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erythro-2-(2,6-Dimethoxy-4-methylphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)propane-1,3-diol

In the title compound, $C_{20}H_{26}O_8$, the molecules adopt a conformation in which the torsion angle C(aryl)—C—C—O(aryloxy) is $-70.8\,(2)°$ and the torsion angle C(aryl)—O—C—C(benzylic) is $-152.71\,(18)°$, leading to a C(aryl)···C(aryl) distance of 4.426 (3) Å. This distance is identical, within experimental error, to the calculated maximum value obtained when the torsion angle C(aryl)—O—C—C(benzylic) is varied and the torsion angle C(aryl)—C—C—O(aryloxy) is kept constant. The angle between the aromatic ring planes is 64.13 (7)°. The conformation is compared with those of related lignin model compounds. The hydrogen-bonding pattern reveals intramolecular interactions, and the formation of centrosymmetric dimers and chains of molecules by intermolecular interactions.

Comment

This paper describes the crystal structure of the lignin model compound (I), which is representative of *erythro* forms of structural elements in lignins of the syringylglycerol β-syringyl ether type. The crystal structures of three compounds of this type, *viz.* (II)–(IV), have been reported previously (Stomberg & Lundquist, 1989; Langer & Lundquist, 2001; Langer *et al.*, 2002). A perspective drawing of (I) and the atomic numbering are shown in Fig. 1. The methyl H atoms at C19 are disordered with two orientations rotated from each other by 60°.

(I)

(II) R= H, R'= CH₂OH
(III) R= CH₃, R'= H
(IV) R= R'= H
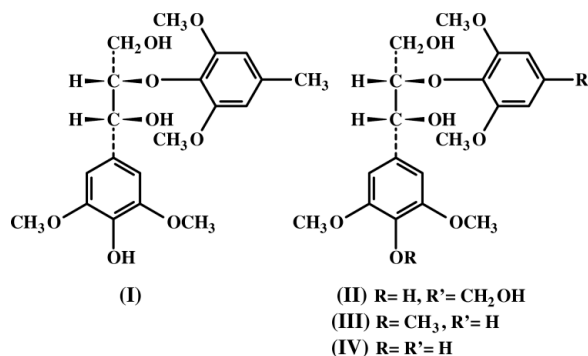
Interestingly, the conformations of (I) and (II) are very similar. The torsion angle C1—C7—C8—O4 is $-70.8\,(2)°$ in (I) and the corresponding angle in (II) is $-71.0\,(4)°$. Furthermore, the magnitude of the torsion angle C11—O4—C8—C7 $[-152.71\,(18)°]$ is very similar to the corresponding angle in (II) $[-150.5\,(4)°]$. The angle between the aromatic ring planes is 64.13 (7)° in (I) and 63.1 (1)° in (II). The conformations of (III) and (IV) are similar but differ dramatically from those of (I) and (II). The torsion angles corresponding to C1—C7—C8—O4 are, for instance, close to 180°. The distance C1···C11 [4.426 (3) Å] can be taken as a
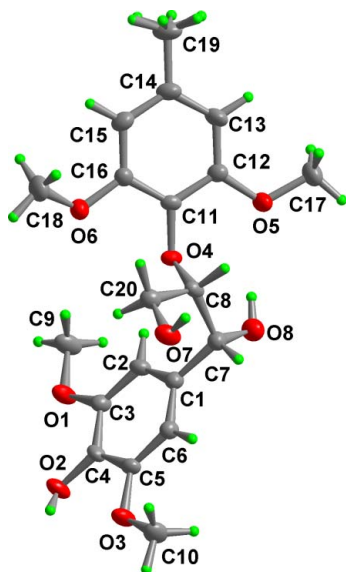
Figure 1
A perspective drawing of (I) showing the atom-numbering. Displacement ellipsoids are shown at the 50% probability level.

measure of the separation of the bulky 2,6-dimethoxy-4-methylphenyl and 4-hydroxy-3,5-dimethoxyphenyl groups. This distance is not close to the maximum possible value (*ca* 5 Å), but agrees with the calculated maximum value of 4.43 Å obtained when the torsion angle C11—O4—C8—C7 is varied and the torsion angle C1—C7—C8—O4 is kept constant at $-70.8 (2)°$.

In the crystal structure of (I), there are three intramolecular and three intermolecular hydrogen bonds of the O—H···O type and one intramolecular and two intermolecular hydrogen
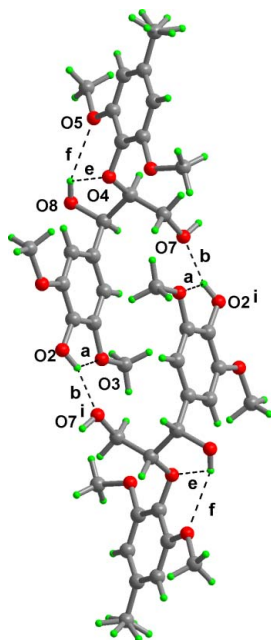

Figure 2
The hydrogen-bonding (dashed lines) pattern of (I). Centrosymmetric dimers are formed [symmetry code: (i) $-x + 2$, $-y + 1$, $-z+2$]. The hydrogen-bond labels match those given in Table 1.

bonds of the weak C—H···O type (Table 1). Intermolecular hydrogen bond *b* (see Table 1 and Fig. 2) gives rise to centrosymmetric dimers. On the first-level graph-set (Bernstein *et al.*, 1995; Grell *et al.*, 1999), the hydrogen bonds are classified as $S(5)$ for bonds *a* and *e*, $S(8)$ for *f* and $S(6)$ for *g*. The centrosymmetric dimer, formed by hydrogen bond *b*, is classified as ring $R_2^2(20)$, while hydrogen bonds *c* and *d* form $C(9)$ and $C(10)$ chains, respectively (Fig. 3). The weak intramolecular hydrogen bonds *h* and *i* form rings $R_2^2(20)$ and $R_2^2(16)$, respectively. On the second-level graph-set, many chains and rings could be identified, the most important being rings $R_4^4(8)$, formed by bonds *b* and *d*, and $R_2^1(5)$, formed by hydrogen bonds *c* and *d*. The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999).

It is notable that the conformations adopted by (I) and (II) in the crystal structures are those that are most favored, as judged from computational studies (Besombes *et al.*, 2003). The conformations adopted by (III) and (IV) are conceivable but not favored according to such studies (Besombes *et al.*, 2003). A plausible assumption is that the conformations of β-ether models are largely governed by hydrogen bonding. Attempts to obtain unequivocal proof of this have so far failed. In a previous paper (Langer & Lundquist, 2001), it was proposed that the different hydrogen-bonding patterns are the main reason for the conformational differences between (II) and (III). However, compounds (I) and (II) adopt very similar conformations in spite of a difference in hydrogen-bonding patterns (see above, also Stomberg & Lundquist, 1989), due to the fact that a hydroxymethyl group in (II) has been exchanged for a methyl group in (I). In a recent paper, it is concluded, based on NMR studies, that intramolecular hydrogen bonding is of minor importance for the conformations adopted by β-ethers in solution (Besombes *et al.*, 2004).

Experimental

The synthesis of (I) has been described by Miksche (1973). Crystals suitable for X-ray analysis were obtained from ethyl acetate (m.p. 420–422 K).

Crystal data

$C_{20}H_{26}O_8$	$Z = 2$
$M_r = 394.41$	$D_x = 1.356$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.6930 (2)$ Å	Cell parameters from 4159
$b = 8.8976 (2)$ Å	reflections
$c = 13.1057 (3)$ Å	$\theta = 1.6–25.5°$
$\alpha = 73.852 (1)°$	$\mu = 0.11$ mm^{-1}
$\beta = 86.150 (1)°$	$T = 173 (2)$ K
$\gamma = 83.062 (1)°$	Prism, colorless
$V = 965.96 (4)$ Å^3	$0.24 \times 0.12 \times 0.08$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	3607 independent reflections
	2409 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.047$
Absorption correction: multi-scan	$\theta_{max} = 25.5°$
(*SADABS*; Sheldrick, 2002)	$h = -10 \rightarrow 10$
$T_{min} = 0.715$, $T_{max} = 0.992$	$k = -10 \rightarrow 10$
10 905 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 0.3785P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
3607 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
261 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
H-atom parameters constrained	

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

Label	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
a	O2—H2$A\cdots$O3	0.84	2.29	2.666 (2)	108
b	O2—H2$A\cdots$O7^i	0.84	1.92	2.676 (2)	148
c	O7—H7$A\cdots$O1^{ii}	0.84	2.61	3.316 (2)	142
d	O7—H7$A\cdots$O2^{ii}	0.84	1.91	2.662 (2)	149
e	O8—H8$A\cdots$O4	0.84	2.35	2.766 (2)	112
f	O8—H8$A\cdots$O5	0.84	2.43	3.201 (3)	154
g	C2—H2$\cdots$O4	0.95	2.50	3.022 (3)	114
h	C19—H19$B\cdots$O8^{iii}	0.98	2.59	3.428 (3)	144
i	C20—H20$B\cdots$O3^i	0.99	2.57	3.323 (3)	132

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

H atoms were constrained to ideal geometry using an appropriate riding model. The C—H distance was kept fixed at 0.95 Å for aromatic H atoms, at 0.99 Å for secondary H atoms and at 1.00 Å for tertiary H atoms. For the hydroxyl groups, the O—H distance (0.84 Å) and C—O—H angle (109.5°) were kept fixed, while the torsion angle was allowed to refine with the starting position based on a circular Fourier synthesis. 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 threefold-averaged circular Fourier syntheses. The methyl H atoms on C19 were treated as disordered with two orientations rotated from each other by 60° with half occupancy. U_{iso} values were fixed at $1.2U_{eq}$ of the pivot atom for aromatic, secondary and tertiary H atoms, while for hydroxyl and methyl H atoms, the U_{iso} values were fixed at $1.5U_{eq}$ of the pivot atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* (Siemens, 1995) and *SADABS* (Sheldrick, 2002; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXTL*.
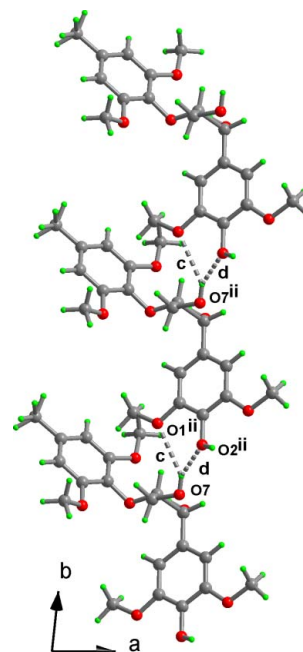

Figure 3
The hydrogen-bonding (dashed lines) pattern of (I). Chains of molecules (I) parallel to the b axis are formed [symmetry code: (ii) x, $y + 1$, z]. The hydrogen-bond labels match those given in Table 1.

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