

Stereoisomers of 1,2-diaryl-1,3-propanediols: *erythro* formsVratislav Langer,<sup>a\*</sup> Shiming Li<sup>b</sup> and Knut Lundquist<sup>b</sup><sup>a</sup>Environmental Inorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and<sup>b</sup>Forest Products and Chemical Engineering, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden

Correspondence e-mail: langer@chalmers.se

Received 12 January 2007

Accepted 15 January 2007

Online 10 February 2007

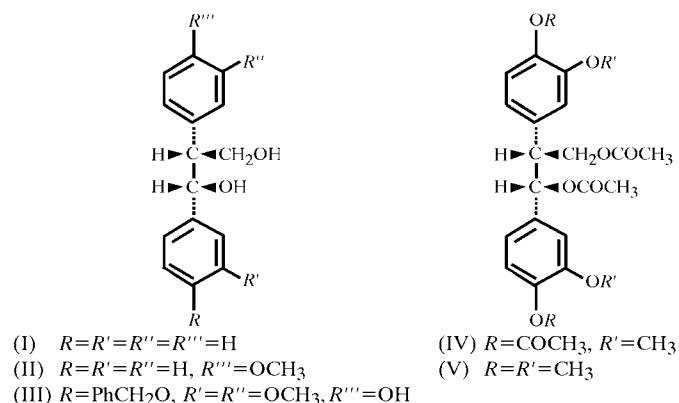
Racemic *erythro*-1,2-diphenyl-1,3-propanediol, C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>, is a model compound representative of *erythro* forms of structural elements of the 1,2-diaryl-1,3-propanediol type in lignins. In the crystal structure, the torsion angle between the bulky phenyl groups is  $-62.26(11)^\circ$ . Strong hydrogen bonds take part in a directed co-operative O—H...O—H...O—H...O—H pattern that is assumed to have a decisive influence on the conformation. This is supported by comparisons with the geometries of related compounds.

## Comment

The stereochemistry of lignin models of the 1,2-diaryl-1,3-propanediol type was investigated in a previous paper (Lundquist & Stomberg, 1987). The crystal structure of one of the compounds examined, namely *erythro*-1,2-diphenyl-1,3-propanediol, (I), is reported in this paper. Previous reports describe the crystal structures of the related compounds *erythro*-2-(4-methoxyphenyl)-1-phenyl-1,3-propanediol, (II) (Lundquist & Stomberg, 1987), and *erythro*-1-(4-benzyloxy-3-methoxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-1,3-propanediol, (III) (Stomberg *et al.*, 1997). The crystal structure of the tetraacetate, (IV), of another related compound, *erythro*-1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol, (VI), has also been determined (Stomberg & Lundquist, 1995). Some results from attempts to determine the crystal structure of the diacetate, (V), of *erythro*-1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol, (VII) (Li *et al.*, 1993; Aoyama *et al.*, 1995), are reported in this paper. The stereochemistry of *threo* forms of lignin models of the 1,2-diaryl-1,3-propanediol type is discussed in a recent paper (Stomberg *et al.*, 2006).

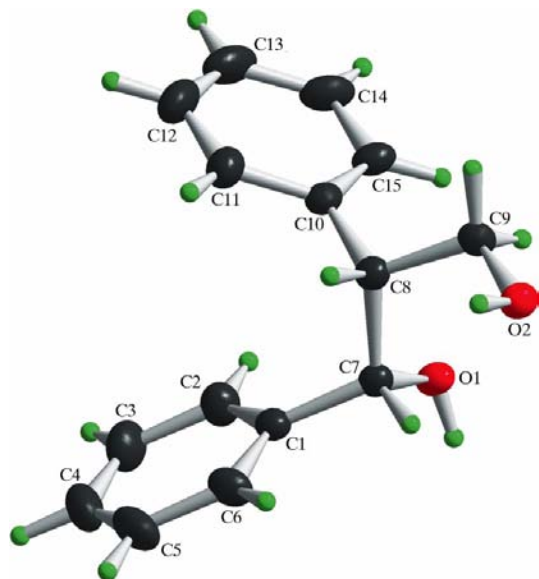
Syntheses of the compounds discussed above are described in the literature referred to or in references therein. Syntheses of other *erythro* forms of lignin models of the 1,2-diaryl-1,3-propanediol type have been published by Parkäs *et al.* (2004) [for (VIII)], Li *et al.* (1994) [for (IX)], Ahvonen *et al.* (1983) [for (X)], Li *et al.* (1996) [for (XI)] and Kristersson & Lundquist (1980) [for (XII)].

A perspective drawing and the atom numbering of (I) are shown in Fig. 1. Geometric details of (I) are given in Table 1 in which, for comparison, the corresponding geometric data for the related compounds (II) and (III) are also included.

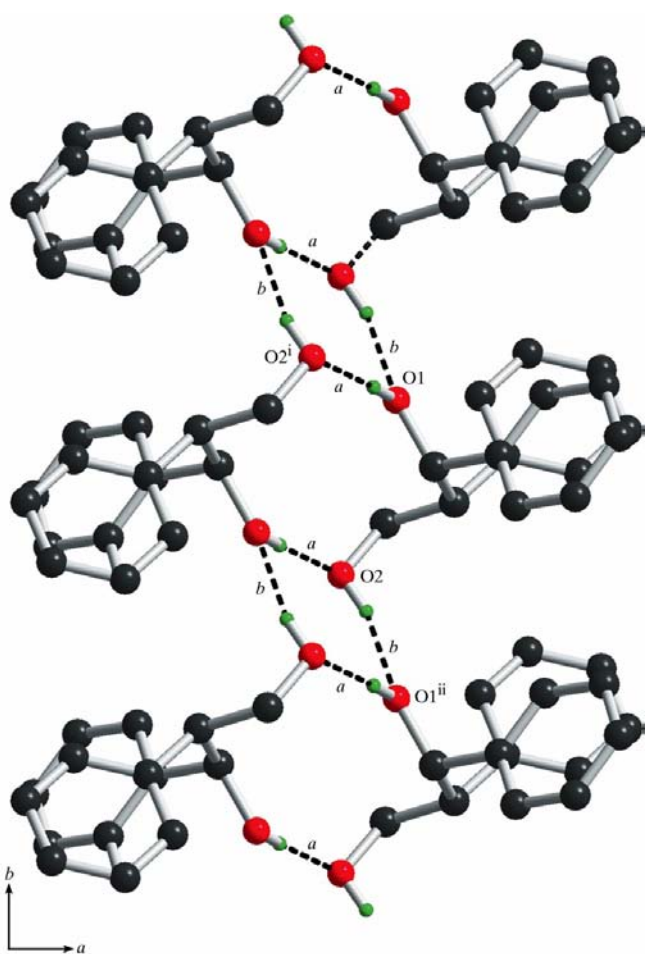


There are strong O—H...O hydrogen bonds (Fig. 2) present in the crystal structure of (I); for geometric details and hydrogen-bond notation, see Table 2. On the first-level graph set, defined by Bernstein *et al.* (1995) and Grell *et al.* (1999),  $R_2^2(12)$  rings, formed by hydrogen bonds *a* between pairs of molecules related by an inversion centre and  $C(6)$  chains formed by hydrogen bonds *b* were identified. On the second-level graph-set,  $R_4^4(8)$  directed four-membered co-operative O—H...O—H...O—H...O—H rings formed by hydrogen bonds *a* and *b* could be recognized.

Disregarding angles between aromatic ring planes, the corresponding geometric details in (I) and related compounds (II) and (III) are very similar (Table 1 and Fig. 3). Hydrogen bonding may explain the conformational similarities exhibited by these compounds. The overall patterns are different [an  $R_4^4(8)$  ring in (I), a  $C_4^4(8)$  chain in (II) and an  $R_6^6(12)$  ring in (III)], but there are strong hydrogen bonds involved in directed co-operative O—H...O—H...O—H...O—H patterns in the three compounds. The importance of hydrogen bonding for the conformations of compounds (I)–(III) is supported by the conformations adopted by the acetates (IV) and (V). In these compounds, which lack strong hydrogen bonds, the torsion angles between the aromatic groups are

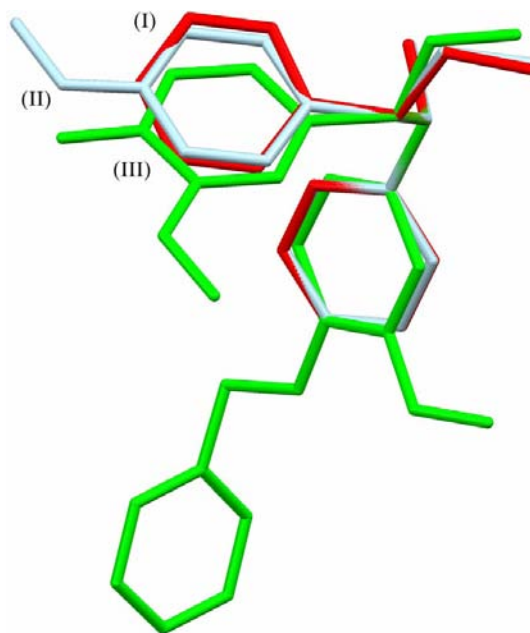


**Figure 1**  
A perspective drawing of (I), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
The hydrogen bonds forming chains of molecules in the *b*-axis direction. H atoms not included in the hydrogen-bonding pattern have been omitted for clarity. For labels and symmetry codes, see Table 2.

close to  $180^\circ$  [ $-178.8(4)^\circ$  in (IV) (Stomberg & Lundquist, 1995) and  $-172(2)^\circ$  in (V) (this work)], implying that the bulky aromatic groups are almost as far apart as possible. This probably governs the conformations adopted by (IV) and (V).



**Figure 3**  
A projection of the overlaid structures of (I), (II) and (III). H atoms have been omitted for clarity.

## Experimental

*erythro*-1,2-Diphenyl-1,3-propanediol, (I), was prepared according to the method of Kristersson & Lundquist (1980). Crystals (m.p. 379–380 K) were obtained from a solution in benzene. *erythro*-1,2-Bis(3,4-dimethoxyphenyl)-1,3-propanediol, (VII), and the isomeric *threo* form were acetylated by treatment with acetic anhydride–pyridine (1:1) for 24 h. The diacetate, (V), of compound (VII) was obtained in crystalline form (m.p. 363 K). The crystal structure of (V) was solved, but refinement resulted in residuals too high for publication.  $^{13}\text{C}$  NMR spectra [100.6 MHz, solvent  $\text{CDCl}_3$ , reference  $(\text{CH}_3)_4\text{Si}$ , 300 K] for (V):  $\delta$  20.8 ( $\text{CH}_3\text{CO}$ ), 21.0 ( $\text{CH}_3\text{CO}$ ), 49.8 ( $\text{H}-\text{C}-\text{CH}_2$ ), 55.8–55.9 (4C,  $\text{OCH}_3$ ), 64.7 ( $\text{CH}_2$ ), 75.4 ( $\text{H}-\text{C}-\text{O}$ ); 110.2, 110.9 (2C), 112.1, 119.7, 121.1, 130.1, 130.8, 148.2, 148.6, 148.8, 148.9 (12C, aromatic C atoms); 169.8 ( $\text{C}=\text{O}$ ), 170.7 ( $\text{C}=\text{O}$ ); for the diacetate of *threo*-1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol:  $\delta$  20.9 ( $\text{CH}_3\text{CO}$ ), 21.2 ( $\text{CH}_3\text{CO}$ ), 49.6 ( $\text{H}-\text{C}-\text{CH}_2$ ), 55.8–55.9 (4C,  $\text{OCH}_3$ ), 64.7 ( $\text{CH}_2$ ), 76.2 ( $\text{H}-\text{C}-\text{O}$ ); 110.5, 110.6, 110.9, 112.1, 119.7, 121.2, 130.1, 130.7, 148.1, 148.5 (2C), 148.7 (12C, aromatic C atoms); 169.9 ( $\text{C}=\text{O}$ ), 170.9 ( $\text{C}=\text{O}$ ).

### Crystal data

$\text{C}_{15}\text{H}_{16}\text{O}_2$   
 $M_r = 228.28$   
 Monoclinic,  $P2_1/n$   
 $a = 13.9047(7) \text{ \AA}$   
 $b = 5.4818(3) \text{ \AA}$   
 $c = 16.8837(9) \text{ \AA}$   
 $\beta = 104.243(1)^\circ$   
 $V = 1247.36(11) \text{ \AA}^3$

$Z = 4$   
 $D_x = 1.216 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.08 \text{ mm}^{-1}$   
 $T = 173(2) \text{ K}$   
 Needle, colourless  
 $0.64 \times 0.08 \times 0.06 \text{ mm}$

## Data collection

Siemens SMART CCD area detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.846$ ,  $T_{\max} = 0.995$

19374 measured reflections  
 3816 independent reflections  
 2877 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 30.6^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.126$   
 $S = 1.00$   
 3816 reflections  
 172 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 0.2365P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ) for compound (I), and corresponding data for related compounds (II) and (III).

	(I)	(II)	(III)
<b>Bonds</b>			
C1—C7	1.5148 (14)	1.513 (4)	1.515 (2)
O1—C7	1.4312 (12)	1.433 (5)	1.433 (2)
C7—C8	1.5456 (14)	1.538 (4)	1.538 (3)
C8—C9	1.5329 (14)	1.526 (4)	1.528 (2)
C8—C10	1.5120 (14)	1.520 (4)	1.519 (2)
O2—C9	1.4277 (13)	1.420 (4)	1.428 (2)
<b>Angles</b>			
C1—C7—C8	113.19 (8)	112.1 (2)	113.22 (14)
C1—C7—O1	111.80 (8)	111.0 (3)	110.52 (16)
O1—C7—C8	108.39 (8)	110.9 (2)	110.83 (13)
C7—C8—C10	113.49 (9)	116.2 (3)	116.68 (16)
C7—C8—C9	110.90 (8)	110.9 (2)	111.36 (14)
C9—C8—C10	111.52 (8)	109.8 (2)	109.12 (13)
C8—C9—O2	112.79 (8)	113.0 (2)	110.31 (14)
<b>Torsion angles<sup>†</sup></b>			
C1—C7—C8—C10	-62.26 (11)	-61.2 (4)	-49.8 (2)
C1—C7—C8—C9	171.29 (8)	172.6 (4)	-175.98 (15)
O1—C7—C8—C10	62.36 (11)	63.5 (4)	75.04 (17)
O1—C7—C8—C9	-64.09 (11)	-62.8 (4)	-51.1 (2)
O2—C9—C8—C7	-60.71 (11)	-56.1 (4)	-49.5 (2)
O2—C9—C8—C10	171.76 (8)	174.1 (4)	-179.70 (15)
<b>Dihedral angles</b>			
between aromatic ring planes	44.43 (6)	115.2 (2)	68.03 (8)

<sup>†</sup> The enantiomer with an *S* configuration at the C atom in the benzyl alcohol group is considered.

Table 2

Hydrogen-bonding geometry ( $\text{Å}$ ,  $^\circ$ ).

Label	$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
<i>a</i>	O1—H1 $\cdots$ O2 <sup>i</sup>	0.84	1.90	2.7317 (10)	173
<i>b</i>	O2—H2 $\cdots$ O1 <sup>ii</sup>	0.84	1.95	2.7523 (11)	158

Symmetry codes: (i)  $-x, -y, -z + 2$ ; (ii)  $x, y - 1, z$ .

H atoms were constrained to ideal geometry using an appropriate riding model (C—H = 0.95–1.00  $\text{Å}$ ) and refined isotropically. For the hydroxyl groups, the O—H distances (0.84  $\text{Å}$ ) and C—O—H angles (109.5 $^\circ$ ) were kept fixed, while the torsion angles were refined from starting positions based on the circular Fourier synthesis.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT and SADABS (Sheldrick, 2003); program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3092). Services for accessing these data are described at the back of the journal.

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