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(R)-(–)-8-Hydroxy-3-methyl-3,4-dihydro-1H-2-benzopyran-1-one

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The title compound, $C_{10}H_{10}O_2$, was isolated from *Eniconsanthum membranifolium* J. Sinclair. There are six independent molecules in the unit cell. Intramolecular hydrogen bonds from the hydroxy H atoms to the carbonyl O atoms are observed in the crystal structure.

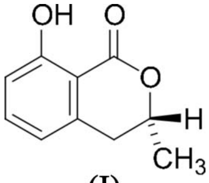
Key indicators

Single-crystal X-ray study
T = 118 K
Mean σ(C–C) = 0.011 Å
R factor = 0.098
wR factor = 0.211
Data-to-parameter ratio = 7.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

(R)-(−)-Mellein [(R)-(−)-8-hydroxy-3-methyl-3,4-dihydro-1H-2-benzopyran-1-one], (I), has been shown to possess an impressive array of biological activities, such as pheromone, bactericidal, fungicidal and algicidal properties (Hoeller *et al.*, 1999; Sun & Toia, 1993; Tan & Zou, 2001). In order to study the structure–biological activity relationship of the compound, it is essential to determine the configuration of mellein. (R)-(−)-Mellein has been isolated from an n-hexane extract of *Eniconsanthum membranifolium* J. Sinclair. This is the first report of the isolation of mellein from this plant. The absolute configuration of the enantiomer was determined based on optical rotation using a polarimeter; $[\alpha]_D = -85.2$ (c 0.0027, MeOH, 295 K), indicating the R enantiomer (Dimitriadis *et al.*, 1997; Mori & Gupta, 1985). An intramolecular hydrogen bond between the hydroxy H atom and the carbonyl O atom was observed by ^{1}H NMR spectroscopy (δ 11.0).



(I)

The molecular structure of one of the independent molecules of (I) is shown in Fig. 1. There are six independent molecules in the unit cell. For clarity, similar atom numbering is used for all independent molecules, which are labelled with the suffixes A to F (Fig. 2). There are no significant structural differences between these molecules.

The intramolecular hydrogen bond from the hydroxy H atom to the carbonyl O atom that is suggested from the NMR data is observed in the crystal structure (Table 1). Each molecule is nearly planar, except for atoms C2 and C10 (Table 2). These structural features are also observed in related compounds (Krohn *et al.*, 1997; Wang, Fang *et al.*, 2003; Wang, Zhang *et al.*, 2003; Wang *et al.*, 2005).

The molecules of (I) are almost parallel to each other, forming layers which are interconnected by weak C—H⋯O interactions (Table 1, Fig. 3).

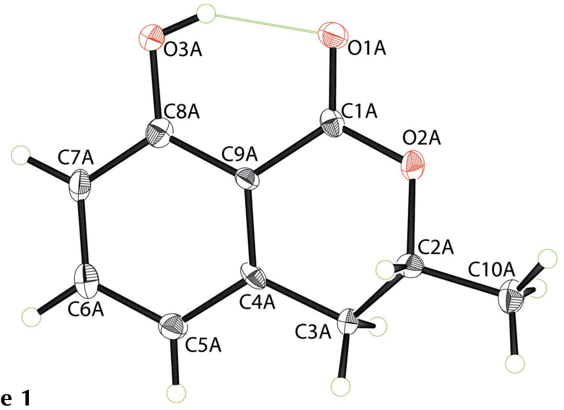


Figure 1
The molecular structure of one of the independent molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a thin line.

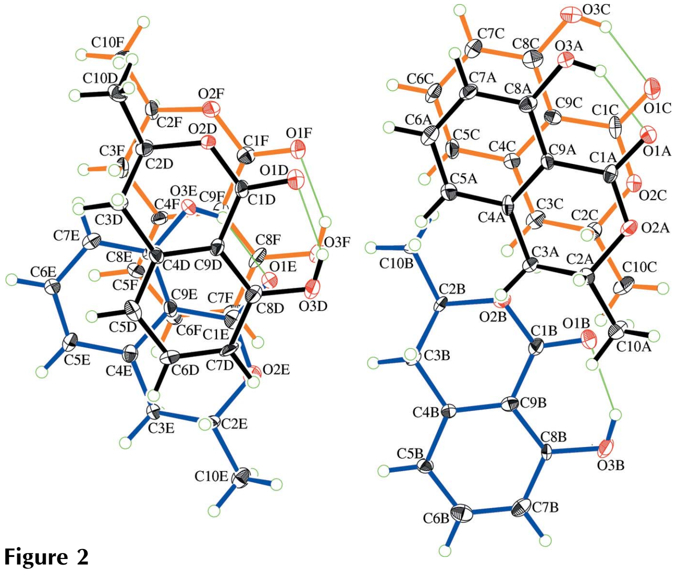


Figure 2
The molecular structures of all the independent molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as thin lines. For clarity, the bonds in molecules B and E are drawn in blue and those in molecules C and F are drawn in brown.

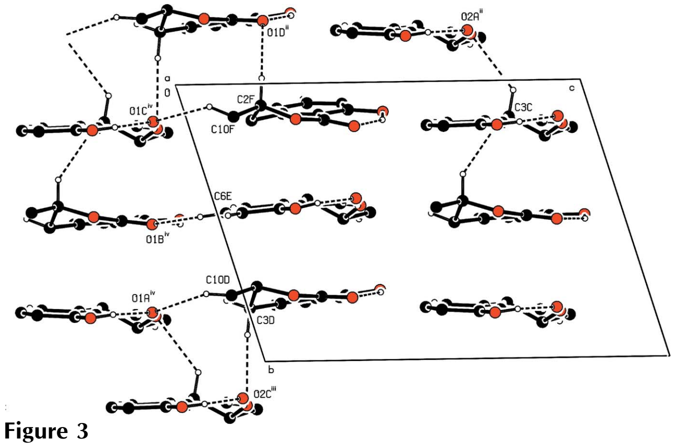


Figure 3
A partial view of the packing of (I), showing the C—H···O hydrogen-bonding interactions (dashed lines) between the different molecules. H atoms not involved in the hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii) $x, y-1, z$; (iii) $x, 1+y, z-1$; (iv) $x, y, z-1$.]

Experimental

A methanol extract (369 g) of branches of *Eniconsanthum membranifolium* J. Sinclair was partitioned successively with *n*-hexane, ethyl acetate and *n*-butyl alcohol. The *n*-hexane extract (64 g) was fractionated on a silica-gel 60 (Cica Reagents, 40–50 μm) column (6 × 50 cm, 700 g), eluted with *n*-hexane—ethyl acetate and acetone in turn. This fractionation process gave ten fractions (fractions A to J). Fraction C (6 g) was subjected to silica-gel chromatography (Merck, 240 g), eluted with $CHCl_3$–acetone. Fractions having the same R_f values were combined and seven fractions (C1 to C7) were obtained. Fraction C1 (270 mg) was repeatedly separated *via* column chromatography on silica gel (Cica Reagents, 20 g) and eluted with *n*-hexane–$CHCl_3$–acetone (5:2:1) to give four fractions (C1*a*–C1*d*). Purification of fraction C1*a* (80 mg) by high-performance liquid chromatography (250 × 20 mm internal diameter, Wako Co. Ltd., Tokyo) and PTLC (preparative thin-layer chromatography) [1 mm layer thickness, *n*-hexane–$CHCl_3$–acetone (5:2:1)] afforded mellein (12.0 mg). Analysis: $[\alpha]_D = -85.2$ (c 0.0027, MeOH, 295 K) (Dimitriadis *et al.*, 1997; Mori & Gupta, 1985); m.p. 328–329 K.

Crystal data

$C_{10}H_{10}O_3$
$M_r = 178.19$
Triclinic, $P1$
$a = 8.375$ (8) Å
$b = 10.826$ (11) Å
$c = 15.321$ (14) Å
$\alpha = 70.80$ (4)°
$\beta = 75.25$ (5)°
$\gamma = 79.05$ (5)°
$V = 1260$ (2) Å^3
$Z = 6$
$D_x = 1.409$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 118$ (2) K
Block, colourless
0.40 × 0.10 × 0.10 mm

Data collection

Rigaku/MSC Mercury CCD area-detector diffractometer
ω scans
Absorption correction: none
10247 measured reflections
5676 independent reflections
4555 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\rm max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.098$
$wR(F^2) = 0.211$
$S = 1.11$
5676 reflections
715 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 2.6686P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*A*—H7*A*···O1*A*	0.84	1.85	2.583 (8)	146
O3*B*—H7*B*···O1*B*	0.84	1.85	2.574 (8)	144
O3*C*—H7*C*···O1*C*	0.84	1.82	2.564 (8)	147
O3*D*—H7*D*···O1*D*	0.84	1.88	2.612 (8)	145
O3*E*—H7*E*···O1*E*	0.84	1.83	2.564 (8)	145
O3*F*—H7*F*···O1*F*	0.84	1.85	2.579 (8)	145
C2*B*—H1*B*···O3*C*$^{\rm i}$	1.00	2.59	3.450 (11)	144
C2*F*—H1*F*···O1*D*$^{\rm ii}$	1.00	2.60	3.474 (11)	147
C3*C*—H2*C*···O2*A*$^{\rm ii}$	0.99	2.60	3.362 (10)	134
C3*D*—H3*D*···O2*C*$^{\rm iii}$	0.99	2.59	3.569 (10)	170
C6*A*—H5*A*···O1*D*	0.95	2.51	3.269 (11)	138
C6*B*—H5*B*···O2*B*$^{\rm i}$	0.95	2.48	3.422 (10)	173
C6*D*—H5*D*···O2*D*$^{\rm i}$	0.95	2.47	3.412 (10)	170
C6*E*—H5*E*···O1*B*$^{\rm iv}$	0.95	2.57	3.328 (10)	137

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D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10*D*—H9*D*···O1*A*$^{\rm iv}$	0.98	2.49	3.402 (10)	156
C10*B*—H9*B*···O1*E*	0.98	2.44	3.371 (10)	159
C10*F*—H9*F*···O1*C*$^{\rm iv}$	0.98	2.48	3.306 (11)	142

Symmetry codes: (i) $x-1, y, z$; (ii) $x, y-1, z$; (iii) $x, y+1, z-1$; (iv) $x, y, z-1$.

Table 2

R.m.s. deviations (Å) of the plane of atoms C1/C3–C9/O3 and deviations (Å) of selected atoms from this plane for the six independent molecules of (I).

Molecule	R.m.s. deviation	O1	O2	C2	C10
A	0.0209	−0.175 (8)	0.126 (8)	0.655 (10)	0.444 (12)
B	0.0288	0.141 (10)	−0.254 (9)	−0.714 (11)	−0.541 (13)
C	0.0236	−0.172 (9)	0.213 (9)	0.707 (10)	0.504 (13)
D	0.0186	0.195 (9)	−0.172 (9)	−0.688 (10)	−0.478 (13)
E	0.0322	−0.133 (9)	0.275 (9)	0.774 (10)	0.100 (12)
F	0.0230	0.153 (9)	−0.243 (8)	−0.710 (10)	−0.516 (13)

All H atoms were placed in idealized positions and treated as riding, with C—H distances in the range 0.98–1.00 Å and an O—H distance of 0.84 Å, and with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C,O) for methyl and hydroxy H atoms or $1.2U_{\rm eq}$(C) for the remaining H atoms. The torsion angles involving the methyl and hydroxy group were refined. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged; the absolute configuration shown is that established by optical rotation measurements.

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *TEXSAN*.

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