Studies on Lignin Model Compounds of the β-O-4 Type: Crystal Structures of *threo*-1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol and 3-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone–Methanol (1/1)

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Structural elements of the β-O-4 type in lignins can be divided into three categories: arylglycerol β-aryl ethers (I), derivatized arylglycerol β-aryl ethers (II) and remaining structures of the β-O-4 type (III), e.g. 2-aryloxypropiophenones (IIIa). Within these categories there are structural variations arising from the nature of the aromatic groups and the stereochemistry. The crystal structures of a lignin model of category I type [*threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**)] and of the methanol solvate of a lignin model of category III type [3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone (**2**)] have been determined from single-crystal X-ray diffraction data. Compound **1** crystallizes in space group $P\bar{1}$ with $a = 7.220(3)$, $b = 10.747(7)$, $c = 12.045(6)$ Å, $\alpha = 109.41(4)$, $\beta = 90.57(4)$, $\gamma = 103.28(4)°$ and $Z = 2$. Full-matrix least-squares refinement of 314 structural parameters gave $R = 0.052$ for 2208 observed $[I > 3\sigma(I)]$ reflexions. The methanol solvate of compound **2** crystallizes in space group $Pca2_1$ with $a = 27.534(14)$, $b = 5.139(2)$, $c = 12.868(5)$ Å and $Z = 4$. Full-matrix least-squares refinement of 339 structural parameters gave $R = 0.042$ for 1092 observed $[I > 3\sigma(I)]$ reflexions.

It is well established that β-O-4 structures constitute the major type of structural element in lignins. According to recent ^{1}H NMR studies[1] 30–40 % of the units in a softwood lignin (spruce) and 40–50 % of the units in a hardwood lignin (birch) are linked to adjacent units by a β-O-4 linkage. These estimates are based on integration of the signal from H_α in β-O-4 structures in lignin acetates and comprise primarily β-O-4 structures belonging to what in this paper is denoted category I (Fig. 1); structural elements of this type could be termed arylglycerol β-aryl ethers. Category II comprises what could be called 'derivatized arylglycerol β-aryl ethers'. Several of the structural elements belonging to category II are not included in the above-mentioned estimates. The main reason for this is that the position of the signal from H_α is shifted upfield when an ether group is introduced into the α-position. There is considerable uncertainty regarding the number of β-O-4 structures of category II but it seems as if they occur much less frequently than those of category I structures. The remaining types of β-O-4 structures are grouped as category III (see Fig. 1). It can be assumed that the proportion of units involved in category III structures is rather small and is probably not included in the above-mentioned estimates to any great extent. Thus the relative distributions of the structures belonging to categories I, II and III are not known with

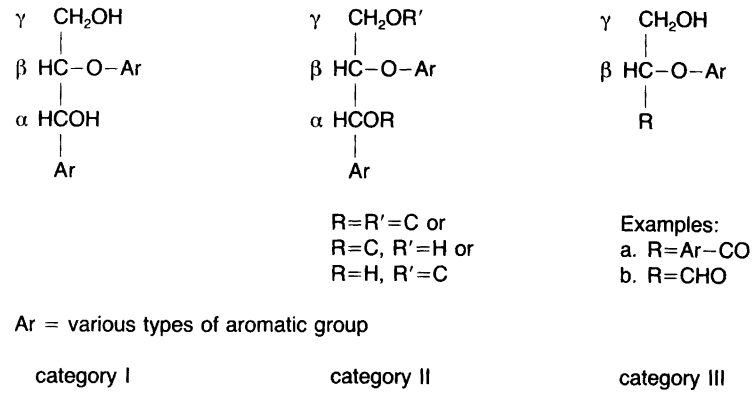


Fig. 1. Structural elements of the β-O-4 type in lignins.

certainty. However, it seems that category I structures occur in greater numbers. Questions which are of relevance in this context have been discussed recently in a paper dealing with the alcoholysis of lignins.[2]

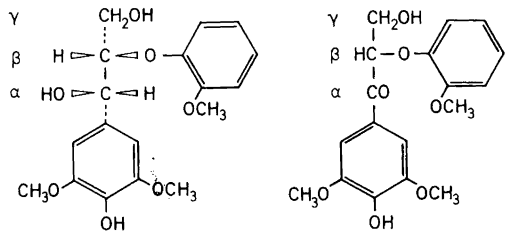
Discrepancies found in the literature regarding the numbers of β-O-4 structures in lignins are sometimes apparent and can be explained by the fact that all the structural elements shown in Fig. 1 have not always been included in the estimates. The classification of β-O-4 structures introduced in this paper is intended to facilitate the discussion of the occurrence of such structures in lignins. It should be remembered that within each category there is structural variation connected with the nature of the aromatic groups and the stereochemistry.

We have recently elucidated the stereochemistry of lignin model compounds representative of β-O-4 structures of the category I, in addition to other structural elements in lignin, on the basis of single-crystal X-ray analyses and ^{1}H NMR spectroscopic comparisons.[3-6] At the same time, X-ray studies of lignin model compounds performed by other groups appeared in the literature (Refs. 7 and 8, see also Ref. 9). As far as comparisons are possible the results reported are in agreement with those derived from our studies.

In this paper the crystal structure of *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**) is described. This complements our earlier X-ray studies since model compounds representing the corresponding type of lignin structures (syringylglycerol β-guaiacyl ethers) have not been examined by single-crystal X-ray analysis previously and, furthermore, no *threo* isomer of β-O-4 models has hitherto been subjected to such analysis. Evidence for the *threo* configuration of compound **1** has previously been obtained from ^{1}H NMR spectral comparisons.[3] The X-ray results confirm the *threo* configuration and enable conclusions to be drawn about the geometry of structural elements of the syringylglycerol β-guaiacyl ether type in lignins.

The crystal structure of the methanol solvate of 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone (**2**) is also described. Compound **2** is a model compound for β-O-4 structures of the 2-aryloxypropiophenone type, which, according to the terminology used in this paper, belongs to category III (Fig. 1). In this case there is no diastereoisomerism requiring elucidation. The data from the X-ray investigation provides, however, an idea about the bond distances and, to some extent, the bond angles in the corresponding structural elements in lignins. Structural elements of the 2-aryloxypropiophenone type seem to occur only rarely in lignins.[1,10]

The synthesis of compounds **1** and **2** has been described previously (Ref. 1, see also Refs. 12



1 **2**

Table 1. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**), $C_{18}H_{22}O_7$. Space group $P\bar{1}$. $B_{eq} = {}^4/_3 \Sigma_i \Sigma_j B_{ij} \mathbf{a}_i \mathbf{a}_j$.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
C(1)	0.7024(4)	0.5631(2)	0.7925(2)	3.42(7)
C(2)	0.7107(4)	0.7013(2)	0.8412(2)	3.53(7)
C(3)	0.7416(4)	0.7672(2)	0.9628(2)	3.55(7)
C(4)	0.7639(3)	0.6954(2)	1.0370(2)	3.37(7)
C(5)	0.7554(3)	0.5570(2)	0.9869(2)	3.46(7)
C(6)	0.7242(4)	0.4906(2)	0.8660(2)	3.72(7)
C(7)	0.7448(8)	0.9816(4)	0.9456(4)	6.7(1)
C(8)	0.7669(5)	0.3538(3)	1.0243(3)	4.29(9)
C(9)	0.6631(4)	0.4914(3)	0.6602(2)	3.58(7)
C(10)	0.4719(4)	0.3862(2)	0.6243(2)	3.36(7)
C(11)	0.3055(4)	0.4490(3)	0.6610(2)	3.93(8)
C(12)	0.4277(4)	0.1887(2)	0.4426(2)	3.72(7)
C(13)	0.5651(5)	0.1395(3)	0.3733(2)	4.71(9)
C(14)	0.5299(8)	0.0023(4)	0.3094(3)	6.9(1)
C(15)	0.361(1)	−0.0827(4)	0.3159(4)	8.3(2)
C(16)	0.2271(9)	−0.0350(4)	0.3843(4)	8.5(2)
C(17)	0.2606(6)	0.1030(3)	0.4486(3)	6.1(1)
C(18)	0.873(1)	0.196(1)	0.3055(7)	11.0(3)
O(1)	0.7514(3)	0.9023(2)	1.0185(2)	4.98(7)
O(2)	0.7963(3)	0.7622(2)	1.1558(2)	4.62(6)
O(3)	0.7848(3)	0.4966(2)	1.0668(1)	4.67(6)
O(4)	0.8130(3)	0.4257(2)	0.6189(2)	4.58(6)
O(5)	0.4624(3)	0.3286(2)	0.4967(1)	3.75(5)
O(6)	0.1432(3)	0.3466(2)	0.6635(2)	4.38(6)
O(7)	0.7286(3)	0.2350(3)	0.3765(2)	6.69(9)
H(C2)	0.696(3)	0.751(2)	0.783(2)	1.0(5)
H(C6)	0.723(4)	0.392(3)	0.831(3)	2.6(6)
H1(C7)	0.841(7)	0.977(5)	0.887(4)	7(1)
H2(C7)	0.627(7)	0.948(4)	0.893(4)	6(1)
H3(C7)	0.765(5)	1.074(5)	1.002(4)	5.4(9)
H1(C8)	0.634(5)	0.304(4)	0.990(3)	3.9(8)
H2(C8)	0.855(4)	0.328(3)	0.968(3)	2.3(6)
H3(C8)	0.789(4)	0.328(3)	1.094(3)	3.0(7)
H(C9)	0.669(3)	0.563(2)	0.622(2)	0.7(4)
H(C10)	0.465(3)	0.312(2)	0.662(2)	0.6(4)
H1(C11)	0.286(5)	0.493(3)	0.601(3)	3.6(7)
H2(C11)	0.336(4)	0.520(3)	0.741(3)	3.1(7)
H(C14)	0.618(6)	−0.032(4)	0.267(4)	5(1)
H(C15)	0.344(6)	−0.178(4)	0.269(4)	6(1)
H(C16)	0.101(7)	−0.091(5)	0.389(4)	6(1)
H(C17)	0.173(5)	0.139(4)	0.497(3)	4.3(9)
H1(C18)	0.97(1)	0.249(8)	0.316(9)	13(3)
H2(C18)	0.868(9)	0.115(7)	0.332(5)	9(2)
H3(C18)	0.827(8)	0.161(6)	0.221(6)	9(2)
H(O2)	0.793(4)	0.712(3)	1.195(3)	2.6(7)
H(O4)	0.797(5)	0.384(4)	0.544(4)	4.8(9)
H(O6)	0.051(5)	0.374(4)	0.668(3)	3.5(8)

Table 2. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone–methanol (1/1), $C_{18}H_{20}O_7 \cdot CH_3OH$. Space group $Pca2_1$. $B_{eq} = {}^4/_3 \Sigma_i \Sigma_j B_{ij} \mathbf{a}_i \mathbf{a}_j$. C(19) and O(8) are the carbon and oxygen atoms belonging to the methanol molecule.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
C(1)	0.1543(2)	0.255(1)	0.274570	3.1(1)
C(2)	0.1462(2)	0.355(1)	0.3732(5)	3.4(1)
C(3)	0.1703(2)	0.248(1)	0.4574(5)	3.6(1)
C(4)	0.2040(2)	0.053(1)	0.4450(5)	3.4(1)
C(5)	0.2125(2)	−0.043(1)	0.3446(5)	3.3(1)
C(6)	0.1880(2)	0.053(1)	0.2599(5)	3.4(1)
C(7)	0.1287(2)	0.523(1)	0.5789(6)	4.8(2)
C(8)	0.2611(2)	−0.343(2)	0.2479(5)	4.5(2)
C(9)	0.1277(2)	0.380(1)	0.1872(5)	3.4(1)
C(10)	0.1374(2)	0.287(1)	0.0758(5)	3.3(1)
C(11)	0.1845(2)	0.394(1)	0.0336(6)	3.6(1)
C(12)	0.0564(2)	0.260(1)	0.0053(5)	3.6(1)
C(13)	0.0245(2)	0.351(1)	−0.0718(5)	3.7(1)
C(14)	−0.0207(2)	0.242(1)	−0.0804(6)	4.7(2)
C(15)	−0.0355(2)	0.045(1)	−0.0161(7)	5.2(2)
C(16)	−0.0039(2)	−0.050(1)	0.0588(6)	5.1(2)
C(17)	0.0423(2)	0.059(1)	0.0684(5)	4.1(1)
C(18)	0.0121(3)	0.635(2)	−0.2171(7)	5.5(2)
C(19)	0.1291(3)	0.020(2)	0.7950(7)	5.6(2)
O(1)	0.1637(1)	0.3240(8)	0.5595(4)	5.0(1)
O(2)	0.2273(1)	−0.0448(8)	0.5274(4)	4.09(9)
O(3)	0.2470(1)	−0.2355(8)	0.3439(4)	4.6(1)
O(4)	0.0982(1)	0.5528(8)	0.2023(4)	4.4(1)
O(5)	0.1009(1)	0.3833(7)	0.0069(4)	3.62(8)
O(6)	0.1868(1)	0.6688(7)	0.0302(4)	3.94(9)
O(7)	0.0420(1)	0.5460(8)	−0.1345(4)	4.38(9)
O(8)	0.1321(2)	−0.188(5)	0.8644(5)	6.5(2)
H(C2)	0.119(2)	0.54(1)	0.381(5)	1(1)
H(C6)	0.190(2)	−0.046(9)	0.181(5)	1.3(9)
H1(C7)	0.124(2)	0.53(1)	0.643(5)	1(1)
H2(C7)	0.140(2)	0.70(1)	0.554(5)	3(1)
H3(C7)	0.097(3)	0.47(1)	0.557(6)	3(2)
H1(C8)	0.270(2)	−0.20(1)	0.204(4)	1(1)
H2(C8)	0.230(2)	−0.41(1)	0.200(6)	4(2)
H3(C8)	0.282(3)	−0.46(1)	0.259(6)	4(2)
H(C10)	0.138(1)	0.088(9)	0.066(3)	0.2(8)
H1(C11)	0.209(2)	0.333(8)	0.072(3)	−0.2(7)
H2(C11)	0.189(2)	0.32(1)	−0.032(6)	3(1)
H(C14)	−0.039(2)	0.29(1)	−0.122(5)	2(1)
H(C15)	−0.073(2)	−0.04(1)	−0.019(5)	4(1)
H(C16)	−0.015(3)	−0.20(1)	0.111(5)	4(1)
H(C17)	0.061(2)	−0.01(1)	0.118(5)	2(1)
H1(C18)	0.005(3)	0.49(2)	−0.259(7)	4(2)
H2(C18)	0.026(3)	0.78(2)	−0.256(7)	5(2)
H3(C18)	0.018(3)	0.74(1)	−0.190(6)	4(2)
H1(C19)	0.121(4)	−0.02(2)	−0.27(1)	8(3)
H2(C19)	0.111(3)	0.15(1)	−0.175(6)	4(2)
H3(C19)	0.157(4)	0.14(2)	−0.208(8)	7(3)
H(O2)	0.247(4)	−0.14(2)	0.500(9)	7(3)
H(O6)	0.164(2)	0.70(1)	−0.044(5)	2(1)
H(O8)	0.101(3)	−0.22(1)	−0.118(6)	5(2)

Table 3. Bond distances (Å) and angles (°) in *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**), $C_{18}H_{22}O_7$, and 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone–methanol (1/1) (**2**, methanol solvate), $C_{18}H_{20}O_7 \cdot CH_3OH$. The average C–H and O–H bond distances are 0.96(7) and 0.83(4) Å, respectively, in **1** and both 1.0(1) Å in **2**, methanol solvate. $T = 290$ K. C(19) and O(8) are the carbon and oxygen atoms belonging to the methanol molecule in the latter compound.

Distance	1	2	Distance	1	2
C(1)–C(2)	1.390(3)	1.388(6)	C(10)–C(11)	1.509(4)	1.510(7)
C(1)–C(6)	1.388(3)	1.405(7)	C(10)–O(5)	1.448(3)	1.428(7)
C(1)–C(9)	1.513(3)	1.486(7)	C(11)–O(6)	1.420(3)	1.413(7)
C(2)–C(3)	1.389(3)	1.385(8)	C(12)–C(13)	1.387(4)	1.405(8)
C(3)–C(4)	1.391(3)	1.376(7)	C(12)–C(17)	1.358(5)	1.371(8)
C(3)–O(1)	1.366(3)	1.382(8)	C(12)–O(5)	1.385(3)	1.380(6)
C(4)–C(5)	1.393(3)	1.403(8)	C(13)–C(14)	1.379(5)	1.370(8)
C(4)–O(2)	1.360(3)	1.337(7)	C(13)–O(7)	1.366(4)	1.374(7)
C(5)–C(6)	1.382(3)	1.374(8)	C(14)–C(15)	1.369(8)	1.370(10)
C(5)–O(3)	1.366(3)	1.371(6)	C(15)–C(16)	1.354(8)	1.387(10)
C(7)–O(1)	1.419(4)	1.427(8)	C(16)–C(17)	1.388(5)	1.397(8)
C(8)–O(3)	1.421(3)	1.408(9)	C(18)–O(7)	1.408(8)	1.420(10)
C(9)–C(10)	1.522(4)	1.535(9)	C(19)–O(8)	–	1.398(10)
C(9)–O(4)	1.430(3)	1.220(6)			

Angle	1	2	Angle	1	2
C(2)–C(1)–C(6)	119.8(2)	120.2(4)	C(9)–C(10)–O(5)	104.6(2)	110.5(4)
C(2)–C(1)–C(9)	120.0(2)	116.9(5)	C(11)–C(10)–O(5)	110.3(2)	104.8(5)
C(6)–C(1)–C(9)	120.3(2)	122.8(4)	C(10)–C(11)–O(6)	109.5(2)	114.4(4)
C(1)–C(2)–C(3)	120.4(2)	119.4(5)	C(13)–C(12)–C(17)	120.6(3)	119.5(5)
C(2)–C(3)–C(4)	120.2(2)	121.5(6)	C(13)–C(12)–O(5)	117.1(2)	114.4(5)
C(2)–C(3)–O(1)	124.5(2)	124.7(5)	C(17)–C(12)–O(5)	122.1(3)	126.1(5)
C(4)–C(3)–O(1)	115.3(2)	113.8(5)	C(12)–C(13)–C(14)	119.3(3)	119.3(6)
C(3)–C(4)–C(5)	118.7(2)	118.4(5)	C(12)–C(13)–O(7)	115.2(3)	116.0(4)
C(3)–C(4)–O(2)	119.3(2)	120.3(5)	C(14)–C(13)–O(7)	125.5(3)	124.7(5)
C(5)–C(4)–O(2)	122.0(2)	121.2(5)	C(13)–C(14)–C(15)	119.4(4)	121.6(6)
C(4)–C(5)–C(6)	121.4(2)	121.4(5)	C(14)–C(15)–C(16)	121.4(4)	119.5(6)
C(4)–C(5)–O(3)	114.2(2)	112.0(5)	C(15)–C(16)–C(17)	119.8(5)	119.5(6)
C(6)–C(5)–O(3)	124.4(2)	126.6(5)	C(12)–C(17)–C(16)	119.6(4)	120.5(6)
C(1)–C(6)–C(5)	119.6(2)	119.0(5)	C(3)–O(1)–C(7)	117.0(2)	117.2(5)
C(1)–C(9)–C(10)	113.0(2)	119.2(4)	C(5)–O(3)–C(8)	118.1(2)	118.7(5)
C(1)–C(9)–O(4)	108.6(2)	121.4(6)	C(10)–O(5)–C(12)	119.4(2)	118.3(4)
C(10)–C(9)–O(4)	109.2(2)	119.4(6)	C(13)–O(7)–C(18)	119.3(5)	118.2(5)
C(9)–C(10)–C(11)	112.3(2)	111.9(5)			

Hydrogen bonds in **1** (distances and angles)

O(2)···O(6)	$(1-x,1-y,2-z)$	2.863(3)	O(2)–H(O2)···O(6)	158(3)
O(4)···O(7)	(x,y,z)	2.916(4)	O(4)–H(O4)···O(7)	163(4)
O(6)···O(4)	$(x-1,y,z)$	2.811(3)	O(6)–H(O6)···O(4)	160(3)

Hydrogen bonds in **2**, methanol solvate (distances and angles)

O(2)···O(3)	(x,y,z)	2.614(7)	O(2)–H(O2)···O(3)	124(10)
O(2)···O(6)	$(^1/_2-x,y-1,^1/_2+z)$	2.788(5)	O(2)–H(O2)···O(6)	141(11)
O(6)···O(8)	$(x,y+1,z-1)$	2.712(7)	O(6)–H(O6)···O(8)	166(5)
O(7)···O(8)	$(x,y+1,z-1)$	2.831(6)	O(7)···H(O8)–O(8)	148(7)

contd

Table 3. (contd)

Selected torsion angles	**1**	**2**
C(2)–C(3)–O(1)–C(7)	−5.3(4)	1.4(8)
C(2)–C(3)–C(4)–O(2)	179.2(3)	179.1(8)
C(3)–C(4)–O(2)–H(O2)	171(3)	−173(9)
C(4)–C(5)–O(3)–C(8)	176.2(3)	−177.3(7)
C(2)–C(1)–C(9)–O(4)	125.3(3)	−3.8(8)
C(2)–C(1)–C(9)–H(C9)	9(2)	–
C(2)–C(1)–C(9)–C(10)	−113.5(3)	176.6(7)
C(1)–C(9)–C(10)–C(11)	61.2(3)	−77.4(7)
C(1)–C(9)–C(10)–O(5)	−179.2(2)	166.2(7)
C(1)–C(9)–C(10)–H(C10)	−59(2)	47(3)
C(1)–C(9)–O(4)–H(O4)	−179(3)	–
C(9)–C(10)–C(11)–O(6)	−159.9(3)	−59.6(7)
C(9)–C(10)–C(11)–H1(C11)	78(2)	63(3)
C(9)–C(10)–C(11)–H2(C11)	−40(2)	175(5)
C(9)–C(10)–O(5)–C(12)	126.3(3)	−78.5(7)
O(4)–C(9)–C(10)–O(5)	−58.3(2)	−13.4(7)
O(4)–C(9)–C(10)–C(11)	−177.8(3)	102.9(8)
O(4)–C(9)–C(10)–H(C10)	62(2)	−133(3)
O(5)–C(12)–C(13)–O(7)	6.4(3)	0.4(9)
H(C9)–C(9)–C(10)–H(C10)	179(2)	–
H(C9)–C(9)–O(4)–H(O4)	−63(3)	–
C(10)–C(9)–O(4)–H(O4)	57(3)	–
C(10)–C(11)–O(6)–H(O6)	−167(3)	−79(3)
C(10)–O(5)–C(12)–C(13)	−120.8(3)	−174.0(7)
C(11)–C(10)–C(9)–H(C9)	−60(2)	–
C(11)–C(10)–O(5)–C(12)	−112.8(3)	160.8(7)
O(6)–C(11)–C(10)–O(5)	83.9(3)	60.1(7)
H1(C11)–C(11)–C(10)–H(C10)	−159(3)	−64(4)
H2(C11)–C(11)–C(10)–H(C10)	82(3)	48(5)
H1(C11)–C(11)–O(6)–H(O6)	−50(4)	158(4)
H2(C11)–C(11)–O(6)–H(O6)	72(4)	43(6)
O(5)–C(10)–C(11)–H1(C11)	−38(2)	−177(3)
O(5)–C(10)–C(11)–H2(C11)	−157(2)	−65(5)
O(6)–C(11)–C(10)–H(C10)	−37(1)	173(3)
O(5)–C(10)–C(9)–H(C9)	59(2)	–
C(12)–O(5)–C(10)–H(C10)	6(2)	46(3)
C(12)–C(13)–O(7)–C(18)	−177.2(7)	176.7(8)

and 13); **1** is obtained by the reduction of **2**. Crystals of the latter compound, obtained from methanol, contained 1 mol of the solvent per mole of ketol **2**, as shown by the X-ray analysis. The presence of methanol was also revealed by a singlet at δ 3.49 (CH_3 in methanol) in the ^1H NMR spectrum. The crystals underwent changes at 99 °C and the resulting product melted at 107 °C. Crystals obtained from acetone–water melted at 107 °C. Observations made in connection with studies on a related compound, 1-(3,4-dimethoxyphenyl) - 3 - hydroxy - 2 - (2 - methoxyphenoxy)-1-propanone,[14] suggest that this compound also forms crystals containing methanol; this has, however, not been completely elucidated.

The crystal structures of **1** *and the methanol solvate of* **2**. Fractional atomic coordinates and equivalent isotropic thermal parameters are given in Tables 1 and 2, and bond distances, bond angles and selected torsion angles in Table 3. Figs. 2 and 3 show stereoscopic views of the unit cells and Figs. 4 and 5 the molecules and the atomic labelling. Crystal data and experimental data for **1** and the methanol solvate of **2** are given in Table 5.

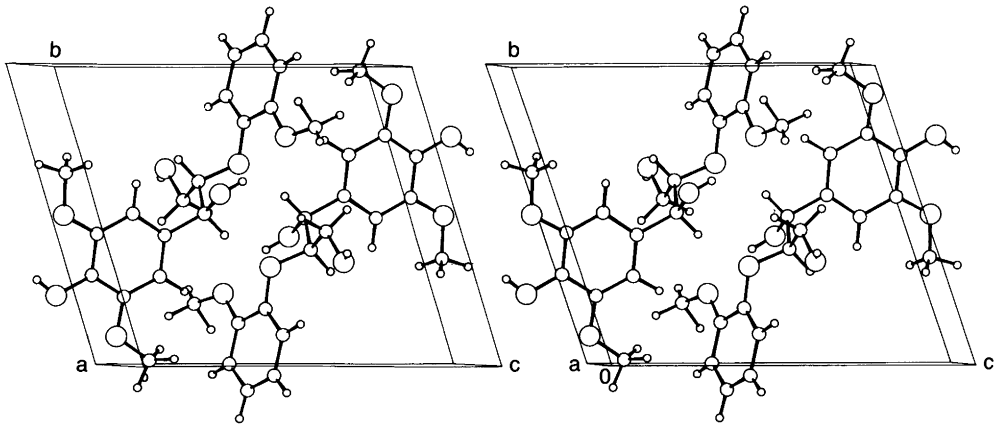


Fig. 2. Stereoscopic view[21] of the unit cell of *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**).

The crystals of both compounds consist of monomeric molecules held together by van der Waals forces and moderately strong hydrogen bonds. The hydroxy oxygen atom O(2) forms an intermolecular hydrogen bond to O(6) in both **1** and the methanol solvate of **2**. In **1** O(6) is also intermolecularly hydrogen-bonded to O(4). In the methanol solvate of **2**, O(6) forms a rather strong hydrogen bond to the methanol molecule [O(6)···O(8) is 2.712(7) Å], which is further hydrogen-bonded to the same molecule of **2** through the methoxy oxygen atom O(7). There

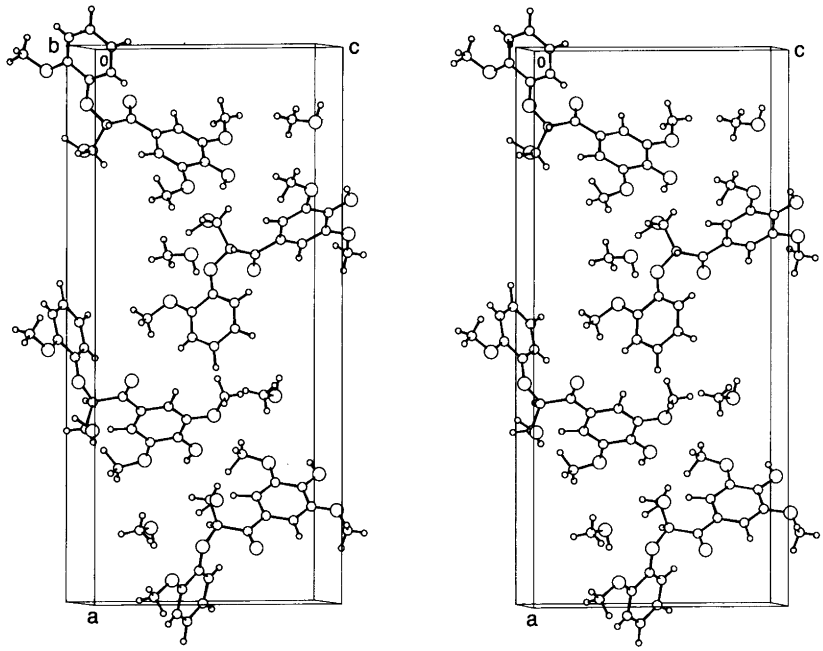


Fig. 3. Stereoscopic view[21] of the unit cell of 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone–methanol (1/1) (**2**, methanol solvate).

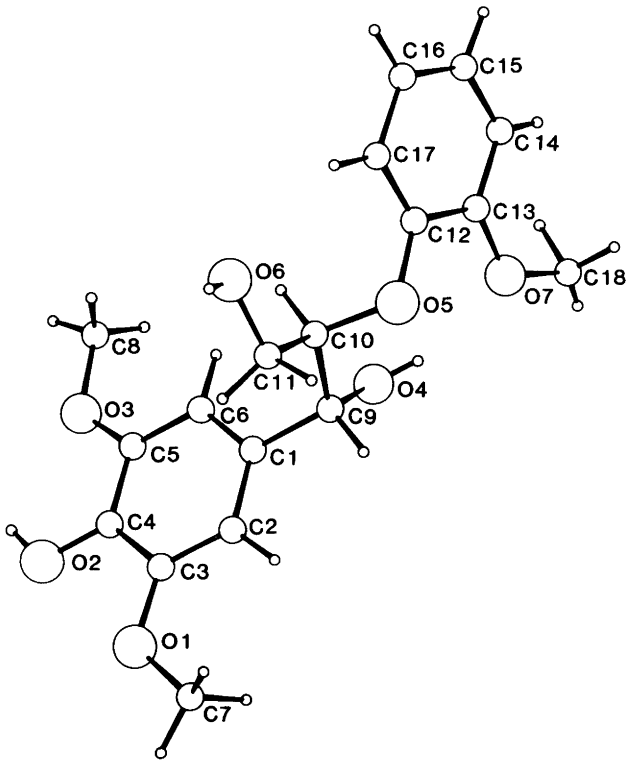


Fig. 4. The *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**) molecule showing the atomic numbering.

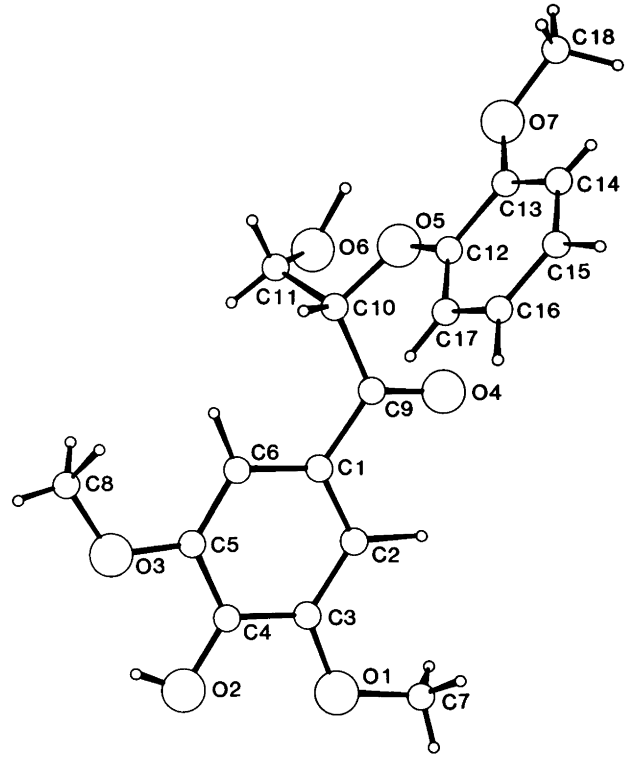


Fig. 5. The 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone (**2**) molecule showing the atomic numbering.

Table 4. Distances (Å) from certain atoms to least-squares planes[a] in **1** and **2**. Defining atoms are:

Plane I C(1)–C(6) in **1** Plane III C(12)–C(17) in **1**
Plane II C(1)–C(6) in **2** Plane IV C(12)–C(17) in **2**

Atom	Plane I	Plane II	Atom	Plane III	Plane IV
C(1)–C(6)	<0.003(2)	<0.016(5)	C(12)–C(17)	<0.004(6)	<0.011(4)
C(7)	0.106(7)	−0.100(12)	C(18)	−0.024(14)	−0.129(14)
C(8)	−0.036(5)	0.103(13)	O(7)	0.028(6)	−0.038(10)
C(9)	−0.039(4)	0.043(10)	C(10)	0.926(7)	0.110(13)
C(10)	1.330(5)	0.104(11)	O(5)	−0.118(5)	0.005(10)
O(1)	−0.004(4)	−0.056(9)			
O(3)	0.041(4)	0.034(9)			
O(2)	0.015(4)	−0.010(9)			
H(O2)	−0.11(4)	0.10(12)			
O(4)	1.068(4)	0.028(11)			

[a]The angle between planes I and III is 73.8(1)° and between II and IV 84.1(2)°.

are also intramolecular hydrogen bonds. In **1** an intramolecular hydrogen bond exists between the hydroxy oxygen atom O(4) and the methoxy oxygen atom O(7). In the methanol solvate of **2**, the hydroxy oxygen atom O(2) also forms an intramolecular hydrogen bond to the neighbouring methoxy oxygen atom O(3).

As is evident from Table 4, all aromatic rings are planar to within 0.016(5) Å. The methoxy oxygen atoms are almost coplanar with the respective rings. As found in a series of lignin model compounds[4–6,15] the methoxy carbon atoms are also near the corresponding ring plane (Table 4). In **2** the phenoxy atom O(5) is situated in the ring plane, defined by C(12)–C(17). In **1** the phenoxy oxygen atom O(5) is slightly twisted [0.118 (5) Å] out of the ring plane as was also found in two other β-O-4 compounds of category I type, namely *erythro*-veratrylglycerol β-guaiacyl ether[4,15] [deviation, 0.116(5) Å] and *erythro*-syringylglycerol β-(4-hydroxymethyl)syringyl ether[6,15] [deviation, 0.091(6) Å]. In these last two compounds, as in **1**, the β-carbon atom [C(10)] is about 1 Å remote from the corresponding benzene ring plane [C(12)–C(17)] and, notably, is situated on the opposite side of the plane compared with the phenoxy oxygen atom. The torsion angle H_α–C–C–H_β is 179(2)° in **1**; in *erythro*-veratrylglycerol β-guaiacyl ether and *erythro*-syringylglycerol β-(4-hydroxymethyl)syringyl ether the corresponding angles are −176(3) and −50(3)°, respectively.

Experimental

X-Ray work. Crystal and experimental data for **1** and the methanol solvate of **2** are given in Table 5. Rotation and Weissenberg photographs were taken of both compounds (Cu K_α radiation) from which crystal symmetry, conditions for reflexions, approximate cell dimensions, and information about the suitability for the data collection, were obtained. Diffracted intensities were measured with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo K_α radiation. Periodic measurements of test reflexions showed 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 reflexions for each compound.

Structure determination. (a) threo-*1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol* (**1**). All but five of the non-hydrogen atoms were obtained by direct methods (MITHRIL[17]). The remaining atoms were obtained from electron-density difference maps.[18] Least-squares refinement of the 25 non-hydrogen atoms led to the *R*-values 0.156 (isotropic thermal parameters) and 0.085 (anisotropic thermal parameters), respectively. An electron-density difference map based on these last parameters revealed all hydrogen atomic positions. The introduction of these and isotropic thermal para-

Table 5. Crystal and experimental data for *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**), $C_{18}H_{22}O_7$, and 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone–methanol (1/1) (**2**, methanol solvate), $C_{18}H_{20}O_7 \cdot CH_3OH$. $T = 290$ K.

	$C_{18}H_{22}O_7$	$C_{18}H_{20}O_7 \cdot CH_3OH$
M_r	350.37	380.39
Crystal system	Triclinic	Orthorhombic
Space group[a]	$P\bar{1}$ (No. 2)	$Pca2_1$ (No. 29)
Unit-cell dimensions/Å or °	a = 7.220(3)	a = 27.534(14)
	b = 10.747(7)	b = 5.139(2)
	c = 12.045(6)	c = 12.868(5)
	α = 109.41(4)	V = 1821(1)
	β = 90.57(4)	
	γ = 103.28(4)	
	V = 854.0(8)	
Z	2	4
D_c/g cm^{-3}	1.363	1.388
m.p./°C	168–169	99–107 (see text)
μ(Mo K_α)/mm^{-1} (no absorption correction)	0.113	0.117
Crystal size/mm	0.18×0.27×0.48	0.16×0.25×0.31
Reflexions for cell determination	15	15
(No., θ range/°)	5.8–11.9	6.2–12.0
Scan mode	ω–2θ	ω–2θ
2θ range/°	3.5–56.0	3.5–50.0
2θ scan speed/° min^{-1}	1.8–5.9	1.5–3.9
Total no. of independent reflexions measured	4159	1938
No. of observed independent reflexions [$I > 3\sigma(I)$]	2208	1092
Test reflexion; standard deviation/%	0 0 3; 1.4	0 0 2; 1.0
Method used to solve structure	Direct methods (MITHRIL);[b] electron-density difference maps (DRF)[c]	
No. of parameters refined	314	339
Weights calculated according to $w = (a + \lvert F_o\rvert + c\lvert F_o\rvert^2 + d\lvert F_o\rvert^3)^{-1}$ [d]	a = 6.0	a = 5.0
	c = 0.018	c = 0.02
	d = 0.0025	d = 0.015
R (R_w)	0.052 (0.062)	0.042 (0.051)
Maximum residual electron density/e Å^{-3}	0.21	0.17

[a]Ref. 16a. [b]Ref. 17. [c]Ref. 18. [d]Ref. 19.

meters for the hydrogen atoms gave a final R-value of 0.052.

(b) *3-Hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone–methanol (1/1)* (**2**·MeOH). The structure was solved by direct methods (MITHRIL[17]) and electron-density calculations. All non-hydrogen atoms belonging to the 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone molecule were obtained from the first MITHRIL solution. Full-matrix least-squares refinement of positional and isotropic thermal parameters for these 25 atoms gave $R = 0.19$; with anisotropic thermal parameters the R-value was only slightly reduced (to 0.167) and there were large differences between F_o and F_c. In the electron-density difference map two peaks appeared (electron density about 3 e Å^{-3}) indicating the presence of further atoms in the crystal. The introduction of these, with scattering power as carbon atoms, reduced the R-value to 0.116 (isotropic thermal parameters) and 0.076 (anisotropic thermal parameters), respectively. Judging from the values of the thermal parameters and the subsequent electron-density map one of the two additional atoms should be an oxygen atom. With this assumption, the R-values became 0.111 (isotropic thermal parameters) and 0.069 (anisotropic thermal parameters), respectively. From the following electron-density difference map

(maximum electron density 0.43 e $Å^{-3}$) all hydrogen atoms were located and it became clear that the additional atoms belonged to a methanol molecule. The presence of methanol in the sample was also indicated in the ^1H NMR spectrum (270 MHz; $CDCl_3$; internal reference, $SiMe_4$): δ 3.49 (3 H, s, CH_3 in methanol), 3.85 (3 H, s, CH_3–O–Ar), 3.91 (6 H, s, CH_3–O–Ar), 4.09 (2 H, m, CH_2), 5.34 (1 H, m, H_β), ca. 7 (6 H, m, aromatic protons). Inclusion of atomic coordinates and isotropic thermal parameters for the hydrogen atoms in the refinement reduced *R* to 0.042.

Further details concerning the refinement of the structures are summarized in Table 5. Atomic scattering factors were taken from Ref. 16b. Calculations were carried out on an IBM 3081 computer, using the crystallographic programs described in Refs. 18 and 20. Lists of structure factors and anisotropic thermal parameters are available from one of the authors (R.S.) on request.

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