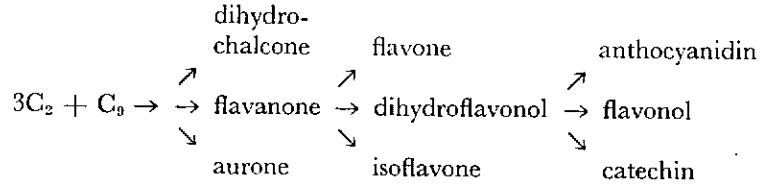
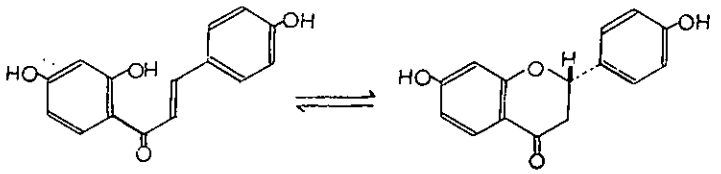


Fig. 2. Probable biogenetic interrelationships among the different classes of flavonoids, based on tracer and chemico-genetical studies.



III IV

as obligatory intermediates in biosynthesis of other flavonoids.

To settle this important question a double-labelling experiment was devised where a mixture of equal amounts of ^{14}C-chalcone and (-)-T-flavanone was fed as precursor. The ^{14}C/T ratio of the flavonoid product as a function of time was determined and used to indicate whether the product was formed more directly from the chalcone or the flavanone. The general plan of the experiment is illustrated in Fig. 3. Results obtained[7] showed that, contrary to expectations, flavanone is not a more immediate precursor for other classes of flavonoids than chalcone. This novel finding has been substantiated by other experimental evidence[8] and the biogenetic scheme shown in Fig. 2 has now accordingly to be modified as follows:

flavanone

$\Downarrow\Uparrow$

$3C_2 + C_9 \rightarrow$ chalcone $\rightarrow$ other flavonoids

Since the different classes of flavonoids are derived from chalcone without prior heterocyclic ring formation, and since they differ from the latter only in the state of oxidation of the central C_3 fragment, biochemical oxidation (and reduction) reactions involving the chalcone nucleus would seem to be key steps in the elaboration of these compounds. As a possible example of the types of reaction involved, the finding of hydroxybenzalcoumaranone (VI) as an oxidation product of chalcone (V) by cell-free extracts of soybean is of interest.[9] This compound readily dehydrates to an aurone, and its existence strongly suggests a mechanism for aurone biosynthesis as shown in Fig. 4. Other modes of oxidation of chalcone conceivably would lead to intermediates for other classes of flavonoids. Work in progress in this laboratory with isolated enzymes promises to be of interest in this connection.

Biosynthesis of the isoflavone nucleus from intermediates of the flavonoid pathway requires a rearrangement step involving the aromatic B ring. This step most probably takes place also at the chalcone stage. On the basis of comparative structural anatomy and other indirect evidence, it can be argued[10] that this is also the key step to other classes of biologically interesting compounds such as rotenoids, pterocarpans and coumestans having in common the branched C_{15} skeleton.

REFERENCES

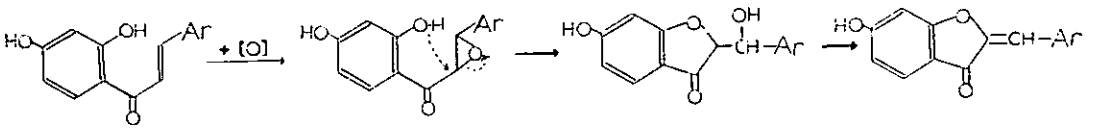
1. For reviews see: H. Grisebach, in *Chemistry and Biochemistry of Plant Pigments* (edited by T. W. Goodwin) p. 279, Academic Press, London (1965); H. Grisebach in *Recent Advances in Phytochemistry* (edited by T. J. Mabry, R. E. Alston and V. C. Runeckles), Vol. 1, p. 379, Appleton-Century-Crofts, New York (1968).

2. Wong, E., Biosynthesis of Flavonols, *Chem. & Ind.*, (1964) 1985; Wong, E., Flavonoid Biosynthesis in *Cicer arietinum, Biochim. Biophys. Acta*, (1965), **111**, 358; Wong, E., Occurrence and Biosynthesis of 4′,6-Dihydroxyaurone in Soybean, *Phytochem.* (1966), **5**, 463; Wong, E. and Moustafa, E., Flavanone Biosynthesis, *Tetrahedron Letters*, (1966), 3021.

$^{14}C/T > 1$ $^{14}C/T > 1$ $^{14}C/T = 1$ $^{14}C/T < 1$ $^{14}C/T < 1$

flavonoid products ← chalcone ← [^{14}C-chalcone ⇌ (-)-T-flavanone] → (-)-flavanone → flavonoid products

Fig. 3. General plan of double labelling experiment and expected results depending on whether chalcone or flavanone is the more immediate precursor.



Ar = —p-C_6H_4OH

Possible mechanism for aurone biosynthesis

Fig. 4

3. Wong, E., Mortimer, P. I. and Geissman, T. A., Flavonoid Constituents of *Cicer arietinum*, *Phytochem.*, (1965), **4**, 89.

4. Wong, E. and Francis, C. M., Flavonoids in Genotypes of *Trifolium subterraneum*. I—The Normal Flavonoid Pattern of the Geraldton Variety, *Phytochem.*, (1968), **7**, 2123; II—Mutants of the Geraldton Variety, *ibid.*, 2131; III—Varietal Differences, *ibid.*, 2139.

5. Moustafa, E. and Wong, E., Purification and Properties of Chalcone-Flavanone Isomerase from Soya Bean Seed, *Phytochem.*, (1967), **6**, 625.

6. Hahlbrock, K., Wong, E., Schill, L. and Grisebach, H., Comparison of Chalcone-flavanone Isomerase Heteroenzymes and Isoenzymes, *Phytochem.*, (1970), **9**, 947.

7. Wong, E. and Grisebach, H., Further Studies on the Role of Chalcone and Flavanone in Biosynthesis of Flavonoids, *Phytochem.*, (1969), **8**, 1419.

8. Wong, E., The Role of Chalcones and Flavanones in Flavonoid Biosynthesis, *Phytochem.*, (1968), **7**, 1751.

9. Wong, E., Aurone Biosynthesis II. Formation of 4′,6-Dihydroxy-2-(α-hydroxybenzyl)-coumaranone from 2′,4,4′-Trihydroxychalcone by Cell-free Extracts of Soybean, *Phytochem.*, (1967), **6**, 1227.

10. Wong, E., Structural and Biogenetic Relationships of Isoflavonoids, *Fortschritte d. Chem. org. Naturst.*, (1970), **28**, 1.

Current Chemistry

STRUCTURE-CYTOKININ ACTIVITY RELATIONSHIPS

H. Young, B.Sc.(Hons.), Ph.D.

Plant Diseases Division, D.S.I.R., Auckland

Cytokinins are a class of growth-promoting plant hormones originally defined as compounds which stimulated cell division in certain plant tissues. However, this limited definition is no longer sufficient. These chemicals have been shown to evoke a range of responses, many of which overlap with those caused by the gibberellins and auxins. The situation is further complicated by the fact that cytokinins, gibberellins, auxins and other plant hormones, e.g. abscisic acid (an inhibitory hormone), interact with each other in the plant to produce a given biological response. The interaction of the different plant hormones in regulating normal growth appears to be complex but little is yet known about it. The main effects of cytokinins are induction of cell division, enlargement of leaf disks of dicotyledonous plants, breaking dormancy of seeds and buds, causing lateral bud development and formation of parthenocarpic fruit. Cytokinins also have an inhibitory effect on certain types of growth. Natural cytokinins have been shown to occur in germinating seeds, developing fruits, roots and sap, but always at very low levels.

The majority of compounds which have cytokinin activity are derivatives of adenine with substituents at two positions. At one position the substituent may be alkyl, substituted alkyl and alkenyl, cycloalkyl, benzyl, substituted benzyl etc. The other position is usually occupied by hydrogen or ribofuranosyl. Adenine derivatives with substituents at other ring positions, e.g. 2-methylthio,[1] and some urea and thiourea derivatives also possess cytokinin activities.[2]

The first naturally occurring compound with cytokinin activity to be isolated in a crystalline form is zeatin, 6-(4-hydroxy-3-methybut-*trans*-2-enylamino) purine. Letham [see Letham, Shannon, and McDonald; Tetrahedron, *23*, 479 (1967) and references cited], then working at the Fruit Research Division, D.S.I.R., obtained approximately 1 mg of highly active crystals from 60 kg of sweet corn. This compound has been synthesized and small quantities are commercially available.

We have been interested in the relationship between molecular structure and cytokinin activity[3]. Adenine derivatives with a variety of functional groups on the exocyclic nitrogen and at the 9-position were required for biological testing on intact plants or excised plant parts. Under these conditions 6-benzylamino-9-(tetrahydropyran-2-yl) purine, (*1* R′=benzyl, R″=tetrahydropyranyl) has been shown to be more active than 6-benzylaminopurine (1 R′=benzyl, R″=H). The 9-tetra-hydropyranyl group therefore appears to be a desirable structural feature.

The usual method of synthesizing N^6-substituted adenine is by the condensation of the appropriate amine with 6-chloropurine in n-butanol. The hydrogen chloride produced by the reaction is neutralised by an excess of the amine or by the addition of an indifferent amine, e.g. tri-ethylamine. A similar reaction with 6-chloro-9-tetrahydropyran-2-ylpurine would give the desired compounds but this method suffers from the fact that the amines

are not readily available. Therefore a reaction which uses the more readily available halides or alcohols (as tosylates) was sought. Adenosine condenses with 3-methylbut-*trans*-2-enyl bromide or benzyl bromide in dipolar aprotic solvents to give 1-substituted adenosine. The 1-substituted adenosine then readily rearranges to the 6-(N-substituted amino)-9-β-D-ribofuranosylpurine. It was hoped that a similar reaction could be carried out with 9-tetrahydropyranyladenine. However the hydrogen bromide produced by the reaction caused hydrolysis of the 9-tetrahydropyranyl group. Addition of an organic or inorganic base, e.g. sodium carbonate, as a hydrogen bromide scavenger resulted in the recovery of the starting materials. However if a strong base like sodium hydride was used to form the anion of the 9-tetrahydropyranyladenine before the halide was added, a reasonable yield (20-50%) of the 6-(N-substituted amino)-9-tetrahydropyranyl purine could be obtained after chromatography. The reaction is complicated by the formation of the 6-(N-disubstituted amino)-9-tetrahydropyranylpurine; even when less than one mole of sodium hydride per mole of 9-tetrahydropyranyladenine was used. Fortunately 9-tetrahydropyranyladenine could be acetylated in high yield at the exocyclic nitrogen with acetic anhydride in the absence of a base. Alkylation of the anion of 6-acetamido-9-tetra-hydropyranylpurine (*1* $R' = CH_3CO$, $R'' =$ THP) followed by alkaline hydrolysis, furnished 6-(N-substituted amino)-9-tetrahydropyranylpurines in good yields. Using this reaction, compounds of structure *1* in which; $R'' =$ tetrahydropyranyl and $R' =$ 3-methylbut-*trans*-2-enyl; 2-, 3-, and 4-fluorobenzyl; 2-methylbenzyl; 3-methylbut-3-enyl; 3-methyl-4-(tetrahydropyran-2-yloxy)but-*trans*-2-enyl; and 2,4-dinitrophenyl, were prepared. Of these 6-(3-methylbut-*trans*-2-enylamino)-9-(tetrahydropyran-2-yl) purine and 6-(3-fluorobenzylamino)-9-(tetrahydropyran-2-yl) purine showed high cytokinin activity in the tobacco leaf disk senescence assay. Two compounds, 6-(3-methylbut-3-enylamino)-9-(tetrahydropyran-2-yl) purine and 6-(3-methyl-4-tetrahydropyran-2-yloxybut-*trans*-2-enylamino)-9-(tetrahydropyran-2-yl) purine, have not been tested but should show high cytokinin activity.

The 9-tetrahydropyranyl group is easily cleaved from the purine ring by mild acid hydrolysis and in the plant it could be subject to chemical or enzymic cleavage. To test whether these 9-tetrahydropyranyl purines are active *per se* or cleavage of the 9-tetrahydropyranyl is necessary for cytokinin activity 9-methoxymethyl-6-(3-methyl-but-*trans*-2-enylamino) purine and 9-cyclohexyl-6-(3-methylbut-*trans*-2-enylamino) purine have been synthesized. The 9-methoxymethyl group is more resistant than the 9-tetrahydropyranyl group to acid hydrolysis. The cyclohexyl group is resistant to acid hydrolysis but has approximately the same steric requirement as the tetrahydropyranyl group. A comparison of these three compounds showed a definite correlation between cytokinin activity and acid lability of the 9-substituent. It is probable that the cytokinin activity of this type of compound is due partly to the 9-substituted molecule and partly due to the hydrolysis product since it is unlikely that the 9-cyclohexyl group would be easily cleaved, if at all, in the plant tissue.

References

1. S. M. Hecht, N. J. Lenard, W. J. Burrows, D. J. Armstrong, F. Skoog, and J. Occolowitz; *Science*, **166**, 1272 (1969).
2. D. S. Letham, *Ann. Rev. Plant Physiol.*, **18**, 349 (1967) and ref. cited.
3. H. Young and D. S. Letham; *Phytochemistry*, **8**, 1199 (1969).

OBITUARY

Professor N. L. Edson, B.Med.Sc., M.B., Ch.B.(N.Z.), Ph.D.(Cantab.), F.R.S.N.Z., Hon.F.N.Z.I.C.

The death of Professor Norman Lowther Edson on 12 May 1970, saw the end of a life devoted to the development of biochemistry and of biochemical education in New Zealand.

Born in Auckland in 1904, Norman Edson reecived his early education at Auckland Grammar School. He entered the University of Otago as a Junior National Scholar and graduated B.Med.Sc. in 1927 and M.B., Ch.B. in 1931. He then spent two years in the Chemistry Department at Otago and was awarded a Certificate of Proficiency (M.Sc. Standard) in Chemistry before proceeding to post-graduate biochemical studies in Sir Frederick Gowland Hopkins's laboratory at Cambridge University.

In 1937 Dr. Edson returned to Otago University to a lectureship in biochemistry within the Department of Physiology, a position he held until 1940, when he resigned to become full-time Director of the recently-established Travis Laboratory, an independent research unit within the Medical School devoted to the study of tuberculosis. In 1944 Dr. Edson returned to full-time teaching as Associate Professor of Biochemistry and in 1949, with the creation of a separate Department of Biochemistry, he was appointed first Professor of Biochemistry in the University of Otago. He held this position until his retirement in 1967.

Professor Edson was a dedicated teacher under whose guidance many young biochemists now holding important positions throughout the world were first introduced to biochemistry as a discipline in its own right. His research interests in intermediary metabolism, stimulated by his fruitful association at Cambridge with H.A. (now Sir Hans) Krebs, subsequently developed in many directions. His studies of the metabolism of polyols and of the biochemistry of the Mycobacteria were pioneering work of the greatest significance.

Professor Edson was a member of the Medical Research Council in its early years and made an important contribution to public health as a member of the Committee on Fluoridation of Water Supplies. He was a foundation member of the Otago Medical School Research Society, and first editor of the Proceedings of the University of Otago Medical School.

Professor Edson was forced by ill health to retire in 1967 at the early age of 63 and his lifelong dedication to biochemistry was recognised upon his retirement by his appointment as an Emeritus Professor in the University of Otago and his election to the Honorary Fellowship of the Institute. His death at the age of 66 deprived New Zealand of one of its most respected biochemists. The sympathy of the Institute of Chemistry is extended to Mrs. Edson and to his family of two sons and a daughter.

NORMAN LOWTHER EDSON (1904 - 1970)

A committee has been formed to organise a fund for a memorial to the late Professor N. L. Edson, first Professor of Biochemistry in the University of Otago.

It is hoped that sufficient funds will be raised to endow two prizes, one for biochemistry in the medical course, the other for biochemistry in a science course.

All friends, colleagues and students of Professor Edson are invited to support this project. Please send your contribution to Mr. C. A. Monroe, Secretary to the Faculty of Medicine, University of Otago, P.O. Box 913, Dunedin.

Please make cheques payable to the Edson Memorial Prize Fund. All contributions will be acknowledged.

For the Edson Prize Committee,

G. B. PETERSEN, *Chairman.*

RETIREMENT

MR. RONALD HICKS, ARIC, FIPHE, FInstWPC, FNZIC

Mr. Hicks retires from his position as Chief Chemist and Treatment Works Superintendent, Drainage Department, Auckland Regional Authority on 27 March 1971.

Mr. Hicks began his career with Melling and Hardern, Public Analysts, in Manchester. He was educated at Salford Technical College (now the University of Salford) and was appointed Chemist at the Manchester Sewage Works in 1927. From 1933 to 1940 Mr. Hicks served as Manager and Chemist of the Gravesend Sewage Works, and he then became General Manager of the Drainage and Purification Department at Hamilton, Scotland, 1940-49. Mr. Hicks joined the Auckland Metropolitan Drainage Board in 1949, and has been closely associated with the major developments in sewage treatment in Auckland over a period of 21 years.

Throughout his career Mr. Hicks has been active in the fields of effluent treatment and pollution. He spent 1958 in San Jose, California working on methods for the treatment of wastes from the canning industry. In recent years he has investigated odour control in sewage treatment, plastic media as filters, improved methods for treating meat works wastes, and other applied research topics.

Mr. Hicks is a member of the governing body of the International Association for Water Pollution Research. He attended the International Conference of this association in San Francisco in 1970. He was a foundation member of the Auckland Air Pollution Research Committee, and submitted a paper (with Mr. C. G. Martin) to the International Conference on Air Pollution in Washington in 1970.

Mr. Hicks has been a member of the Institute since 1952, and is well respected for his achievements in the difficult field of waste treatment. He plans to make an overseas tour in 1971 to study recent developments in waste water technology, before returning to Auckland. Members of the Institute wish him an enjoyable trip, and a long and happy retirement.

CHEMISTRY TODAY

A Refresher Course for Secondary School Teachers 10 - 14 May 1971

A 5-day full-time course will be held in the first week of the May vacation 1971 at the University of Auckland. The course will consist of a series of lectures, seminars and laboratory sessions. Modern developments in the major branches of chemistry will be covered, and there will be special emphasis on the subject matter of the sixth and seventh form chemistry curricula.

A brochure will be published in February 1971; copies may be obtained from the Department of University Extension, University of Auckland, Private Bag, Auckland.

IUPAC INFORMATION

Information has been received from IUPAC on forthcoming international symposia as follows:

1. Vth International Conference on Organometallic Chemistry — Moscow — 16-21 August 1971.
2. International Conference on Chemical Education — Sao Paulo, Brazil — 30 August - 3 September 1971.
3. EUCEPA (European Committee on Cellulose and Paper) — Symposium on Man-made Polymers in Papermaking — Helsinki, Finland — 5-8 June 1972.

C. J. Wilkins, Secretary,
National Committee for Chemistry.

BRANCH NOTES

AUCKLAND

Auckland Regional Authority

Mr. R. Hicks will retire on 27 March 1971 from his position as Chief Chemist and Treatment Works Superintendent. Mr. D. J. Ogilvie transferred from the Palmerston North City Council in March, and is now Water Chemist for the Authority. Mr. J. B. Richardson (formerly Lecturer at Auckland University) has been appointed Chemist (Drainage). Mr. P. Welsby is Senior Chemist at the Mangere Treatment Works.

N.Z. Fertiliser Manufacturers' Research Association

Mr. J. C. M. Devereaux has recently taken up a position as research chemist.

University of Auckland

Dr. B. F. Anderson and Dr. G. G. Dodson (both Auckland graduates) visited Auckland recently. They are both Research Fellows in Crystallography at Oxford University. Dr. Anderson has recently solved the structure of a new antibiotic, thiostrepton. Dr. Dodson and two other Auckland graduates, Dr. Sylvia Rumball and Dr. E. N. Baker, were collaborators with Professor Dorothy Hodgkin in the recent determintion of the structure of crystalline insulin.

Dr. John Aggett has returned from study leave at Imperial College, London, where he carried out research on spectroscopic techniques in collaboration with Professor T. S. West.

THE REGISTRY — 2/12/70

The following elections includes the first group of Graduate Members to be elected as Associates.

Election as Associates:

AIRD, Ronald Murray, B.E.(Chem.), B.Sc., N.Z. Dairy Research Institute, Palmerston North (Product Development Manager).

BOWMAKER, Graham Arthur, B.Sc.(Hons.), Ph.D.(Sydney), Chemistry Dept., Auckland University (Lecturer).

BROOK, David William, M.Sc.(Otago), King's High School, Dunedin (Teacher).

CHADDERTON, William Frederick, B.Sc., King's College, Otahuhu (Teacher).

COOKE, Alan, B.Sc., L.R.I.C., Cawthron Institute, Nelson (Senior Analyst).

DROMGOOLE, Sydney Herbert, M.Sc.(Auck.), Dept. of Medicine, Auckland University (Scientific Officer).

FERGUS, Brian Joseph, M.Sc.(Auck.), Ph.D. (McGill), N.Z. Forest Products Ltd., Auckland (Research Chemist).

GLASBY, Geoffrey Philip, M.A.(Oxon.), Ph.D. (Imp. Coll.), D.I.C., A.R.I.C., N.Z. Oceanographic Institute, Wellington (Scientist).

GUNN, Marcus Keith, B.Sc., U.E.B. Industries Ltd., Auckland (Research Chemist).

LAING, Kerry Richard, M.Sc.(Auc.), Chemistry Dept., Auckland University (Ph.D. Student).

LAWRENCE, Miss Valerie, B.Sc., Mt. Roskill Grammar School, Auckland (Senior Chemistry Teacher).

PERCIVAL, Henry Joseph, M.Sc., Ph.D.(Well.), N.Z. PACRA, Lower Hutt (Research Chemist).

TAYLOR, Allan Maurice, M.Sc.(N.Z.), Ph.D. (Penn.), F.G.A., Victoria University (Senior Lecturer in Geochemistry).

TURNER, John, B.Sc., International Paints of N.Z. Ltd., Wellington (Chief Chemist).

Graduate Members elected as Associates:

DAVEY, Kalvyn Frederick, B.Sc., Ivon Watkins Dow Ltd., New Plymouth (Production Supervisor).

ERCEG, Ivan Joseph, M.Sc.(Auck.), A. C. Hattrick Ltd., Auckland (Industrial Chemist).

HAY, Douglas Miller, B.Sc., B.E.(Chem.), N.Z. PACRA, Lower Hutt (Research Engineer).

MITCHELL, James William, B.Sc.(Hons.) (Cantuar.) Chemistry Dept., University of Canterbury (Ph.D. Student).

MOIR, Colin Harley, B.Sc.(Hons.) (Cantuar.), Kempthorne Prosser & Co. Ltd., Hornby (Asst. Works Manager).

NORRIS, Rodney John, B.Sc., Chemistry Division D.S.I.R., Gracefield (Scientist).

PAPPS, Murray Douglas, B.Sc.(Hons.) (Cantuar.), Unilever N.Z. Ltd., Petone (Production Manager).

WADDINGHAM, Donald Markham, B.Sc., B.A.L.M. Paints (N.Z.) Ltd., Auckland (Group Leader, Automotive Section, Technical Service Lab.).

Graduate Members:

BARRON, Peter Kenneth, M.Sc.(Auc.), Fletcher Industries Ltd., Auckland (Res. Chemist).

BARRY, Bernard John, Chemistry Dept., University of Waikato (Ph.D. Student).

DIXON, Alan Sydney, B.Sc.(Hons.) (Cantuar.), Lactose Co. of N.Z. Ltd. (Industrial Chemist).

EVANS, Alan Bruce, B.Sc.(Well.), Kodak N.Z. Ltd., Wellington (Quality Control Officer).

GAINSFORD, Allan Ross, B.Sc.(Hons.) (Cantuar.), Chemistry Dept., University of Canterbury (Ph.D. Student).

JORDAN, Stuart Andrew, M.Sc.(Auck.), Formica (N.Z.) Ltd., Papakura (Industrial Chemist).

JULL, Warwick Lloyd, B.Sc., Chemistry Dept., Auckland University (Student).

MILESTONE, Neil Brennan, M.Sc.(Well.), School of Science, University of Waikato, Hamilton (D.Phil. Student).

MOHI, Mrs. Heather Jeannette, B.Sc.(Hon.) (Otago),, c/o Drs. Perry and Fitzgerald, Dunedin (Graduate Technologist).

PARNELL, David Laurence, M.Sc.(Auck.), Formica N.Z. Ltd., Papakura (Industrial Chemist).

ROBINSON, Peter Graham, M.Sc.(Auck.), Chemistry Dept., Auckland University (Teaching Fellow).

ROWDEN, Murray Walker, M.Sc.(Cantuar.), B.A.L.M. Paints Ltd., Lower Hutt (Chemist).

WOOLHOUSE, Anthony David, M.Sc.(Well.), Pathology Dept., Wellington Hospital (Chemist).

WONG, Ronald James, M.Sc.(Auck.), Chemistry Dept., Auckland University (Ph.D. Student).

Resignations:

Miss S. Merrick, D. C. Rhodes.

Deaths:

The following deaths were recorded with regret. F. B. Cousins, L. W. Ruddle.

BOOK REVIEW

Noble-Gas Chemistry, by John H. Holloway, published by Methuen, London, 1968. 213 pages. Price U.K. 42s.

The author, a lecturer in chemistry at the university of Aberdeen, has divided this monograph into three parts: discovery and properties of the noble gas elements (40 pps, 100 refs.); weakly bonded species including clathrates (45 pps, 221 refs.); and chemical compounds (115 pps, 318 refs.). There is an index covering the work as a whole.

The first part includes an account of early attempts to promote reactions of the noble gases, particularly argon, which lead to the appreciation of the significance of their electronic structure to valence theory. Data on their physical properties is tabulated and the analytical determination by spectra, mass spectrometry and vapour-phase chromatography is described. Uses are considered; those on the largest scale being those of helium and argon as an inert shield in arc welding and metallurgy, e.g. helium in titanium refining. Balloons (helium) and light bulbs (argon) are smaller volume users. Helium, neon and argon are used in attaininig low temperatures, and neon, krypton and xenon are used in lighting equipment. Radon and Kr^{85} have some use in radiography.

Under weakly bonded "compounds" the writer discussed a wide range of short-lived species observed spectroscopically including ions, e.g. HeH+ (which has a bond strength about half that of the isoelectronic molecule H_2) and diatomic molecules such as HgHe and ArXe. Noble-gas clathrates include hydrates which have been known since 1896 and organic clathrates, especially those of hydroquinone. The specific binding of xenon by haemoglobin and myoglobin is briefly considered.

The third part describes the post-1962 chemistry of xenon and related work on krypton and radon. This section includes detailed reviewing of the range of known compounds, which is now fairly extensive, although still largely dependent on bonding of the noble gas atom to either fluorine or oxygen. Experimental details for preparations and reactions, spectroscopic and allied analyses of structures, and theoretical aspects of bonding are well covered. Under the heading of applications, the potential of xenon fluorides and xenic acid as oxidants is indicated.

This book makes interesting reading, especially because of the unusual attention given to reactions which do not occur and experiments which just failed (Yost and Kaye in 1933 ran out of xenon after trying to prepare chlorides but had planned further experiments with fluorine which would almost certainly have met with success).

M. J. TAYLOR.

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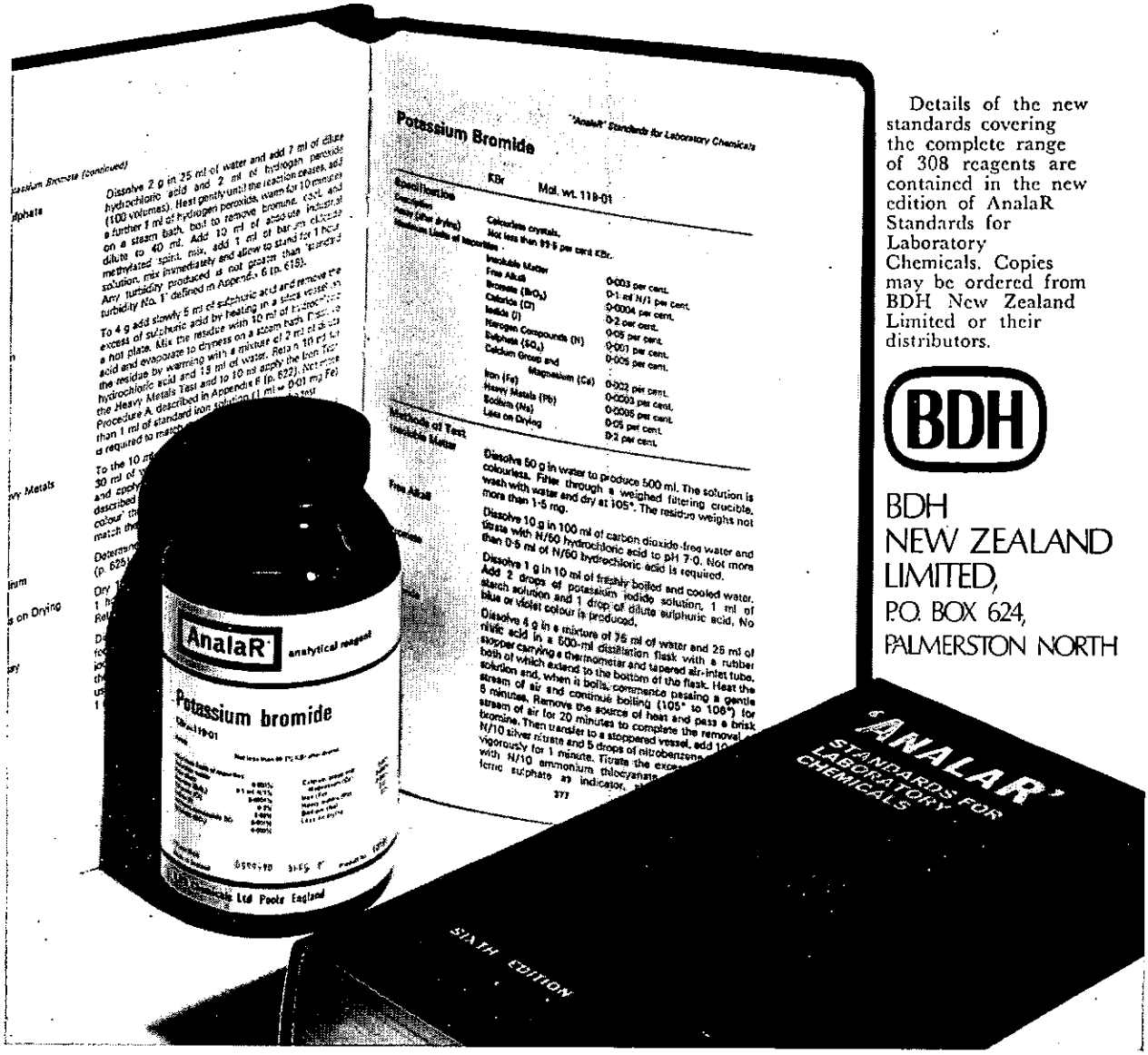

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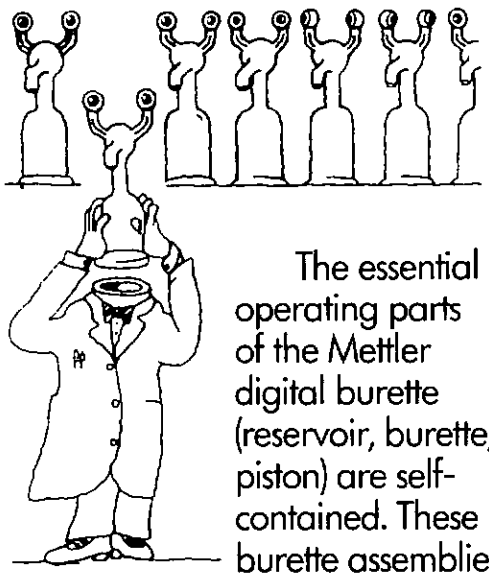

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