

A chiral furocoumarin

Fereshteh Haddadian Billiot, Damon R. Billodeaux,
Steven F. Watkins and Frank R. Fronczek*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804,
USA

Correspondence e-mail: fronz@chxray1.chem.lsu.edu

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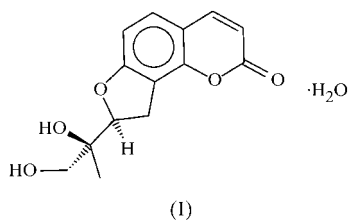
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The furocoumarin 1,2-dihydro-2-(1,2-dihydroxyprop-2-yl)-8*H*-furo[2,3-*h*]benzopyran-8-one crystallizes from methanol–water as the monohydrate $C_{14}H_{14}O_5 \cdot H_2O$. Both chiral centers have the *S* configuration. Both OH groups and both H atoms of the water molecule form intermolecular hydrogen bonds with O···O distances in the range 2.7686 (18)–2.8717 (18) Å.

Comment

Isolation of furocoumarins from the roots of *Angelica* species has been reported by Harmala *et al.* (1992). The structure of the title furocoumarin, (I), was studied in order to determine the stereochemistry of the two chiral centers, C11 and C12. The complete sphere of Cu $K\alpha$ data proved adequate to determine not only the relative configurations of these centers, but also the absolute configurations in the absence of elements heavier than oxygen. Both centers are found to have the *S* configuration. The bond lengths and angles of the coumarin rings are similar to those found in other recently reported coumarin structures (Chinnakali *et al.*, 1998; Yip *et al.*, 1995). Both six-membered rings are fairly planar, with maximum deviations from their respective rings of 0.0087 (13) Å for O1 and 0.0077 (12) Å for C10. The furan ring is much less planar, having a flattened envelope conformation with C11 at the flap position, lying 0.0541 (9) Å from the best plane of the five-membered ring. All potential donors of the OH groups and H_2O are involved in nearly linear intermolecular O—H···O hydrogen bonds, as detailed in Table 1.



Experimental

Crystals were kindly provided by Professor O. Sticher (ETH, Zürich), having been crystallized from a methanol–water mixture.

Crystal data

$C_{14}H_{14}O_5 \cdot H_2O$
 $M_r = 280.27$
Monoclinic, $P2_1$
 $a = 7.1304$ (4) Å
 $b = 6.9381$ (4) Å
 $c = 13.4150$ (7) Å
 $\beta = 90.901$ (4)°
 $V = 663.58$ (6) Å³
 $Z = 2$

$D_x = 1.403$ Mg m⁻³
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 13$ – 44°
 $\mu = 0.932$ mm⁻¹
 $T = 297$ K
Lath, colorless
 $0.58 \times 0.18 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.614$, $T_{\max} = 0.954$
3733 measured reflections
2519 independent reflections
2428 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$
 $\theta_{\max} = 74.84^\circ$
 $h = -8 \rightarrow 8$
 $k = -8 \rightarrow 8$
 $l = -16 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 0.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.097$
 $S = 1.07$
2519 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 0.0326P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³
Extinction correction: Zachariasen (1963)
Extinction coefficient: 0.0075 (12)
Absolute structure: Flack (1983); 1040 Friedel pairs
Flack parameter = -0.06 (15)

Table 1

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O4	0.85 (3)	2.04 (3)	2.8717 (18)	165 (3)
O1W—H2W···O2 ⁱ	0.91 (2)	1.87 (2)	2.7686 (18)	173 (2)
O4—H4O···O5 ⁱⁱ	0.87 (2)	2.04 (2)	2.8519 (15)	156 (2)
O5—H5O···O1W ⁱⁱⁱ	0.86 (2)	1.97 (2)	2.8083 (18)	165 (3)

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

The absolute configuration was determined by refinement of the Flack (1983) parameter, based on 1040 Friedel pairs. The reported configuration yielded $x = -0.06$ (15), while the inverse configuration yielded $x = 1.06$ (15). The OH and H_2O H atoms were refined isotropically. Other H atoms were placed in calculated positions with C—H distances of 0.93 (Csp²), 0.97 (CH₂) and 0.96 Å (CH₃), and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached C atom (1.5 for methyl), and thereafter treated as riding. A torsional parameter was refined for the methyl group.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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