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REVIEW ARTICLE

FORMATION AND PROPERTIES OF SOME WOOD EXTRACTIVES*

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Abstract—Chemical and other data concerning the location and site of formation of heartwood extractives are discussed. The biological conditions in the transition zone adjacent to the heartwood boundary are briefly described and some properties of extractives are given. The classes of polyphenolic compounds found in the wood of *Eucalyptus* species are listed together with the details of ellagic acid derivatives which are the most common class in this genus.

INTRODUCTION

IT HAS been estimated that, on a value basis, about one-half of the wood used in a few years time will end up in the fibrous form. Also, the world's wood requirements for these purposes will double in the 1965–1980 period and triple by the year 2000.[1] Another estimate[2] indicates that the world increase in consumption in the 1965–1985 period for sawnwood, plywood and particle board will be 26, 154 and 345% respectively.[2] To meet these demands, increasing proportions of the world's wood requirements will come from new resources and from plantations. Some of the material from the new resources will be of a lower or a different quality to the wood currently used and may require modifications of the usual utilization procedures. On the other hand the quality of the plantation material will be improved to make it more suitable for utilization, for example by the large, automatic-production, low-pollution pulping units of the future.

One important feature of the quality of wood is uniformity and uniformity can be affected by the amount and type of extractives present. Extractives are defined as the non-structural components or secondary constituents of plants. Usually they can be removed with neutral solvents although dilute alkali is sometimes necessary. The amount of extractives in the wood of a tree is dependent on several factors and prominent amongst these is the amount of heartwood.

With the increasing use of new and different timbers and with the increasing standards required of plantation timbers, more information of extractives will be needed. A knowledge of the location of the extractives in wood is required so as to understand their effect in different conditions. Determination of the constitution of extractives is needed in order to rationally devise methods to control their effects in utilization processes. Also, knowledge of their formation in the tree will contribute to an understanding of the constitution of the

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[1] J. L. KEAYS, *Forest Prod. Lab. Rep.* VP-X-64, Canadian Forest Service, Vancouver (1970).

[2] J. C. WESTOBY, *Seventh All-Australia Timber Congress*, Perth (1969).

complex and polymerized components which form more than 75% of many extractives. There is also a need for geneticists to select superior trees, from an extractives point of view, for the establishment of new plantations. This paper gives a general discussion of these aspects and also summarizes information on the wood extractives of *Eucalyptus* species (Myrtaceae) which are being grown on an increasing scale throughout the world as a source of wood.

DISCUSSION

Location of Extractives

Extractives are present in greater amounts in the heartwood than in the sapwood. The changes in extractives content can be very abrupt at the heartwood periphery. Phenolic extractives are largely found in the wood rays but also can be found in the vessels and fibres and in some cases in specialised cells. Large amounts can be present in some species; for example, between 30 and 40% in some eucalypts. More is found in the outer heartwood than the inner heartwood.[3]

Most attention has been given in the past to the extractives which occur in the lumen of the cells. Extractives can also form coatings on the cell wall and on the pits so that in some cases they could interfere with the permeability and penetration of the wood. This loss of permeability is probably the reason why the drying of wet pockets in green wood is slowed[4] and why the collapse of some timbers is promoted.[5] However, it has been demonstrated[6] that in *Eucalyptus delegatensis* the lignin content must also be considered. The penetration of some woods with aqueous preservatives can be affected for the same reason. Phenolic coatings[4,5] of the lumens have been observed in some species and fatty coatings[7] in others.

Extractives can also be located in the capillaries in the cell walls. There is evidence that in the fresh sapwood of *Pinus resinosa* there is 25% free space in the hydrated S2 layers of the tracheid cell walls.[8] This space appears to exist as capillaries having cross-sections between 2 and 6 nm. Many compounds are small enough to diffuse into free space of this size, for example, the largest dimension of glucose is 0·63 nm and that of a flavonoid monomer about 1·5 nm. There is evidence from different studies that when the heartwood extractives are formed and the membranes containing them rupture, the smaller components may soak into the cell wall. Physical measurements have indicated that significant amounts of extractives are in the cell wall of the heartwood of some species.[9–11] In some cases, solvents which cause wood to swell can remove phenolic materials from the cell wall,[12] but in other cases they are not completely removed.[4,13] The cell wall extractives are probably largely responsible for the difference in dimensional stability, durability and strength that has been found between sapwood and heartwood. They might have a direct influence on the ease of pulping by reacting with lignin.

[3] W. E. HILLIS, in *Wood Extractives* (edited by W. E. HILLIS), p. 59, Academic Press, New York (1962).
[4] R. L. KRAHMER, R. W. HEMINGWAY and W. E. HILLIS, *Wood Sci. Technol.* **4,** 122 (1970).
[5] R. W. MEYER and G. M. BARTON, *Forest Prod. J.* **21,** 58 (1971).
[6] D. E. BLAND, *Wood Sci. Technol.* **5,** 17 (1971).
[7] A. B. WARDROP and G. W. DAVIES, *Austral. J. Bot.* **6,** 96 (1958).
[8] G. P. BERLYN, *Am. J. Bot.* **56,** 498 (1969).
[9] H. TARKOW and J. KRUEGER, *Forest Prod. J.* **11,** 228 (1961).
[10] F. F. WANGAARD and L. A. GRANADOS, *Wood Sci. Technol.* **1,** 253 (1967).
[11] D. E. BLAND and W. E. HILLIS, *Appita* **23,** 204 (1969)
[12] J. W. W. MORGAN and R. J. ORSLER, *Holzforschung* **23,** 48 (1969).
[13] W. E. HILLIS, unpublished data.

Localized Concentration of Extractives

Specialized cells or groups of cells (such as the resin canals in conifers) are found in some woods[14] and these may contain compounds appreciably different from those in the surrounding tissues. In addition, an injury to the developing cambial cells often gives rise to the formation of traumatic intercellular canals. They can vary greatly in size and are exemplified by the resin pockets in conifers and kino pockets in eucalypts.[14] Resin-soaked patches of wood are also found in coniferous species, and damage to living trees of some species can result in discoloured damaged wood of different types.

Site of Formation of Extractives

A previous summary[15] of evidence supported the view that phenolic extractives in heartwood or injured areas are formed *in situ* at the periphery of these areas. The following recent studies also support this view.

In Norway spruce (*Picea abies*) and many other trees, the fungus *Fomes annosus* is transmitted through the root system and spreads out from the centre of the tree as it moves upwards. A reaction zone is formed in the inner ray cells in the sapwood in front of the fungal attack and in spruce this zone contains appreciable amounts of lignans. GLC analyses of the reaction zone has shown increased amounts of lignans, of which hydroxymatairesinol is by far the major component.[16] In one case, the reaction zone contained 28 times more hydroxymatairesinol than that found in undamaged heartwood. Bioassay studies have shown that hydroxymatairesinol is inhibitory to *Fomes annosus*, whereas the other lignans studied have little effect.[16] The analysis of the different zones show that it is unlikely the lignans would be translocated from the cambial or sapwood regions of the tree to the reaction zones as their composition of lignans is different.

Frequently, clusters of cells of Western hemlock (*Tsuga heterophylla*) wood contain small deposits known as floccosoids. Microscopic examination shows that the contents of different cells varied in their appearance. The contents of different cells were dissected and amounts of about 1 ng have been analysed by gas chromatography. This showed that cells that are a few cells apart had different compositions. Some contain very largely conidendrin, others contain largely hydroxymatairesinol and some contain an unidentified lignan.[4] It is unlikely that these different compounds could be translocated so selectively through the rays to the heartwood periphery and appear as discrete entities in neighbouring cells. It is possible, however, that different degrees of acidity in the cells may have resulted in different lignans. The UV absorption spectra of the material in the rays of Western hemlock and the adjacent tracheids have been examined *in situ* with a microspectrophotometer. The ray contained non-aromatic material and this is presumably transformed to the lignan-like material in the tracheids at some point between these two cells.[4]

Examination of cross-sections of *Pinus radiata* trees showed there were marked changes in the relative proportions and compositions of the resin acids, fatty acids and fatty acid esters associated with heartwood formation. The proportion of resin acids and fatty acids increased substantially in the heartwood. There was little change in resin acid composition from outer sapwood to inner heartwood. However, the composition of sapwood fatty acids differed from that in the heartwood and from that of the sapwood fatty acid esters. Large

[14] H. E. DADSWELL and W. E. HILLIS, in *Wood Extractives* (edited by W. E. HILLIS), p. 3, Academic Press, New York (1962).
[15] W. E. HILLIS, *Wood Sci. Technol.* **2**, 241 (1968).
[16] L. SHAIN and W. E. HILLIS, *Phytopath.* **61**, 841 (1971).

reductions in the proportions and a marked change in the composition of fatty acid esters occurred from outer sapwood to heartwood.[17] These data support the view that these materials are formed *in situ* at the heartwood boundary.

The stereospecific isomers of the di- and tri-meric flavans found in the heartwood of *Acacia* species indicate that at least some of the polymeric processes responsible for their formation at the heartwood boundary are enzymically controlled.[18]

If the conclusions from the above chemical evidence are correct, then there must be considerable biological activity in the transition zone between sapwood and the heartwood or the injured area. Recently in these laboratories, evidence was obtained of increased respiration and of increased enzyme activity in the transition zone between sapwood and heartwood. The enzymes concerned were 6-phosphogluconate dehydrogenase and malate dehydrogenase, which are concerned with increased carbohydrate metabolism, and peroxidase and phenol oxidase. A more detailed knowledge of the biological conditions in the transition zone will help in understanding the processes forming heartwood extractives. This knowledge will also help in the elucidation of the structure of the polymeric compounds which form the major portion of extractives and whose constitution is largely unknown.

Alteration of the amount of heartwood and extractives commonly formed can probably be achieved by the selection of suitable trees for breeding. There are cases where normal heartwood formation in *Pinus radiata*, *Eucalyptus delegatensis* and *Callitris columellaris* is delayed for several years. These examples indicate that a breeder developing plantations for the pulping industry may be able to select material which can be harvested before heartwood formation occurs. Also, there are *Pinus* spp. with a range of extractives content in the heartwood and those with low content could be used for breeding in cases where heartwood formation takes place before the trees are suitable for harvesting.

Effect of Extractives on Wood Properties

Extractives are responsible for a number of the properties of wood. The varied range of properties is due to the diverse nature of the compounds that have been isolated from or are known to exist in different species of wood. Chemotaxonomic information, e.g.[19–21] assists the prediction of the nature and constitution of the extractives that will be found in new species.

With the increased use of the wood of new species, the plywood industry has encountered problems due to the properties of extractives. In some cases these can hinder the satisfactory adhesion of the glue to the veneer surface and in others they react with the glue to prevent satisfactory polymerization. Similar effects can be expected in the manufacture of particle board, the production of which is increasing rapidly. Few detailed studies have been made of these effects of extractives. Hemingway[22] has studied the effect of heat-induced changes in the wood fats of *Betula lutea* in relation to the surface wettability since such changes could affect adhesion. The migration of fatty acids to the surface of white spruce veneers during drying has also recently been studied[23] but found to play a

[17] R. W. HEMINGWAY and W. E. HILLIS, *Appita* **24**, 439 (1971).
[18] D. G. ROUX, personal communication.
[19] H. ERDTMAN, in *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 89, Academic Press, London (1963).
[20] M. HASEGAWA, *J. Jap. Forest. Soc.* **40**, 111 (1958).
[21] W. E. HILLIS and R. H. ORMAN, *J. Linn. Soc.* (*Bot.*) **58**, 371 (1962).
[22] R. W. HEMINGWAY, *Tappi* **52**, 2149 (1969).
[23] G. E. TROUGHTON and S-Z. CHOW, *Wood Sci.* **3**, 129 (1971).

secondary role. Extractives can also influence the adhesion and stability of paint and varnish films[24–26] and corrode metals.[27–29]

Some of the difficulties encountered in the increasing use of the wood of new species by the pulp and paper industry are caused by polyphenols. These substances are often present in appreciable amounts, particularly in species growing in tropical and semi-tropical regions. Polyphenols lower the yield of pulp, increase consumption of and affect the recovery of pulping chemicals. Some extractives can inhibit pulping reactions and others corrode equipment.[30] Recent work has shown how phenolic extractives can affect the colour of pulp[31] particularly when they contain vicinal tri-hydroxy groups as in eucalypt extractives. The penetration pathway of alkaline pulping liquors into wood is such that a concentrated solution of the reaction products of extractives and pulping liquor is present at the cell wall before delignification commences.[31] The nature of the reaction products will depend on the conditions of pulping. The products from eucalypt extractives produce pulps which are initially darker than those from coniferous pulps.

The Wood Extractives of Eucalyptus *species*

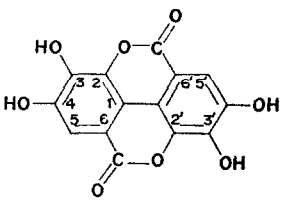
As some species of *Eucalyptus* can be among the fastest growing trees in the world their use for many purposes has risen sharply during the last half-century. Mature Australian-grown trees are being used increasingly within Australia and Japan as a source of paper pulp. In some cases the raw material contains up to 25% or more extractives. A number of problems were encountered for the first time when eucalypt woods were used in such applications. They indicate the type of properties which may be encountered in the utilization of new tropical and semi-tropical species. Extractives problems are further accentuated in Australian grown eucalypts, since almost all logs contain only a narrow (less than 2·5 cm) sapwood.

The genus *Eucalyptus* contains about 500 species, varieties and sub species growing under a wide range of environmental conditions and is one of the most highly variable genera in the plant kingdom. In these laboratories the wood extractives of 60 species have been examined[13] so far. From this study and published information the known components of the extractives are as follows; (a) polyphenolic carboxylic acids and their esters, (b) flavanols and their polymers, (c) stilbenes, (d) chromatographically unresolved fractions, (e) other components. At this stage, the polyphenols appear to have a limited use as chemotaxonomic markers.

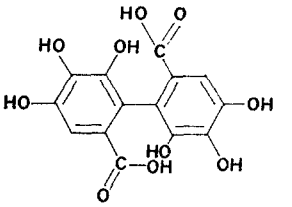
Polyphenolic Carboxylic Acids

Ellagic (I) and gallic acids and their esters (hydrolysable tannins or ellagitannins[32,33]) are present in almost all the eucalypt heartwoods so far examined.[13,30] Ellagic acid exists as essentially planar molecules arrayed in planes extending throughout the crystal.[34] Its mass spectra and that of related compounds has been studied.[35] When pure it has a

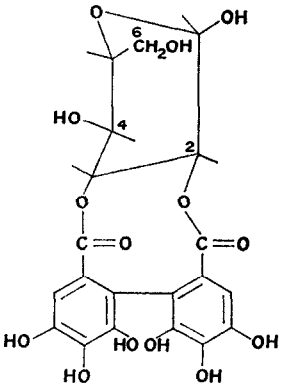
[24] J. A. F. GARDNER, *Official Digest, J. Paint Technol. & Engineering*, p. 698, June (1965).
[25] W. SANDERMANN and M. PUTH, *Farbe u. Lack* **71**, 13 (1965).
[26] M. FRACHEBOUD, J. W. ROWE, R. W. SCOTT, S. M. FANEGA, A. J. BUHL and J. K. TODA, *Forest Prod. J.* **18**, 37 (1968).
[27] J. A. F. GARDNER, in *Wood Extractives* (edited by W. E. HILLIS), p. 317, Academic Press, New York (1962).
[28] W. E. HILLIS and W. M. MCKENZIE, *Forest. Prod. J.* **14**, 310 (1964).
[29] W. M. MCKENZIE and W. E. HILLIS, *Wear* **8**, 238 (1965).
[30] J. A. F. GARDNER and W. E. HILLIS, in *Wood Extractives* (edited by W. E. HILLIS), p. 367, Academic Press, New York (1962).
[31] W. E. HILLIS, *Appita* **23**, 89 (1969).



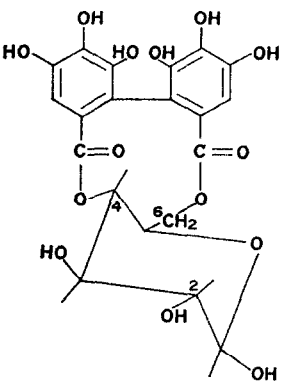
(I) Ellagic acid



(II) Hexahydroxydiphenic acid



(III) D-1



(IV) D-4

very low solubility in water and all the common organic solvents. However, if it is associated with other naturally occurring extractives in woody tissues, ellagic acid can be removed readily with these solvents.

The amount of ellagic acid in eucalypts varies not only from species to species but also from tree to tree of the same species. The outer heartwood contains more ellagic acid than the inner heartwood, particularly when taken from old trees. Amounts up to 4·0% have been recorded. The amount in sapwood is appreciably lower. If free ellagic acid is heated in oxygen-free alkaline conditions it is decarboxylated in about an hour to give hexahydroxydiphenyl.[36] Gallic acid can be similarly decarboxylated to yield pyrogallol. The diphenyl oxidizes rapidly, particularly under alkaline conditions, to form dark brown materials which adhere strongly to pulp. These materials may be partly responsible for the dark colour of the raw pulp and the black liquor which are features of eucalypt pulping.

Under pulping and other conditions, free ellagic acid in wood forms very insoluble green–yellow complexes with metallic ions such as magnesium, calcium, sodium and aluminium.[30,37–39] These substances contain about 60% of organic material but are not readily obtained with definite stoichiometric composition although 2:1 ellagic acid:metal complexes have been produced. A crystallographic examination indicates that the cations

[32] L. JURD, in *Wood Extractives* (edited by W. E HILLIS), p. 229, Academic Press, New York (1962).
[33] E. HASLAM, *Chemistry of Vegetable Tannins*, Academic Press, London (1966).
[34] A. MCL. MATHIESON and B. J. POPPLETON, *Acta Crystallogr.* **24B**, 1456 (1968).
[35] P. F. NELSON and Q. N. PORTER, *Holzforschung* **21**, 107 (1967).
[36] R. W. HEMINGWAY and W E. HILLIS, *Tappi* **54**, 933 (1971).
[37] D. G. HEWITT and P. F. NELSON, *Holzforschung* **19**, 97 (1965).
[38] G. J. LEES and P. F. NELSON, *Appita* **20**, 113 (1967).
[39] P. F. NELSON, *Holzforschung* **19**, 102 (1965).

are accommodated in a region of high concentration of oxygen atoms of adjacent ellagic acid molecules.[34] These complexes stabilize the ellagic acid to degradation by heat under alkaline conditions (at least below pH 11) and their separation at various stages of the pulping provides the distinctive green–yellow material of eucalypt mills. The complexes adhere to steel and other surfaces and cause malfunctioning of much pulp mill equipment. They can be removed with sodium hypochlorite solution at pH 8·5–10[40] or strong nitric acid. Apart from causing difficulties in the burning of spent pulping liquor the complexes are carried forward into the pulp and consume excessive amounts of bleaching chemicals.

Recent work[41] has shown the existence of 3,3′-di- and 3,3′,4-tri-*O*-methyl ellagic acids in some *Eucalyptus* species. A small number of species, such as those in the Heterophloiae series contain appreciable amounts of the 3,3′,4-tri-*O*-methyl ellagic acid 4′-glucoside.

Gallic acid has been observed in a number of species and the amount varies considerably but it is less than that of ellagic acid. The amount in the inner and outer heartwoods of a sample of *E. delegatensis* was respectively 0·08 and 0·17%.[42]

Ellagitannins have been detected in most of the eucalypt woods examined. So far, only those that are esters of hexahydroxydiphenic acid (II) (and in one case gallic acid also) have been found. Ellagitannins form a major portion of the extractives of the low-density, pale-coloured species which are the raw material for the Australian paper industry. In these species 10–20 different ellagitannins have been recognized.[31,42–44] The ellagitannins are very soluble in water and react strongly with iron. In mature heartwoods up to 25% extractives and 4% of ellagic acid can be present in some species of this type. About 15% of the extractives are monomers which are best detected by spraying with a mixture of 1% sodium carbonate and 4·3% sodium sulphite.[31]

In addition to the very similar chromatographic properties of the monomeric ellagitannins, the lack of stability of some of them has made their separation more difficult. The procedure finally adopted[44] was to extract the monomeric ellagitannins from freeze-dried extractives with anhydrous acetone. After purification with the aid of Sephadex G-50, most of the separations of this mixture were carried out on Sephadex G-25, G-15 or G-10 using water as eluant. During the separation, some monomers begin to hydrolyse necessitating rapid removal of water by freeze-drying. Owing to the difficulties associated with the separations, the amounts of individual compounds obtained pure were very small limiting the choice of identification methods which can be used. These have been acid, alkaline and enzyme hydrolysis of the original compound or its methyl derivative for different times and chromatographic examination of the products, and IR and NMR studies.

Qualitative hydrolysis of the ellagitannins of *E. delegatensis* revealed the presence of ellagic acid and glucose and, in one case, (compound D-3) the presence of gallic acid also. There was a different behaviour in the time course of hydrolysis of the different compounds. Compounds D-1 and D-4 have been identified by IR and NMR spectral and chromatographic comparisons as the 2,3- and 4,6-(hexahydroxydiphenyl)-glucose respectively. The postulated conformation of the glucose in D-1 is 3B or C1 (III) and in D-4 it is C1 (IV).[44,45]

[40] A. W. McKenzie, A. J. Pearson and J. R. Stephens, *Appita* **21** (2), XIX (1968).
[41] W. E. Hillis and Y. Yazaki, unpublished data.
[42] W. E. Hillis and A. Carle, *Biochem. J.* **74,** 607 (1960).
[43] W. E. Hillis and A. Carle, *Holzforschung* **12,** 136 (1958).
[44] M. K. Seikel and W. E. Hillis, *Phytochem.* **9,** 1115 (1970).
[45] J. C. Jochims, G. Taigel and O. T. Schmidt, *Annalen* **717,** 169 (1968).

Several points have been observed[44] in the NMR 100 MHz spectra which support the view that D-2 is 2,3;1,6 di-(HHDP)-glucose (V). D-2 is identical with pedunculagin for which Schmidt *et al.*[45,46] give the constitution of 2,3;4,6-di-(HHDP)-glucose. The latter workers have strong evidence to support their view. However water, acid and enzyme hydrolysis produces 2,3-(HHDP)-glucose and minor amounts of other compounds but never 4,6-(HHDP)-glucose. The NMR spectrum with a sharp downfield signal at δ 6·30 and the easy hydrolysis, both very similar to corilagin, point to aroylation of the anomeric hydroxyl group. Schmidt *et al.*[46] had difficulty in fully methylating pedunculagin and this is in contrast to the reported ease of methylation of the anomeric hydroxyl of glucose by diazomethane.[47]

Recently we treated solutions of ellagitannins with *Penicillium waksmani* which has strong α-glucosidase activity on gallyl or diphenyl esters. Whereas it does not affect D-1 or D-4 it hydrolyses corilagin slowly and D-2 relatively quickly. The latter gave 2,3-(HHDP)-glucose, but not the 4,6 isomer, and another main compound.[41] This is further supporting evidence for the proposal previously published that D-2 is 2,3:1,6 di-(HHDP)-glucose[44] (V).

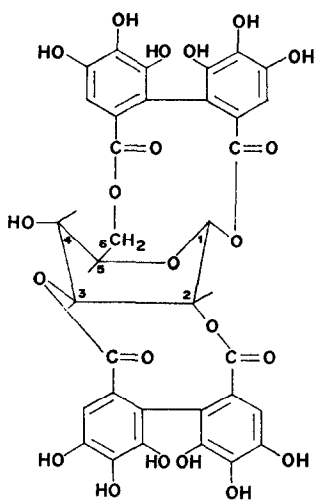
The chromatographic properties of D-3 are also altered by treatment with *P. waksmani* indicating the existence of an ester on the α hydroxyl of the anomeric carbon of glucose. The NMR spectrum of this compound also has a singlet at 6·44 ppm. The structure of compound D-3 is currently being investigated.

Ellagic acid and glucose are the only recognizable acid hydrolysis products from compound D-6 present in *E. delegatensis* and are formed in about equal proportions. It does not react with aniline phthalate indicating substitution of the carbon 1 hydroxyl. Hydrolysis with *P. waksmani* gives D-6-2 and ellagic acid indicating the presence of hexahydroxydiphenic acid as an aroyl ester on the α hydroxyl of glucose carbon 1. Both D-6 and D-6-2 have an IR band at 832 ν indicative of α-glucose. On acid hydrolysis D-6-2 gives ellagic acid and glucose. Assuming D-6 contains 2 glucose and 2 HHDP moieties and D-6-2 only 1 HHDP moiety, the yield of D-6-2 was 95% theory. The NMR spectrum of D-6 contains 3 singlets (6·36, 6·50 and 6·60 ppm) in the aromatic region whereas D-6-2 contains only a very sharp singlet identical with the middle one. It appears that 1 peak can represent the 2 protons on the HHDP moieties which accordingly must be in magnetically equivalent environments. Because D-6-2 reacts weakly with aniline phthalate, it is concluded that the HHDP is esterified with the carbon 2 hydroxyls of the two glucose moieties. We[41] provisionally propose that D-6 has the constitution of 2 HHDP and 2 glucose moieties with 1,1′ and 2,2′ linkages (VI). The glucose moieties could exist as 1C conformers, with the one on the right being turned over from left to right.

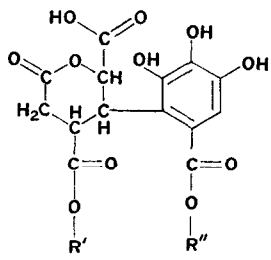
The elegant hypothesis for the biosynthesis of the ellagitannin series suggests that the initial step is from penta-gallyl glucose.[48] The work of Haslam[49] indicates that the gallyl rings project radially from the glucose core and lie in a plane perpendicular to it. NMR data indicate the lack of planarity between the phenyl ring and carbonyl groups of the HHDP moieties in ellagitannins.[44] The existence of ellagitannins with such structures raises the question whether the intramolecular dehydrogenation of two gallyl groups in gallotannin to form an ellagitannin can be achieved enzymically.

Examination of the rates of hydrolysis of different ellagitannins under mild pulping and oxygen-free conditions has shown that some are notably resistant to hydrolysis.[36] In

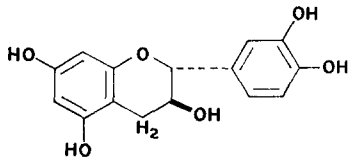
[46] O. T. SCHMIDT, L. WÜRTELE and A. HARRÉUS, *Annalen* **690**, 150 (1965).
[47] R. KUHN and H. H. BAER, *Chem. Ber.* **86**, 724 (1953).
[48] O. T. SCHMIDT and W. MAYER, *Angew. Chem.* **68**, 103 (1956).
[49] E. HASLAM, *J. Chem. Soc.* C, 1734 (1967).



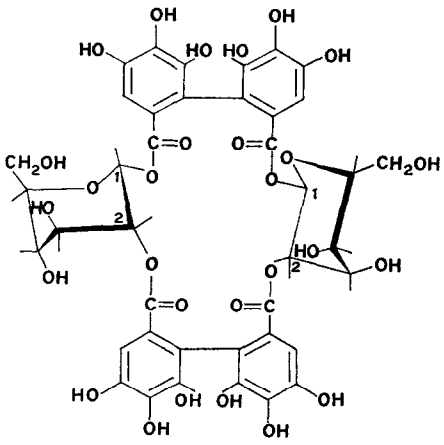
(V) D-2



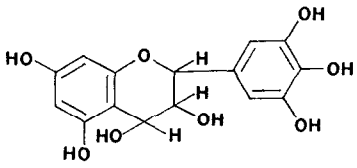
(VII)



(VIII) (+) Catechin



(VI)



(IX) Leucodelphinidin

the time taken to hydrolyse they partly form highly coloured materials and D-6 and D-13 appear to be more chromogenic than the others.[31] The eucalypt extractives form much more colour during alkali pulping than does lignin[31] and this colour is absorbed by the pulp. The removal of small amounts of chromophores during bleaching necessitates the removal of much non-coloured material as well.[50] Consequently it is desirable to remove the potentially chromogenic material before pulping.

It is notable that whereas the hexahydroxydiphenoyl radical exists in the eucalypt extractives, some plant tissues (such as the dried fruit of *Terminalia* spp.) contain an oxidized form in which one aromatic ring is opened (VII) such as found in chebulagic acid. Apparently this oxidation is readily brought about biologically. Accordingly we studied the *in vitro* reactions of ellagitannins, ellagic and gallic acids with alkali and oxygen. The aromatic

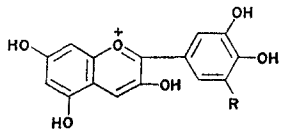
[50] P. F. Nelson, J. C. Smith and W. D. Young, *Appita* **24**, 107 (1970).

ring of the extractives is ruptured under mild conditions to non-phenolic materials. A pretreatment of eucalypt chips with alkali and oxygen before pulping destroys the extractives so that the kraft pulp subsequently prepared has a lighter colour.[51] The process has potential in improving the quality of eucalypt raw material.

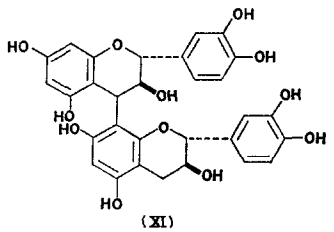
Flavanols and Their Polymers

Flavanols in their polymeric and sometimes monomeric forms are present in all eucalypts and in some, such as *E. marginata*, the amounts may be large. The flavanols present belong to the classes represented by catechin (VIII) and leucodelphinidin (IX). The leucoanthocyanins give a red colour and sometimes an anthocyanidin when heated with butanol-hydrochloric acid. Catechin has been detected in some eucalypts and the leucoanthocyanins are usually in the polymeric form but on acid treatment yielded cyanidin (X, R=H) in the case of *E. fasciculosa*, *E. marginata*[52] and delphinidin (X, R=OH) and cyanidin in the case of *E. tereticornis*[52] and delphinidin with *E. sieberi*.[53]

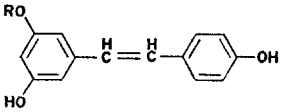
More recently Nisi and Panizzi[54] isolated 0·6 per cent of a dimeric proanthocyanidin or leucoanthocyanin from the wood of *E. camaldulensis* (which gave cyanidin with acid).



(X) Cyanidin R=H
Delphinidin R=OH



(XI)



(XII) R=H
(XIII) R=Glucose

From chemical and spectroscopic evidence they concluded the material was a dimeric compound (XI) with the same stereochemistry as (+)-catechin. This compound is one factor responsible for the red colour in the wood of this species.[55] A further proanthocyanidin has been isolated and is considered to be the octameric compound,[56] and another, which gave delphinidin, was also present in the wood, in addition to catechin, protocatehuic, gallic and ellagic acids.[57]

The main constituents of eucalypt kinos[3] (polyphenolic exudates) appear to be polymerized forms of leucoanthocyanins, or occasionally, of catechins. In at least one species (*E. sieberi*[58]), the kino is almost entirely polymerized leucodelphinidin. In another species *E. hemiphloia*, the kino appears to be very largely polymerized catechins.[59] The amount of kino present in the wood depends on the species and the amount of damage to the active cambium that the tree has received. Kinos give much more colour with alkaline pulping liquors than the ellagitannin extractives.[31] However, if oxygen is passed through hot alkaline solutions decoloration takes place.[51]

[51] R. W. HEMINGWAY and W. E. HILLIS, *Appita*, in press.
[52] G. M. ROBINSON and R. ROBINSON, *Biochem. J.* **17,** 206 (1933).
[53] W. E. HILLIS, *Austral. J. Biol. Sci.* **9,** 263 (1956).
[54] D. NISI and L. PANIZZI, *Gaz. Chim. Ital.* **96,** 803 (1966).
[55] D. NISI, *Cellulosa e Carta* **17,** 18 (1966).
[56] D. NISI, *Cellulosa e Carta* **20,** 13 (1969).
[57] L. CAPITO and L. PANIZZI, *Annali Chem. (Roma)* **49,** 771 (1959).
[58] W. E. HILLIS and A. CARLE, *Biochem. J.* **92,** 516 (1964).
[59] W. E. HILLIS and A. CARLE, *Austral. J. Chem.* **16,** 147 (1963).

Stilbenes

Hathway[60] has shown that resveratrol (XII) and its glucoside (XIII) is present in the heartwood of a small number of subseries of eucalypts namely the Tesselatae, Eucorymbosae, Neocorymbosae, Maculatae, Dealbatae, Pedicellatae and the series Subcornutae. Although the stilbenes are useful in classifying members of the Longiores subsection they they have been found in a few other species of the genus.[13,61] Stilbenes do not form significant amounts of colour during alkaline pulping[31] but wood containing them darkens appreciably on exposure to sunlight.[62] They are largely responsible foı the high durability of the woods containing them.[63]

Chromatographically Unresolved Fractions

The major portion of the extractives of any species are polymeric or high molecular weight polyphenols that are poorly resolved by the available chromatographic methods. Attempts to completely separate this fraction from *E. delegatensis* have been unsuccessful but it comprises more than 80% of the extractives.[38,44] In more than 30 eucalypt heartwoods examined so far, the unresolved material showing mobility in the chromatographic solvents 6% acetic acid or butanol–acetic acid–water reacts positively with vanillin–hydrochloric acid showing different proportions of polymerized flavans. The yield of ellagic acid obtained by hydrolysis of this material from *E. delegatensis* indicates that if the components are polymers of ellagic acid and ellagitannins then the hexahydroxydiphenic acid moiety is not greatly affected.

Other Components

When young fast-grown eucalypts such as *E. globulus* is used for pulp, a different group of extractives becomes important. Samples from 6 to 10-yr-old trees grown in Portugal have been examined[64] and it would be expected these trees would contain a small proportion of heartwood. The acetone soluble content of the samples was low (1·5–1·9%) and the ether insoluble part, which contained mainly condensed tannins, was only 1·2–1·6%. The amounts of ellagic and gallic acids in the free form were 0·02 and 0·03% respectively and in the combined form 0·23 and 0·06% respectively. Vanillic and syringic acids were found and resin acids were absent. The very low amount of fatty acids contained mainly linoleic then oleic and palmitic acids; β-sitosterol was isolated in very small amounts. During kraft pulping, the polyphenols, nearly all the fatty acids and about one-third of the unsaponifiable substances were dissolved, leaving in the unbleached pulp a resin which was mainly unsaponifiables (β-sitosterol).[65]

Wood resins have been isolated from other eucalypts and in particular from the wood of *E. microcorys* (tallowwood) in a yield of 2–3% and *cyclo*eucalenol (yield 0·7%), a new triterpene similar to the *cyclo*artenol sub-group, has been examined.[66]

CONCLUSIONS

A study of the chemistry of wood extractives can assist the understanding of the mechanism of their formation and that of heartwood. More detailed information of this type will

[60] D. E. Hathway, *Biochem. J.* **83,** 80 (1962).
[61] J. H. Hart and W. E. Hillis, unpublished data.
[62] J. W. W. Morgan and R. J. Orsler, *Holzforschung* **22,** 11 (1968).
[63] H. Lyr, *Enzymologia* **23,** 231 (1961).
[64] B. Swan and I-S. Åkerblom, *Svensk Papperstidn.* **70,** 239 (1967).
[65] B. Swan, *Svensk Papperstidn.* **70,** 616 (1967).
[66] J. S. G. Cox, F. E. King and T. J. King, *J. Chem. Soc.* 1384 (1956).

clarify the routes to the polymeric materials and enable the unravelling of their constitution. Also an in depth study of one group of eucalypt extractives has provided an understanding of their behaviour and indicated a way in which their deleterious effects in the pulping industry can be reduced. In addition, the reduction in amounts of deleterious components in fast grown trees with little heartwood show some of the advantages in forest management practices of this type.

Key Word Index—Eucalyptus; Myrtaceae; wood extractives; flavanoids; ellagic acid; tannins; stilbenes.