# organic papers

# threo-2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxy-phenyl)-1,3-propanediol

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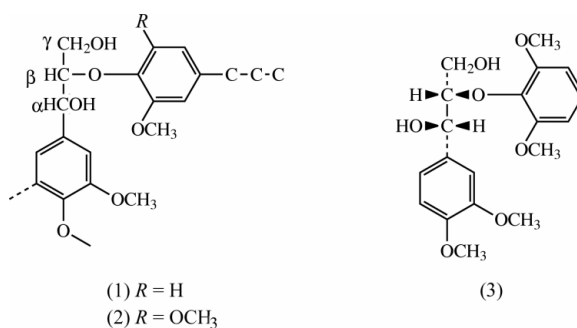Correspondence e-mail:
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**Key indicators**

Single-crystal X-ray study
$T = 183$ K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.051
$wR$ factor = 0.123
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystals of the title compound, $C_{19}H_{24}O_7$, the molecules adopt a conformation in which the torsion angle C(aryl)—C—C—O(aryloxy) is −70.5 (2)° and the torsion angle C(aryl)—O—C—C(benzylic) is −148.25 (19)°. This leads to a closest C(aryl)$\cdots$C(aryl) distance of 4.319 (3) Å. This distance is, within experimental error, identical 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 75.79 (7)°. The hydrogen-bonding pattern reveals intramolecular interactions and formation of ribbons of molecules, parallel to the $a$ axis.

## Comment

Roughly one half of the phenylpropane units in lignins are arylglycerols attached to an adjacent unit by a $\beta$-aryl ether linkage. The majority of these ether structures can be grouped as arylglycerol $\beta$-guaiacyl ethers, (1), and arylglycerol $\beta$-syringyl ethers, (2). Assignments of *erythro* and *threo* forms of lignin model compounds representative of structures of type (2) were originally based on ^{1}H NMR spectral comparisons with model compounds for structures of type (1) (Miksche, 1973). Assignment using this method is undoubtedly justified, but we considered that confirmation by an independent method was desirable, and this was accomplished by assigning the *threo* (3) and *erythro* forms of the model compound 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol based on crystal structure determinations of synthetic intermediates (Lundquist *et al.*, 1987). This, together with crystal structure determinations of a series of *erythro* forms of syringylglycerol $\beta$-syringyl ethers (Stomberg & Lundquist, 1989; Langer & Lundquist, 2001; Langer *et al.*, 2002), provides a basis for the steric assignment of lignin models representative of lignin structures of type (2).
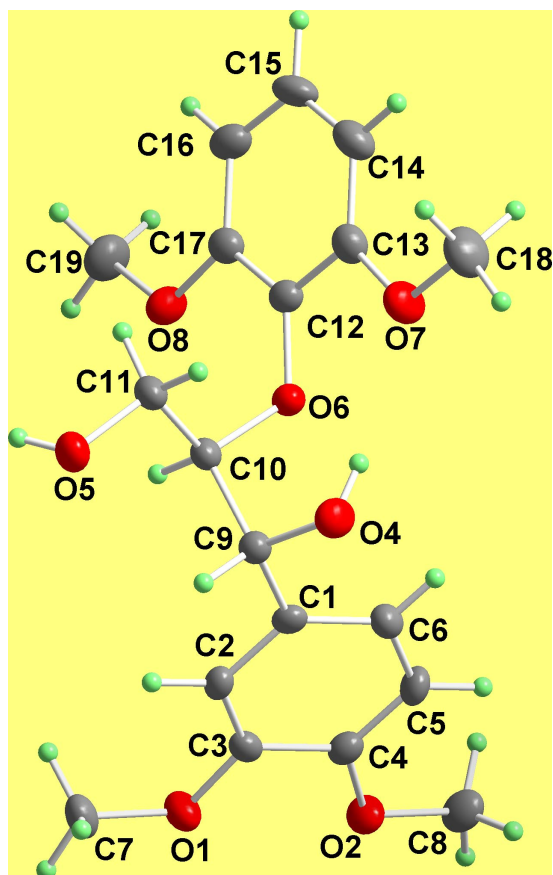


(1) $R$ = H
(2) $R$ = $OCH_3$

(3)

The study of the crystal structure of (3) reported in this paper is primarily directed towards establishing the confor-

**Figure 1**
The numbering scheme for the title compound. Displacement ellipsoids are shown at the 50% probability level.

mation of the compound. We have previously examined three *erythro* forms of models representative of lignin structures of type (2). Compound (3) represents *threo* forms of such structures. In the crystals of (3), the molecules adopt a conformation in which the torsion angle C1—C9—C10—O6 is −70.5 (2)° and the torsion angle C12—O6—C10—C9 is −148.25 (19)° (Fig. 1). This leads to a C1—C12 distance of 4.319 (3) Å, which is taken as a measure of the separation of the bulky 2,6-dimethoxyphenyl and 3,4-dimethoxyphenyl groups. This distance is not close to the maximum possible value (*ca* 5 Å), but it agrees with the calculated maximum value 4.32 Å obtained when the torsion angle C12—O6—C10—C9 is varied and the torsion angle C1—C9—C10—O6 is kept constant at −70.5 (2)°. The angle between the aromatic ring planes is 75.79 (7)°. It is notable that the positions of the aromatic rings are interrelated in a similar way in the crystal structures of (3) and *erythro*-1-(4-hydroxy-3,5-dimethoxy-phenyl)-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-pro-panediol (Stomberg & Lundquist, 1989). Hydrogen bonding can be expected to influence the conformation. There are two intramolecular hydrogen bonds formed by H(O4) and the atoms O6 and O7. A ribbon of molecules, parallel to the *a* axis, is formed by intermolecular hydrogen bonding between H(O5) and O4 (Fig. 2 and Table 1).
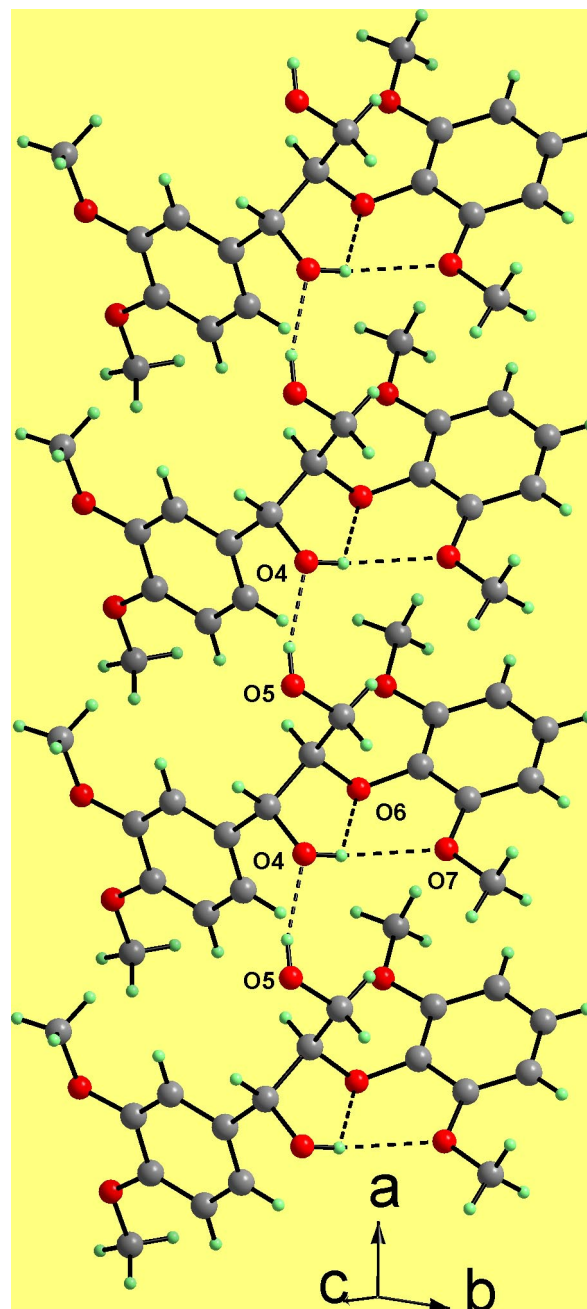


**Figure 2**
The hydrogen-bonding pattern for (3).

Three lignin model compounds representative of *threo* forms of lignin structures of type (1) have been examined by X-ray crystallography (Stomberg *et al.*, 1988; Lundquist *et al.*, 1996). In the crystals, these compounds adopt conformations with the aromatic groups almost as far apart as possible.

## Experimental

The synthesis of the diastereomeric forms of 2-(2,6-dimethoxy-phenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol has been described by von Unge *et al.* (1988). Crystals of the *threo* form (3) suitable for X-ray analysis were obtained from ethyl acetate (m.p. 383–385 K).

## Crystal data

$C_{19}H_{24}O_7$
$M_r = 364.38$
Triclinic, $P\bar{1}$
$a = 6.1632\ (2)$ Å
$b = 9.1891\ (3)$ Å
$c = 15.9231\ (5)$ Å
$\alpha = 98.913\ (1)°$
$\beta = 90.664\ (1)°$
$\gamma = 97.328\ (1)°$
$V = 883.17\ (5)$ Å$^3$

$Z = 2$
$D_x = 1.370$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3859
  reflections
$\theta = 2.3–25.4°$
$\mu = 0.10$ mm$^{-1}$
$T = 183\ (2)$ K
Plate, colourless
$0.25 \times 0.10 \times 0.02$ mm

## Data collection

Siemens SMART CCD
  diffractometer
$\omega$ scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 2001)
  $T_{min} = 0.974$, $T_{max} = 0.998$
9676 measured reflections

3238 independent reflections
2141 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25.4°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 19$

## Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.123$
$S = 1.01$
3238 reflections
265 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2$
$\quad + 0.2595P]$
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| O4—H4···O6 | 0.84 | 2.20 | 2.669 (2) | 115 |
| O4—H4···O7 | 0.84 | 2.24 | 3.051 (2) | 163 |
| O5—H5···O4$^i$ | 0.84 | 1.99 | 2.807 (2) | 164 |
| C8—H8B···O8$^{ii}$ | 0.98 | 2.55 | 3.359 (3) | 139 |
| C9—H9···O5 | 1.00 | 2.52 | 2.940 (3) | 105 |
| C19—H19B···O2$^{iii}$ | 0.98 | 2.56 | 3.418 (3) | 146 |

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

H atoms were refined isotropically and were constrained to 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 match the observed 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 a threefold averaged circular Fourier synthesis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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