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REVIEW ARTICLE

RECENT ADVANCES IN THE CHEMISTRY AND CHEMICAL UTILIZATION OF THE NATURAL CONDENSED TANNINS*

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Abstract—Catechins and 5-deoxyflavan-3,4-diols are regarded as the immediate biosynthetic precursors of the commercially-used condensed tannins. Variations of structure and stereochemistry of a variety of biflavanoids constituted from these and from a wider range of flavan-3,4-diol analogues, is briefly reviewed. Emphasis is placed on the limitations imposed on structural interpretation by rotational isomerism about sp^2–sp^3 hybridized C—C interflavanoid bonds. A high incidence of this phenomenon is recorded among the triflavanoids, the smallest of the polyflavanoids to exhibit significant tanning properties, and is illustrated in the case of a decamethylether triacetate of all-*trans*-bileucofisetinidin-(+)-catechin. The unique isolation of the first pure derivative of a tetraflavanoid tannin, an analogue of the above triflavanoid, is recorded. Structural, stereochemical and conformational aspects are discussed as representative of those of condensed tannins. Chemical modifications of similar molecular species, notably those from wattle bark extract, has led to the development in South Africa of cold- and thermosetting adhesives, precipitants for clay suspensions, mud thinning agents for oil well drilling and surface coatings for woods. Many of these are finding highly significant and increasing industrial application.

INTRODUCTION

REAPPRAISAL of an early study of the affinity of wattle bark extract (from *Acacia mearnsii*) for collagen substrates[1] on the basis of more recent knowledge of tannin structure,[2] indicates that biflavanoids do not possess significant tanning properties. Adsorptive effects become prominent only at the triflavanoid level, and thereafter increase exceedingly rapidly with molecular weight.

Although for this reason, mono- and biflavanoids do not fall within the strict definition of condensed tannins, they are invariably associated with, and apparently represent biogenetic precursors of the more highly condensed units. Their structures, stereochemistry, modes of condensation and condensation aptitudes are accordingly significant. A brief review of the development of these classes follows as an introduction to the more recent and still somewhat tentative advances amongst their higher oligomers or true tannins. Earlier reviews of tannin precursors and bimolecular flavanoids have been made by Freudenberg and Weinges[3] and by Weinges *et al.*[4]

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* Based on a paper read at the Wood Extractives Symposium, 161st Meeting of the American Chemical Society in Los Angeles in April, 1971; and in abbreviated form at the meeting of the South African Chemical Institute, Grahamstown on 2 February, 1971.

[1] D. G. Roux, *J. Soc. Leather Trades' Chem.* **39,** 80 (1955); R. L. Sykes and D. G. Roux, *ibid.* **41,** 14 (1957).

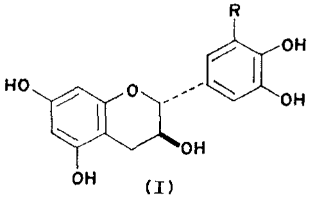
[2] D. G. Roux, *Tydskrif vir Natuurwetenskappe* 139 (1970).

[3] K. Freudenberg and K. Weinges, in *The Chemistry of Flavonoid Compounds* (edited by T. A. Geissman), p. 197, Pergamon Press, Oxford (1962).

[4] K. Weinges, W. Bähr, W. Ebert, K. Göritz and H.-D. Marx, *Progress in the Chemistry of Organic Natural Products*, Vol. 27, p. 158, Springer, Vienna (1969).

FLAVAN-3,4-DIOLS, CATECHINS AND BIFLAVANOIDS AS TANNIN PRECURSORS

The chemistry of (+)-catechin (I, R = H), and that of its 3-epimer, (—)-epicatechin, provides the basis of much of this work. These compounds also constitute the terminal units of most condensed tannins, and their structures must be traced back to the pioneering work by Freudenberg *et al.*[5] over many years, and to the final confirmation of their absolute configurations by Hardegger *et al.*[6] In turn, Mayer and Bauni[7] related the stereochemistry of (+)-gallocatechin (I, R = OH) to that of (+)-catechin.



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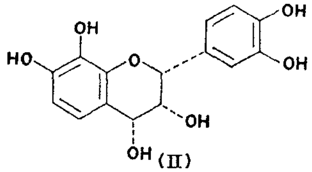

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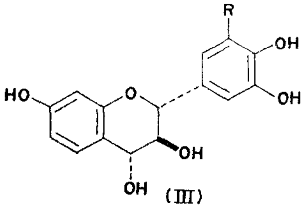

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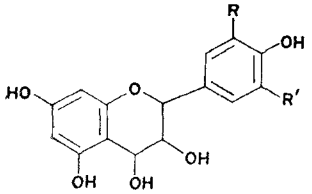

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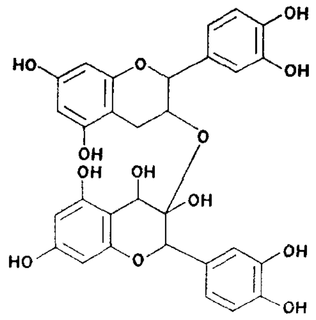

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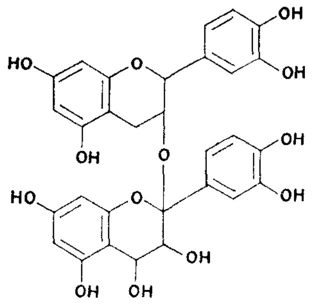

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Other units involved in tannin structure are the flavan-3,4-diols. The first of these to be isolated, (—)-melacacidin (II), was recognized by King and Bottomley,[8] while the first synthesis from dihydroflavonols was a leucorobinetinidin (III, R = OH) by Freudenberg and Roux[9] and a leucocyanidin (IV, R = OH, R′ = H) by Swain.[10] Natural compounds representative of the latter classes were isolated by Keppler[11] [(+)-mollisacacidin (III, R = H)], by Weinges[12] [(+)-leucorobinetinidin (III, R = OH)], by Roux[13] and Freudenberg and Weinges[14] [the enantiomer[15] of (+)-mollisacacidin] and by Seshadri *et al.*[16]

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[5] K. Freudenberg, *Sci. Proc. Royal Dublin Soc.* **27**, 153 (1956).

[6] E. Hardegger, H. Gempeler and A. Zust, *Helv. Chim. Acta*, **40**, 1819 (1957); A. Zust, F. Lohse and E. Hardegger, *ibid.* **43**, 1274 (1960).

[7] W. Mayer and G. Bauni, *Annalen* **611**, 264 (1958).

[8] F. E. King and W. Bottomley, *Chem. & Ind.* 1368 (1953); *J. Chem. Soc.* 1399 (1954).

[9] K. Freudenberg and D. G. Roux, *Naturwiss.* **41**, 450 (1954); D. G. Roux and K. Freudenberg, *Annalen* **613**, 56 (1958).

[10] T. Swain, *Chem. & Ind.* 1144 (1954).

[11] H. H. Keppler, *J. Chem. Soc.* 2721 (1957).

[12] K. Weinges, *Annalen* **615**, 203 (1958).

[13] D. G. Roux, *Chem. & Ind.* 161 (1958); D. G. Roux and S. R. Evelyn, *Biochem. J.* **70**, 344 (1958).

[14] K. Freudenberg and K. Weinges, *Annalen* **613**, 61 (1958).

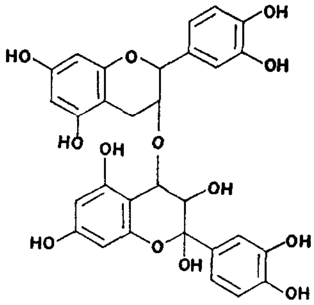
[15] J. W. Clark-Lewis and D. G. Roux, *J. Chem. Soc.* 1402 (1959).

[16] A. K. Ganguly and T. R. Seshadri, *J. Sci. Ind. Res. India* **17B**, 168 (1958); *Tetrahedron* **6**, 21 (1959); G. R. Nagarajan and T. R. Seshadri, *Current Sci.* **29**, 178 (1960); A. K. Ganguly, T. R. Seshadri and P. Subramanian, *Tetrahedron* **3**, 225 (1958).

[leucopelargonidin (IV, R = R′ = H), leucocyanidin (IV, R = OH, R′ = H) and leucodelphinidin (IV, R = R′ = OH)]. Their stereochemistry was placed on a firm basis mainly by Clark-Lewis[17] by using NMR spectrometry, while Drewes[18] examined their mass spectrometry.

Following relatively closely upon the initial flavan-3,4-diol chemistry was the recognition of natural oligomeric leucocyanidins by Forsyth and Roberts[19] from the cocoa bean (*Theobroma cacao*) (V) and by Freudenberg and Weinges[20,21] from *Gleditschia triancanthos* and *Craetagus oxycantha* (VI or VII) during the early sixties. However, structure V is of doubtful validity, and VI and VIII require additional confirmation.

Geissman and Dittmar,[22] Weinges and Freudenberg[23] and Creasy and Swain[24] in 1965 provided advances in a direction which would later prove significant, by the isolation of C—C linked leucocyanidin biflavanoids corresponding to VIII from avocado seed[22] (*Persea gratissima*), cola nuts[23] (*Cola acuminata*) and the strawberry[24] (*Fagaria vesca*).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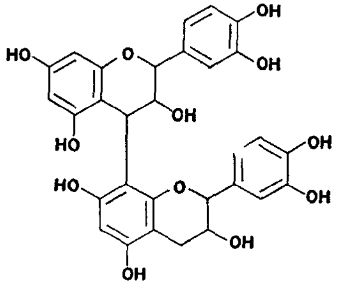
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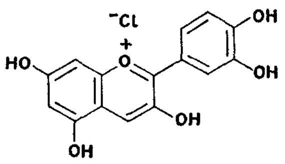
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Geissman and Dittmar[22] provided an acceptable mechanism for the rather remarkable fission of a C—C interflavanoid bond under hydrolytic conditions. The products of hydrolysis of the leucocyanidin (VIII) were cyanidin chloride (IX) and a catechin (I) or epicatechin together with phlobaphenes which result from the strongly competing phenol-oxidative self-condensation. Formation of the latter is expecially troublesome with higher polyflavanoid tannins, and may be minimised by adopting the procedure due to Pigman *et al.*,[25]—high dispersion in alcoholic HCl solution under pressure—which facilitates generation of the products of hydrolysis.

However, the precise structural details of the above C—C linked biflavanoid compounds were not described and biflavanoid VIII from the avocado gave an ill-defined 60 MHz NMR spectrum from which structural deductions were barely possible, and no details as regards mode of linkage between flavanoid units or their stereochemistry could be established.

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[17] J. W. Clark-Lewis, L. M. Jackman and T. M. Spotswood, *Austral. J. Chem.* **17**, 632 (1964); M. I. Baig, J. W. Clark-Lewis and M. J. Thompson, *ibid.* **22**, 2645 (1969).

[18] S. E. Drewes, *J. Chem. Soc.* **C**, 1140 (1968).

[19] W. G. C. Forsyth and J. B. Roberts, *Biochem. J.* **74**, 374 (1960).

[20] K. Freudenberg and K. Weinges *Tetrahedron Letters* 267 (1961).

[21] K. Freudenberg and K. Weinges, *Angew. Chem.* **74**, 182 (1962).

[22] T. A. Geissman and H. F. Dittmar, *Phytochem.* **4**, 359 (1965).

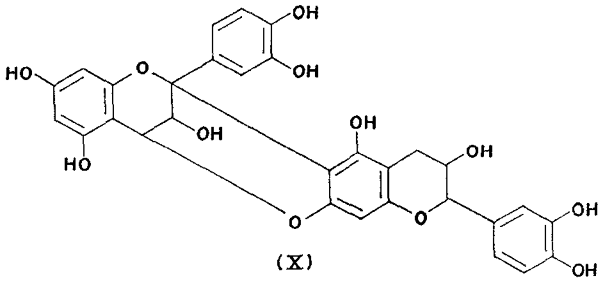
[23] K. Weinges and K. Freudenberg, *Chem. Commun.* 220 (1965).

[24] L. L. Creasy and T. Swain, *Nature, Lond.* **208**, 151 (1965).

[25] W. Pigman, E. Anderson, R. Fischer, M. A. Buchanan and B. L. Browning, *Tappi* **36**, 4 (1953).

Credit for the first natural crystalline biflavanoid leucocyanidin goes to Mayer *et al.*[26] who isolated a remarkable doubly-linked compound X from the chestnut (*Aesculus hippocastanum*). Although this yielded (—)-epicatechin on hydrolysis and gave a clearly-defined NMR spectrum, no attempts were made at stereochemical interpretation.

Related biflavanoids with C—C bonds (similar to VIII) were isolated during contemporary studies by Nisi and Panizzi[27] (from *Eucalyptus camaldulensis*), Krishnamoorthy and Seshadri[28] (*Myrica nagi*) and Delle Monache *et al.*[29] (*Ouratea* spp.), but it fell to the author and his co-workers[30,31] to characterize a group of crystalline leucofisetinidins (XI–XIII) from the wood of *Acacia mearnsii* in terms of their stereochemistry and mode of linkage for the first time, and similarly to determine the stereochemistry of a homologous series of related all-*trans*-5-deoxyleucoanthocyanidin-(+)-catechins [leucofisetinidin and leucorobinetinidins (XIV–XVI)] from the bark extract of the same tree.



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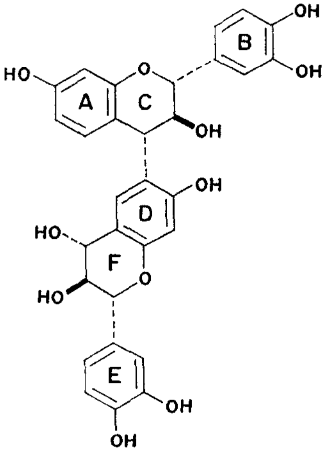

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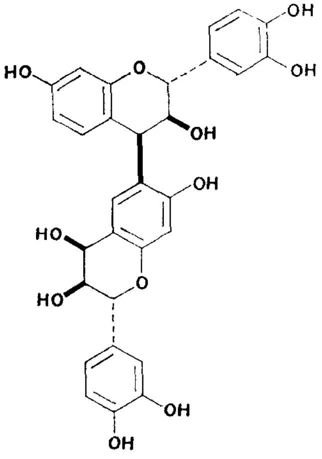

(XII)

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[26] W. Mayer, L. Goll, E. M. von Arndt and A. Mannschreck, *Tetrahedron Letters* 429 (1966).

[27] D. Nisi and L. Panizzi, *Gazetta* **96**, 803 (1966).

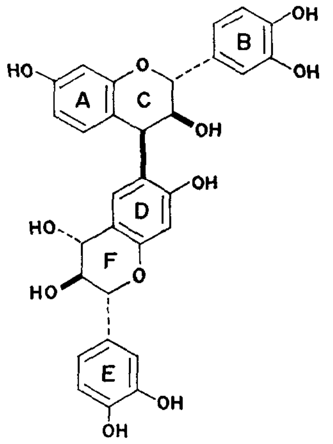
[28] V. Krishnamoorthy and T. R. Seshadri, *Tetrahedron* **22**, 2367 (1966).

[29] F. Delle Monache, I. L. d'Albuquerque, F. Ferrari and G. B. M. Bettóle, *Tetrahedron Letters* 4211 (1967); *Il Farmaco*, **25**, 96 (1970).

[30] S. E. Drewes, D. G. Roux, S. H. Eggers and J. Feeney, *Chem. Commun.* 368 (1966); *J. Chem. Soc.* **C**, 1217 (1967).

[31] S. E. Drewes, D. G. Roux, H. M. Saayman, J. Feeney and S. H. Eggers, *Chem. Commun.* 370 (1965); *J. Chem. Soc.* **C**, 1302 (1967).

The C- and F-ring heterocyclic systems were shown to have half-chair conformations for most individual flavanoid moieties, exceptions being twisted boat conformations were 2,3-*trans*-3,4-*cis* relative configurations pertained in the upper units (C rings of XII and XIII). The 4,6-coupling for bileucofisetinidins (XI–XIII) were evident from sharp singlets in the high-field aromatic region, whereas confirmation of similar assignment for the all-*trans*-5-deoxyleucoanthocyanidins (XIV–XVI) was obtained more recently from chemical shift data.[32]



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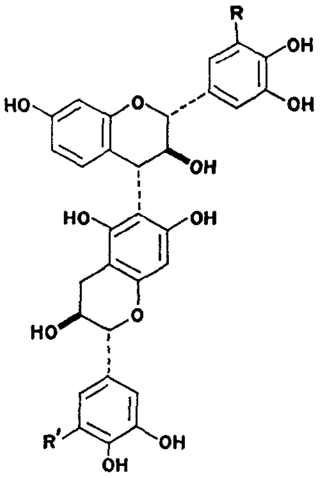
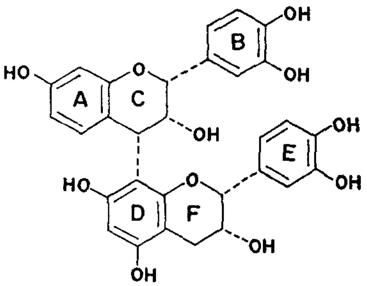


(XIV) R = R′ = H
(XV) R = OH, R′ = H
(XVI) R = R′ = OH



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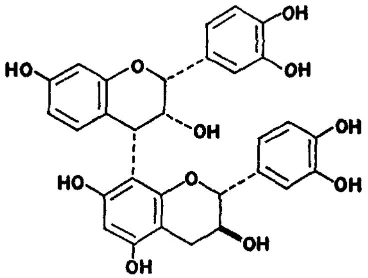

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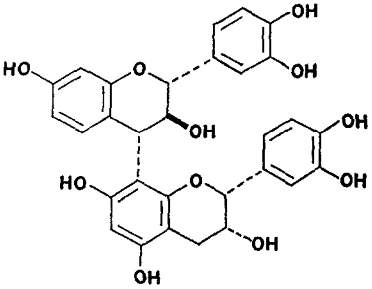

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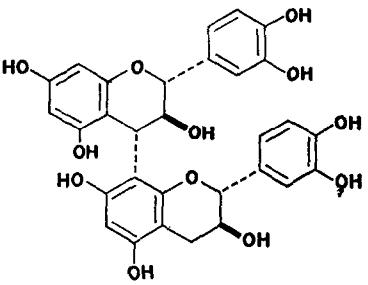

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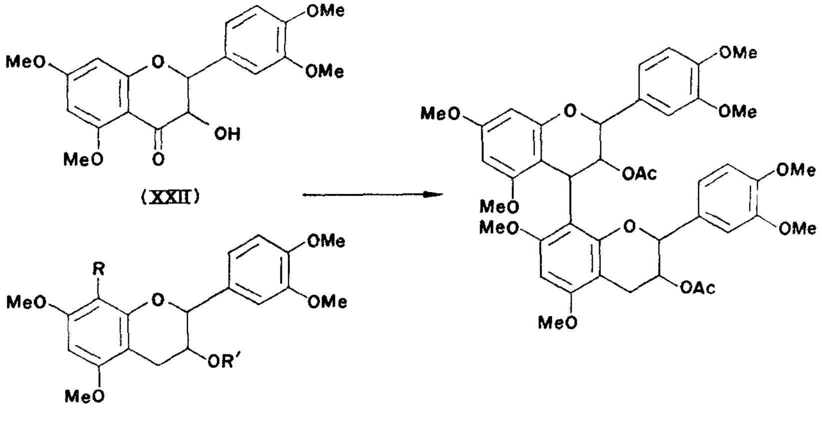
[32] I. C. du Preez and D. G. Roux, unpublished work.

The bileucofisetinidins from wattle wood are still unique in having a 3,4-diol function in the terminal group, one of them (XIII) being converted into an acetonide after epimerization of the 4-OH of the F-ring.[30] These compounds are accompanied by a high concentration of their apparent precursor 2,3-*trans*-3,4-*trans*-(+)-mollisacacidin (III, R = H), as well as traces of (+)-2,3-*trans*-3,4-*cis* and (+)-2,3-*cis*-3,4-*cis* diastereoisomers[33] which may well be artefacts of epimerization.[34] Tri-, penta- and undeca-flavanoid analogues also exist[35] but could not be purified sufficiently hitherto for structural determination.

The biflavanoids (XIV–XVI) from the barks are also accompanied by their apparent precursors, (+)-leucofisetinidin (III, R = H), (+)-leucorobinetinidin (III, R = OH), (+)-catechin (I, R = H) and (+)-gallocatechin (I, R = OH), and by higher oligomeric analogues.[2] Combined these constitute the tannins of 'mimosa' or wattle extract of commerce, the mixture having a number average molecular weight of 1250.[36]

Shortly afterwards Weinges *et al.*[37,38] isolated C—C 4,8-linked biflavanoid leucocyanidins from various sources. These (XVII–XX) were representative of all the possible combinations of (+)-catechin (I, R = H) and (−)-epicatechin in both 'upper' and 'lower' units. Their stereochemistry at C-4 of the C-ring was not specified where (−)-epicatechin formed the 'upper' unit. However, from their coupling constants ($J_{2,3} < 1$, $J_{3,4}$ 2·0–2·1 Hz), and with the knowledge that their bulky 2-aryl and 4-flavanoid substituents will assume predominantly *equatorial* positions, these 'upper' (−)-epicatechin units should have half-chair conformations and 2 *eq*, 3 *ax*, 4 *eq* or 2,3-*cis*-3,4-*cis* arrangements of substituents as indicated in XVII and XVIII (see ref.[30]). From a variety of fruits a number of doubly-linked leucocyanidins similar to those first found by Mayer *et al.*[26] were also characterized by Weinges *et al.*[38]



Scheme 1. Synthesis of 4,8-linked procyanidin derivative.[39]

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[33] S. E. Drewes and H. A. Ilsley, *Phytochem.* **8**, 1039 (1969).
[34] S. E. Drewes and D. G. Roux, *Biochem. J.* **94**, 482 (1965).
[35] D. G. Roux and E. Paulus, *Biochem. J.* **82**, 320 (1962).
[36] S. R. Evelyn, *J. Soc. Leather Trades' Chem.* **38**, 142, 309 (1954); S. R. Evelyn, D. R. Cooper and P. C. van Berge, *J. Polymer Sci.* **33**, 53 (1954).
[37] K. Weinges, K. Göritz and F. Nader, *Annalen* **715**, 164 (1968).
[38] K. Weinges, W. Kaltenhäuser, H. D. Marx, E. Nader, F. Nader, J. Perner and D. Seiler, *Annalen* **711**, 184 (1968).
[39] K. Weinges and J. Perner, *Chem. Commun.* **351** (1967); K. Weinges, J. Perner and H. D. Marx, *Chem. Ber.* **103**, 2344 (1970).

In recent years the significant advances were the synthesis by Weinges and Perner[39] of a 4,8-linked leucocyanidin derivative by means of a Grignard-type reaction between metallated catechin derivative (XXI) and the methylated dihydroflavonol, taxifolin (XXII) (see Scheme 1), as proof of structure of some natural leucocyanidins; the study of the reaction of mercaptoacetic acid with flavan-4-ol model compounds and its possible use as selective splitting agent for the tannins of common heather (*Calluna vulgaris*) by Brown *et al.*,[40,41] and by Sears and Casebier[42] for splitting C—C links at 4-aryl substituted flavanoid units; the use by Pelter *et al.*[43] of solvent induced shifts in NMR spectrometry to determine the position of linkage from C-4 of the 'upper' flavanoid unit to the alternatives of the 6- or 8-positions of the phloroglucinol ring when present in the terminal unit of biflavanoids; and the demonstration by the author and his coworkers[44] of the presence of biflavanoid carboxylic acids, e.g. the leucoguibourtinidin carboxylic acids in *Acacia luederitzii* and *A. reficiens*.

TRIFLAVANOID TANNINS: RECOGNITION OF ROTATIONAL ISOMERS

Some of the above work employing degradative reagents was performed on tannin mixtures of unknown composition and structure, and in no previous work was a unit more complex than a biflavanoid accurately defined. Drewes and Roux,[45] for example, studied the mass spectrometry of a trileucofisetinidin from the wood of *Acacia mearnsii*, but its NMR spectrum proved complex. Similarly Seshadri *et al.*[46] reported natural triflavanoid leucocyanidin units, but without precise definition of their mode of link or stereochemistry. The reason for the above lies mainly in the very complex NMR spectra due to multiplicity of all signals. These are characteristic of a wide variety of chromatographically homogeneous triflavanoid fractions from different sources, and is especially evident in the acetyl-proton region (τ 7·9–8·4), where only three or at most four acetyl-methyl resonances are anticipated from compounds of this order of complexity.

This high incidence of multiplicity provided a serious barrier to work on even the smallest of those units which possess tanning properties. The phenomenon could conceivably be due to three factors; (i) impurities due to related flavanoids, as a result of separation difficulties with complex mixtures of such highly polar oligomers; (ii) impurities in the sense of structural isomers, i.e. polyflavanoids with differing points of interflavanoid linkage, and (iii) closer to actual purity, signals resulting from a mixture of rotameric forms about an interflavanoid bond—a phenomenon predicted by the author as early as 1967.[30]

The impact of the latter on NMR spectra is rarely evident amongst biflavanoids, but notable exceptions are the leucoguibourtinidin-(+)-catechins and -(−)-epicatechins from *A. luederitzii* and *A. reficiens*.[44] An example[47] is the 4,6-linked all-*trans*-leucoguibourtinidin-(+)-catechin derivative (XXIII) which at 100 MHz exhibits the following NMR phenomena; (i) multiplicity of acetyl-methyl resonances—three (τ 8·07, 8·19 and 8·36) instead of the two anticipated, but together integrating to a total of six protons, (ii) split methoxyl signals, and (iii) a tendency for heterocyclic protons to be either broadened or duplicated. Following

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[40] M. J. Betts, B. R. Brown, P. E. Brown and W. T. Pike, *Chem. Commun.* 1110 (1967).

[41] M. J. Betts, B. R. Brown and M. R. Shaw, *J. Chem. Soc.* C, 1178 (1969).

[42] K. D. Sears and R. L. Casebier, *Chem. Commun.* 1437 (1968).

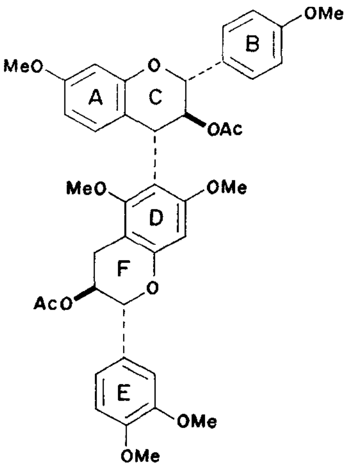
[43] A. Pelter, P. I. Amenechi, R. Warren and S. H. Harper, *J. Chem. Soc.* C, 2572 (1969).

[44] I. C. du Preez, A. C. Rowan and D. G. Roux, *Chem. Commun.* 492 (1970).

[45] S. E. Drewes and D. G. Roux, *Chem. Commun.* 1 (1968).

[46] V. Narayanan and T. R. Seshadri, *Indian J. Chem.* 7, 213 (1969); V. K. Bhatia, R. Madhav and T. R. Seshadri, *ibid.* 7, 123 (1969).

[47] I. C. du Preez, A. C. Rowan and D. G. Roux, *Chem. Commun.* 315 (1971).



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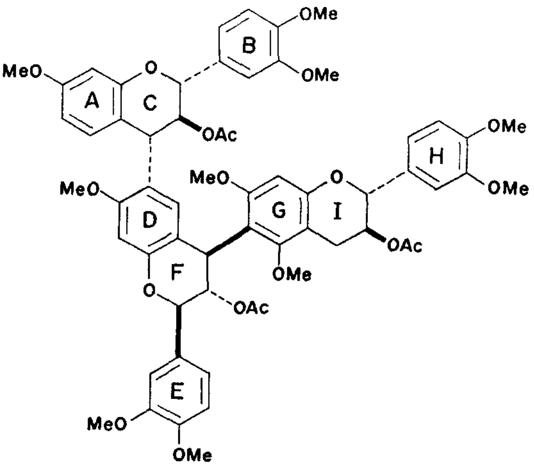

(XXIV*)

progressive temperature elevation these anomalies are resolved with, for example, coalescence of those two acetyl methyl resonances (τ 8·07, 8·19) which together integrate as three protons, and sharpening of the triplet (τ 4·12) attributed to the 3-H of the C-ring.

These effects provide proof in this instance that a rotational barrier about the 4,6-link exists, and that separation of rotamers does not follow from highly selective chromatographic procedures. With this knowledge similar effects are discernable in the NMR spectrum at 220 MHz of a triflavanoid all-*trans*-bileucofisetinidin-(+)-catechin (XXIV), M^+ 1100, from *Colophospermum mopane*.[47] From the spectrum may be observed; (i) 6 methoxyl resonances [τ 8·21, 8·26, 8·32, 8·37 and 8·50 (slight split—double signal)] instead of the 3 anticipated, (ii) four identical triplets [τ 3·68, 4·88 (two), 3·99] each with ΣJ_s 19·5 Hz due to two heterocyclic 3-protons of rings C and F, and (iv) two pairs of octets [τ 6·55–6·80 and τ 7·12–7·45] due to a single 4-methylene function in the I-ring. These phenomena are symptomatic of rotational isomerism about both interflavanoid bonds.

Proof is provided by the coalescence of signals, in this instance at differential rates, for both methoxy and acetoxy proton resonances over the range 26·5–94°. Differential rates of coalescence may be attributed to two factors; (a) differences in the chemical shifts between doublets, and (b) differences in the Arrhenius activation energies required for rotation. The fact that chemical shift differences are relatively small, while the temperature requirements for rotation are large, suggests differences in the activation energies needed for rotation about each of the $C(sp^2)$—$C(sp^3)$ hybridized bonds.

About these bonds two different conformations may be recognized; (a) that in which a bond of the sp^3-hybridized C-atom eclipses the double bond, and (b) the alternative, where the bonds of the sp^3-hybridized C-atom are bisected by the double bond of the sp^2-hybridized C-atom. The rotational barrier in such cases is very low—of the order of 5 kcal/mol—and thus for the di- and triflavanoids other factors, equivalent to the well-known steric hindrance in *ortho*-substituted diphenyls, may be responsible for the high energy requirements. Weinges *et al.*[48] has recently shown that 4,4-linked *O*-dimethylresorcinol-poly-

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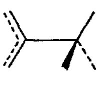
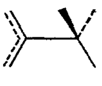
* The stereochemistry about 4,6-interflavanoid bonds in XXIV is unknown. Note the inverted representation of flavanoid units containing the F heterocyclic ring in XXIV, and F and L heterocyclic rings in XXV, i.e. units which are structurally and stereochemically identical to III, R = H and I, R = H.

[48] K. Weinges, H. D. Marx and K. Göritz, *Chem. Ber.* **103**, 2336 (1970).

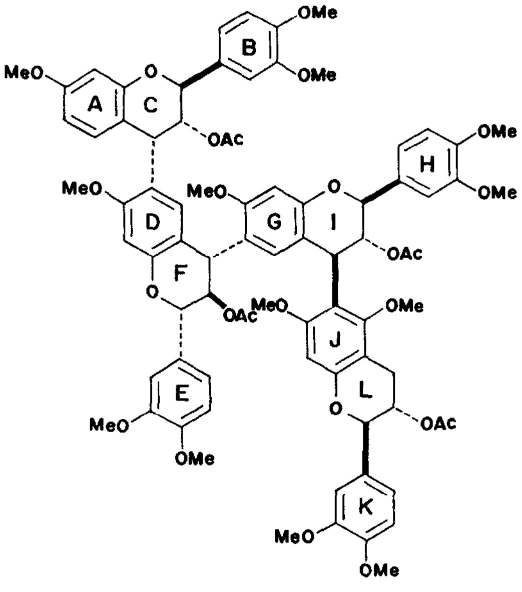

(a)


(b)

methoxyflavans exhibit no rotational isomers at ambient temperatures, whereas their existence is apparent when *O*-trimethylphloroglucinol replaces *O*-dimethylresorcinol in the same units. The above work demonstrates for the first time rotational isomerism about both interflavanoid bonds in triflavanoid tannins, and also emphasizes the ubiquitous distribution of a phenomenon which the author and co-workers predicted in 1967.[30,31]

TETRAFLAVANOID TANNINS

Very rare exceptions to the above do, however, exist. The only example hitherto is the pure diastereoisomeric form of a tridecamethylethertetra-acetate of 2,3-*trans*-3,4-*cis*:$2',3'$-*trans*-$3',4'$-*trans*: $2'',3''$-*trans*-$3'',4''$-trans:$2''',3'''$-*trans*-trileucofisetinidin-(+)-catechin (XXV), M^+1456, from the heartwood of the well-known South African karee tree (*Rhus lancea*).* The criteria of purity used are, of course, chromatographic homogeneity, but more specifically NMR spectrometry at 220 MHz in view of the general prevalence of rotational isomers. In this instance duplication of signals is completely absent, and a series of spectra obtained by 10% incremental additions of C_6D_6 to a $CDCl_3$ solution shows four acetyl methyl resonances, thirteen methoxyl resonances and three *AMX* and one *ABXY* heterocyclic ring systems. These systems were analysed by spin-decoupling techniques.



(XXV†)

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* The 4,6-interflavanoid bond and the sequence of flavanoid units have been confirmed recently by degradative and NMR spectrometric methods respectively.[49]

† The stereochemistry about 4,6-interflavanoid bonds in XXIV is unknown. Note the inverted representation of flavanoid units containing the F heterocyclic ring in XXIV, and F and L heterocyclic rings in XXV, i.e. units which are structurally and stereochemically identical to III, R = H and I, R = H.

[49] D. Ferreira, H. K. L. Hundt and D. G. Roux, *Chem. Commun.* 1257 (1971).

The position of linkage to the terminal (+)-catechin unit (4,6) is determined by solvent-induced chemical shifts of methoxyl signals[43] over the above range of spectra, while the assignment of links between other units is tentatively 4,6 based on the presence of singlets to high (8-protons) and low fields (5-protons) in the benzenoid region.

The flavanoid moiety with a 2,3-*trans*-3,4-*cis* configuration is tentatively assigned to the 'uppermost' unit on the basis of the identical coupling constants shown by the corresponding unit of a (+)-2,3-*trans*-3,4-*cis*:2,3-*trans*-3,4-*trans*-bileucofisetinidin.[30] From the coupling constants this heterocyclic ring has a boat conformation with 2(*eq*), 3(*ax*), 4(*eq*) arrangement of substituents,[30] whereas the remainder have 2(*eq*), 3(*eq*), 4(*eq*) [2(*eq*), 3(*eq*) in terminal catechin group] arrangements associated with half-chair conformations. From the above it is evident that the 2- and 4-aryl linkages to all heterocyclic ring are *equatorial*. On the assumption that strong intramolecular hydrogen bonds exist between functional groups in the free phenolic form, the original tannin molecule as a whole assumes an approximately planar conformation.

The tetraflavanoid is accompanied by related tannins and by its apparent precursors (—)-leucofisetinidin (the enantiomer of III, R = H) and (+)-catechin (I, R = H). The formula XXV illustrates the relative configurations, but also reflects the absolute configurations of these presumed parent units. The absence of rotational isomers, and the ordered sequence of units suggests as before[50-52] that enzymic systems are involved at the rapid transformation which occurs at the sapwood-heartwood interface in this and in many other hardwood species.

INDUSTRIAL UTILIZATION OF CONDENSED TANNINS BY CHEMICAL MODIFICATION

Industrial use of any product demands its standardization in order to ensure reproduceable results during the narrow range of conditions normally applied. This requirement is met by the wattle or 'mimosa' bark extract industry where afforestation is on a sustained-yield basis, and both extraction and spray-drying are carefully controlled to meet the demands of the tanning industry. Furthermore, there exists a large supply potential of extract.

The tannins present in wattle extract consist of a molecular gradation of poly-flavanoids (number-average molecular weight of *ca.* 1250) structurally similar to the tannins described above, and of constant composition. Chemical conversion of the tannins has been studied over a number of years in South Africa with the development of several industrial products.

Precipitant for Clay Suspensions in Municipal Water

The synthesis of this substance is based on the conversion of the tannin to an amphoteric compound by means of the Mannich reaction involving ethanolamine and formaldehyde.[53] The product (XXVI, as hypothetical single unit of the polyflavanoid tannin), a secondary amine, is water-soluble as the hydrochloride, and causes immediate flocculation of clay suspensions in municipal water where clay contamination results from erosion or thunderstorms. The flocculant is removed quantitatively during the precipitation, the product known as 'Floccotan' has been applied on a considerable scale locally and elsewhere.

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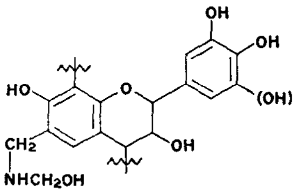
[50] D. G. Roux, *Nature, Lond.* **181**, 1454 (1958); *ibid* **180**, 973 (1957).

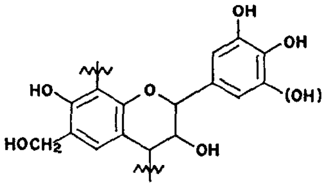
[51] S. E. Drewes and D. G. Roux, *J. Chem. Soc.* **C**, 1644 (1966); *ibid.* 1407 (1967).

[52] H. M. Saayman and D. G. Roux, *Biochem. J.* **96**, 36 (1965).

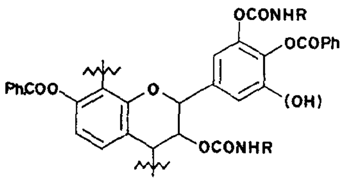
[53] The process was developed by the Natal Tanning Extract Co., Pietermaritzburg, Natal, in partial collaboration with the South African Council of Scientific and Industrial Research.



(XXVI)



(XXVII)



(XXVIII)

Adhesives for Composite Boarding

The base-catalysed reaction of phenol with formaldehyde is almost too well known for illustration. Tannins with their high degree of hydroxylation offer strong nucleophilic centres as anions for attack by the formaldehyde, and the ensuing benzyl alcohol (XXVII) or benzyl carbonium ion is highly reactive. Methylene cross-links between tannin units result. Due to the large average molecular weight of the tannins the formaldehyde requirements of the adhesives are relatively low. The extract has to be tailored to meet the individual demands of particleboard and plywood manufacture, and widely divergent products are employed in each of these areas of manufacture.

Current use in South Africa is about 1000 tons wattle extract annually[54] whereas in Australia some 1000 tons annual use has been reported.[55] The South African use lies exclusively in chipboard, the Australian in plywood, but both are based on wattle bark extract. An advantage of wattle-formaldehyde over phenol-formaldehyde adhesives in particleboard manufacture lies in the relatively low degree of wet swelling in boards manufactured from the former.

Cold-Setting Adhesive as Substitute for Resorcinol

Recent temporary but world-wide shortages of resorcinol prompted the development of a cold-setting adhesive.[56] The product, representing a highly modified wattle tannin, has considerable economic advantage over resorcinol adhesives, and has undergone completely successful composite beam-lamination tests under local industrial conditions.

Surface Coatings for Wood

Partially benzoylated wattle tannins (two benzoyl groups per flavanoid unit) readily precipitate from the aqueous system in which reaction occurs (conventional Schotten–Baumann method). After drying, the derivative is toluene-soluble, and furnishes an inexpensive source of hydroxyl function for reaction with diisocyanates to form carbamates or polyurethanes (XXVIII). The product[56] affords a surface coating for wood with high gloss, colour stability, high scratch resistance and excellent resistance against weathering relative to the best polyurethanes in commercial use.

Thinning Agent for Drilling Muds

A mud-thinning agent for oil-well drilling has been formulated by incorporation of chrome salts as complexing agent into wattle tannins.[56] The industrially prepared spray-dried product has economic advantages, forms a filter-cake which shows low water loss, has

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[54] Developed by Uovobord Ltd., Port Elizabeth.

[55] Developed by the CSIRO Forest Products Laboratory, Melbourne.

[56] Developed by the Leather Industries Research Institute, Grahamstown, South Africa.

remarkable ageing properties at elevated temperatures, caused no corrosion of high-stress steel surfaces, and has proved highly satisfactory under drilling conditions of up to 6000 feet.

Of the above, the adhesives and mud-thinning agents perhaps offer the best prospect of further development and increasing commercial exploitation with the eventual diversified industrial use of natural tannins in prospect.

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Key Word Index—Condensed tannins; oligomers; catechins; flavan-3,4-diols; adhesives.