

(E)-6-Methoxy-3-(α -methoxybenzylidene)benzo[*b*]furan-2(3*H*)-one at 173 K

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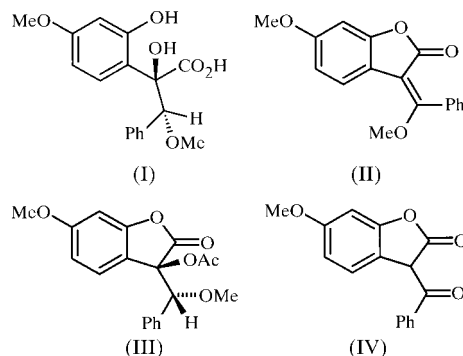
The title compound, C₁₇H₁₄O₄, is an unprecedented new synthetic isoaurone-type enol ether that has the *E* configuration. The planar furanone ring is fused to a methoxybenzene ring system, with an interplanar angle of 175.7 (1)°. Due to this ring fusion, the six-membered ring has a significant amount of ring strain, as shown by the internal ring angle range of 115.8 (1)–124.7 (1)°, whereas the vinylic phenyl ring has internal angles between 119.7 (1) and 120.2 (1)°. The molecules form infinite hydrogen-bonding layers along the *b* direction of the form C—H...O, where the keto O atom acts as a bifurcated acceptor. These layers are connected along the *c* direction by another hydrogen bond with a methoxy H atom as donor. In addition to this connection, the layers are stacked *via* centres of symmetry by a pair of symmetry-related benzofuranone ring systems.

Comment

Isoaurones [3-arylidenebenzofuran-2(3*H*)ones] are an uncommon class of flavonoid compounds isomeric with aurones [2-arylidenebenzofuran-3(2*H*)-ones], some of which are naturally occurring, *e.g.* *E*-marginalin (Barbier, 1987). Like the aurones, isoaurones can exist in either the *E* or the *Z* form. This class of compound has been of synthetic interest over the years (Gripenberg & Juselius, 1954; Walter *et al.*, 1966; Moriarty *et al.*, 1984; Litinas & Stampelos, 1992; Rossi *et al.*, 1995). In the course of our studies in the flavonoid field we have synthesized the unusual title isoaurone-type enol ether compound, (II) (Burke & O'Sullivan, 1997) *via* lactonization and subsequent dehydration of (2*R*,3*R*)-2-hydroxy-2-(2-hydroxy-4-methoxyphenyl)-3-methoxy-3-phenylpropan-1-oic acid, (I).

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We have determined on the basis of the following X-ray crystallographic analysis that the novel isoaurone compound, (II), has the *E*-configuration. This result clearly indicates that the glycolic acid product, (I), possesses the (2*R*,3*R*) [or (2*S*,3*S*)] configuration, if the dehydration step leading to the isoaurone (II) occurs by the expected concerted anti-periplanar *E2* elimination reaction at (I). In the original paper



reporting the synthesis of (I) as the result of a benzoic acid rearrangement on 1-(2-hydroxy-4-methoxyphenyl)-3-methoxy-3-phenylpropan-1,2-dione (Brady *et al.*, 1989), compound (I) was assigned the (2*R*,3*S*)-configuration on the basis of a mechanistic postulate. At present the mechanism of this reaction is being re-evaluated. In the original paper (Brady *et al.*, 1989) the diagram clearly shows that the glycolic acid product had the (2*R*,3*S*)-configuration, but it was inadvertently named (2*R*,3*R*) in the text. This error was carried over into our subsequent paper (Burke & O'Sullivan, 1997).

The furanone ring of the title compound, (II), which is essentially planar, is fused to a methoxybenzene ring system. Both ring systems are approximately coplanar, the angle between the furanone moiety and the fused benzene ring being 175.7 (1)°. Selected bond lengths and angles in Table 1 show that the benzene ring C4–C9 has a remarkable amount of angle strain arising from the ring fusion. The internal bond angles [C7 115.8 (1), C8 124.7 (1), C9 118.5 (1) and C4 118.9 (1)°] are all somewhat different from 120.0°, whereas the vinylic phenyl ring has internal angles between 119.7 (1) and 120.2 (1)°. In accordance with an earlier nuclear Overhauser effect experiment, the present X-ray experiment shows the

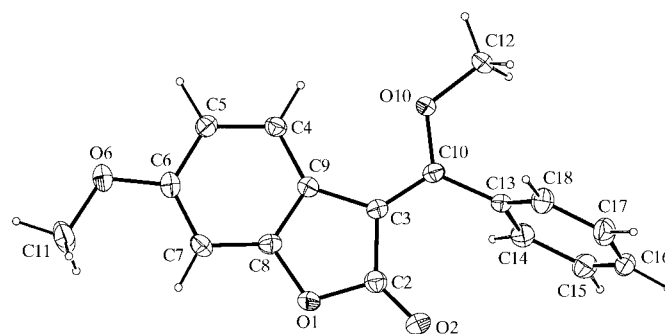


Figure 1
PLATON (Spek, 1990) displacement ellipsoid plot of (II) at the 50% probability level with the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

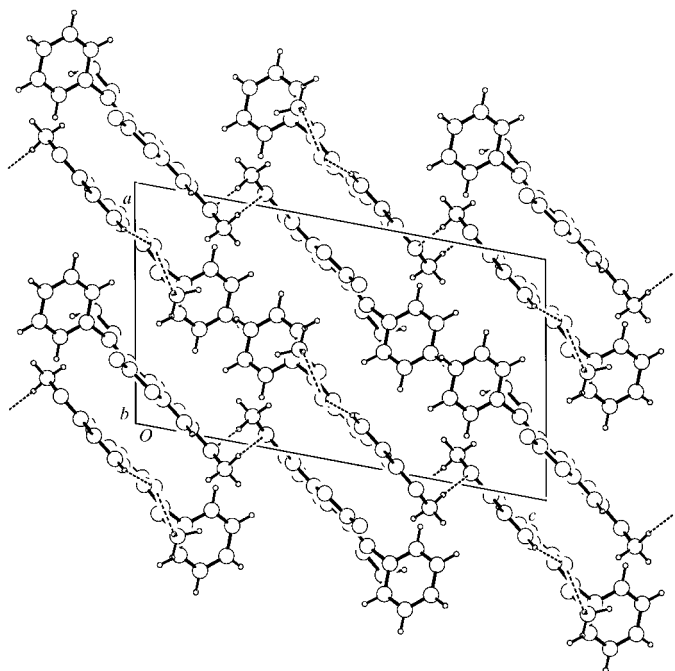


Figure 2
PLUTON (Spek, 1991) packing diagram for (II) exhibiting the layered structure along *b* and the stacking of the layers *via* centres of symmetry. The hydrogen bonds are shown as dashed lines.

large distance of 3.703 (16) Å between H4 and the C12 methyl of the vinylic methoxyl group (Fig. 1). It is also worth observing that the vinylic phenyl group is rotated out of the plane with the benzofuranone moiety by 78.8 (1)°. This had already been predicted using Dreiding molecular models. Some prominent torsion angles are also shown in Table 1.

The molecules in the crystal of (II) are packed together *via* intermolecular C—H...O interactions and stacking between the benzofuranone ring systems. If we consider the intramolecular hydrogen bond C4—H4...O10 and the intermolecular hydrogen bond C4—H4...O2(*x*, *y* − 1, *z*), then H4 has a bifurcated donor function. With the intermolecular C12—H123...O2(*x*, *y* − 1, *z*) bond the keto oxygen O2 is a bifurcated acceptor. The above mentioned hydrogen bonds form discrete layers along *b*. The view along the *b* axis (Fig. 2) shows that these layers are connected along the *c* direction *via* another intermolecular hydrogen bond, C11—H112...O6(−*x*, $\frac{1}{2} + y$, $\frac{1}{2} - z$), where the methoxy H atom acts as a donor. Details of the hydrogen bonding system are given in Table 2. Furthermore, stacking of the benzofuranone moieties is also displayed in Fig. 2. The stacking follows the [201] direction; the distance between the centres of gravity of the rings is 3.672 (1) Å.

Experimental

Compound (II) was prepared as follows: a mixture of (2*R*,3*R*)-2-hydroxy-2-(2-hydroxy-4-methoxyphenyl)-3-methoxy-3-phenylpropan-1-oic acid, (I) (0.3 g, 0.94 mmol; Brady *et al.*, 1989), and acetic

anhydride (10 ml) was heated under reflux for 2 h. The cooled solution was poured into iced water (30 ml). The resulting yellow solid was collected and crystallized from ethanol as green–yellow elongated plates of (II) (yield 0.079 g, 30%; m.p. 435–437 K). Analysis, found: C 72.05, H 5.01%; C₁₇H₁₄O₄ requires: C 72.32, H 5.01%; IR (ν_{\max} , KBr, cm^{−1}): 1762, 1626 and 1587; (λ_{\max} , 95% EtOH, nm): 206.1 (ϵ dm^{−3} mol^{−1} cm^{−1} 23, 709), 233.2 (13, 923), 256.6 (11, 895) and 342 (13, 861); ¹H NMR (270 MHz, CDCl₃, p.p.m.): 3.71 (s, 3H), 3.83 (s, 3H), 6.66 (*d*, *J* = 2.2 Hz, 1H), 6.70 (*dd*, *J* = 8.2, 2.4 Hz, 1H), 7.41 (*m*, 2H), 7.52 (*m*, 3H), and 7.70 (*d*, *J* = 8.2 Hz, 1H); ¹³C NMR (67.80 MHz, CDCl₃, p.p.m.): 55.63, 57.72, 96.63, 103.18, 109.19, 116.82, 123.87, 128.74, 128.99, 130.32, 130.56, 152.56, 159.95, 168.02 and 168.21; MS (EI) *m/z*: 282.1 (*M*⁺, 100), 267.1 (23), 239.1 (50), 211.1 (3) and 105 (50%). Evaporation of the filtrate to half its volume yielded cubes of (3*R*)-3-acetoxy-6-methoxy-3-[(*R*)-methoxyphenylmethyl]benzo[*b*]furan-2(3*H*)-one, (III) (yield 0.129 g, 40%; m.p. 409–411 K). Analysis, found: C 66.94, H 5.35%; C₁₉H₁₈O₆ requires: C 66.66, H 5.30%; IR (ν_{\max} , KBr, cm^{−1}): 1821, 1752 and 1635; ¹H NMR (270 MHz, CDCl₃, p.p.m.): 2.03 (s, 3H), 3.24 (s, 3H), 3.79 (s, 3H), 4.78 (s, 1H), 6.14 (*d*, 8.2 Hz, 1H), 6.46 (*dd*, *J* = 8.2, 2.3 Hz, 1H), 6.71 (*d*, *J* = 2.3 Hz, 1H), 7.32 (*m*, 2H) and 7.42 (*m*, 3H); ¹³C NMR (67.80 MHz, CDCl₃, p.p.m.): 20.37, 55.55, 57.72, 79.33, 83.93, 97.28, 109.29, 113.70, 126.02, 127.90, 128.51, 128.81, 134.5, 156.30, 162.05, 168.45 and 173.84; MS (EI) *m/z*: 342 (*M*⁺, 1), 282 (3), 252 (4), 209 (5), 165 (2) and 121 (100%). An alternative synthesis of (II) proceeds as follows: a mixture of 3-benzoyl-6-methoxybenzofuran-2-one, (IV) (0.076 g, 0.284 mmol; Brady, Burke & O'Sullivan, unpublished results), dimethyl sulfate (0.1 ml, 1.06 mmol), anhydrous potassium carbonate (3 g, 21.7 mmol) and dry acetone (20 ml) heated under reflux for 2 h. The cooled mixture is then filtered free of inorganic matter and diluted with ice and water. The resulting precipitate crystallizes from ethanol as green–yellow elongated plates of (II) (yield 0.05 g, 62%; m.p. 436 K). All the chiral compounds discussed or shown in this paper existed as racemic mixtures; only one member of the enantiomeric pair is mentioned in each case for the sake of convenience.

Crystal data

C ₁₇ H ₁₄ O ₄	$D_x = 1.396$ Mg m ^{−3}
$M_r = 282.28$	Mo $K\alpha$ radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 8000 reflections
$a = 10.5235$ (8) Å	$\theta = 2.7$ –30.3°
$b = 7.1136$ (3) Å	$\mu = 0.100$ mm ^{−1}
$c = 18.2587$ (13) Å	$T = 173$ (1) K
$\beta = 100.632$ (9)°	Plate, green–yellow
$V = 1343.38$ (15) Å ³	0.54 × 0.35 × 0.06 mm
$Z = 4$	

Data collection

Stoe IPDS diffractometer	$\theta_{\max} = 30.29^\circ$
φ oscillation scans	$h = -14 \rightarrow 14$
Absorption correction: numerical (Coppens <i>et al.</i> , 1965)	$k = 0 \rightarrow 9$
$T_{\min} = 0.948$, $T_{\max} = 0.994$	$l = 0 \rightarrow 25$
13 623 measured reflections	Between 50 and 200 standard reflections every image
3849 independent reflections	frequency: 6 min
2237 reflections with $I > 2\sigma(I)$	intensity decay: none
$R_{\text{int}} = 0.037$	

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.012$	$(\Delta/\sigma)_{\max} = 0.001$
3849 reflections	$\Delta\rho_{\max} = 0.22$ e Å ^{−3}
246 parameters	$\Delta\rho_{\min} = -0.19$ e Å ^{−3}

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.3905 (16)	C4—C5	1.3885 (16)
O1—C2	1.4024 (14)	C5—C6	1.4007 (18)
C2—O2	1.1993 (15)	C6—C7	1.3860 (19)
C2—C3	1.4644 (18)	C7—C8	1.3781 (16)
C3—C10	1.3550 (16)	C8—C9	1.3857 (17)
C3—C9	1.4605 (17)	C10—O10	1.3426 (15)
O6—C6	1.3733 (14)	C10—C13	1.4879 (17)
O6—C11	1.4273 (18)	O10—C12	1.4447 (15)
C4—C9	1.3883 (18)		
C8—O1—C2	107.67 (9)	C7—C6—C5	121.57 (11)
O2—C2—O1	119.04 (11)	C8—C7—C6	115.81 (11)
O2—C2—C3	133.17 (11)	C7—C8—C9	124.66 (12)
O1—C2—C3	107.77 (10)	C7—C8—O1	123.08 (11)
C10—C3—C9	129.73 (12)	C9—C8—O1	112.21 (10)
C10—C3—C2	123.86 (11)	C8—C9—C4	118.49 (11)
C9—C3—C2	106.33 (10)	C8—C9—C3	105.97 (11)
C6—O6—C11	116.80 (11)	C4—C9—C3	135.32 (11)
C9—C4—C5	118.87 (11)	O10—C10—C3	115.77 (11)
C4—C5—C6	120.59 (12)	O10—C10—C13	120.71 (10)
O6—C6—C7	123.42 (11)	C3—C10—C13	123.52 (12)
O6—C6—C5	115.00 (12)	C10—O10—C12	120.41 (10)
C9—C3—C10—C13	176.25 (11)	C3—C10—C13—C18	106.79 (14)
C2—C3—C10—C13	-7.45 (18)	O10—C10—C13—C14	108.86 (14)
O10—C10—C13—C18	-72.54 (16)	C3—C10—C13—C14	-71.80 (17)

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...O2 ⁱ	0.985 (14)	2.480 (14)	3.4454 (16)	166.6 (10)
C4—H4...O10	0.985 (14)	2.582 (13)	3.0598 (15)	109.9 (10)
C11—H112...O6 ⁱⁱ	1.016 (18)	2.47 (2)	3.460 (2)	163.7 (15)
C12—H123...O2 ⁱ	1.00 (2)	2.547 (17)	3.2606 (18)	128.0 (12)

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

The positions of the H atoms were determined from difference electron-density maps and they were refined with isotropic displacement parameters. The C—H bond lengths range between 0.960 (15) and 1.062 (15) Å.

Data collection: *IPDS Software* (Stoe & Cie, 1999); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *PLUTON* (Spek, 1991); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: *JZ1387*). Services for accessing these data are described at the back of the journal.

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