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Journal of Wood Chemistry and Technology

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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-cate-chinyl) methane and the two diastereomers of 2-furyl-(6-catechinyl)-(8-catechinyl) methane in low yield, with 65% of the catechin unreacted.

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 petro-
leum 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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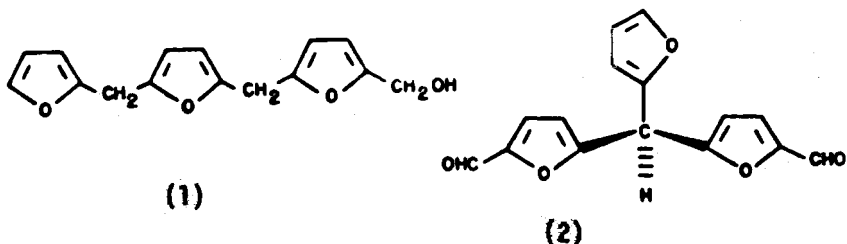
self-condensation reactions of these compounds, there is
question about the degree of intermolecular tannin-furan chemi-
cal bonding required to produce copolymers in adhesive appli-
cations. In addition, suitable model compounds, necessary for

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]


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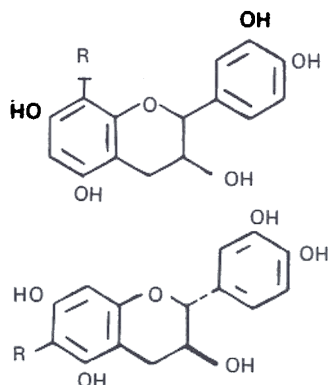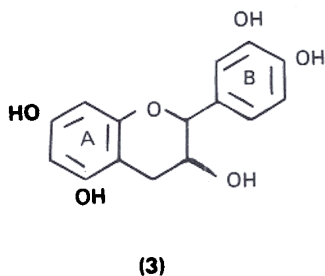
where R = Br
        = o- or -p-hydroxybenzyl
        = 4-flavanyl

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).

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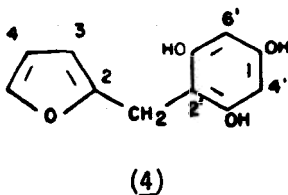
Attempts to make the di- and tri-substituted phloroglucinol
derivatives through use of a higher molar ratio of furfuryl
alcohol to phloroglucinol only resulted in a decrease in yield
of product (4) and an increase in yield of oligomers.
Considerable unreacted phloroglucinol was recovered from these
reactions, 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 deri-
vatives 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					Methylene Bridge	Furan Unit			
	C2	C3	C4	C6	C8		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 Bridge	Furan Unit		
	H2	H3	H4	H6	H8		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

$(\underline{5})$ $(\underline{6})$
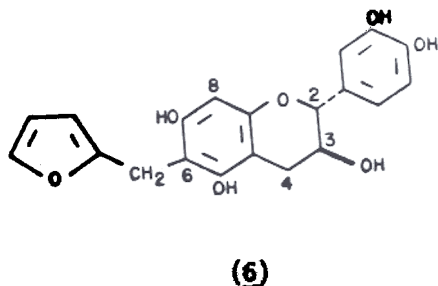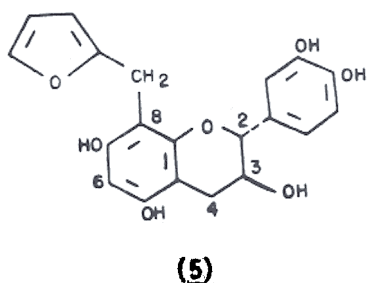
structures of these compounds were further corroborated by the
^{1}H-NMR data of the penta-acetate derivatives. Though there was
little difference in the chemical shifts of the A-ring protons,
the methylene bridge protons differed by 0.18 PPM with the C-6
substituted isomer more downfield than the C-8 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 down-
field shift of the C-6 substituted peracetates was probably cause
by the exposure of the methylene protons to the deshielding regic
of the two neighboring acetate functions, whereas only one acetal
at C-7 was adjacent to the methylene protons in the C-8 substitu:
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	C2	Catechin Unit 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.
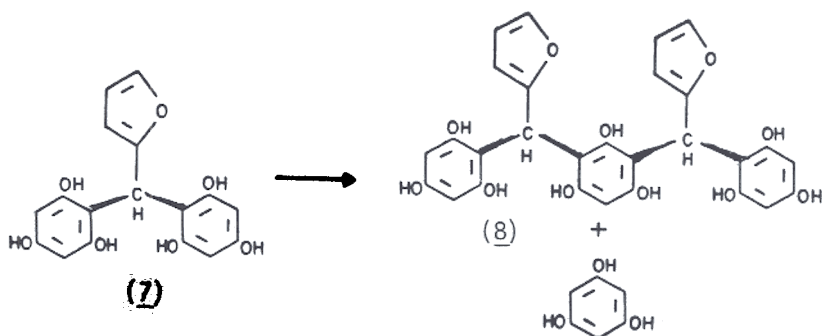
Although product (7) was readily separated from starting materials and oligomers by chromatography on Sephadex LH-20, cellulose TLC of the freeze-dried products invariably showed the presence of phloroglucinol and oligomers as impurities, even after repeated chromatography and drying. The TLC of the 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	H2	H3	Catechin Unit 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-catechin- yl)-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-catechin- yl)-(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-catechin- yl)-(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 substi-
tution 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)
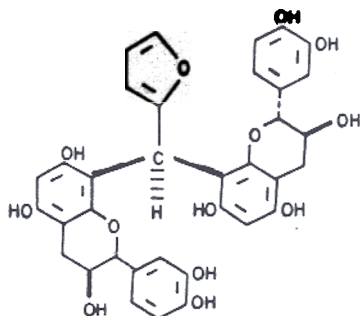
However, the C-8, C-8 substituted product (9) was isolated by
repeated chromatography on Sephadex LH-20 by first eluting with

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 fur-
furaldehyde 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

(10)   (11)
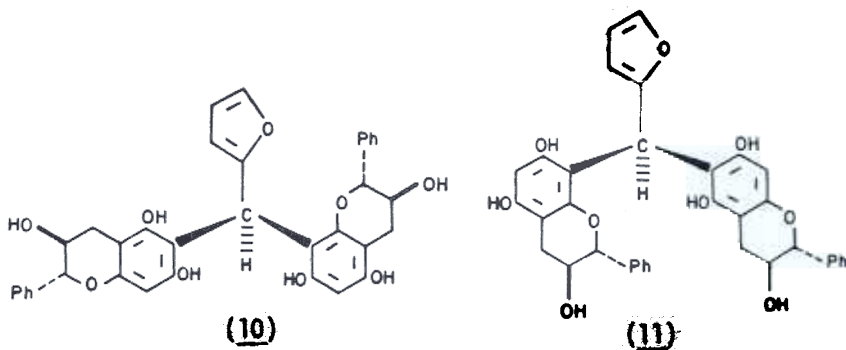
that these two compounds are C-6 and C-8 substituted diastereomers,
assignment of the configuration of the two products has not yet
been possible. Efforts to resolve this question are continuing.
The C-6 and C-6 substituted isomer was not isolated. Difficulty in
obtaining this product was not unexpected, 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 electro-
philes.

     The products of the reaction of catechin with fur-
furaldehyde, 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 dimen-
sional 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 devel-
oped 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$_2$O (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$_2$O (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$_2$O (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 ($\underline{5}$) 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 ($\underline{5}$) 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 ($\underline{7}$)

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$_2$O (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 phloro-
glucinol 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: ⋏ 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-H2O (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-H2O,
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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