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# Conformation of 1-aryl-2-aryloxy-1-propanols: *threo*-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol

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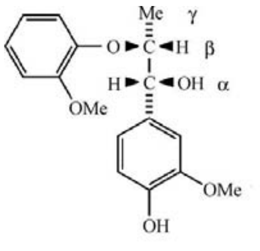
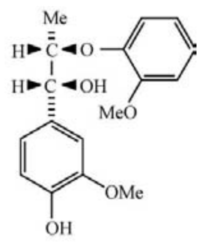
The title compound, $C_{17}H_{20}O_5$, (I), is structurally related to naturally occurring 1-aryl-2-aryloxy-1-propanols. Such compounds are of interest as lignin models, and neolignans of this type have been detected in a large number of plants. In the crystal structure of (I), the molecules adopt a conformation in which the aryl groups are far apart from each other. The O(aryloxy)—C—C—C(aryl) torsion angle is 177.76 (14)°. The conformation is compared with those of other compounds (neolignans and lignin model compounds) of the 1-aryl-2-aryloxy-1-propanol type (including some acetate derivatives). The comparison shows that in all the examined compounds the above-mentioned torsion angle is close to 180°, and the distance between the centers of the aromatic rings approaches the maximum achievable in most of the compounds. The hydrogen-bonding pattern of (I) is discussed in terms of graph-set theory.

## Comment

1-Aryl-2-aryloxy-1-propanols are of interest as lignin model compounds (Adler *et al.*, 1966; Wallis *et al.*, 1991; Stomberg *et al.*, 1993; Li & Lundquist, 2001). Quite a few neolignans with this type of structure have been isolated from plants (Stomberg *et al.*, 1993; Wallis, 1998; Lee & Ley, 2003; Kónya *et al.*, 2004; Hanessian *et al.*, 2006). The crystal structures of a number of 1-aryl-2-aryloxy-1-propanols have been reported (Jakobsons *et al.*, 1986; Wallis *et al.*, 1991, 1996; Stomberg *et al.*, 1993; Lee & Ley, 2003). The crystal structure of *threo*-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol, (I) (Fig. 1), is reported in the present paper. Jakobsons *et al.* (1986) have reported the crystal structure of the *erythro* form of this compound, hereafter (II). The synthesis of the *threo* and *erythro* forms by reduction of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone has been described by Adler *et al.* (1966). The *erythro*/*threo* ratio in the reaction products obtained depends on the particular reducing reagent used and the reaction conditions (Brunow *et al.*, 1988). Reduction with borane dimethyl sulfide complex gives predominantly the *threo* form (Li & Lundquist, 2001).



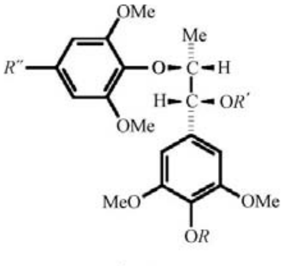
(I)



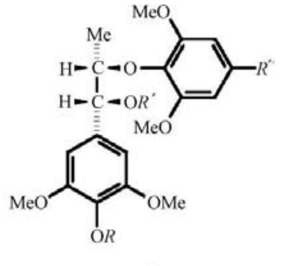
(II)

There are strong O—H···O hydrogen bonds (Fig. 2) present in the crystal structure of (I) (for geometrical details of the hydrogen bonds, see Table 1). Three of the hydrogen bonds are intramolecular, supporting the rigidity of the molecule, and one is intermolecular, forming *C*(8) chains on the first-level graph set, as defined by Bernstein *et al.* (1995) and Grell *et al.* (1999). There are also two weak C—H···O hydrogen bonds present in the crystal structure, consolidating the crystal framework, both of them forming *C*(5) chains on the first-level graph set (Fig. 3).

Geometric details of (I) are given in Table 2. For comparison, the corresponding geometric data for the related compounds (II), (III)–(VI) and acetate derivatives (VII)–(IX) are included in the table. To enable comparison, we have consistently considered the reference molecule as having the *R* configuration at Cα. The C(aryl)—O—Cβ—Cα and O(aryloxy)—C—C—C(aryl) torsion angles [C11—O4—C9—C8 and O4—C9—C8—C1 for (I)], the distances between the centers of the aromatic rings, and the angles between the aromatic ring mean planes are given in Table 2.



*threo*



*erythro*

(III) $R$ = H, $R'$ = H, $R''$ = (*Z*)-MeCH=CH
(IV) $R$ = Me, $R'$ = H, $R''$ = $MeCH_2CH_2$
(V) $R$ = Me, $R'$ = H, $R''$ = $CH_2$=$CHCH_2$
(VI) $R$ = Me, $R'$ = H, $R''$ = *p*-Tos–NH–N=CH
(VII) $R$ = Ac, $R'$ = Ac, $R''$ = (*E*)-MeCH=CH
(VIII) $R$ = Ac, $R'$ = Ac, $R''$ = (*E*)-MeCH=CH
(IX) $R$ = Ac, $R'$ = Ac, $R''$ = (*Z*)-MeCH=CH

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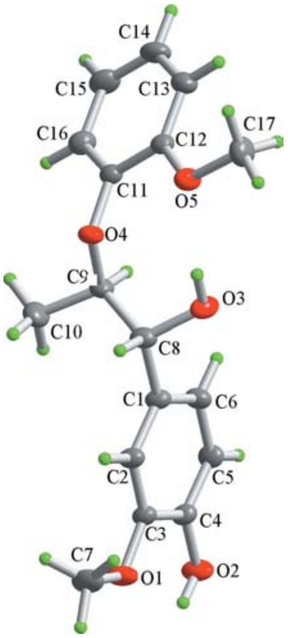

**Figure 1**
A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

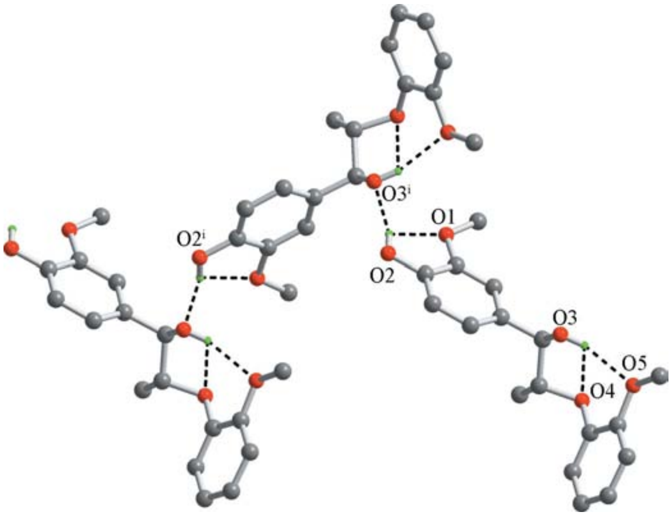

**Figure 2**
Hydrogen bonds (broken lines) forming chains of molecules in (I). H atoms not included in the hydrogen-bonding pattern have been omitted for clarity. For symmetry codes, see Table 1.

In all the compounds, the O(aryloxy)—C—C—C(aryl) torsion angle is close to 180°. In most of the compounds, the distance between the centers of the aromatic rings is close to the maximum achievable. The *erythro* acetate (IX) constitutes an exception in the sense that the C(aryl)—O—C$\beta$—C$\alpha$ torsion angle is comparatively small, and as a consequence of this the distance between the ring centers deviates notably from the maximum. The separation of the aromatic rings in (I)–(IX) might be attributed to $\pi$–$\pi$ electron repulsion (Hunter & Sanders, 1990). The orientations of the C(aryl)—O—C$\beta$—C$\alpha$ torsion angle for the *threo* and *erythro* forms (I) and (II) differ considerably, which explains the larger distance between the aromatic ring centers for (II) (see Table 2). The aromatic plane angles of the acetate derivatives (VII)–(IX) deviate considerably from the average of those of (I)–(VI).

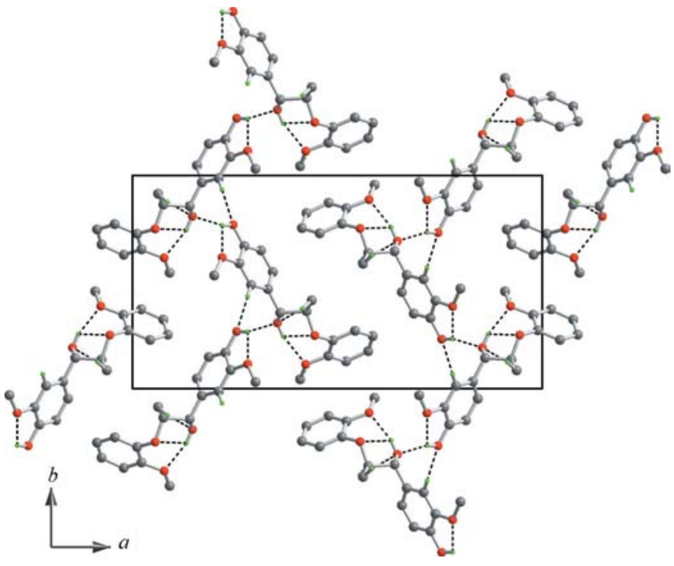

**Figure 3**
A projection of the content of the unit cell along the *c* axis. Hydrogen bonds are shown as broken lines. H atoms not included in the hydrogen-bonding pattern have been omitted for clarity.

## Experimental

Compound (I) was synthesized by reduction of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-1-one with $BH_3 \cdot S(CH_3)_2$ in tetrahydrofuran solution (under an argon atmosphere). Excess $BH_3 \cdot S(CH_3)_2$ was decomposed by addition of methanol. Work-up gave a product consisting primarily of (I) ($^1$H NMR). Crystals of melting point 386–387 K were obtained from acetone (Li & Lundquist, 2001). The brittleness of the crystals made it difficult to isolate a crystal of the usual size for data collection, so a larger uncut crystal was employed.

*Crystal data*

$C_{17}H_{20}O_5$
$M_r = 304.33$
Orthorhombic, $Pna2_1$
$a = 23.2847\ (11)$ Å
$b = 12.1184\ (6)$ Å
$c = 5.5709\ (3)$ Å
$V = 1571.96\ (14)$ Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm$^{-1}$
$T = 153\ (2)$ K
1.00 × 0.17 × 0.07 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.461$, $T_{\max} = 0.993$
27834 measured reflections
3175 independent reflections
2688 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.112$
$S = 1.00$
3175 reflections
204 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{\max} = 0.36$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.18$ e Å$^{-3}$

### Table 1
Hydrogen-bond geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O2—H2⋯O1 | 0.84 | 2.23 | 2.6813 (18) | 114 |
| O2—H2⋯O3$^{i}$ | 0.84 | 1.95 | 2.7438 (18) | 157 |
| O3—H3⋯O4 | 0.84 | 2.41 | 2.7606 (17) | 106 |
| O3—H3⋯O5 | 0.84 | 2.07 | 2.8781 (15) | 162 |
| C2—H2$A$⋯O2$^{ii}$ | 0.95 | 2.42 | 3.3545 (19) | 168 |
| C10—H10$A$⋯O3$^{iii}$ | 0.98 | 2.52 | 3.491 (3) | 171 |

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

### Table 2
C(aryl)—O—C$_{\beta}$—C$_{\alpha}$ and O(aryloxy)—C—C—C(aryl) torsion angles (°), distances between centers of aromatic rings ($D$, Å), and angles ($A$, °) between the aromatic ring mean planes for compounds (I)–(IX).

For comparison, we have consistently considered the isomer with the $R$ configuration at C$\alpha$.

| Compound/ CSD[a] refcode | C—O—C—C | O—C—C—C | $D$ | $A$ |
|---|---|---|---|---|
| (I)[b] | 122.83 (14) | 177.76 (14) | 7.128 (2) | 75.68 (8) |
| (II)[c]/not in CSD | −141.69 | 173.29 | 7.259 | 56.32 |
| (III)[d]/WALSUX | 116.29 | −178.60 | 7.126 | 94.60 |
| (IV)[d]/WALTAE | 113.47 | 175.02 | 7.141 | 74.39 |
| (V*a*)[e]/IMICEM | 140.69 | 171.70 | 7.333 | 92.36 |
| (V*b*)[e]/IMICEM | 114.55 | 178.99 | 7.024 | 72.09 |
| (VI)[e]/IMICIQ | 142.84 | 169.62 | 7.360 | 110.17 |
| (VII)[f]/TAHKIW | −175.87 | 172.78 | 7.487 | 133.74 |
| (VIII)[g]/TAHKOC01 | 169.56 | 169.15 | 7.391 | 123.83 |
| (IX)[d]/WALTEI | −44.09 | 168.51 | 6.435 | 39.09 |

Notes: (*a*) Cambridge Structural Database (Allen, 2002). References: (*b*) this work; (*c*) Jakobsons *et al.* (1986); (*d*) Stomberg *et al.* (1993); (*e*) Lee & Ley (2003); (*f*) Wallis *et al.* (1991); (*g*) Wallis *et al.* (1996).

Friedel pairs were averaged and the reference molecule for this racemic crystal was chosen to have the $R$ conformation for atoms C8 and C9. H atoms were constrained to an ideal geometry using an appropriate riding model, with C—H distances of 0.95–1.00 Å and O—H distances of 0.84 Å. For the hydroxy and methyl groups, the O—H (or C—H) distances and C—O—H (C—C—H or O—C—H for methyl groups) angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting positions based on the circular Fourier synthesis. $U_{\rm iso}$(H) values were set at $1.5U_{\rm eq}$(O), $1.5U_{\rm eq}$(C$_{\rm methyl}$) and $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3086). Services for accessing these data are described at the back of the journal.

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