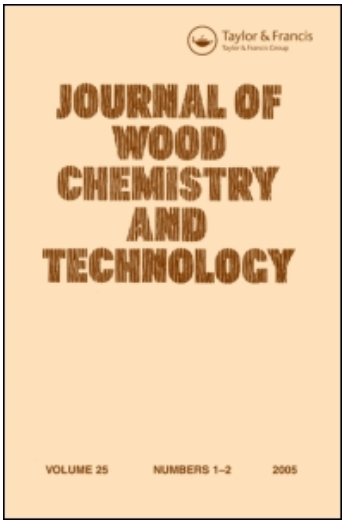

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CONDENSED TANNINS: REACTIONS OF MODEL COMPOUNDS WITH FURFURYL ALCOHOL AND FURFURALDEHYDE

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ABSTRACT

Reaction products of phloroglucinol or catechin with furfuryl alcohol and furfuraldehyde were studied. In reactions of furfuryl alcohol with phloroglucinol, only 2-furyl-(1',3',5'-trihydroxyphenyl) methane was obtained as product, and 53% of the phloroglucinol was recovered. Reactions of furfuryl alcohol with catechin gave 2-furyl-(8-catechinyl) methane and 2-furyl-(6-catechinyl) methane in 4.0% and 1.5% yields, respectively, while 62% of the catechin was unreacted. Polymeric furans with few catechin moieties made up the oligomeric products (38% of catechin). Reaction of phloroglucinol with furfuraldehyde gave 2-furyl-di(1',3',5'-trihydroxyphenyl) methane, an unstable product that readily polymerized during isolation. The solid state ^{13}C-NMR spectrum of the higher polymers suggested one phloroglucinol moiety per furan unit, but lower oligomers contained more furan-furan condensation products. Reactions of catechin with furfuraldehyde gave 2-furyl-di(8-catechinyl) methane and the two diastereomers of 2-furyl-(6-catechinyl)-(8-catechinyl) methane in low yield, with 65% of the catechin unreacted.

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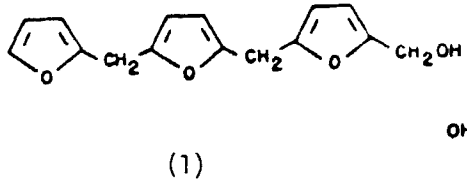
INTRODUCTION

Rapid development of new composite wood products has placed the forest products industry in a position of heavy reliance on chemical manufacturers for adhesives. The petroleum shortage of the mid-1970's, in juxtaposition with a strong housing demand, caused the forest products industry to intensify the search for alternative adhesives based on their own resources, such as lignins, tannins, and furans. Reports[1-3] on the use of condensed tannin-furan systems as wood adhesives have suggested that the combination of these two renewable resources may hold promise as an approach that would permit the forest products industry to be more self-sufficient.

The apparent advantages of replacing formaldehyde with furfuraldehyde in tannin-based adhesives could include more controllable condensation reactions because of possible steric constraints and also could afford an opportunity to overcome possible health concerns associated with the use of formaldehyde. Both furfuryl alcohol and furfuraldehyde undergo self condensation in the presence of acid catalysts to give polymers primarily of types (1)[4-6] and (2)[7], respectively. In view of the facile



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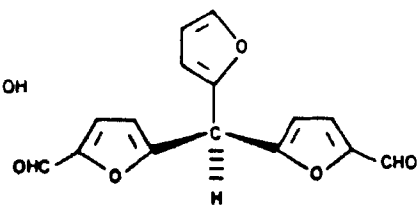


(2)

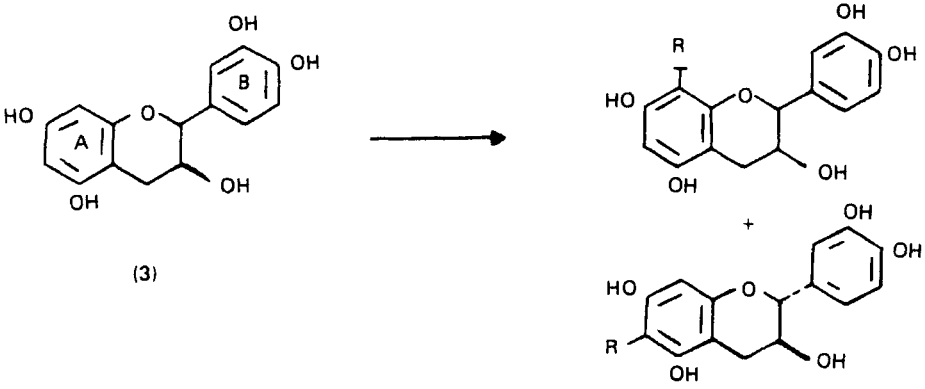
self-condensation reactions of these compounds, there is question about the degree of intermolecular tannin-furan chemical bonding required to produce copolymers in adhesive applications. In addition, suitable model compounds, necessary for

interpretation of the structure and properties of the polymers, have not been described. This study was undertaken to make appropriate model compounds and to gain more information about how readily furfuryl alcohol and furfuraldehyde react with flavanoids bearing a phloroglucinol A-ring representative of the condensed tannins from conifer barks.

RESULTS AND DISCUSSION

Reactions With Furfuryl Alcohol

The phloroglucinol A-ring in catechin (3) has been demonstrated to readily undergo electrophilic substitution.[8,9]



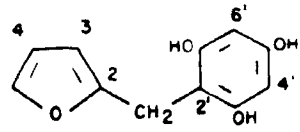
(3)

where R = Br
= o- or -p-hydroxybenzyl
= 4-flavanyl

The ready acid-catalyzed condensation of furfuryl alcohol probably proceeds via a carbocation intermediate, so it may be captured by the phloroglucinol A-ring of the flavanoid unit.

When phloroglucinol was reacted with furfuryl alcohol in alcohol solution with an acetic acid catalyst, little or no phenol reacted. Both hydrochloric and p-toluene sulfonic acids were used in attempts to force the condensation, but this only resulted in rapid resinification of the furfuryl alcohol. To promote intermolecular condensation and to minimize furan self-

condensation, aqueous solutions of phloroglucinol and furfuryl alcohol were treated at 100°C in the presence of acetic acid. These conditions provided a phloroglucinol reaction product in low yield (10%) together with some oligomeric materials. The phloroglucinol derivative was shown to be 2-furyl-(1',3',5'-trihydroxyphenyl)-methane (4) from ^{13}C-and ^{1}H-NMR data (Tables 1 and 2). Both the phloroglucinol and furan rings were clearly discernible, with the methylene protons appearing at δ 3.90 PPM and the carbon chemical shift at 21.6 PPM. Acetylation of this product gave the triacetate as colorless crystals whose ^{13}C- and ^{1}H-NMR spectra were fully consistent with the proposed structure (4).



(4)

Attempts to make the di- and tri-substituted phloroglucinol derivatives through use of a higher molar ratio of furfuryl alcohol to phloroglucinol only resulted in a decrease in yield of product (4) and an increase in yield of oligomers. Considerable unreacted phloroglucinol was recovered from these reactions, suggesting that these oligomers were predominantly polymeric furans.

When catechin was used in place of phloroglucinol, two low molecular weight phenolic products were obtained and purified by reverse-phase HPLC. ^{13}C-NMR data of these products clearly showed that both were made up of equimolar proportions of catechin to furan units and were hence regioisomeric to one another. Studies of proton chemical shifts of substituted catechin derivatives by Hundt and Roux[10] and by Batterham and Highet[11] have established that, in flavanoid systems, the H-8 chemical shift

TABLE 1

Selected ^{13}C-NMR Chemical Shifts of Products with Furfuryl Alcohol

Compound	Catechin Unit C2	C3	C4	C6	C8	Methylene Bridge	Furan Unit C2	C3	C4	C5
	δ PPM FROM TMS									
Furfuryl Alcohol							155.6	106.9	110.4	142.2
Penta-acetate of catechin (3)	77.8	68.4	24.0	110.2	108.8					
2-Furyl-(1',3',5'-trihydroxyphenyl)-methane (4)				107.3*	95.0**	21.6	157.2	104.8	110.3	140.3
Tri-acetate of (4)				120.5*	114.1**	21.0	152.2	106.0	110.4	141.2
2-Furyl-(8-catechinyl)-methane (5)	82.3	68.1	28.4	95.7	107.5	21.9	154.2	105.1	110.5	140.4
Penta-acetate (5)	78.0	68.3	24.3	109.9	116.2	22.5	152.6	105.9	110.5	142.2
2-Furyl-(6-catechinyl)-methane (6)	81.9	67.8	28.6	107.5	95.4	21.9	155.0	105.1	110.3	140.6
Penta-acetate of (6)	78.0	68.4	24.8	116.8	109.0	23.2	152.0	106.1	110.5	141.4

*Substituted phloroglucinol carbon
**Unsubstituted phloroglucinol carbon

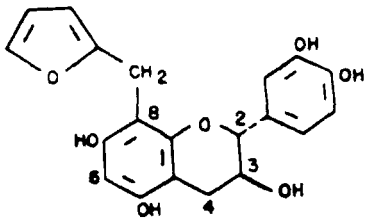
TABLE 2

Selected ^{1}H-NMR Chemical Shifts for Products of Reaction with Furfuraldehyde

Compound	Catechin Unit					Methylene	Furan Unit		
	H2	H3	H4	H6	H8	Bridge	H3	H4	H5
	δ PPM from TMS								
2-Furyl-(1',3',5'-trihydroxyphenyl)-methane (4)				6.0*	6.0*	3.90	5.84	6.20	7.25
Tri-acetate of (4)				6.89*	6.89*	3.83	5.85	6.22	7.23
2-Furyl-(6-catechinyl)-methane (6)	4.60	3.90	2.6-2.9	-	6.13	3.85	5.80	6.15	7.21
Penta-acetate of (6)	5.1---5.20		2.7-2.8	-	6.63	3.93	5.91	6.24	7.12
2-Furyl-(8-catechinyl)-methane (5)	4.55	3.90	2.6-2.9	6.03	-	3.95	5.85	6.16	7.20
Penta-acetate of (5)	5.0---5.20		2.7-2.9	6.69	-	3.75	5.90	6.23	7.19

*Phloroglucinol protons

occurs at lower field than does the corresponding H-6 signal. Examination of the ^{1}H-NMR of the two compounds showed that the more mobile compound had a phloroglucinol A-ring proton at δ 6.03 PPM and that the other compound had an A-ring at δ 6.13 PPM. On this basis, the more mobile compound was assigned structure (5) with substitution at C-8, and the other compound was assigned structure (6) of the C-6 substituted isomer. The assignments of



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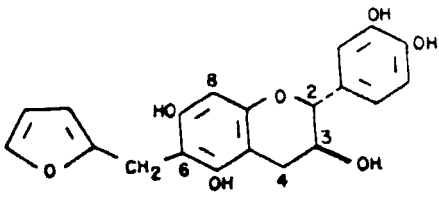


(6)

structures of these compounds were further corroborated by the ^{1}H-NMR data of the penta-acetate derivatives. Though there was little difference in the chemical shifts of the A-ring protons, the methylene bridge protons differed by 0.18 PPM with the C-6 substituted isomer more downfield than the C-8 substituted derivative. Similar differences in the chemical shifts of methylene bridge protons were observed in the peracetates of *o*- and *p*-hydroxybenzyl substituted catechin.[8] The larger downfield shift of the C-6 substituted peracetates was probably caused by the exposure of the methylene protons to the deshielding regions of the two neighboring acetate functions, whereas only one acetate at C-7 was adjacent to the methylene protons in the C-8 substituted derivative.

The yields of the two isomers were low, about 4.0% for the C-8 substituted product and 1.5% for the C-6 substituted isomers. The ratio of yields of 2.7:1 for the C-8 to C-6 isomer reflects the greater reactivity at the C-8 position, which is in

agreement with ratios obtained in other studies.[8,12] Unreacted catechin was recovered in about a 62% yield, while oligomeric materials accounted for about 38% of the catechin. Most of the latter material precipitated out of the aqueous reaction mixture as a gummy solid. The yield of the precipitate increased from 38% after 2.5 hours of heating to about 49% after 4.5 hours. A sample of these oligomeric products was fractionated on Sephadex LH 20[13] using ethanol as the solvent. The low molecular weight products and unreacted starting materials were eluted in the first fractions, and the oligomeric products were separated into more (A) and less mobile (B) fractions. Small samples of each fraction were acetylated, and the number average molecular weights were determined by vapor pressure osmometry, both for the parent and acetylated derivatives (Table 3). The separation obtained on the Sephadex column was a function of molecular weight, the more mobile fraction being of lower molecular weight. The carbon and hydrogen analyses of the two fractions and of their peracetate derivatives were nearly identical, suggesting very similar compositions. However, the larger change in molecular weight obtained by acetylation of the higher molecular weight fraction suggests a higher proportion of catechin moieties in these oligomers than in the less condensed fractions, an observation counter to that which would be expected from a simple linear polymer structure.

Evidence for the presence of catechin functionality in the oligomers was obtained from their ^{13}C-NMR spectra.[14] Prominent signals observed at chemical shifts of 67.8 and 81.8 PPM were attributable to the C-3 and C-2, respectively, of the catechin heterocyclic ring. Also apparent were signals consistent with the furan ring and the methylene bridge carbon at 22.0 PPM. The location and shape of the furan signals were in many respects similar to those observed in a homogeneous furan polymer obtained by heating furfuryl alcohol alone in aqueous

TABLE 3

Molecular Weight and Composition of Oligomers from Reaction of Catechin with Furfuryl Alcohol

	Mw_n	%C	%H
Sample A	1096	63.9	5.3
Peracetate of A	1232	62.8	5.0
Sample B	1679	64.3	5.3
Peracetate of B	2170	63.1	5.0

solution with an acetic acid catalyst. The broad signal at 107 PPM is assigned to the C-3 and C-4 of the furan unit, with di-substitution at the C-2 and C-5 positions.[15] Though a large proportion of intermolecular linkages are between furan units themselves, it is clear that there are some bonds between furan and catechin units in these oligomers.

Reactions With Furfuraldehyde

Unlike reactions with furfuryl alcohol, acetic acid readily catalyzes the condensation of furfuraldehyde with the formation of black glassy products in alcohol solutions heated at 100°C. The reactions of furfuraldehyde with phloroglucinol and catechin were more controllable when carried out at ambient temperature. Formation of excess polymeric products could be avoided by restricting the reaction time to several hours and stopping the reaction as soon as the gummy precipitate appears. Overnight reactions at ambient temperature gave mostly insoluble polymers.

In the reaction of furfuraldehyde with phloroglucinol, only one low molecular weight product was obtained. The ^{13}C-NMR spectra clearly showed furan carbon chemical shifts at 105.9, 110.0, and 141.0 PPM, together with the quarternary carbon at 154.9 PPM (Table 4). The phloroglucinol carbon shifts occurred

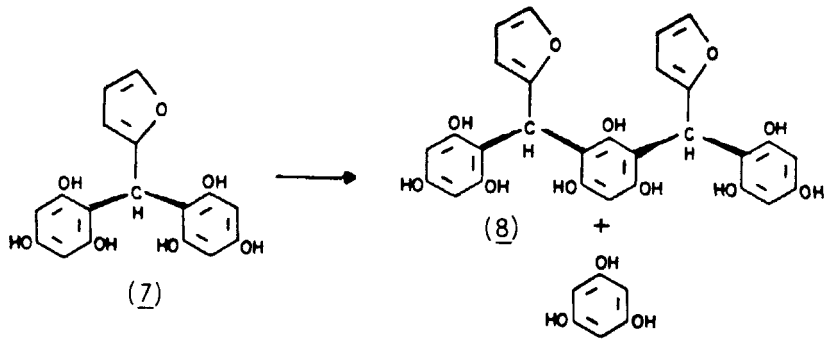
TABLE 4

Selected ^{13}C-NMR Chemical Shifts of Products with Furfuraldehyde

Compound	Catechin Unit C2	C3	C4	C6	C8	Methylene Bridge	Furan Unit C2	C3	C4	C5
	δ PPM from TMS									
Furfuraldehyde							154.1	122.0	114.0	148.0
Catechin	82.0	67.9	28.1	96.7	95.7					
2-Furyl-di(1',3',5'-trihydroxyphenyl)-methane (7)				106.5*	93.3**	30.3	154.9	105.9	110.0	141.0
Hexa-acetate of (7)				121.6*	114.5**	33.4	-	107.9	110.2	142.0
2-Furyl-di-(8-catechinyl)-methane (9)	82.1 82.4	67.4 67.6***	27.8	96.6	106.7	30.0	156.3	105.4	110.0	140.8
2-Furyl-(6-catechinyl)-(8-catechinyl)-methane) A	82.0 83.0	66.9 67.8	28.5	107.4 97.0	95.8 106.4	30.8	155.3	106.2	110.1	141.1
2-Furyl-(6-catechinyl)-(8-catechinyl)-methane B	81.9 83.3	67.3 67.8	28.8	107.4 96.9	95.8 106.2	30.7	155.2	106.0	110.1	141.1

*Substituted phloroglucinol
**Unsubstituted phloroglucinol
***Rotational isomers

at 106.5 PPM for the substituted carbon and at 96.3 PPM for the unsubstituted carbons. The bridging methine carbon signal was at 30.3 PPM. On the basis of the ^{13}C-NMR spectrum, the product could be assigned structure (7). This structure could also be confirmed by the ^{1}H-NMR data (Table 5). The phloroglucinol ring protons occurred at δ 6.05 PPM. Also, the signal at δ 7.30 PPM is attributable to the furan H-5, and the multiplets that integrated for two protons at δ 6.25 PPM account for the H-3 and H-4 protons.



Although product (7) was readily separated from starting materials and oligomers by chromatography on Sephadex LH-20, cellulose TLC of the freeze-dried products invariably showed the presence of phloroglucinol and oligomers as impurities, even after repeated chromatography and drying. The TLC of the eluate from the Sephadex column showed that complete separation had been achieved. These observations suggest that product (7) is unstable and possibly undergoes self-condensation to oligomers (i.e., 8) with the release of phloroglucinol. A sample of the purified compound (7) when heated in water or alcohol gave high yields of phloroglucinol and oligomers. Additionally, product (7) also decomposed after standing for several days in ethyl acetate at ambient temperature. In comparison, 2-furyl-(1',3',5'-trihydroxyphenyl) methane (4) is stable, so the methine

TABLE 5

Selected ^{1}H-NMR Chemical Shifts for Products of Reaction with Furfuraldehyde

Compound	Catechin Unit H2	H3	H4	H6	H8	Methylene Bridge	Furan Unit H3	H4	H5
	δ PPM from TMS								
2-Furyl-di(1',3',5' trihydroxyphenyl)-methane (7)				6.0*	6.0*	6.05	6.25	6.25	7.30
Tri-acetate of (7)				6.86*	6.86*	5.83	5.87	6.22	7.28
2-Furyl-di(8-catechinyl)-methane (9)	4.33d 4.57d	3.7-4.1	2.3-3.0	6.03 6.06	- -	6.30	5.70	6.15	7.23
Deca-acetate of (9)	4.30d 4.70d	4.75-5.1	2.3-3.1	6.48 6.50	- -	6.02	5.80	6.20	7.20
2-Furyl-(6-catechinyl)-(8-catechinyl)-methane A	4.55d 4.58d	3.7-4.3	2.3-3.0	5.94	6.19	6.05	5.90	6.10	7.27
Deca-acetate of (A)	4.9----5.2		2.4-2.9	6.52	6.59	5.88	5.85	6.20	7.23
2-Furyl-(6-catechinyl)-(8-catechinyl)-methane (B)	4.57d 4.65d	3.8-4.2	2.4 3.0	6.14	6.14	6.45** 6.40	5.76** 5.97	6.25** 6.16	7.25** 7.20
Deca-acetate of (B)	4.75---5.25		2.4-3.1	6.53	6.56	5.90	5.85	6.20	7.20

*Phloroglucinol protons
**Signals approximately 35% of those below may be due to rotational isomers.

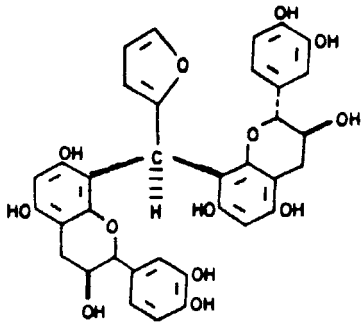
carbon in (7) must be particularly reactive as a result of the extra phloroglucinol moiety attached to it. The ready substitution at this bridging carbon may be compared with the C-4 in procyanidins where two phloroglucinol A-rings are attached. The interflavanoid bond of procyanidins is also labile, but much less so than (7). Steric barriers around the C-4 of the interflavanoid bond in procyanidins may slow this reaction in comparison to a compound such as (7). However, the instability of (7) is another example of the reactivity of a methine carbon substituted with two units of phloroglucinol functionality, as occurs in the condensed tannins of most conifer barks in contrast to the tannins of wattle, which consist of flavan units with resorcinol A-rings and which are considerably more stable to cleavage.[16]

When the reaction of phloroglucinol and furfuraldehyde was conducted in ethanol at higher solids content, highly condensed insoluble products were obtained. Only small amounts of phloroglucinol were detected when the precipitate was washed with organic solvents. The fact that phloroglucinol was a major constituent of the polymer was also shown by a solid state ^{13}C-NMR spectrum that was consistent with structure (8). The chemical shifts of the solid sample appeared approximately 2 PPM downfield from those of the solution spectrum of (7). The distinctive methine carbon, which bridges the furan and phloroglucinol rings observed at 30.3 PPM in the solution spectrum of (7), is at 32 PPM in the spectrum of the solid sample. Unlike solution ^{13}C-NMR signals, the solid probe provides chemical shifts of comparable intensity as a result of close proximity to a hydrogen in the solid state. Hence, to determine the ratio of the furan to the phloroglucinol functionality, the relative areas of the signals at 154, 143, 109, and 99 PPM were measured, since the number of furan moieties may not necessarily be the same as the number of phloroglucinol units. The signal at 143 PPM is attributable to only C-5 of the furan ring, and the signal at 99 PPM is

attributable to only unsubstituted carbon of the phloroglucinol ring. Since the areas of these two signals are approximately equal, there is about one furan unit for every phloroglucinol unit in the polymer. In the solution spectrum of furfuraldehyde, the carbon β to the aldehyde group has a chemical shift of 123 PPM. The solid state ^{13}C spectrum of the insoluble polymer also has signals at 124 and 126 PPM, indicating the presence of furfuraldehyde self-condensation products. Further indications of self-condensation of the furan are the distinctive signals at 14 and 17 PPM, which can be attributed to methyl carbons in methyl furan[15] presumably brought about by disproportionation of the aldehyde functionality.

Catechin shows less reactivity than phloroglucinol in condensation reactions with furfuraldehyde. Unlike reactions with phloroglucinol, catechin and furfuraldehyde did not react to form a gel under conditions of high solids content. The combined yield of low molecular weight products was also smaller, and over 60% of the catechin was recovered after reaction.

In reactions of catechin with furfuraldehyde, substitution occurred at both the C-6 and C-8 positions to give rise to several regio-isomers that were difficult to separate.



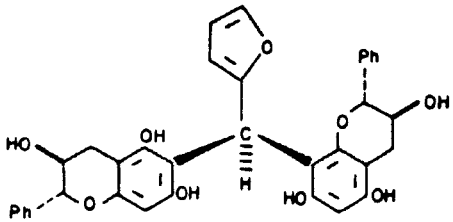
(9)

However, the C-8, C-8 substituted product (9) was isolated by repeated chromatography on Sephadex LH-20 by first eluting with

ethanol and then rechromatography of the partially purified product using ethanol-water (1:1, v/v) solvent. In both the ^{13}C- and ^{1}H-NMR spectra, signals attributable to catechin and furan units were readily apparent, and the methine carbon appeared at 30.0 PPM, which is consistent with the bridging carbon in (7) (Tables 4 and 5). The ^{13}C-NMR spectrum showed the substituted and unsubstituted carbons of the phloroglucinol A-rings at chemical shifts of 106.6 and 96.6 PPM, which are consistent with substitution at the C-8 positions of both catechin units.[16] It is interesting to note that the C-2 (82.1 and 82.4 PPM), C-3 (67.4 and 67.6 PPM), and the substituted C-8 (106.5 and 106.7 PPM) chemical shifts of the two catechin units were not coincident, suggesting unusual phenomenon of internal atropisomerism arising from steric constraint to free rotation about the interflavanoid bond.

Two other products of the reaction of catechin with furfuraldehyde were isolated by chromatography on Sephadex LH-20 and then separated further by HPLC on Zorbax CN columns eluted with methanol-water (15:85, v/v). The ^{13}C-NMR data of both compounds were in many respects similar to the spectrum of (9) and almost identical to each other. The presence of two separate chemical shifts at 95.8 and 97.0 PPM for the more mobile compound on HPLC and at 95.8 and 96.9 PPM for the other compound that were attributable to unsubstituted C-8 and C-6 catechin A-ring carbons, respectively, clearly showed that the two compounds must have two catechin units, one substituted at the C-6 position and the other at the C-8 position.[16] This conclusion was also corroborated by the two distinct substituted A-ring carbon signals at 106.4 and 107.4 PPM that were assigned to the substituted C-8 and C-6 carbons, respectively, in the more mobile compound. Similar differences in the chemical shifts of the substituted A-ring carbons were observed for the other compound at 106.4 and 107.4 PPM, respectively. These two

compounds are therefore diastereomers. In the R and S convention, the C-8 substituted catechin has priority over its C-6 substituted counterpart, so the R isomer is compound (10) and the S isomer is compound (11). Although the ^{13}C- and ^{1}H-NMR data clearly show



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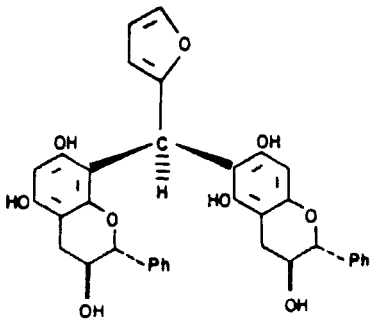

(11)

that these two compounds are C-6 and C-8 substituted diastereomers, assignment of the configuration of the two products has not yet been possible. Efforts to resolve this question are continuing. The C-6 and C-6 substituted isomer was not isolated. Difficulty in obtaining this product was not unexpected, since other studies[8,12] have shown that the C-6 position is only about one-third as reactive as the C-8 position in substitutions with bulky electrophiles.

The products of the reaction of catechin with furfuraldehyde, such as (9), are relatively stable in comparison to the phloroglucinol derivative (7). This is possibly caused by the bulk of the catechin function inhibiting further condensation, possibly through nucleophilic displacement reactions such as that proposed for the formation of (8). However, under acidic conditions and in the presence of phloroglucinol or phenyl-methane thiol as nucleophiles, product (9) readily released catechin as in the acid-catalyzed cleavage of the interflavanoid bond of procyanidins.[16]

EXPERIMENTAL

^{1}H-NMR spectra at 80 MHz and ^{13}C-NMR spectra at 20 MHz were recorded with a Varian FT-80A spectrometer.[13] High performance liquid chromatography (HPLC) was carried out on a Waters Associates M-6000 liquid chromatograph.[13] Two dimensional thin-layer chromatography (TLC) was with Schleicher and Schull F-1440[13] cellulose sheets in the solvent systems (A) t-butanol-acetic acid-water (3:1:1, v/v/v) and (B) 6% acetic acid (v/v). Plates were visualized after spraying with either vanillin-HCl, ferric chloride-potassium ferricyanide on cellulose, or formalin-H_2SO_4 on Si-gel plates. Column chromatography was with Sephadex LH-20[13] in columns 15 mm or 25 mm (i.d.) x 900 mm long.

2-Furyl-(1',3',5'-trihydroxyphenyl) methane (4)

Phloroglucinol (3.2 g) and furfuryl alcohol (2.0 g) were suspended in water in the presence of HOAc (1.0 ml) in a sealed vial and the mixture heated at 105°C for 2 hours. The soluble reaction mixture was separated from the precipitated gum and freeze-dried. The dried product was fractionated by chromatography on Sephadex LH-20, using EtOH-H_2O (1:1, v/v) as the solvent. Fractions were monitored by cellulose TLC developed with 6% HOAc. The product was isolated and freeze-dried to give 0.43 g of a light-colored solid, Rf (A), 0.80; Rf (B), 0.90. ^{1}H-NMR in acetone-d_6: δ 7.93 (br,OH); 7.25 (m,1H); 6.20 (m,1H); 6.00 (s,2H); 5.84 (m,1H); and 3.90 (2H). ^{13}C-NMR in acetone-d_6: 21.6, 95.0, 104.8, 107.3, 110.3, 140.3, and 157.2 PPM.

Acetylation with pyridine-acetic anhydride gave the triacetate, which was crystallized from EtOH-H_2O as colorless plates, m.p. 98-99°C. Found: C, 61.3; H, 4.9%; $C_{17}H_{16}O_7$ requires C, 61.4; H, 4.8%. ^{1}H-NMR in $CDCl_3$: δ 7.23 (m,1H); 6.89 (s,2H); 6.22 (m,1H); 5.86 (m,1H); 3.83 (bs,2H); and 2.25,

2.22 (9H). ^{13}C-NMR in $CDCl_3$: 20.7, 21.6, 23.4, 106.0, 110.2, 114.1, 120.5, 141.0, 152.0, and 168 PPM.

2-Furyl-(6-catechinyl) methane (6)

Catechin (2.9 g) and furfuryl alcohol (1.0 g) were dissolved in H_2O (100 ml) containing HOAc (1.0 ml) in a sealed vial, and the mixture was heated at 100°C for 2 hours. The soluble reaction mixture was separated from the precipitated gum and freeze-dried. The product was fractionated by chromatography on Sephadex LH-20 by eluting with EtOH-H_2O (1:1, v/v) as the solvent. Fractions (20 ml) were collected, and tubes 104-113 gave 0.10 g of crude product. The compound was purified by HPLC on a DuPont Zorbax CN column (9.4 mm x 25 cm) by eluting with MeOH-H_2O (20:80, v/v) at a flow rate of 2.0 ml/min, where compound (6) was eluted at a retention of 33.0 ml. Two dimensional cellulose TLC showed one compound at Rf (A) 0.60 and Rf (B) 0.85. ^{1}H-NMR in acetone-d_6: δ 7.80 (vb,OH); 7.21 (d,1H); 6.75-6.87 (3H); 6.15 (m,1H); 6.13 (s,1H); 5.80 (m,1H); 4.60 (m,1H); 3.85 (s,2H); and 2.6-2.9 (m,2H). ^{13}C-NMR in acetone-d_6: 21.9, 28.6, 67.8, 81.9, 95.4, 105.1, 107.5, 110.3, 140.6, and 155.0 PPM. MS, m/e (%): 370 (55), 265 (30), 219 (100), 177 (50), and 152 (45).

Acetylation of compound (6) with acetic anhydride and purification on TLC (Si-gel, benzene-acetone 4:1, v/v, Rf 0.63) gave the penta-acetate. Found: C, 61.9; H, 4.9%; $C_{30}H_{28}O_{12}$ requires C, 62.1; H, 4.8%. ^{1}H-NMR in $CDCl_3$: δ 7.1-7.3 (m,3H); 7.12 (m,1H); 6.63 (s,1H); 6.24 (m,1H); 5.91 (m,1H); 5.1-5.2 (m,2H); 3.93 (s,2H); 2.7-2.80 (m,2H); 1.99 (s,3H); and 2.26 (br s,12H). ^{13}C-NMR in acetone-d_6: 23.2, 24.8, 68.4, 78.0, 106.1, 109.0, 110.5, 116.8, 141.4, and 152.0 PPM.

2-Furyl-(8-catechinyl) methane (5)

Further elution of the Sephadex LH-20 column with the same solvent gave the crude product in fractions 122-140 (160 mg).

A sample was purified by HPLC on a DuPont Zorbax CN column under the conditions above to obtain compound (5) at a retention volume of 27.0 ml. Two dimensional cellulose TLC showed one compound at Rf (A) 0.65 and Rf (B) 0.55. ^{1}H-NMR in acetone-d_6: δ 7.75 (vb,OH); 7.25 (m,1H); 6.50-6.85 (m,3H); 6.15 (m,1H); 6.03 (s,1H); 5.85 (m,1H); 4.55 (m,1H); 3.90 (br s,2H); and 2.6-2.9 (m,2H). ^{13}C-NMR in acetone-d_6: 21.9, 28.4, 68.1, 82.3, 95.7, 105.1, 107.5, 110.4, 140.4, and 154.2 PPM. MS, m/e (%): 370 (100), 219 (80), 218 (70), 251 (70), and 123 (75).

Acetylation of compound (5) with pyridine-acetic anhydride gave the penta-acetate that was purified on TLC (Si-gel, benzene-acetone, 4:1, v/v, Rf 0.65). Found: C, 61.9; H, 4.9%; $C_{30}H_{28}O_{12}$ requires C, 62.1; H, 4.8%. ^{1}H-NMR in $CDCl_3$: δ 7.21-7.31 (m,3H); 7.19 (br s,1H); 6.69 (s,1H); 6.23 (m,1H); 5.90 (m,1H); 5.0-5.2 (m,2H); 3.75 (s,2H); 2.6-2.83 (m,2H); 2.26, 2.23 (12H); and 1.97 (s,3H). ^{13}C-NMR in acetone-d_6: 22.5, 24.3, 68.3, 78.0, 105.9, 109.9, 110.5, 116.2, 141.2, and 152.6 PPM.

2-Furyl-di(1',3',5'-trihydroxyphenyl) methane (7)

A mixture of phloroglucinol (6.5 g) and furfuraldehyde (2.0 g), water (100 ml) containing EtOH (10.0 ml), and acetic acid (1.0 ml) was stirred for 4.5 hours at ambient temperature. The resulting dark green suspension was filtered over glass-wool, and the filtrate was freeze-dried. The dried product was chromatographed on Sephadex LH-20, using EtOH-H_2O (1:1, v/v) as the solvent. Phloroglucinol was recovered in tubes 18-30, and a crude isolate of the product was recovered in tubes 64-106. Oligomeric products were collected in tubes 130 and up. The crude product was rechromatographed on Sephadex LH-20, using the same solvent system to remove further quantities of phloroglucinol and oligomers. Although cellulose TLC of the eluate in tubes 64-106 showed only one product, after freeze-drying and sample work-up the cellulose plates showed phloroglucinol and oligomeric impurities. A sample of comparatively pure com-

pound was finally obtained in which the cellulose TLC showed one predominate spot at Rf (A) 0.68 and Rf (B) 0.80. ^{1}H-NMR in acetone-d_6: δ 8.2-8.8 (br,OH); 7.30 (br s,1H); 6.25 (m,2H); 6.05 (s,4H); and 5.98 (s,1H). ^{13}C-NMR in acetone-d_6: 30.3, 96.3, 105.9, 106.5, 110.0, 141.0, and 154.9 PPM.

Acetylation of (7) with pyridine-acetic anhydride gave the hexa-acetate, which was purified by preparative TLC (Si-gel, benzene-acetone, 4:1, v/v, Rf 0.55). Crystallization from MeOH gave colorless plates, m.p. 184°C. Found: C, 59.6; H, 4.7%; $C_{29}H_{26}O_{13}$ requires C, 59.8; H, 4.5%. ^{1}H-NMR in $CDCl_3$: δ 7.28 (br s,1H); 6.86 (s,4H); 6.22 (m,1H); 5.89 (m,1H); 5.83 (br s,1H); and 2.24, 1.97 (m,18H). ^{13}C-NMR in acetone-d_6: 33.4, 107.9, 110.2, 114.5, 121.6, and 142.0 PPM; the quarternary carbon signal was obscured.

Phloroglucinol-furfuraldehyde polymers (8)

Furfuraldehyde (10.0 g) and HOAc (3.0 ml) were added to a solution of phloroglucinol (10.0 g) in EtOH (100 ml), and the mixture was allowed to stand at ambient temperature overnight. The hard, dark-colored solid product was broken up and thoroughly washed with EtOAc, acetone, and finally EtOH. The washings contained only small amounts of phloroglucinol. The solid residue was dried under vacuum for two days and sent to Dr. R. H. Newman, Chemistry Division, Department of Scientific and Industrial Research, Petone, New Zealand, who recorded the solid state ^{13}C-NMR spectrum on an XL-200. The spectrum showed strong resonance at 109 PPM assignable to C-3 and C-4 of the furan unit and the substituted carbon of the phloroglucinol unit. Another strong signal at 154 PPM was assigned to the quarternary carbon of the furan unit and the hydroxylated carbons of the phloroglucinol unit. The methine bridge carbons were apparent at 32 PPM, and less intense signals were apparent at 99 PPM of the unsubstituted phloroglucinol ring and at 143 PPM of C-5 of the furan unit. Small signals were also observed at 124 and 127 PPM,

which were assigned to the C-2 carbon of the furan unit in which an aldehyde function was retained, and at 14 and 17 PPM, which were assigned to a methyl carbon that may have been obtained from a disproportionation of the furfuraldehyde.

2-Furyl-di(8-catechinyl) methane (9)

Furfuraldehyde (6.7 g) and HOAc (1.0 ml) were added to a solution of catechin (10.0 g) in EtOH (100 ml), and the mixture was allowed to stand at ambient temperature overnight. The reaction mixture was concentrated on a rotary evaporator at low temperature, and the residue was diluted with H_2O. This product was freeze-dried and then fractionated by chromatography on Sephadex LH-20 with EtOH solvent by collecting 15 ml fractions. Unreacted catechin (7.0 g) was recovered in tubes 22-37. Crude products were obtained from fractions 38-58 (1.0 g) and from 59-84 (0.45 g). Fractions 38-58 were combined and rechromatographed on Sephadex LH-20 eluting with EtOH-H_2O (1:1, v/v). As before, 15-ml fractions were collected, and fractions 29-35 gave nearly pure compound (9) in a yield of 175 mg. A small sample of this product was purified further by HPLC (DuPont Zorbax CN, 9.4 mm x 24 cm, MeOH-H_2O, 15:85, v/v) to obtain the product at a retention volume of 22.2 ml at a flow rate of 2.0 ml/min. Two dimensional cellulose TLC showed one compound at Rf (A) 0.70 and Rf (B) 0.70, Found: C, 59.4; H, 5.1%; $C_{35}H_{30}O_{13}.3H_2O$ requires C, 59.0; H, 5.1%. ^{1}H-NMR in acetone-d_6: δ 7.6-8.2 (br,OH); 7.23 (m,1H); 6.5-6.8 (m,6H); 6.30 (s,1H); 6.06 (s,1H); 6.03 (s,1H); 5.70 (m,1H); 4.59 (d,J=8Hz,1H); 4.32 (d,J=8Hz,1H); 3.7-4.1 (m,2H); and 2.3-3.0 (m,4H). ^{13}C-NMR in acetone-d_6: 27.8, 30.0, 67.4, 67.6, 82.1, 82.4, 96.6, 105.4, 106.5, 106.7, 110.0, 140.8, and 156.3 PPM.

Acetylation with pyridine-acetic anhydride and preparative TLC (Si-gel, benzene acetone, 4:1, v/v, Rf 0.43) gave the deca-acetate. Found: C, 61.0; H, 4.8%; $C_{55}H_{50}O_{23}$ requires C, 61.2; H, 4.6%. ^{1}H-NMR in $CDCl_3$: δ 6.7-7.2 (m,7H); 6.50 (s,1H); 6.48

(s,1H); 6.20 (m,1H); 6.02 (s,1H); 5.80 (m,1H); 4.75-5.1 (m,2H); 4.70 (d,J=8Hz,1H); 4.30 (d,J=8Hz,1H); 2.2-3.1 (m,4H); and 1.7-2.3 (m,30H).

2-Furyl-(6-catechinyl)-(8-catechinyl) methane (A)

Continued elution of the above Sephadex LH-20 column with EtOH-H_2O (1:1, v/v) to fractions 54-68 gave a mixture of two 2-furyl-di-catechinyl methanes. These two compounds were separated by HPLC (DuPont Zorbax CN, 9.4 mm x 25 cm, MeOH-H_2O, 15:85, v/v, 2 ml/min) to give the product A at a retention volume of 26.5 ml. After preparative HPLC the product appeared as primarily one compound on cellulose TLC Rf (A) 0.60, Rf (B) 0.75. Found: C, 58.0; H, 5.0%; $C_{35}H_{30}O_{13}\cdot 4H_2O$ requires C, 57.5; H, 5.20%. ^{1}H-NMR in acetone-d_6: δ 7.5-8.3 (br,OH); 7.27 (m,1H); 6.7-6.9 (m,6H); 6.19 (s,1H); 6.10 (m,1H); 6.05 (s,1H); 5.94 (m,1H); 5.90 (m,1H); 4.58 (d,J=8Hz,1H); 4.55 (d,J=8Hz,1H); 3.7-4.3 (m,2H); and 2.3-3.0 (m).

Acetylation with pyridine-acetic anhydride and preparative TLC (Si-gel, benzene-acetone, 4:1, v/v, Rf 0.36), gave an off-white solid. ^{1}H-NMR in $CDCl_3$: δ 6.9-7.25 (m); 6.59 (s,1H); 6.52 (s,1H); 6.20 (m,1H); 5.88 (s,1H); 5.85 (m,1H); 4.9-5.25 (m); 2.4-2.9 (m); and 1.25-2.2 (m).

2-Furyl-(6-catechinyl)-8-catechinyl) methane (B)

The isomeric 2-furyl-di-(catechinyl) methane (B) was obtained from the same mixture by collection of the peak on HPLC eluted at a retention volume of 28.6 ml. Two dimensional cellulose TLC showed that the product obtained by preparative HPLC was predominantly one compound at Rf (A) 0.60 and Rf (B) 0.75. Found: C, 57.5; H, 5.1%; $C_{35}H_{30}O_{13}\cdot 4H_2O$ requires C, 57.5; H, 5.2%. ^{1}H-NMR in acetone-d_6: δ 7.6-8.3 (br,OH); 7.20 (m,1H); 6.7-6.95 (m,6H); 6.45 (s,1/2H); 6.40 (s,1/2H); 6.25 (s,1/2H); 6.16 (m,1H); 6.14 (s,2H); 5.97 (m,1H); 5.76 (m,1/2H); 4.65 (d,J=8Hz,1H); 4.57 (d,J=8Hz,1H); 3.8-4.2 (m); and 2.3-3.0 (m).

Acetylation with pyridine-acetic anhydride and preparative TLC on Si-gel as before gave the deca-acetate at Rf 0.40. ^{1}H-NMR in $CDCl_3$: δ 6.9-7.3 (m,6H); 6.56 (s,1H); 6.53 (s,1H); 6.20 (m,1H); 5.90 (m,1H); 5.85 (s,1H); 4.90-5.3 (m,3H); 4.75 (d,J=8Hz,1H); 3.85 (s,2H); 2.4-3.1 (m,4H); and 1.25-1.30 (m).

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