

threo-2-(2,6-Dimethoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)propane-1,3-diol: a conformational study

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Received 24 February 2005

Accepted 1 March 2005

Online 18 March 2005

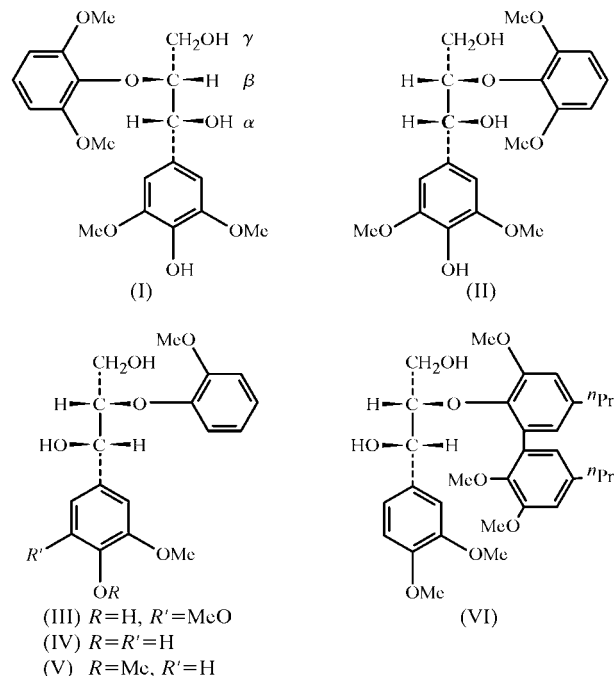
In the crystal structure of the title compound, C₁₉H₂₄O₈, the molecules adopt a conformation in which the bulky 2,6-dimethoxyphenoxy and 4-hydroxy-3,5-dimethoxyphenyl groups are almost as far apart as possible. The C(aryl)···C(aryl) distance is 4.8766 (19) Å, which is close to the calculated maximum value (4.92 Å). The C(aryl)–C–C–O(aryloxy) torsion angle is 173.76 (11)° and the C(benzylic)–C–O–C(aryl) torsion angle is 149.09 (11)°. The conformation is compared with those of related lignin model compounds. The hydrogen-bonding pattern is discussed in terms of graph-set theory.

Comment

This paper describes the crystal structure of the title compound, (I), the *threo* form of a lignin model compound representative of structural elements in lignin of the arylglycerol β-syringyl ether type. The crystal structure of the *erythro* form, (II), has been reported previously (Langer, Li & Lundquist, 2002). Arylglycerol β-syringyl ethers constitute a major type of structural elements in hardwood lignins, e.g. in birch lignin (Larsson & Miksche, 1971). The *erythro* form of such structural elements predominates (Lundquist & von Unge, 1986; Bardet *et al.*, 1998; Akiyama *et al.*, 2003).

In (I), the C9–C10–O6–C12 torsion angle is 149.09 (11)° and the C1–C9–C10–O6 torsion angle is 173.76 (11)° (the enantiomer with the *R* configuration at the benzylic C atom is considered throughout the discussion of torsion angles in this paper), and the C1···C12 distance is 4.8766 (19) Å. In the *erythro* form, the corresponding data are –75.26 (13)°, –177.27 (10)° and 4.4458 (17) Å, respectively. The C1···C12 distance in (II) is about the same as the corresponding distances in other examined *erythro* forms of the arylglycerol β-syringyl ether type (Stomberg & Lundquist, 1989; Langer &

Lundquist, 2001; Langer *et al.*, 2005). Obviously, the aromatic rings in the *erythro* form, (II) (and related compounds), are not separated as much as they are in the *threo* form, (I). The angle between the aromatic ring planes is 67.66 (6)° in (I) and 57.27 (5)° in (II). The C1···C12 distance in (I) [4.8766 (19) Å] is very close to the calculated maximum value (4.92 Å).



In the crystal structure of (I), there are three intramolecular (Fig. 1) and two intermolecular hydrogen bonds of the O–H···O type and four weak intermolecular hydrogen bonds of the C–H···O type (Table 1). On the first-level graph-set (Bernstein *et al.*, 1995; Grell *et al.*, 1999), the intramolecular hydrogen bonds are classified as *S*(5) for bonds *a* and *c*, and *S*(8) for *d* (see Fig. 1). The intermolecular hydrogen bonds *b* and *e* form *C*(10) and *C*(6) chains, respectively (Fig. 2). The weak intramolecular hydrogen bonds *f*, *g*, *h* and *i* form *R*₂²(8) rings and *C*(8), *C*(13) and *C*(7) chains, respectively. On the second-level graph-set, many chains and rings could be identified, the most important ones being *C*₂²(10) and *C*₂²(16) chain types, both formed by bonds *b* and *e*. These two hydrogen bonds thus form *R*₃³(22) rings (Fig. 2). The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999). The hydrogen-bonding patterns of *threo*-(I) and *erythro*-(II) (Langer, Li & Lundquist, 2002) forms are similar with respect to intramolecular hydrogen bonds.

As pointed out above, the title *threo* β-syringyl ether adopts a conformation in which the aryl groups are almost as far apart as possible. This is actually what could be expected from computational studies (Besombes *et al.*, 2003a). In a second *threo* form of an arylglycerol β-syringyl ether, namely *threo*-2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol, the C(aryl)–C–C–O(aryloxy) torsion angle is –70.5 (2)° and the C(aryl)–O–C–C(benzylic) torsion angle is –148.25 (19)° (Langer, Lundquist *et al.*, 2002). This leads to a C(aryl)···C(aryl) distance of 4.319 (3) Å, which deviates

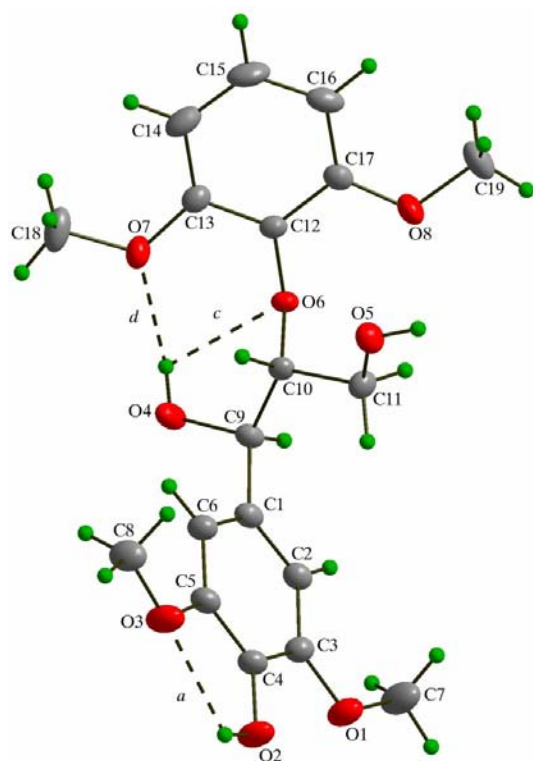


Figure 1
A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The intramolecular hydrogen bonds are shown as dashed lines and their notation is given in Table 1.

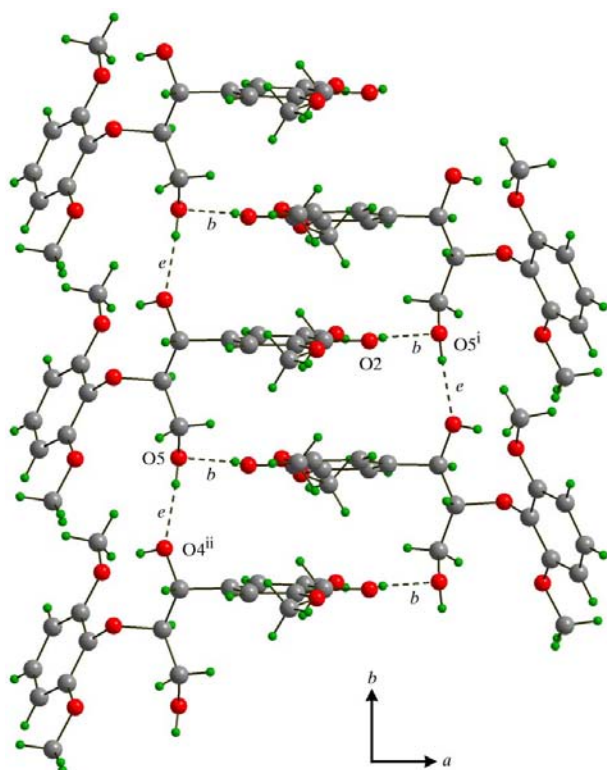


Figure 2
The hydrogen-bonding pattern (dashed lines) of (I) in projection along the *c* axis. The hydrogen-bond notation is given in Table 1.

significantly from the maximum value (*ca* 4.91 Å). However, according to computational studies, the conformation adopted by this compound is fairly favoured (Besombes *et al.*, 2003*a*). All the *threo* forms of models of the arylglycerol β -guaiacyl ether type which have been examined to date [(III) (Stomberg *et al.*, 1988), (IV) and its triacetate (Lundquist *et al.*, 1996), and (V) (Langer & Lundquist, 2002)] adopt conformations in which the aromatic groups are far apart from each other. This is in accordance with expectations based on computational studies (Simon & Eriksson, 1998; Besombes *et al.*, 2003*b*). The crystal structure of the *threo* form of a trimeric model compound of the arylglycerol β -aryl ether type, (VI), has been reported by Karhunen *et al.* (1996). Calculations based on their data show that this compound also adopts an extended conformation: the C(aryl)–C–C–O(aryloxy) torsion angle is 175.7° and the C(aryl)–O–C–C(benzylic) torsion angle is 171.9°.

Experimental

Compound (I) was synthesized according to the procedure of Li *et al.* (2000). Separation of the *erythro* and *threo* forms was accomplished by ion-exchange chromatography (*cf.* Li *et al.*, 1994). Crystals of (I) (m.p. 415–417 K) suitable for X-ray crystallography were obtained from 2-butanone/ethyl acetate (3:1).

Crystal data

$C_{15}H_{24}O_8$	$D_x = 1.398 \text{ Mg m}^{-3}$
$M_r = 380.38$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7395 reflections
$a = 24.0634 (1) \text{ \AA}$	$\theta = 1.9\text{--}30.7^\circ$
$b = 7.3465 (1) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 22.4459 (3) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\beta = 114.332 (1)^\circ$	Prism, colourless
$V = 3615.56 (7) \text{ \AA}^3$	$0.28 \times 0.24 \times 0.22 \text{ mm}$
$Z = 8$	

Data collection

Siemens SMART CCD area-detector diffractometer	5566 independent reflections
ω scans	4423 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.768$, $T_{\text{max}} = 0.976$	$\theta_{\text{max}} = 30.7^\circ$
28 856 measured reflections	$h = -34 \rightarrow 34$
	$k = -10 \rightarrow 10$
	$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 4.0089P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.146$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$
5566 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
275 parameters	
H atom parameters constrained	

H atoms were refined isotropically and were constrained to ideal geometry using an appropriate riding model. For aromatic H atoms, the C–H distances were kept fixed at 0.95 Å, for secondary H atoms at 0.99 Å and for tertiary H atoms at 1.00 Å. 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 distance (0.98 Å) and C–C–H angle (109.5°) were kept fixed, while the torsion angles were allowed to refine, with the starting positions based on a threefold averaged circular Fourier synthesis.

Table 1

Hydrogen-bonding geometry (Å, °).

Label	D—H...A	D—H	H...A	D...A	D—H...A
<i>a</i>	O2—H2...O3	0.84	2.22	2.6707 (16)	114
<i>b</i>	O2—H2...O5 ⁱ	0.84	2.02	2.7851 (15)	152
<i>c</i>	O4—H4...O6	0.84	2.31	2.7424 (14)	112
<i>d</i>	O4—H4...O7	0.84	2.13	2.9123 (16)	154
<i>e</i>	O5—H5...O4 ⁱⁱ	0.84	1.99	2.8284 (15)	173
<i>f</i>	C9—H9...O6 ⁱⁱⁱ	1.00	2.56	3.5139 (17)	159
<i>g</i>	C11—H11A...O3 ^{iv}	0.99	2.50	3.2171 (18)	129
<i>h</i>	C18—H18C...O2 ^v	0.98	2.57	3.466 (2)	153
<i>i</i>	C19—H19C...O7 ⁱⁱ	0.98	2.52	3.491 (2)	169

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1820). Services for accessing these data are described at the back of the journal.

References

Akiyama, T., Matsumoto, Y., Okuyama, T. & Meshitsuka, G. (2003). *Phytochemistry*, **64**, 1157–1162.
 Bardet, M., Robert, D., Lundquist, K. & von Unge, S. (1998). *Magn. Reson. Chem.* **36**, 597–600.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Besombes, S., Robert, D., Utille, J.-P., Taravel, F. R. & Mazeau, K. (2003a). *J. Agric. Food Chem.* **51**, 34–42.
 Besombes, S., Robert, D., Utille, J.-P., Taravel, F. R. & Mazeau, K. (2003b). *Holzforchung*, **57**, 266–274.
 Brandenburg, K. (2005). *DIAMOND*. Version 3.0b. Crystal Impact GbR, Bonn, Germany.
 Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Grell, J., Bernstein, J. & Tinhofer, G. (1999). *Acta Cryst.* **B55**, 1030–1043.
 Karhunen, P., Rummakko, P., Pajunen, A. & Brunow, G. (1996). *J. Chem. Soc. Perkin Trans. 1*, pp. 2303–2308.
 Langer, V., Li, S. & Lundquist, K. (2002). *Acta Cryst.* **E58**, o42–o44.
 Langer, V. & Lundquist, K. (2001). *Acta Cryst.* **E57**, o1219–o1221.
 Langer, V. & Lundquist, K. (2002). *Acta Cryst.* **E58**, o433–o435.
 Langer, V., Lundquist, K. & Miksche, G. E. (2005). *Acta Cryst.* **E61**, o1001–o1003.
 Langer, V., Lundquist, K., Stomberg, R. & von Unge, S. (2002). *Acta Cryst.* **E58**, o90–o92.
 Larsson, S. & Miksche, G. E. (1971). *Acta Chem. Scand.* **25**, 647–662.
 Li, S., Lundquist, K. & Soubbotin, N. (1994). *Holzforchung*, **48**, 509–511.
 Li, S., Lundquist, K. & Westermark, U. (2000). *Nord. Pulp Pap. Res. J.* **15**, 205–210.
 Lundquist, K., Li, S. & Stomberg, R. (1996). *Nord. Pulp Pap. Res. J.* **11**, 43–47.
 Lundquist, K. & von Unge, S. (1986). *Acta Chem. Scand. Ser. B*, **40**, 791–797.
 Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* **B55**, 1044–1056.
 Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.
 Siemens (1995). *SMART* and *SAINT*. Versions 4.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Simon, J. P. & Eriksson, K. E. L. (1998). *Holzforchung*, **52**, 287–296.
 Stomberg, R., Hauteville, M. & Lundquist, K. (1988). *Acta Chem. Scand. Ser. B*, **42**, 697–707.
 Stomberg, R. & Lundquist, K. (1989). *J. Crystallogr. Spectrosc. Res.* **19**, 331–339.