

Structural Considerations in Predicting the Utilization of Tannins

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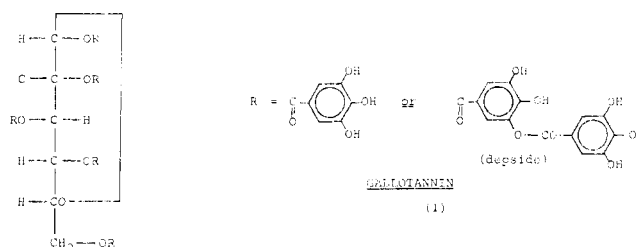
The implications of structural differences between hydrolyzable and condensed tannins are briefly reviewed. A new synthetic approach to condensed tannin chemistry provides perspective as regards the stereochemical course, regioselectivity, and sequence of the carbocation-mediated condensation mechanism at ambient temperatures. Physical methods, particularly ultrahigh-resolution nuclear magnetic resonance spectroscopy and circular dichroism, taken in conjunction with the synthetic method, enable definition of the structure, absolute configuration, and dynamic behavior of tannins in solution up to the triflavonoid level for the first time. The latter were shown to consist of 4,6:4,8-linked "branch-chained" units. The degree to which such finite knowledge of condensed tannin structure and of extract composition predicts their physical and chemical behavior is discussed with emphasis on the tanning process and on established adhesive uses (plywood, particle board, and corrugated cardboard manufacture).

Natural tannin extracts, almost irrespective of their composition or origin, have over many thousands of years been employed in the conversion of hides and skins into nonputrescible leather. This traditional process, based initially on cottage-type industries, was subject to dramatic change during industrialization over the latter half of the last century, resulting in the supplanting of most "hydrolysable" tannins (Freudenberg, 1920), e.g., algarobilla, chestnut, divi-divi, myrabolans, oak, sumach and tara extracts, tannic acid, and Turkish tannin with "condensed tannins" (Freudenberg, 1920), notably wattle ("Mimosa"), quebracho, and mangrove extracts.

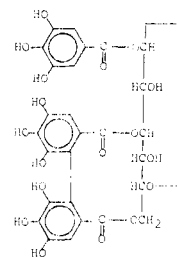
Initial preference for the "hydrolyzable" tannins probably centered in part on local availability, their reputedly lower "astringency" compared with condensed tannins, and their color stability or lack of reddening in polluted atmosphere under industrial conditions. However, the shift in emphasis to condensed tannins was mainly due to their greater availability from natural forests, e.g., quebracho and mangrove, or from scientific afforestation on a sustained-yield basis, e.g., wattle ("Mimosa") extract, in the face of increased demand; the richness of these sources, notably wattle bark (~35% tannins) and quebracho wood (~25%); and the development of modified conditions of tannage which largely overcame the astringency factor.

For both "condensed" and "hydrolyzable" tannins, affinity for the collagen substrate (i.e., hides and skins) is undoubtedly related to their relatively high molecular mass (~800-3000) and relatively low solubility as individual components in aqueous systems. Chemical differences are accordingly less significant from the affinity aspect. However, structural differences play a dominant role when considering alternative uses for tannins.

Thus, hydrolyzable tannins in which ester and depside links predominate [e.g., gallotannins (Haslam et al., 1961; Haslam, 1967) (1), corilagin (2), chebulagic acid (3), and chebulinic acid (4) (Schmidt and Eckert, 1958)] are predictably sensitive to both acid and alkaline conditions and would decompose with ease during a variety of chemical conversion reactions. Also, the gallic acid, depside, and hexahydroxydiphenic acid moieties and their derived units are deactivated as regards electrophilic aromatic substitution by their carboxyl (ester group) function, and sterically hindered residual nucleophilic centers. Therefore, apart from their erstwhile use in the isolation and purification of germanium from ores and for medicinal purposes (treatment of burns, since discontinued), the hy-

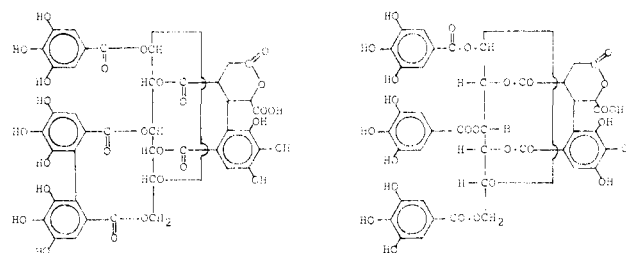


R may be only gallic acid resulting in 2-penta-O-galloylglucose or predominantly the depside resulting in either 2-octa- or nona-galloylated glucose



CORILAGIN

(2)



CHEBULAGIC ACID

(3)

CHEBULINIC ACID

(4)

drolyzable tannins have not found wider application although still used in tannin blends, e.g., myrabolans, *Mimosa*.

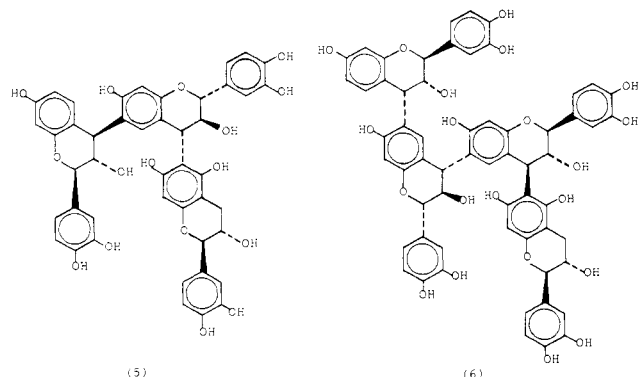
By contrast, the application of condensed tannins, or their extracts as established and freely available natural products, has expanded significantly beyond the domain of leather manufacture to adhesives for composite wood products and corrugated cardboard and to depressants in ore recovery and in a chemically modified form as a flocculant in water purification. These represent areas of accepted and current industrial use.

The chemistry of those condensed tannins which are of commercial significance and of their analogues differs somewhat from that previously visualized, and it is ac-

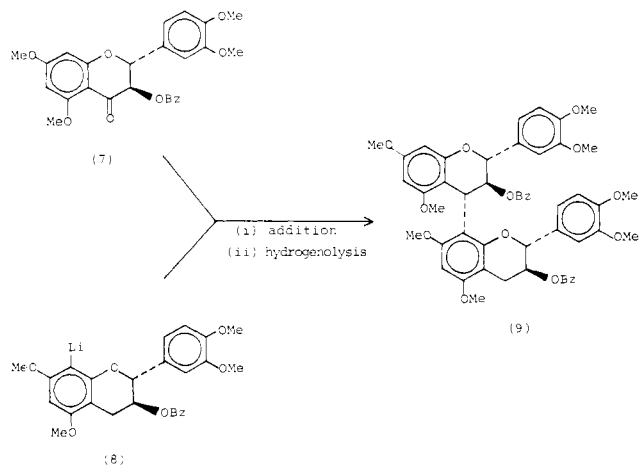
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cordingly important to deal briefly with some of the more recent developments.

As prelude to more recent work, we isolated some 9 years ago two triflavonoids from the mopane tree (*Colophospermum mopane*), one of which was assigned the all-trans structure (5) (du Preez et al., 1971). Also, the phenomenon of rotational isomerism was demonstrated for both bi- and triflavonoids from the same source. Shortly afterward the structure and relative configuration of a tetraflavonoid (6)



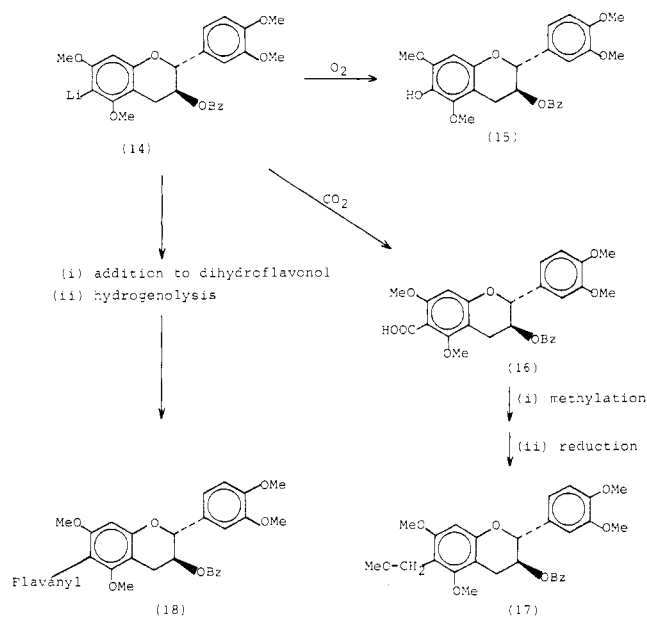
from the karree tree (*Rhus lancea*) was allocated (Ferreira et al., 1971). However, at this juncture we decided that although the structures were based on degradative, ^1H NMR, and MS evidence, they were less than satisfactory because of doubts about certain structural elements and that considerable advantage could accrue from a purely synthetic approach. For example, although Weinges and co-workers (Weinges et al., 1968) were successful in synthesizing a 4,8-linked biflavonoid derivative (9) using a Grignard-type reaction between (+)-taxifolin and (presumed) (+)-8-lithiocatechin derivatives (7 and 8 respectively) no distinction between 4,6- and 4,8-linkages to



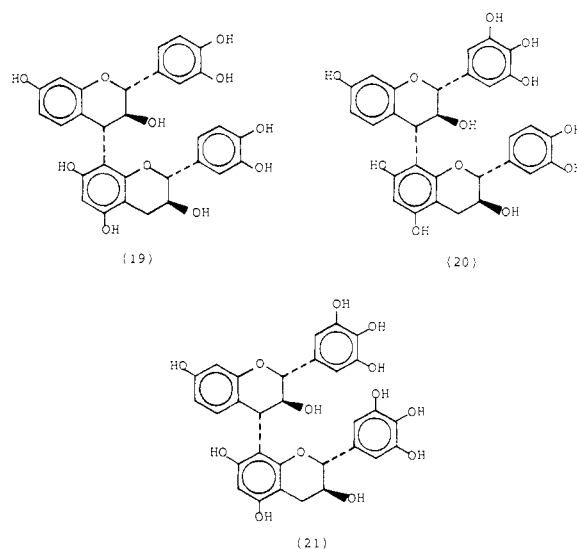
“terminal” units of the phloroglucinol type in bi-, tri-, and tetraflavonoids (cf. 9, 5, and 6) had hitherto been possible.

This problem essentially centered around (i) confirmation of the position of substitution as 8 during direct monobromination of a (+)-catechin derivative (cf. formula 11) and (ii) achievement of 6-bromination of the same compound (cf. formula 13). These products, with the position of bromination firmly established, could provide a sound basis for synthesis of 4,8- and 4,6-linked biflavonoids along the lines previously adopted by Weinges et al. (1968). Monobromination of 3-O-benzyltetra-O-methyl-(+)-catechin (10) produced the hitherto presumed 8-bromo derivative 11, and this was confirmed by us via X-ray analysis of its crystal structure (Engel et al., 1978). This reaction, however, produced no evidence whatsoever of the desired 6-bromo derivative; reaction with 2 mol of

bromine gave the (+)-6,8-dibromocatechin derivative (12) exclusively (Hundt and Roux, 1978). However, partial debromination of the latter with butyllithium afforded the desired (+)-6-bromocatechin derivative 13 for the first time and hence provided the key (via the corresponding 6- and 8-lithiocatechins) to a series of 6- and 8-substituted hydroxyl-, carboxyl-, methoxymethyl-, and (+)-flavanyl-catechins as illustrated for the 6-substituted derivatives only (14 \rightarrow 15, 16, 17, and 18) (Hundt and Roux, 1978).

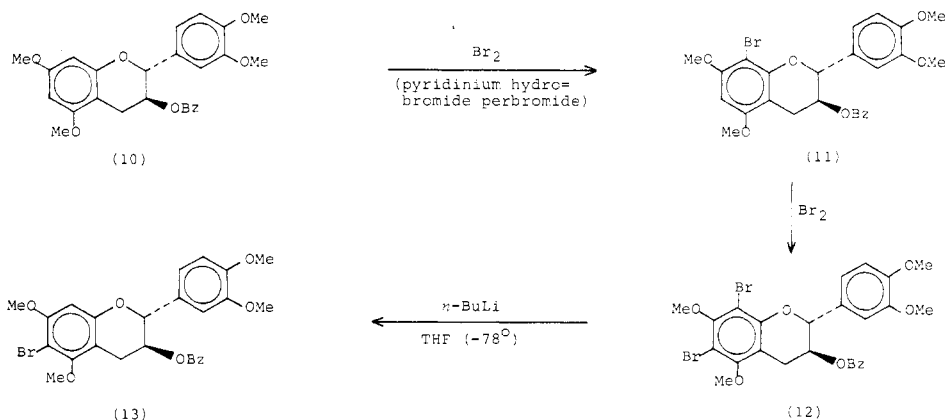


These pairs of 6- and 8-substituted (+)-catechins enabled us to show (Hundt and Roux, 1978) that the residual 8- and 6-protons fall into narrow ranges of NMR chemical shifts which are devoid of overlap [τ (CDCl_3) 3.51–3.70 and 3.76–3.93, respectively]. By using these parameters the biflavonoids from wattle bark extract were shown by NMR spectrometry to be 4,8 linked as illustrated in structures 19–21 and the tetraflavonoid tannin 6 from the karree



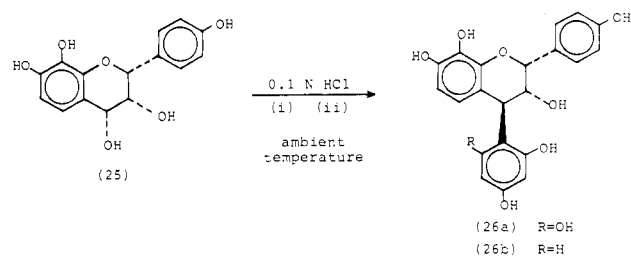
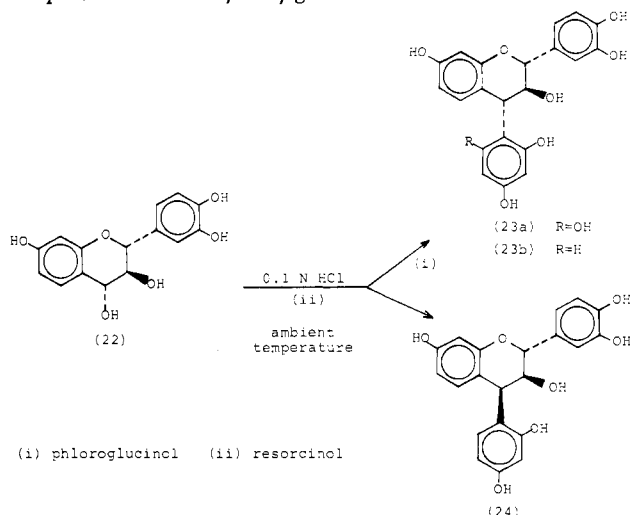
(Ferreira et al., 1971) as 4,6 linked to its “terminal” (+)-catechin unit. Considering the small shift differences, these assignments are made with some reservation, but they appear to be sound in view of the range of compounds examined. Models of biflavonoid compounds also show that residual protons (6 or 8) are always removed from the diamagnetic anisotropy of adjacent benzenoid rings.

Subsequent steps in the evolution of this synthetic approach to condensed tannin structure were aimed at de-



termining the stereochemistry of polyflavonoids at C-4 and also at effecting direct synthesis of biflavonoids via a biogenetic-patterned route. These objectives were inter-related.

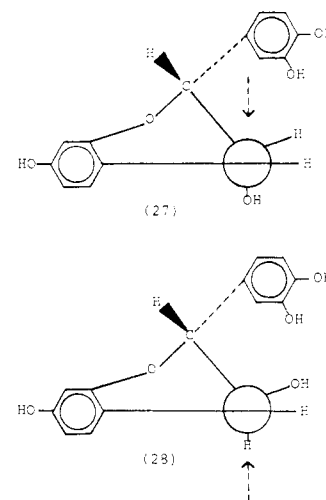
The first of these was achieved by selecting flavan-3,4-diols of known absolute configuration (**22**, **25**) and condensing each in turn with phloroglucinol and resorcinol via a transient 4-carbonium ion mechanism (Botha et al., 1978a). The 2,3-*trans*-3,4-*trans*-flavan-3,4-diol [(+)-mol-lisacacidin, **22**] reacts rapidly at low acidity with a suitable excess of phloroglucinol at room temperature to form the 2,3-*trans*-3,4-*trans*-4-arylflavan-3-ol (**23a**) only, i.e., with complete retention of configuration. Similar reaction with



resorcinol, in place of phloroglucinol, results in both 3,4-*trans* (**23b**) and 3,4-*cis* analogues (**24**), the former predominating (38 and 22% yields, respectively), i.e., the reaction proceeds with high net retention of configuration (Botha et al., 1978a). By contrast the carbonium ion formed under identical conditions from (-)-2,3-*cis*-3,4-*cis*-teracacidin (**25**) is captured stereoselectively by both phloroglucinol and resorcinol to form 2,3-*cis*-3,4-*trans*-4-

arylflavan-3-ol analogues (**26a**, **26b**) with inversion of configuration (Botha et al., 1978a).

On the assumption that both carbonium ion intermediates possess sofa conformations, attack on the 4-carbocation with a 2,3-*cis* configuration (**27**) should proceed

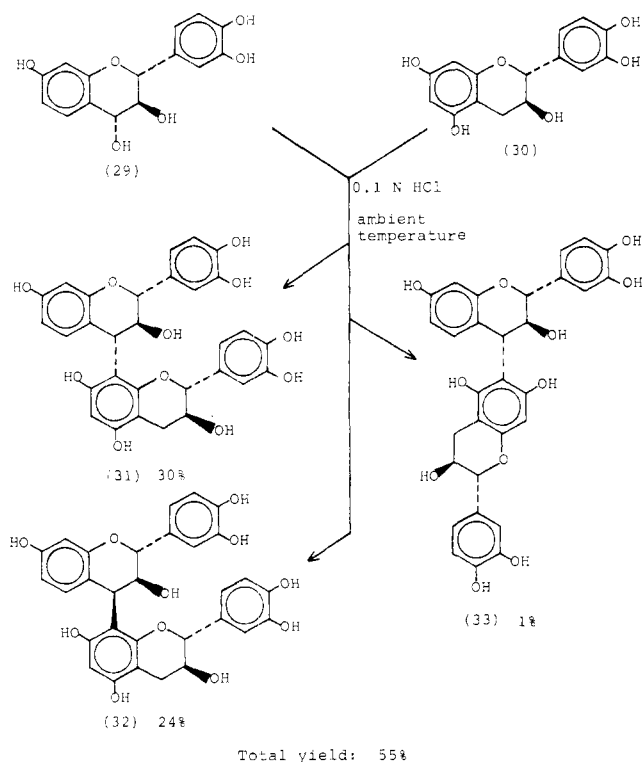


selectively with or without neighboring group participation from the least hindered upper side (i.e., the side removed from the adjacent 3-*axial*-hydroxyl), whereas reaction with the 2,3-*trans* carbocation (**28**) may be expected to occur with nucleophilic attack directed mainly from the opposite or "lower" side, with the larger phloroglucinol ring exercising a higher degree of "steric approach control". The condensation mechanism with flavan-3,4-diols at C-4 is, therefore, subject to a kinetic mechanism, i.e., steric approach control rather than a thermodynamic control (Botha et al., 1978a). [Claims to the contrary have been made by Haslam and co-workers (Thompson et al., 1972; Jacques et al., 1974; Fletcher et al., 1977) for condensed tannins of a different type, probably because their reactions were conducted at relatively elevated temperatures.] Since flavan-3,4-diols and the appropriate catechins accompany related tannins, it is evident that the above mechanism predicts the configuration at C-4 of all 2,3-*trans* and 2,3-*cis* flavonoid units constituting those condensed tannins which have hitherto been found in nature (du Preez, et al., 1971; Ferreira et al., 1971; Thompson et al., 1972; Jacques et al., 1974; Fletcher et al., 1977; Drewes et al., 1966, 1967).

The above work led to the further finding that CD curves of the 4-arylflavan-3-ols (**23a**, **23b**, **24**, **26a**, **26b**) are completely dominated by the multiple Cotton effects of the two phenyl chromophores at C-4, introduced with 4-arylation. Reversal of the sign of high-amplitude Cotton effects at 220–240 nm occurs with inversion at C-4, a

strongly positive effect correlating with 4R and a strongly negative effect with 4S, as defined for the phloroglucinol substituent. The CD method thus provides an unambiguous and direct criterion for assessing the absolute configuration at C-4 for 2,3-*trans*-2',3'-*trans* biflavonoids as shown below (Botha et al., 1978a).

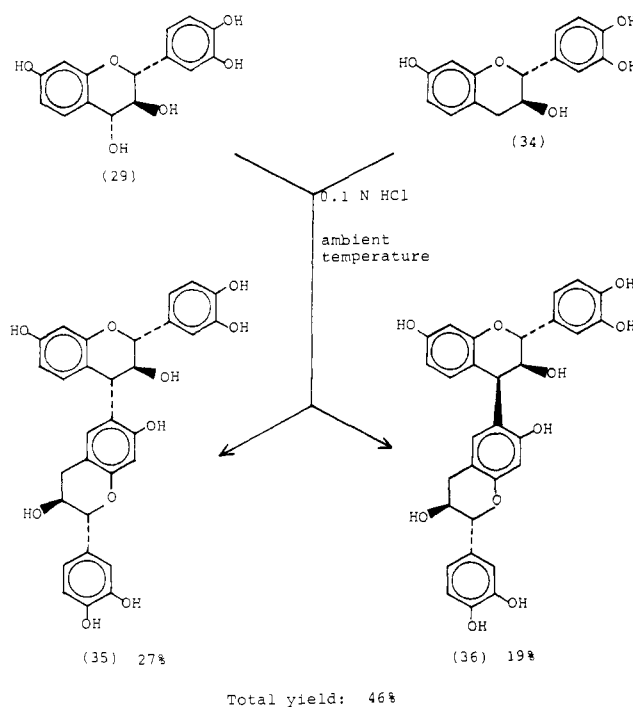
Development of the above carbonium ion mediated synthetic approach, but using (+)-catechin in place of phloroglucinol or resorcinol, enabled us to synthesize two biflavonoids present in wattle bark at ambient temperatures in what we consider to be a biochemical-type synthesis (Botha et al., 1978b). The reaction (29 + 30 → 31, 32, 33) showed the same elements of stereoselectivity as



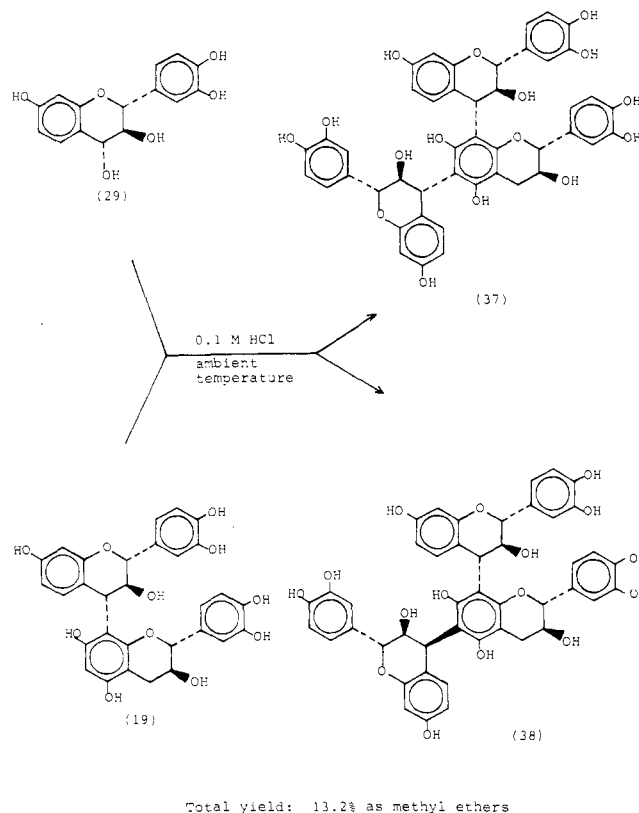
resorcinol, forming the 4,8-linked all-*trans* and *trans*-,*cis*-,*trans* biflavonoids 31 and 32, respectively, and also the 4,6-linked all-*trans* biflavonoid 33 in 30, 24, and 1% yields. The reaction is thus partially regioselective, possibly due to steric factors. The 3,4 *cis* biflavonoid 32 was immediately recognized as a major biflavonoid component of wattle bark extract which had been overlooked (Drewes et al., 1966, 1967). CD spectra confirmed their absolute configuration at C-4 (Botha et al., 1978b).

Substitution of (-)-fisetinidol for (+)-catechin in the same reaction with (+)-mollisacadin (29 + 34 → 35 + 36) on the other hand gave regioselective coupling at C-6 of the resorcinol-type flavan-3-ol unit to give the expected all-*trans* and 2,3-*trans*-3,4-*cis*:2',3'-*trans* biflavonoids 35 and 36, respectively, in yields (27 and 19%) comparable to those obtained with (+)-catechin under identical conditions (Botha, 1978b). From the above, and considering the low degree of 4,6 bonding with (+)-catechin, it would appear that further coupling of (+)-mollisacadin (29) with the 4,8-linked biflavonoid 19 would be mainly confined to the 6 position of the "upper" (-)-fisetinidol unit to give a "linear-type" condensate. This prediction, although based on two separate and noncompeting reactions, proved invalid (Botha et al., 1979).

Coupling of the flavan-3,4-diol, (+)-mollisacadin (29), with synthetic 4,8-linked all-*trans*-(-)-fisetinidol-(+)-catechin (19) under the identical conditions applied before,



results in the regioselective condensation at the vacant 6 position of the biflavonoid to form the novel 4,8:4,6-linked all-*trans* and 2,3-*trans*-3,4-*trans*:2',3'-*trans*:2'',3''-*trans*-



3'',4''-*cis*-bi(-)-fisetinidol-(+)-catechin triflavonoid tannins 37 and 38, respectively, in almost equal proportion (13% yield) (Botha et al., 1979).

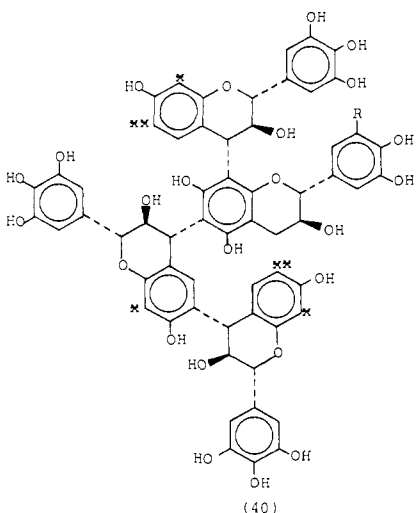
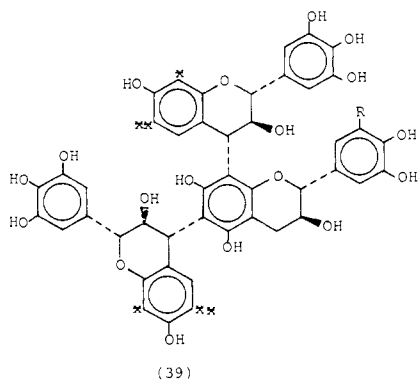
These assignments follow from the presence to high field in the aromatic region of two ABC systems attributable to the resorcinol A-ring protons of two (-)-fisetinidol units and the conspicuous absence of the high-field singlet which differentiates the residual 6-proton on the A ring of the "lower" (+)-catechin unit of the biflavonoid starting ma-

terial (19), when the products are examined by 360-MHz FT NMR spectrometry at $\sim 200^\circ\text{C}$. The structures are further supported by diagnostic multiple Cotton effects in the low-wavelength region of the CD spectra of the methyl ether triacetates of the triflavonoids 37 and 38 when compared with that of biflavonoids (Botha et al., 1978b).

The identical triflavonoids 37 and 38 accompanied by the 4,8-linked biflavonoid 19 and flavan-3,4-diol (29) were isolated in the proportions of 3:2 from the heartwood of the mopane tree (*Colophospermum mopane*) some 7 years ago (du Preez et al., 1971; du Preez, 1971). The same structural and stereochemical relationships also exist between natural mono-, 4,8-linked bi-, and 4,8:4,6-linked triflavonoids of commercial wattle bark (*Mimosa*) extract (*Acacia mearnsii*) (Botha et al., 1979).

In summary, the biochemical condensation processes in wattle extracts appear to occur with logical regard for the nucleophilic character of the benzene rings and for constraints imposed by steric factors (affecting regioselectivity), steric approach control, and the availability of immediate precursors of a suitable type. Under the impact of ultrahigh-resolution NMR, mass spectrometry, circular dichroism, and conformational analysis, and above all the synthetic approach, some of the mysteries of condensed tannin structure have been unraveled up to the triflavonoid level.

Such "branch-chained" (as opposed to "linear") triflavonoid structures of *Mimosa* extract, for example, the all-*trans*-[4,8:4,6]-bi(-)-robinetinidol-(+)-gallocatechin (39, R = OH) and (-)-catechin (39, R = H) have relatively

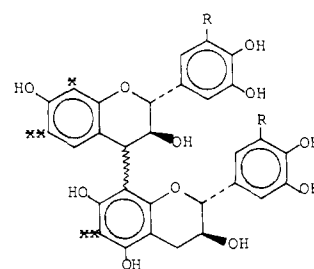


* Reactive nucleophilic centres

reactive and accessible nucleophilic centers on the resorcinol A rings of the (-)-robinetinidol units. These centers, notably the 6 positions on each of the A rings, provide sites

for further biochemical elaboration to the tetraflavonoid and higher oligomeric structures [e.g., the hypothetical structure (40)], and the triflavonoids are, therefore, in a sense key intermediates in tannin formation.

The same accessible reactive sites, as well as those available on the 4,8 biflavonoids (19, 20, 21, and 32), as summarized in structure 41 (R = H or OH), and on higher



(41)

oligomers (hypothetical structure 40, R = H or OH) may now be invoked to rationalize the general reactivity of wattle tannins in electrophilic aromatic substitution. Knowledge of this type is particularly useful in the industrial application (Pizzi, 1977a).

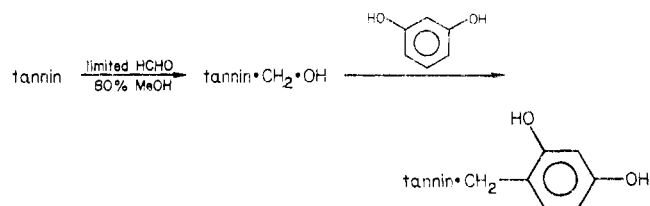
STRUCTURAL CONCEPTS AND ADHESIVE APPLICATIONS

Apart from C-C interflavonoid bond stability and high reactivity, perhaps the greatest single factor which recommends the use of certain of the natural condensed tannin extracts is solubility in cold water. In this respect the oligomeric tannins of *Mimosa* extract with their high degree of hydroxylation and suitable molecular mass distribution (Roux and Evelyn, 1958) offer the best overall prospect of broad application. Quebracho extract is comprised of tannins which we have shown (Botha, 1978) to be structurally similar to those of *Mimosa*, but with a lower degree of hydroxylation (emphasis on catechol and pyrogallol B-ring functions, respectively) and, therefore, lower solubility; hence the necessity of sulfitation of quebracho to ensure sufficient solubility during extraction and use. The tannins of mangrove and pine-bark extracts are, particularly in the latter instance, on an average more highly condensed than either *Mimosa* or quebracho tannins, presumably due to greatly enhanced reactivity of the procyanidin flavan-3,4-diol precursor, thus providing well-known solubility problems.

Structural complexity and degree of hydroxylation are, however, not the only factors affecting solubility, others being the composition of the tannin and "nontannin" admixtures present in natural extracts. Carbohydrates which mainly constitute the nontannin fractions (Saayman and Roux, 1965), for example, not only enhance solubility, but also serve as hydrogen-bond breakers, thus reducing viscosity at the high ($\sim 50\%$) solids content required for industrial adhesive applications, e.g., particleboard manufacture. Artificial addition of phenol to tannin extracts has much the same effect.

Relative immobility of the higher natural oligomers (cf. structure 40) of condensed tannins [phenolic mass range 300-3000 for *Mimosa* tannins; number average mass ~ 1250 (Evelyn, 1954), approximately equivalent to a tetraflavonoid tannin] conceivably results in relatively poor cross-linking via methylene bridges during bonding with formaldehyde and consequent brittleness of the resulting adhesive. The problem is, however, readily surmounted by limited ($\sim 10\%$) addition of suitable phenol-formaldehyde (PF), resorcinol-formaldehyde (RF) (Pizzi, 1977a; Pizzi and Roux, 1978) or urea-formaldehyde (UF) con-

Scheme I



densates (Pizzi, 1977b, 1978a) which ensure a high degree of cross-linking, but without loss of the innate bond stability in the latter instance.

Residual reactive centers located mainly on the resorcinol moieties of bi-, tri-, and (hypothetical) tetraflavonoids (cf. structures 39-41) ensure the required compromise between high adhesive reactivity required for short press cycles and extended precure ("pot-life") stability in thermosetting applications. The reactivity of adhesives based on *Mimosa* extract is, for example, such that short press times are achieved under relatively neutral conditions (pH 7-8), whereas exceptionally high alkalinity (pH >11) is required of conventional PF adhesives for use under similar conditions. As a result, particleboards based on wattle adhesives exhibit low swelling characteristics under cold-soak conditions, contrasting in this respect with those of PF adhesives.

Advantage is taken of the high reactivity of condensed tannins at high alkalinity by using admixtures of wattle and quebracho extracts as accelerators for conventional PF adhesive resins in thermosetting plywood applications.

The "pot-life" or effective precure working life of condensed tannin adhesives probably represents a combined function of the inherent degree of condensation of tannins present in the extract; their relative solubility in the complex natural mixture; the reactivity (nucleophilic character) of the tannin molecules, and the accessibility of nucleophilic centers (steric factor). This may be controlled by pH adjustment over the neutral range (pH 7-8), or by 10% addition of UF resin (Pizzi, 1977b, 1978a).

Reaction of condensed tannins with formaldehyde may be catalyzed by limited addition of divalent metal ions, the most useful being zinc or lead acetates (Pizzi, 1978b).

Finally, the reactivity of condensed tannins in adhesive applications may be enhanced by a variety of methods, one of which is graft condensation in the reaction sequence shown in Scheme I to give a tannin-resorcinol "copolymer" (Pizzi, 1977a; Pizzi and Roux, 1978). This product has cold-set properties and was used for beam lamination ("glulam" application) during the first energy crisis. Other formulations (Pizzi and Roux, 1978) which produce the same effect include use of linear resorcinol-phenol copolymers, in which resorcinol occupies a terminal position, as cross-linking agent. Replacement of resorcinol by *m*-aminophenol in these applications gives a fast setting adhesive which will be used shortly in South Africa in finger-jointing applications (Pizzi and Roux, 1978).

The wattle-urea-formaldehyde (WUF) (Pizzi, 1977b, 1978a) formulation referred to above serves as replacement for resorcinol in strengthening starch adhesives used in corrugated cardboard manufacture in the packaging industry (Custers et al., 1979).

The scope of our achievements in South Africa, now well documented (Pizzi, 1977a,b, 1978a,b,c; Pizzi and Roux, 1978; Custers et al., 1979) is such that about 70% of the industrial phenolic adhesives used in the composite wood industry is based on wattle (*Mimosa*) extract. This is the culmination of some 10-15 years of research effort on the part of a small group. The basic ingredients of such relative success lie in part in the stability of C-C inter-

flavonoid bonds present in wattle tannin molecules (cf. formulas 39-41), their high natural solubility, and their relatively high reactivity due to accessibility of strongly nucleophilic centers in terminal positions on "branch-chain" type (Botha et al., 1979) tannin units (cf. formulas 39 and 40).

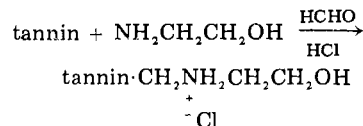
TANNIN STRUCTURE AND MINERAL BENEFICATION

Complexing of metal ions with the predominant pyrogallol and minor catechol B-ring function of *Mimosa* tannins has been studied extensively (Slabbert, 1972). The polyfunctional nature of the tannins in terms of uniformly distributed complexing sites (i.e., on the B ring of each flavonoid unit), their molecular mass, the nature of the complexing sites (i.e., vicinal di- or trihydroxy), and the pH of the aqueous medium determine the stability of the complex.

These factors may play a role in the consumption of some 1000 tons of wattle bark extract by one mining firm. The tannins serve as depressant for calcite (CaCO₃) in the recovery of fluorite (CaF₂) from heavily contaminated ores.

TANNIN MODIFICATION AND WATER TREATMENT

Wattle tannins, ethanolamine, and formaldehyde condense in acidic medium in a Mannich-type reaction under aqueous conditions to form the salt of a secondary amine.



The product termed "Floccotan" (developed by the Natal Tanning Extract Company, Pietermaritzburg 3200, Natal) is ionized and presumably capable of neutralizing electrical charges on clay particles in aqueous suspension, while simultaneously causing their precipitation. Both the precipitant and the suspended clay are, therefore, quantitatively removed and the process serves as excellent clarification agent for muddy water. It has been used in many municipal water reservoir systems, which are dependent on muddy run-off from thunderstorms.

SOME POTENTIAL USES FOR CONDENSED TANNINS

Possible uses of condensed tannins which have been investigated thoroughly, but not as yet applied industrially, are as follows: (i) "*Mimosa* wash primer" (Seavell, 1978) which serves as corrosion inhibitor for iron by the formation of iron tannate through complexing with the vicinal phenolic hydroxyl function of tannins prior to painting; (ii) floral foams (Knauf, 1979) (acid condensation of *Mimosa* extract with furfuryl alcohol in the presence of a suitable "blowing agent"); (iii) antioxidants, as illustrated by the excess of strongly reducing pyrogallol function of *Mimosa* tannins; (iv) removal of chlorine in air-purification systems by simple scrubbing procedure since aqueous solutions of *Mimosa* tannins remove chlorine quantitatively through exceptionally rapid reaction with their highly activated benzenoid ring systems.

In this survey we have avoided rather than overlooked coverage of the traditional use of tannins in leather manufacture and hence the importance of structure in relation to adsorption, retannages, color development (reddening), and sludge formation. Previous reviews (Roux, 1970, 1972, 1978; Roux et al., 1975) have covered some of these aspects.

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Loblolly Pine Bark Polyflavanoids

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The inner bark of *Pinus taeda* L. contains (+)-catechin, the procyanidin B-1 (a C-4 to C-8 linked (-)-epicatechin to (+)-catechin dimer), and three polymeric procyanidins that have distinctly different solubility and chromatographic properties. An ethyl acetate soluble polymer (0.20% of bark, $M_n = 1200$) was purified by chromatography on LH-20 Sephadex. A water-soluble tannin (6.3% of bark, $M_n = 2100$) and an acetone/water-soluble tannin (3.7% of bark, $M_n = 2900$) were purified by chromatography on cellulose columns. Despite differences in their physical properties, thiolysis with benzenethiol and ^{13}C -NMR spectra indicated that the three polymeric procyanidins were composed of C-4 to C-8 (or C-6) linked (-)-epicatechin upper units (chain extenders) and that the lower unit (chain initiator) was (+)-catechin.

Loblolly pine (*Pinus taeda* L.) is the principal commercial softwood of the southeastern United States, accounting for nearly one-half of the total southern pine inventory. At advanced ages, loblolly pine trees may attain diameters of 60 in. and heights of 150 ft. These trees typically are grown on a rotation age of 30-80 years, and the timber is used for a substantial part of the pulp and paper, lumber, plywood, and particle board produced in the United States (Koch, 1972). Large amounts of bark are harvested with the trees, most of which is burned for steam generation. However, loblolly pine bark is a rich source of polyflavanoids and the petroleum shortage of 1973 renewed interest in the possibilities for using these polymers to replace phenol in wood adhesives. Many approaches have been investigated, but none has been found

commercially viable (Hemingway, 1978). More complete knowledge of the structure and properties of these polymers is needed if advances in using them are to be made.

Previous work on loblolly pine bark polyflavanoids concentrated on the water-soluble and alkali-soluble polymers in the outer bark (Hemingway and McGraw, 1976, 1977). Although results of the studies suggested polymers dominated by (-)-epicatechin units linked by C-4 to C-8 (or C-6) bonds, yields of thiolysis products were low ($\leq 5\%$), and some of the analytical data did not fit well with that expected of a simple procyanidin-B type of polymer. During the conversion of inner to outer bark, several processes could cause differences in the chemistry of polymers from the two tissues. Outer-bark polymers of structures that differ from those found in the inner bark may be formed during death of phloem parenchyma, or by the cork cambium in much the same manner as occurs in heartwood formation (Hillis, 1977), or by the deposition of a secondary type of lignin in the outer bark (Hergert,

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