erythro-2-(2,6-Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)-1,3-propanediol

Vratislav Langer[a]* and Knut Lundquist[b]

[a]Department of Environmental Inorganic Chemistry, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and [b]Department of Forest Products and Chemical Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden

Correspondence e-mail:
langer@inoc.chalmers.se

In the crystals of the title lignin model compound, $C_{20}H_{26}O_8$, the molecules adopt a conformation in which the bulky 2,6-dimethoxyphenoxy and 3,4,5-trimethoxyphenyl groups are distant from each other. The O(phenoxy)—C—C—C(phenyl) torsion angle between these groups is 178.58 (7)°. The hydrogen-bonding pattern is discussed in terms of graph-set theory.

Comment

Roughly one half of the phenylpropane units in lignins are arylglycerols attached to an adjacent unit by a β-aryl ether linkage. In hardwood lignins, most of the β-aryl substituents are of the syringyl type. Formula (1) shows a structural element of the arylglycerol β-syringyl ether type. The majority of these structural elements have the erythro configuration (Bardet et al., 1998). erythro-2-(2,6–Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)-1,3-propanediol, (2), is a model compound representative of erythro forms of lignin structures of type (1). The crystal structure of (2) is described in this paper.

(1)

(2) R = CH$_3$, R' = H
(3) R = H, R' = CH$_2$OH
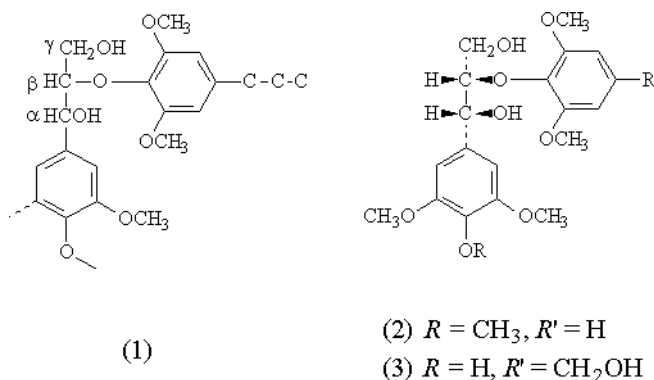
The title compound, (2), adopts a conformation in which the bulky 1-aryl and 2-aryloxy groups are distant from each other. The distance C1···C12 is 4.5030 (13) Å, the torsion angle C1—C9—C10—O6 is 178.58 (7)° and the torsion angle C9—C10—O6—C12 is −89.24 (9)°. The conformation of (2) differs considerably from that of a previously examined compound of the same type, erythro-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propanediol, (3) (Stomberg & Lundquist, 1989). In this latter compound, the distance corresponding to C1···C12 is 4.425 (7) Å, the C1—C9—C10—O6 torsion angle is −71.0 (4)° and the C9—C10—O6—C12 torsion angle is −150.5 (4)°. The angle between the aromatic ring planes is 76.00 (3)° in (2) and 63.1 (1)° in (3).
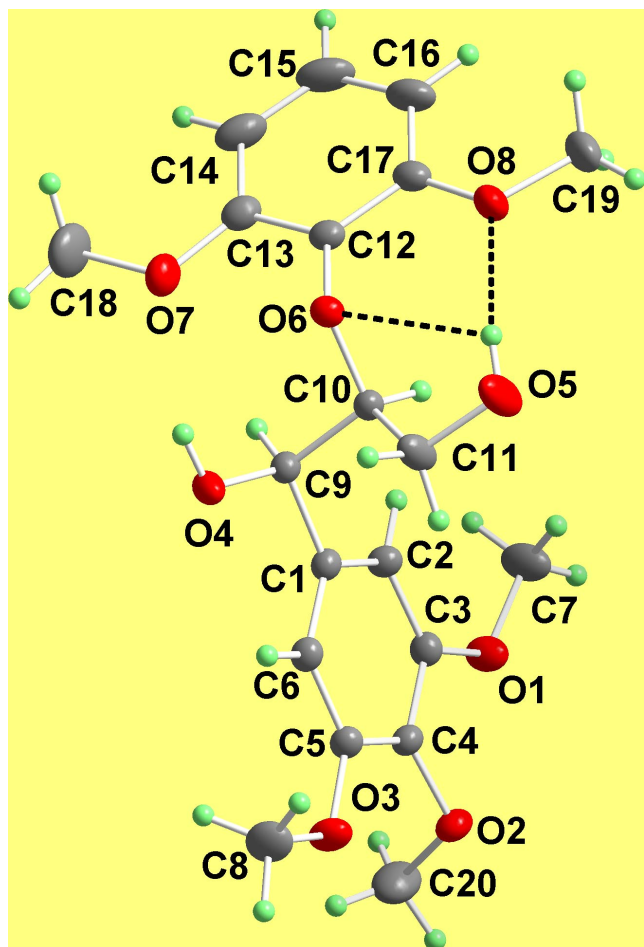
Figure 1
The numbering scheme for (2) with displacement ellipsoids shown at the 50% probability level. The intramolecular hydrogen bonds are shown by broken lines.

Figure 2
The hydrogen-bond network showing a chain of molecules.

$C1,1(6)$, shown in Fig. 2. Generally, the intermolecular hydrogen bonds are weaker in (2) than in (3). This is in agreement with measured melting points: 451–453 K for (3) and 377–378 K for (2). We think that the different hydrogen-bonding patterns are the main reason for the conformational differences between (2) and (3).

Experimental

The synthesis of 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxy-phenyl)-1,3-propanediol has been described by von Unge *et al.* (1988). Separation of the diastereomeric forms was accomplished by ion exchange chromatography [*cf.* Li *et al.* (1994)]. The *erythro* isomer (2) was recrystallized from ethyl acetate.

The hydrogen-bonding patterns of (2) and (3) differ considerably. Both structures exhibit intramolecular hydrogen bonds of approximately the same strength, but in (2) they are formed by H(O5) and both O6 and O8 (Fig. 1 and Table 1), while in (3) they are formed by the H atom in the benzylic hydroxyl group and the O atoms corresponding to O6 and O8. The intermolecular hydrogen bonds also differ as a result of the fact that (3) has two more hydroxyl groups than (2) (a phenolic group and the hydroxyl group in the methylol group denoted R'). As a consequence of this, (3) exhibits a complicated hydrogen-bonding network. Assignment of the hydrogen-bond descriptors using program *PLUTO* (Mother-well *et al.*, 1999) in terms of the graph-set theory (Bernstein *et al.*, 1995) has been carried out. For this purpose, we use symbols of type $Xa,d(n)$, where X is the pattern descriptor, a is the number of acceptors, d is the number of donors and n is the number of atoms comprising the pattern. For (3), there are, on the first level, a chain $C1,1(10)$ and rings $R2,2(20)$ and $R2,2(22)$ and, on the second level, chains $C2,2(19)$, $C2,2(21)$ and rings $R4,4(8)$, $R4,4(38)$, $R4,4(40)$ and $R4,4(42)$. The structure of (2) exhibits just one first-level descriptor, a chain
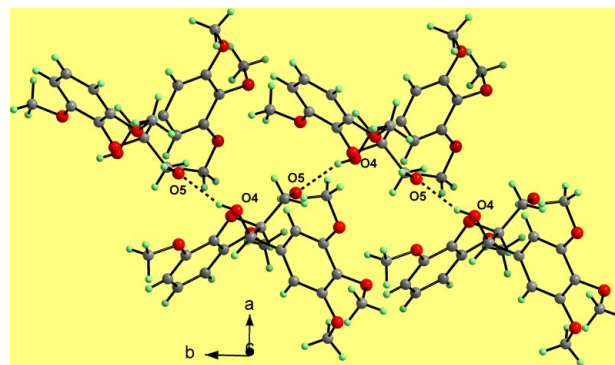
Crystal data

$C_{20}H_{26}O_8$	$D_x = 1.268$ Mg m^{-3}
$M_r = 394.41$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8192
$a = 11.7627 (2)$ Å	reflections
$b = 9.6220 (2)$ Å	$\theta = 1.8$–$32.9°$
$c = 18.7387 (3)$ Å	$\mu = 0.10$ mm^{-1}
$\beta = 103.034 (1)°$	$T = 183 (2)$ K
$V = 2066.22 (6)$ Å^3	Irregular shape, colorless
$Z = 4$	$0.65 \times 0.30 \times 0.20$ mm

Data collection

Siemens SMART CCD	7394 independent reflections
diffractometer	5861 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan	$\theta_{max} = 32.9°$
(*SADABS*, Sheldrick, 2001)	$h = -17 \rightarrow 17$
$T_{min} = 0.939$, $T_{max} = 0.981$	$k = -14 \rightarrow 14$
33473 measured reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 0.5426P]$
$wR(F^2) = 0.125$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
7394 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
286 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O5^{i}	0.84	2.09	2.8569 (11)	152
O4—H4$\cdots$O6	0.84	2.56	2.8731 (10)	104
O4—H4$\cdots$O7	0.84	2.64	3.1934 (12)	125
O5—H5$\cdots$O6	0.84	2.45	2.8504 (11)	110
O5—H5$\cdots$O8	0.84	2.20	2.9876 (12)	157
C6—H6$\cdots$O4	0.95	2.40	2.7360 (12)	101
C9—H9$\cdots$O7	1.00	2.47	3.0947 (12)	120
C11—H11$A\cdots$O7^{ii}	0.99	2.58	3.1676 (14)	118
C19—H19$C\cdots$O4^{iii}	0.98	2.58	3.5465 (15)	171

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

H atoms were refined isotropically and were constrained to the ideal geometry using an appropriate riding model. For hydroxyl groups, the O—H distances (0.84 Å) and C—O—H angles (109.5°) were kept fixed, and the torsion angle was chosen to maximize the electron density. For methyl groups, the C—H distances (0.98 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on the threefold averaged circular Fourier synthesis.

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