

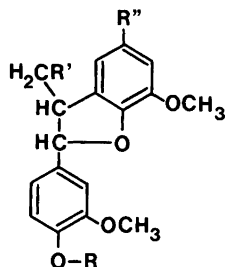
The Crystal Structure of *trans*-2,3-Dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran

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The so-called phenylcoumaran structure (i.e. two lignin units interconnected by the arrangement of linkages exemplified in compounds 1-5) constitutes an important type of structural element in lignins (see, e.g., Ref. 1). Compounds 1-5 represent models for lignin structures of the phenylcoumaran type.



- 1 R = H, R' = H, R'' = CH = CHCH₃
- 2 R = CH₃, R' = H, R'' = CH₂CH₂CH₃
- 3 R = H, R' = OH, R'' = CH = CHCH₂OH
- 4 R = H, R' = OH, R'' = CH₂CH₂CH₂OH
- 5 R = H, R' = OH, R'' = H

In 1933 Erdtman² proposed structure 1 for dehydrodiisoeugenol. This structure was later confirmed (see Ref. 3), and the structural work on 1 was completed in 1963 by Aulin-Erdtman *et al.*³ who elucidated its stereochemistry. It was shown that the methyl and the 4-hydroxy-3-methoxyphenyl substituents of the furan ring are *trans* ori-

ented. Freudenberg and Hübner⁴ showed in 1951 that dehydrodiconiferyl alcohol (3) is formed on oxidation of coniferyl alcohol. Their proof of the structure of 3 included a conversion of 3, via 4, into the derivative 2, a compound which had previously been prepared² from dehydrodiisoeugenol. The conversion of 3 as well as 1 into 2 was conducted under conditions which left the steric arrangement at the furan ring unchanged. It follows from the studies referred to above that the methylol group and the 4-hydroxy-3-methoxyphenyl group in 3 and 4 are *trans* orientated. The structure of 3 has been confirmed in recent work by Nakatsubo and Higuchi.⁵ The synthesis of the lignin-related phenylcoumaran derivative 5 has recently been described.⁶ Primarily on the basis of ¹H NMR spectral comparisons with 4, it was suggested that the synthesized compound was the *trans* isomer of 5 (for NMR studies of the steric arrangement in phenylcoumarans, see Ref. 7). The crystal structure of 5, which is described in this paper, shows that the *trans* configuration is the correct one. Bond distances and to some extent bond angles determined for the dihydrofuran ring of 5 should be representative for the corresponding features of phenylcoumaran elements in lignins.

Experimental

Structure determination. Crystal and experimental data for 5 are given in Table 1. Diffracted in-

Table 1. Crystal and experimental data for *trans*-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran, C₁₇H₁₈O₅ (T = 290 K).

M_r	302.33
Crystal system	Monoclinic
Space group ^a	C2/c (No. 15)
Unit cell dimensions/Å or °	$a = 17.514(8)$ $b = 9.782(5)$ $c = 18.301(7)$ $\beta = 109.81(3)$ $V = 2950(2)$
Z	8
$D_c/g\text{ cm}^{-3}$	1.362
M.p./°C	93–95
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$ (no absorption correction)	0.108
Crystal size/mm	0.16×0.19×0.31
Reflections for cell determination	15
(No./ θ range/°)	2.4 < θ < 11.2
Scan mode	ω -2 θ
2 θ range/°	3.5–50
2 θ scan speed/° min ⁻¹	1.0–3.9
Total No. of independent reflections measured	2779
No. of observed independent reflections [$I > 3\sigma(I)$]	1525
Test reflection; maximum variation/%	223; ±1.7
Method used to solve structure	Direct methods (MITHRIL) ^b ; electron density difference map (DRF) ^c
No. of parameters refined	271
Weights calculated according to	$w = (8.0 + F_o + 0.009 F_o ^2)^{-1}$ ^d
R	0.037
Maximum residual electron density/e Å ⁻³	0.13

^aRef. 8a. ^bRef. 9. ^cRef. 10. ^dRef. 11.

tensities were measured with a Syntex P2₁ diffractometer, using graphite-monochromated MoK α radiation. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method¹² was used to calculate the intensities.¹³ Periodic measurements of a test reflection revealed no loss in intensity during the collection of the data. Correction was made for Lorentz and polarization effects. Unit cell dimensions were determined from diffractometer setting angles for 15 reflections.

The atomic coordinates of all non-hydrogen atoms were determined by direct methods (MITHRIL).⁹ Intensity statistics indicated a centric structure, and a plausible solution was obtained within space group C2/c. Full matrix least-squares refinement^{10,14} of positional and isotropic thermal parameters for the non-hydrogen atoms gave $R = 0.114$. The introduction of anisotropic thermal parameters reduced R to 0.080. From the

subsequent electron density difference map all hydrogen atoms were located (maximum electron density 0.58 e Å⁻³).¹⁰ Inclusion of atomic coordinates and isotropic thermal parameters for the hydrogen atoms in the refinement gave $R = 0.037$.

Further details concerning the refinement of the structure are summarized in Table 1. Atomic scattering factors were taken from Ref. 8b. Calculations were carried out on an IBM 3081 computer, using the crystallographic programmes described in Refs. 10 and 14. Lists of structure factors and anisotropic thermal parameters are available from one of the authors (R.S.) on request.

Results and discussion

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2, and

Table 2. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for *trans*-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran, $\text{C}_{17}\text{H}_{18}\text{O}_5$. All atoms occupy the general eight-fold site 8f of space group $C2/c$.

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
C(1)	0.3193(1)	0.3393(2)	0.1645(1)	3.50(6)
C(2)	0.2766(1)	0.2327(2)	0.1178(1)	3.42(6)
C(3)	0.3158(1)	0.1421(2)	0.0840(1)	3.31(6)
C(4)	0.3984(1)	0.1587(2)	0.0965(1)	3.56(6)
C(5)	0.4403(1)	0.2627(3)	0.1426(1)	4.33(7)
C(6)	0.4012(1)	0.3531(3)	0.1765(1)	4.32(7)
C(7)	0.1962(2)	0.0096(3)	0.0274(2)	4.51(9)
C(8)	0.2738(1)	0.4392(3)	0.1970(1)	3.69(7)
C(9)	0.2509(1)	0.5735(3)	0.1492(1)	3.92(7)
C(10)	0.1666(1)	0.6275(3)	0.1394(2)	4.53(8)
C(11)	0.3532(1)	0.6094(2)	0.2685(1)	3.55(7)
C(12)	0.3155(1)	0.6684(3)	0.1966(1)	3.81(7)
C(13)	0.3389(2)	0.7977(3)	0.1811(2)	4.87(9)
C(14)	0.3991(2)	0.8642(3)	0.2383(2)	5.1(1)
C(15)	0.4366(1)	0.8047(3)	0.3104(2)	4.66(9)
C(16)	0.4140(1)	0.6754(2)	0.3264(1)	3.81(7)
C(17)	0.5068(2)	0.6783(5)	0.4557(2)	6.7(1)
O(1)	0.27964(9)	0.0339(2)	0.03819(9)	3.89(5)
O(2)	0.4383(1)	0.0681(2)	0.0645(1)	4.60(5)
O(3)	0.1084(1)	0.5486(2)	0.0810(1)	5.24(6)
O(4)	0.32484(9)	0.4806(2)	0.27519(8)	3.91(5)
O(5)	0.4470(1)	0.6068(2)	0.39560(9)	4.88(6)
H(C2)	0.218(1)	0.224(2)	0.109(1)	1.2(4)
H(C5)	0.500(2)	0.272(3)	0.149(1)	2.9(6)
H(C6)	0.431(2)	0.428(3)	0.208(1)	2.3(5)
H1(C7)	0.188(1)	-0.001(3)	0.076(2)	1.9(5)
H2(C7)	0.163(2)	0.077(3)	-0.002(2)	2.9(7)
H3(C7)	0.186(2)	-0.079(3)	-0.005(2)	2.4(5)
H(C8)	0.226(1)	0.398(2)	0.200(1)	0.4(4)
H(C9)	0.254(1)	0.551(3)	0.098(1)	1.9(5)
H1(C10)	0.154(1)	0.624(2)	0.187(1)	1.7(5)
H2(C10)	0.158(2)	0.727(3)	0.121(2)	2.8(6)
H(C13)	0.314(2)	0.839(3)	0.129(2)	3.3(6)
H(C14)	0.417(2)	0.957(3)	0.231(2)	4.0(7)
H(C15)	0.482(2)	0.848(3)	0.353(2)	4.2(7)
H1(C17)	0.483(2)	0.767(5)	0.475(2)	7.0(7)
H2(C17)	0.549(3)	0.702(5)	0.440(2)	7.2(7)
H3(C17)	0.522(2)	0.614(4)	0.496(2)	5.9(7)
H(O2)	0.407(2)	0.028(4)	0.024(2)	5.2(9)
H(O3)	0.062(2)	0.555(4)	0.083(2)	5.8(9)

bond distances, bond angles and selected torsion angles in Table 3. Fig. 1 shows a stereoscopic view of the unit cell, and Fig. 2 shows the molecule and the atomic labelling. The crystals of **5** consist of monomeric molecules held together by van der Waals forces and hydrogen bonds between the

hydroxy groups [O(2)ⁱ...O(3)ⁱⁱ is 2.754(3) Å, H(O2)ⁱ...O(3)ⁱⁱ 1.99(4) Å, O(2)ⁱ...O(3)ⁱⁱⁱ 2.897(3) Å and O(2)ⁱ...H(O3)ⁱⁱⁱ 2.08(4) Å; the angle O(2)ⁱ-H(O2)ⁱ...O(3)ⁱⁱ is 148(3)° and

$$^i x, y, z, \quad ^{ii} 1/2 - x, 1/2 - y, \bar{z}, \quad ^{iii} 1/2 + x, -\frac{1}{2} + y, z.$$

Table 3. Bond distances (Å) and angles (°) in *trans*-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran, C₁₇H₁₈O₅. The average C–H and O–H bond lengths are 0.98(4) and 0.84(1) Å, respectively.

Distances

C(1)–C(2)	1.394(3)	C(5)–C(6)	1.386(4)	C(11)–C(12)	1.382(3)
C(1)–C(6)	1.383(3)	C(7)–O(1)	1.426(3)	C(11)–C(16)	1.382(3)
C(1)–C(8)	1.504(3)	C(8)–O(4)	1.464(3)	C(12)–C(13)	1.388(4)
C(2)–C(3)	1.388(3)	C(8)–C(9)	1.554(4)	C(13)–C(14)	1.372(4)
C(3)–O(1)	1.365(3)	C(9)–C(10)	1.520(4)	C(14)–C(15)	1.387(4)
C(3)–C(4)	1.396(3)	C(9)–C(12)	1.493(3)	C(15)–C(16)	1.385(4)
C(4)–C(5)	1.366(3)	C(10)–O(3)	1.428(3)	C(16)–O(5)	1.376(3)
C(4)–O(2)	1.376(3)	C(11)–O(4)	1.375(3)	C(17)–O(5)	1.420(4)

Angles

C(2)–C(1)–C(6)	118.8(2)	C(10)–C(9)–C(12)	111.5(2)
C(2)–C(1)–C(8)	118.9(2)	C(9)–C(10)–O(3)	108.6(2)
C(6)–C(1)–C(8)	122.2(2)	C(12)–C(11)–C(16)	122.0(2)
C(1)–C(2)–C(3)	120.5(2)	C(12)–C(11)–O(4)	113.4(2)
C(2)–C(3)–C(4)	119.6(2)	C(16)–C(11)–O(4)	124.6(2)
C(2)–C(3)–O(1)	124.9(2)	C(9)–C(12)–C(11)	108.5(2)
C(4)–C(3)–O(1)	115.5(2)	C(9)–C(12)–C(13)	131.7(2)
C(3)–C(4)–C(5)	119.9(2)	C(11)–C(12)–C(13)	119.8(2)
C(3)–C(4)–O(2)	120.2(2)	C(12)–C(13)–C(14)	118.9(3)
C(5)–C(4)–O(2)	119.9(2)	C(13)–C(14)–C(15)	121.4(3)
C(4)–C(5)–C(6)	120.6(2)	C(14)–C(15)–C(16)	120.4(3)
C(1)–C(6)–C(5)	120.6(2)	C(11)–C(16)–C(15)	117.8(2)
C(1)–C(8)–C(9)	113.4(2)	C(11)–C(16)–O(5)	116.7(2)
C(1)–C(8)–O(4)	109.7(2)	C(15)–C(16)–O(5)	125.3(2)
C(9)–C(8)–O(4)	105.8(2)	C(3)–O(1)–C(7)	117.0(2)
C(8)–C(9)–C(10)	114.5(2)	C(8)–O(4)–C(11)	106.6(2)
C(8)–C(9)–C(12)	101.4(2)	C(16)–O(5)–C(17)	116.2(2)

Selected torsion angles

C(2)–C(3)–O(1)–C(7)	–2.8(3)	C(8)–O(4)–C(11)–C(12)	10.6(2)
C(3)–C(4)–O(2)–H(O2)	25(3)	C(9)–O(8)–C(4)–C(11)	–19.2(2)
C(2)–C(1)–C(8)–C(9)	–98.1(3)	C(9)–C(12)–C(11)–O(4)	3.1(3)
C(2)–C(1)–C(8)–O(4)	143.9(3)	C(10)–C(9)–C(8)–O(4)	–100.0(3)
C(1)–C(8)–C(9)–C(10)	139.7(3)	C(10)–C(9)–C(12)–C(11)	107.9(3)
C(1)–C(8)–C(9)–C(12)	–100.1(2)	O(4)–C(11)–C(12)–C(13)	–179.0(3)
C(1)–C(8)–O(4)–C(11)	103.4(2)	O(4)–C(11)–C(16)–O(5)	–1.0(3)
C(8)–C(9)–C(10)–O(3)	–77.6(3)	O(4)–C(11)–C(16)–C(15)	179.2(3)
C(8)–C(9)–C(12)–C(11)	–14.4(2)	C(11)–C(16)–O(5)–C(17)	–177.2(3)

O(2)ⁱ...H(O3)ⁱⁱⁱ–O(3)ⁱⁱⁱ 168(4)°]. The next shortest intermolecular contact distances are: H(C6)···H(C6)['] 2.38(5), H3(C7)···H(C9)['] 2.30(4), H3(C17)···H3(C17)['] 2.38(8) and H3(C17)···H(O3)['] 2.35(5) Å.

The aromatic C–C bond distances are normal [mean value 1.384(8) Å; r.m.s. deviation is given in parentheses] as are the C–H bond distances. The C(sp³)–O_{methoxy} bond distances [mean value

1.423(3) Å] agree well with those observed in a series of lignin-related compounds^{16,17} and agree with typical C–O single bond values.^{8c} The C(sp²)–O_{methoxy} bond distances are also similar to those observed in other lignin model compounds and show, like the C(11)–O(4) distance, partial double bond character due to the influence of the aromatic rings (cf. Ref. 8c). The C(sp³)–O_{furan} distance, 1.464(3) Å, is close to the average value of

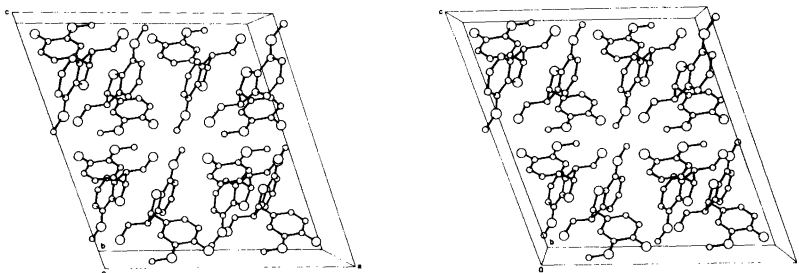


Fig. 1. Stereoscopic view¹⁵ of the unit cell of *trans*-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran, C₁₇H₁₈O₅. Hydrogen atoms are omitted.

1.47(1) Å observed in strained systems, e.g. epoxides.^{8c}

The maximum deviation of the benzene ring carbon atoms from the respective ring plane is 0.004(2) Å. The oxygen atoms connected to the benzene rings are close to the ring planes [maximum deviation 0.024(2) Å], as are the methoxy carbon atoms [maximum deviation 0.097(5) Å]. The deviations of C(8), C(9) and O(4) from the benzene ring plane of the dihydrobenzofuran unit are -0.290(5), 0.058(4) and -0.019(4) Å, respectively. The two benzene ring planes are almost perpendicular to each other [mutual angle 85.4(1)°].

As observed for previously studied lignin models,^{16,17} the C-O_{methoxy} bond angles involving the ring carbon atoms *cis* to the methyl are always

larger [average 125.1(2)°] than those involving the *trans* counterparts [average 116.1(6)°], and the methoxy hydrogen atoms closest to the benzene rings tend to be as remote as possible from the ring planes [on average 0.8(1) Å]; both these effects reduce the repulsion between the hydrogen atoms of C_{ring} and C_{methoxy} [average distance 2.30(9) Å; cf. Refs. 16 and 17].

The bond angles in the dihydrofuran unit deviate in some cases considerably from the tetrahedral value, as also found in a "neolignan" of phenylcoumaran type.¹⁸

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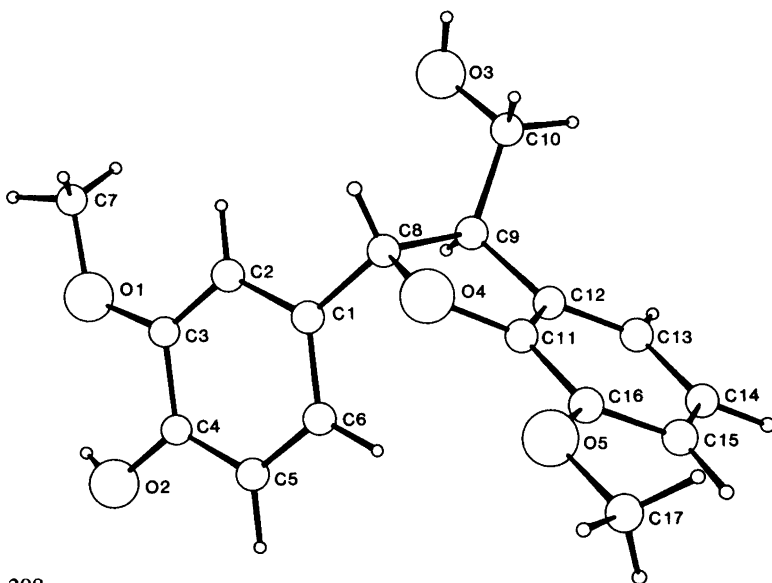


Fig. 2. The *trans*-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran molecule showing the atomic numbering.

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