On the Stereochemistry of Lignin Model Compounds of the 1,2-Diaryl-1,3-propanediol Type. The Crystal Structure of *erythro*-2-(4-Methoxyphenyl)-1-phenyl-1,3-propanediol

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Properties (location of ^{1}H NMR signals, stability of borate complexes) of diastereomers of lignin-related diarylpropanediols are discussed. ^{1}H NMR spectral comparisons with the *threo* and *erythro* forms of 1,2-diphenyl-1,3-propanediol provide a basis for the assignments of diastereomers of lignin model compounds of the 1,2-diaryl-1,3-propanediol type. Final confirmation of the structure of such a compound, *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol, was achieved by single-crystal X-ray analysis. This compound crystallizes in the monoclinic space group $P2_1$ with $a=8.703(4)$, $b=6.060(2)$, $c=13.487(6)$ Å, $\beta=99.84(4)°$ and $Z=2$. The structure was determined by direct methods. Least-squares refinement gave $R=0.039$ for 1311 observed independent reflections.

Nakatsubo and Higuchi[1] assigned the stereochemistry of the *threo* and *erythro* forms of a lignin model compound of the 1,2-diaryl-1,3-propanediol type on the basis of ^{1}H NMR studies of phenyl boronate derivatives. Their results can be used for the elucidation of the stereochemistry of related diarylpropanediols (see, e.g., Refs. 2–4). NMR spectral comparisons with the *erythro*
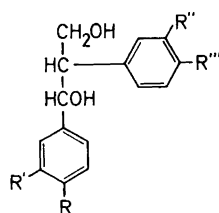
Scheme 1.
1. R=R'=R''=R'''= H
2. R=R'=R''= H, R'''= OCH₃
3. R=R'''= OH, R'=R''= OCH₃

and *threo* forms of 1,2-diphenyl-1,3-propanediol · (1) provide an alternative basis for the assign-

ment of diastereomers of lignin model compounds of the current type, since the *erythro* and *threo* forms of 1 have been described in the literature.[5,6] The diastereomers of 1 can be prepared by reduction of the *erythro* and *threo* forms of 3-hydroxy-1,2-diphenylpropanoic acid, the stereochemistry of which has been elucidated by Zimmerman and Traxler.[7] We have prepared this acid (diastereomeric mixture) via an α-lithiated carboxylic acid intermediate by adaptation of a synthetic method previously used[3] for the synthesis of the diastereomers of 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol (3) (a different, but related synthesis of the latter compound has recently been published by Nonni and Dence[8]). The *threo* form of the acid could be obtained in a pure state by fractional crystallization. Reduction with borane/dimethyl sulfide complex gave the *threo* form of 1. The *erythro* form of 1 can be obtained in a pure state by an alternative synthesis.[2] It is evident from Table 1 that ^{1}H NMR spectral comparisons with acetate derivatives of the *erythro* and *threo* forms of 1 support the stereochemical assignment of the

Table 1. ^{1}H NMR data for acetate derivatives of lignin model compounds of the 1,2-diaryl-1,3-propanediol type. Solvent: $CDCl_3$. Spectrometer frequency: 270 MHz.

Compound	δ/ppm vs. TMS (J/Hz)					
	Hα	Hβ	H(γ₁)	H(γ₂)	OCH₃	COCH₃
1 (*threo*)	6.04 (8.4)	3.48 (m)	4.37 (5.1,11.1)	4.55 (7.3,11.1)		1.96,2.08
1 (*erythro*)	6.13 (7.6)	3.43 (m)	4.12 (6.6,11.2)	4.29 (6.4,11.2)		1.91,1.92
2 (*erythro*)	6.09 (7.3)	3.37 (m)	4.09 (6.6,11.2)	4.29 (6.6,11.2)	3.79	1.94 (6H)
3 (*threo*)	5.98 (7.8)	3.42 (m)	4.36 (5.9,11.2)	4.53 (7.0,11.1)	3.63,3.65	2.03,2.11,2.26,2.27
3 (*erythro*)	6.10 (6.6)	3.38 (m)	4.18 (6.6,11.4)	4.39 (7.0,11.4)	3.69,3.73	1.97,1.98,2.28,2.29

erythro form of **2** and the diastereomers of **3** made in previous work.[2,3] Final confirmation of the structure of the *erythro* form of **2** (synthesis[2]) has been obtained by the determination of its crystal structure; this is described in a separate section of this paper.

The two isomers of **1** can be separated by anion exchange chromatography, using a borate solution as eluent (cf. Ref. 9). The *erythro* form is eluted before the *threo* form, which implies that the latter compound forms the stronger borate complex. The signal from Hγ₂ in the acetate derivatives is located at higher field for the *erythro* form than for the *threo* form (Table 1). In this respect, as well as with respect to the stability of borate complexes, 1,2-diaryl-1,3-propanediols differ from model compounds of the arylglycerol β-aryl ether type.[9,10] We have here, however, to deal with apparent discrepancies. The *erythro* and *threo* forms of the 1,2-diaryl-1,3-propanediols have been defined in such a way that the *threo* form (formula **A**) has structural features in common with the *erythro* form of arylglycerol β-aryl ethers (formula **C**) (this is most easily seen from comparisons with formula **B**); conversely, the *threo* forms of such ethers resemble the *erythro* forms of diarylpropanediols.

The crystal structure of *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2; bond distances, bond angles and selected torsion angles are listed in Table 3. Fig. 1 shows a stereoscopic view of the unit cell, and Fig. 2 the molecule and the atomic labelling.

The crystals of the *erythro* form of **2** consist of monomeric molecules held together by van der Waals forces and hydrogen bonds between the hydroxy groups [O(1)^i···O(2)^{ii} is 2.720(5) Å, O(1)^i···H(O2)^{ii} 1.88(8) Å, O(1)^i···O(2)^{iii} 2.711(3) Å and H(O1)^i···O(2)^{iii} 1.87(4) Å; the angle O(1)^i···H(O2)^{ii}–O(2)^{ii} is 158(6)° and O(1)^i–H(O1)^i···O(2)^{iii} 172(4)°]. The next shortest intermolecular contact distances are: H(C3)···H1(C9)′ 2.39 (6), H(C4)···H(C15)′ 2.54(7) and H(O1)···H (O2)′ 2.44(8) Å.

The aromatic C–C bond distances are normal (mean value 1.384(8) Å; r.m.s. deviation is given in parenthesis) as are the C–H bond distances. The $C(sp^3)$–$O_{methoxy}$ bond distance agrees well with those observed in a series of lignin-related

$^i x,y,z.$ $^{ii}x,y-1,z.$ $^{iii}1-x,-1/2+y, 1-z.$
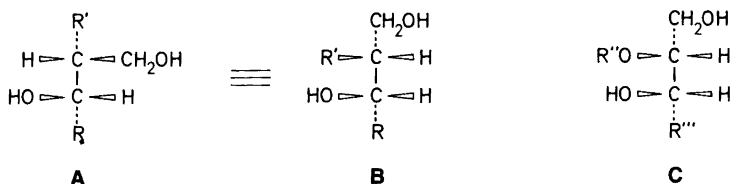
Scheme 2.
R,R′,R″, and R‴ are aromatic groups

Table 2. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol, $C_{16}H_{18}O_3$. The origin is defined by $y_{C(1)} = 0$. $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \, \mathbf{a}_i \cdot \mathbf{a}_j$.

| Atom	x	y	z	$B_{eq}/Å^2$
C(1)	0.0867(3)	0	0.3705(2)	3.43(6)
C(2)	-0.0309(4)	0.1022(8)	0.4110(2)	4.40(8)
C(3)	-0.1792(4)	0.013(1)	0.3971(3)	5.5(1)
C(4)	-0.2112(5)	-0.177(1)	0.3441(3)	5.9(1)
C(5)	-0.0960(5)	-0.2805(9)	0.3019(3)	5.7(1)
C(6)	0.0516(4)	-0.1904(7)	0.3148(2)	4.41(8)
C(7)	0.2484(3)	0.1000(7)	0.3876(2)	3.25(6)
C(8)	0.2747(3)	0.2502(6)	0.3001(2)	3.15(6)
C(9)	0.4300(3)	0.3720(7)	0.3254(2)	3.79(7)
C(10)	0.2622(3)	0.1414(7)	0.1983(2)	3.27(6)
C(11)	0.1587(4)	0.2249(8)	0.1177(2)	4.52(8)
C(12)	0.1475(4)	0.1353(9)	0.0223(2)	5.4(1)
C(13)	0.2390(4)	-0.0409(8)	0.0060(2)	4.61(8)
C(14)	0.3421(4)	-0.1279(8)	0.0850(2)	4.60(9)
C(15)	0.3540(4)	-0.0346(7)	0.1800(2)	4.29(7)
C(16)	0.301(1)	-0.307(1)	-0.1108(4)	9.1(2)
O(1)	0.3656(2)	-0.0680(6)	0.4058(2)	3.85(5)
O(2)	0.4436(3)	0.4969(6)	0.4156(2)	4.56(6)
O(3)	0.2185(3)	-0.1183(8)	-0.0911(2)	6.35(8)
H(C2)	-0.007(4)	0.242(7)	0.445(3)	2.7(8)
H(C3)	-0.266(5)	0.103(9)	0.432(3)	5(1)
H(C4)	-0.314(6)	-0.229(9)	0.333(4)	6(1)
H(C5)	-0.120(5)	-0.404(9)	0.257(3)	4(1)
H(C6)	0.129(4)	-0.259(7)	0.284(3)	3.0(8)
H(C7)	0.263(3)	0.188(5)	0.448(2)	0.1(4)
H(C8)	0.189(3)	0.367(6)	0.294(2)	1.7(6)
H1(C9)	0.510(4)	0.271(7)	0.334(2)	2.1(7)
H2(C9)	0.441(4)	0.466(7)	0.265(3)	2.6(7)
H(C11)	0.088(4)	0.350(7)	0.133(3)	3.7(9)
H(C12)	0.058(4)	0.183(9)	-0.036(3)	4.2(9)
H(C14)	0.407(4)	-0.234(6)	0.072(2)	2.0(7)
H(C15)	0.427(5)	-0.094(9)	0.235(3)	5(1)
H1(C16)	0.295(7)	-0.44(1)	-0.064(5)	8(2)
H2(C16)	0.288(5)	-0.32(1)	-0.172(4)	6(1)
H3(C16)	0.399(9)	-0.26(2)	-0.088(6)	13(4)
H(O1)	0.418(4)	-0.046(8)	0.464(3)	3.3(8)
H(O2)	0.396(7)	0.63(1)	0.403(5)	8(2)
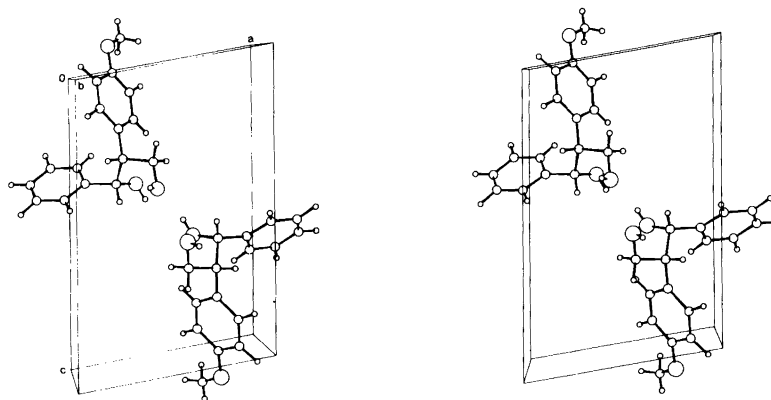
Fig. 1. Stereoscopic view[11] of the unit cell of *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol, $C_{16}H_{18}O_3$.

Table 3. Bond distances (Å) and angles (°) in *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol, $C_{16}H_{18}O_3$. The average C–H bond distance is 0.97(2) Å.

Distance

C(1)–C(2)	1.386(4)	C(7)–O(1)	1.433(5)	C(11)–C(12)	1.384(5)
C(1)–C(6)	1.382(4)	C(7)–C(8)	1.538(4)	C(12)–C(13)	1.372(6)
C(1)–C(7)	1.513(4)	C(8)–C(9)	1.526(4)	C(13)–C(14)	1.375(5)
C(2)–C(3)	1.381(5)	C(8)–C(10)	1.510(4)	C(13)–O(3)	1.373(4)
C(3)–C(4)	1.363(8)	C(9)–O(2)	1.420(4)	C(14)–C(15)	1.388(5)
C(4)–C(5)	1.384(6)	C(10)–C(11)	1.383(4)	C(16)–O(3)	1.399(10)
C(5)–C(6)	1.380(6)	C(10)–C(15)	1.380(5)		

Angle

C(2)–C(1)–C(6)	118.6(3)	C(9)–C(8)–C(10)	109.8(2)
C(2)–C(1)–C(7)	119.4(2)	C(8)–C(9)–O(2)	113.0(2)
C(6)–C(1)–C(7)	122.0(3)	C(8)–C(10)–C(11)	119.4(3)
C(1)–C(2)–C(3)	120.6(4)	C(8)–C(10)–C(15)	123.1(3)
C(2)–C(3)–C(4)	120.3(4)	C(11)–C(10)–C(15)	117.5(3)
C(3)–C(4)–C(5)	120.0(4)	C(10)–C(11)–C(12)	121.3(4)
C(4)–C(5)–C(6)	119.6(5)	C(11)–C(12)–C(13)	120.2(3)
C(1)–C(6)–C(5)	120.9(4)	C(12)–C(13)–C(14)	119.6(3)
C(1)–C(7)–C(8)	112.1(2)	C(12)–C(13)–O(3)	115.7(3)
C(1)–C(7)–O(1)	111.0(3)	C(14)–C(13)–O(3)	124.7(4)
C(8)–C(7)–O(1)	110.9(2)	C(13)–C(14)–C(15)	119.7(4)
C(7)–C(8)–C(9)	110.9(2)	C(10)–C(15)–C(14)	121.7(3)
C(7)–C(8)–C(10)	116.2(3)	C(13)–O(3)–C(16)	118.2(4)

Selected torsion angles

C(2)–C(1)–C(7)–O(1)	140.4(4)	C(9)–C(8)–C(7)–O(1)	−62.8(4)
C(2)–C(1)–C(7)–C(8)	−95.0(4)	C(9)–C(8)–C(10)–C(11)	−108.9(5)
C(1)–C(7)–C(8)–C(9)	172.6(4)	C(10)–C(8)–C(7)–O(1)	63.5(4)
C(1)–C(7)–C(8)–C(10)	−61.2(4)	C(10)–C(8)–C(9)–O(2)	174.1(4)
C(7)–C(8)–C(9)–O(2)	−56.1(4)	C(12)–C(13)–O(3)–C(16)	−175.8(7)
C(7)–C(8)–C(10)–C(11)	124.2(5)	H(C7)–C(7)–C(8)–H(C8)	−64(3)
H(C8)–C(8)–C(7)–O(1)	178(2)		

compounds[12] and is in accordance with typical C–O single bond values.[13a] The $C(sp^2)$–$O_{methoxy}$ bond distance is also similar to those observed in other lignin model compounds, and shows partial double-bond character (cf. Ref. 13a).

The maximum deviation of the benzene ring carbon atoms from the respective ring plane is 0.011(4) Å. The methoxy oxygen atom O(3) does not deviate significantly from the ring plane [0.002(7) Å], while the methoxy carbon atoms C(16) and C(8) do [0.090(12) and 0.044(7) Å, respectively]. The two benzene ring planes form an angle of 115.2(2)° with each other.

As noted for previously studied lignin models,[12] the C–C–$O_{methoxy}$ bond angle involving the ring carbon atoms *cis* to the methyl is larger

[124.7(4)°] than that involving the *trans* counterparts [115.7(2)°].

It should be mentioned in this context that the crystal structure of a diacetate of a 1,2-diaryl-1,3-propanediol related to the phenylcoumaran type of structure has recently been determined.[14]

Experimental

3-Hydroxy-2,3-diphenylpropanoic acid was prepared from benzaldehyde (4.24 g, 0.040 mol) and phenylacetic acid (5.44 g, 0.040 mol), following the procedure previously described for the synthesis of a related compound.[3] According to an ^{1}H NMR examination the crude product (9.1 g)
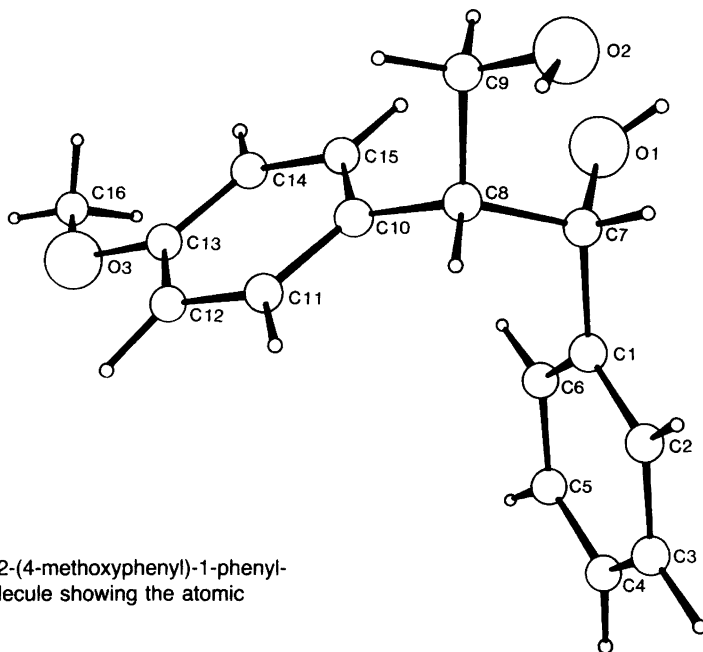
Fig. 2. The *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol molecule showing the atomic numbering.

Table 4. Crystal and experimental data for *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol, $C_{16}H_{18}O_3$ ($T = 290$ K).

M_r	258.32
Crystal system	Monoclinic
Space group[a]	$P2_1$ (No. 4)
Unit cell dimensions/Å or °	$a = 8.703(4)$
	$b = 6.060(2)$
	$c = 13.487(6)$
	$\beta = 99.84(4)$
	$V = 700.8(5)$
Z	2
D_c/g cm^{-3}	1.224
M.p./°C	129–130
μ(Mo$K\alpha$)/mm^{-1} (no absorption correction)	0.090
Crystal size/mm	0.15×0.23×0.46
No. of reflections for cell determination (θ range/°)	15 ($4.8<\theta<10.4$)
Scan mode	ω–2θ
2θ range/°	3.5–60
2θ scan speed/° min^{-1}	1.5–4.9
Total no. of reflections measured	2239
No. of observed independent reflections ($I>3\sigma(I)$)	1311
Test reflection (maximum variation/%)	200($\pm$1.4); 130($\pm$1.3); 004 ($\pm$0.8)
Method used to solve structure	Direct methods (MITHRIL[b], DIRDIF[c]); electron density difference map (DRF)[d]
No. of parameters refined	243
Weights calculated according to	$w=(2.0+|F_0|+0.05|F_0|^2)^{-1}$ [e]
R	0.039
Maximum residual electron density/e Å^{-3}	0.15

[a]Ref. 13*b*. [b]Ref. 15. [c]Ref. 16. [d]Ref. 17. [e]Ref. 18.

consisted primarily of a mixture of the *threo* (77%) and *erythro* (23%) forms of 3-hydroxy-2,3-diphenylpropanoic acid. Crystallization from ethyl acetate gave the *threo* acid slightly contaminated with the *erythro* form. Recrystallization gave 3.8 g of the pure *threo* form (m.p. 178–181°C; lit.[7] 177–178°C)

threo-1,2-Diphenyl-1,3-propanediol was obtained as an oil on reduction of *threo*-3-hydroxy-2,3-diphenylpropanoic acid with borane/dimethyl sulfide complex (cf. Ref. 3). ^{1}H NMR data for the acetate derivative are given in Table 1.

Crystal structure determination. The crystals of the *erythro* form of **2** are plate-like, and twin formation is common. A twin crystal was cleaved along the plate-plane; this yielded a single crystal suitable for the structure determination. Crystal and experimental data are given in Table 4. Diffracted intensities were measured with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation. A 96-step profile was recorded for each reflection, and the Lehmann and Larsen profile-analysis method[19] was used to calculate the intensities.[20] 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[15]; DIRDIF[16]). Intensity statistics indicated a non-centric structure and a plausible solution was obtained assuming space group $P2_1$. Full-matrix least-squares refinement[17,21] of positional and isotropic thermal parameters for the non-hydrogen atoms gave $R=0.120$. The introduction of anisotropic thermal parameters reduced R to 0.076. From the subsequent electron density difference map all hydrogen atoms were located (maximum electron density 0.48 e Å^{-3}).[17] Inclusion of atomic coordinates and isotropic thermal parameters for the hydrogen atoms in the refinement gave $R=0.039$.

Further details concerning the refinement of the structure are summarized in Table 4. Atomic scattering factors were taken from Ref. 13c. Calculations were carried out on an IBM 3081 computer, using the crystallographic programmes described in Refs. 17 and 21. Lists of structure factors and anisotropic thermal parameters are available from one of the authors (R.S.) on request.

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