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8-(2-Bromo-3-methoxy-3-methylbutyl)-7-methoxycoumarin

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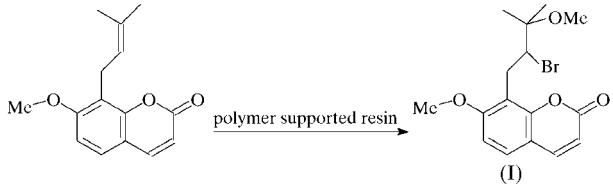
The title compound, $C_{16}H_{19}BrO_4$, is a derivative of osthol, isolated from the seeds of *Imperatoria Osthruthium*. The structure was solved in space group $P\overline{1}$, with two molecules in the asymmetric unit, and was refined to a final *R* factor of 0.064. The two molecules in the asymmetric unit differ in the orientation of their brominated substituent group. The benzopyran ring displays aromatic character. The packing of the molecules in the lattice is mainly due to C—H···O hydrogen bonds.

Comment

The title compound, (I), a derivative of osthol, is an anti-inflammatory and antifungal drug (Akelah & Sherrington, 1981), and is the active ingredient of the seeds of *Imperatoria Osthruthium* used in the traditional Chinese system of medicine (Liu *et al.*, 1998). The aim of the present work was to modify the isoprenyl group in osthol by a microwave-assisted reaction employing polymer-supported reagents and to study the change in activity resulting therefrom (Geetha Gopalakrishnan *et al.*, 2000).



Compound (I) is a racemic mixture and crystallizes in space group $P\overline{1}$, with two molecules, *A* and *B*, in the asymmetric unit. The racemic compound has a chiral centre at the 2-bromo substituent and the asymmetric unit was chosen to have molecule *A* with *S* chirality and molecule *B* with *R* chirality. Fig. 1 shows molecule *A* with *S* chirality at atom C2′*A*.

In the benzopyran ring of (I), the average O1—C2 and C2—C3 distances in the two molecules are 1.381 (7) and 1.447 (9) Å, respectively, indicating that the electrons are delocalized in the ring with the carbonyl group acting as the electron-withdrawing group. This is corroborated by the fact that the benzopyran ring is planar.

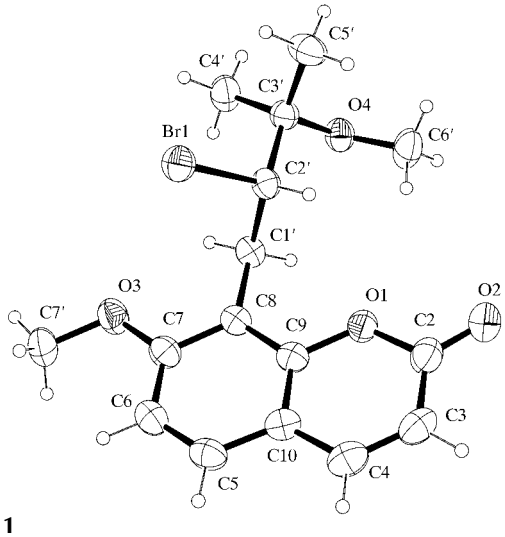


Figure 1
A view of one of the *A* molecules of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Most of the bond lengths are similar in both molecules of (I). The maximum deviation is observed in the C7′—O3 bond [1.420 (5) Å in molecule *A* and 1.440 (5) Å in molecule *B*]. Atoms C1′, C2′, C3′ and C5′ are coplanar and are oriented at angles of 174.1 (3) (molecule *A*) and 173.2 (3)° (molecule *B*) with respect to their corresponding benzopyran rings.

In the packing of (I), molecules *A* and *B* form layers along the *b* axis. The two independent molecules, as well as their symmetry-related molecules, are connected by C—H···O hydrogen bonds (Table 2).

Experimental

The title derivative was prepared by bromomethoxylation of the double bond in the isoprenyl unit of osthol under microwave conditions, employing a new polymer-supported bromine chloride resin. Unlike the normal cohalogenating reagents, such as Br_2/MeOH or *N*-bromosuccinamide in MeOH, which result in multiple products or pose difficulty in isolation (Batluenga & Martinez Gallo, 1985), the bromine chloride resin with osthol was a chemoselective and regioselective reaction, which proceeded quantitatively within 30 s, yielding the desired bromomethoxy compound, (I). The polymer-supported bromine chloride resin [2 g, prepared by passing bromine over commercially available chloride resin (IRA-400)] was added to a solution of osthol (0.024 g, 1 mmol) in MeOH (10 ml) and the mixture was irradiated in a modified domestic microwave oven fitted with a refluxing unit. On completion of the reaction, which was monitored by thin-layer chromatography, the resin was filtered and repeatedly washed with methanol, and the filtrate, after concentration, was purified by column chromatography (silica gel, 60–120 mesh, eluant EtOAc–hexane). The title compound was then crystallized from ethyl acetate by slow evaporation.

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Crystal data

$C_{16}H_{19}BrO_4$
M_r = 355.21
Triclinic, $P\overline{1}$
a = 10.280 (2) Å
b = 10.497 (4) Å
c = 16.175 (4) Å
α = 75.91 (2)°
β = 80.81 (2)°
γ = 68.00 (3)°
V = 1565.1 (8) Å^3
Z = 4
D_x = 1.508 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 15–30°
μ = 3.70 mm^{-1}
T = 293 (2) K
Block, colourless
0.25 × 0.12 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 EXPRESS diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (*XRAYACS*; Chandrasekaran, 1998)
T_{min} = 0.458, T_{max} = 0.709
6666 measured reflections
6133 independent reflections
4992 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 72.7°
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.173
S = 1.31
6133 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −1.41 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2*A*—O2*A*	1.217 (6)	C2*B*—O2*B*	1.220 (5)
C2*A*—O1*A*	1.383 (5)	C2*B*—O1*B*	1.379 (4)
C7*A*—O3*A*	1.360 (5)	C7*B*—O3*B*	1.353 (4)
C2′*A*—Br1	1.977 (4)	C2′*B*—Br2	1.990 (3)
C6′*A*—O4*A*	1.390 (5)	C6′*B*—O4*B*	1.416 (5)
C7′*A*—O3*A*	1.420 (5)		
O2*A*—C2*A*—O1*A*	116.1 (5)	O2*B*—C2*B*—O1*B*	116.9 (4)
C9*A*—C8*A*—C1′*A*	121.0 (3)	C9*B*—C8*B*—C7*B*	117.4 (3)
C1′*A*—C2′*A*—Br1	108.5 (2)	C1′*B*—C2′*B*—Br2	109.2 (2)
C3′*A*—C2′*A*—Br1	110.0 (3)	C3′*B*—C2′*B*—Br2	110.3 (2)
O4*A*—C3′*A*—C5′*A*	111.3 (3)	O4*B*—C3′*B*—C4′*B*	103.2 (3)
C7*A*—O3*A*—C7′*A*	118.9 (4)	C7*B*—O3*B*—C7′*B*	118.4 (3)
C6′*A*—O4*A*—C3′*A*	118.0 (3)	C6′*B*—O4*B*—C3′*B*	118.0 (3)
C7*A*—C8*A*—C1′*A*—C2′*A*	107.5 (4)	C7*B*—C8*B*—C1′*B*—C2′*B*	−112.6 (4)
C8*A*—C1′*A*—C2′*A*—C3′*A*	177.2 (3)	C8*B*—C1′*B*—C2′*B*—C3′*B*	−175.2 (3)
C8*A*—C1′*A*—C2′*A*—Br1	−58.4 (4)	C8*B*—C1′*B*—C2′*B*—Br2	60.6 (3)
C8*A*—C7*A*—O3*A*—C7′*A*	176.1 (4)	C8*B*—C7*B*—O3*B*—C7′*B*	179.1 (4)
C4′*A*—C3′*A*—O4*A*—C6′*A*	170.8 (4)	C4′*B*—C3′*B*—O4*B*—C6′*B*	−172.9 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2′*B*—H11*B*···O1*B*	0.98	2.46	3.078 (4)	120
C1′*B*—H10*C*···O4*B*	0.97	2.49	2.871 (4)	102
C1′*B*—H10*D*···O3*B*	0.97	2.35	2.809 (4)	108
C2′*A*—H11*A*···O1*A*	0.98	2.56	3.143 (5)	118
C1′*A*—H10*B*···O4*A*	0.97	2.57	2.916 (5)	101
C4*B*—H3*B*···O4*A*^{i}	0.93	2.56	3.258 (4)	132

Symmetry code: (i) $-x, 1-y, -z$.

All H atoms were fixed geometrically and refined using a riding model.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST*97 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1573). Services for accessing these data are described at the back of the journal.

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