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Melampodinone

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The title compound, methyl {1a*S*-[1a*R**,2a*R**,3a*R**,4*E*,5a*S**,8a*R**,9*R**(2*S**,3*S**),9a*R**]}-9-{[(2,3-dimethyloxiranyl)carbonyl]oxy}-2a,3a,5a,7,8,8a,9,9a-octahydro-4-methyl-8-methylene-2,7-dioxobisoxireno[4,5:7,8]cyclodeca[1,2-*b*]furan-1a(2*H*)-carboxylate, $C_{21}H_{22}O_{10}$, is an oxidation product of melampodin A. It has $Z' = 2$, and the conformations of the ten-membered rings in the two molecules are quite similar, with a mean difference of 2.4° between endocyclic torsion angles.

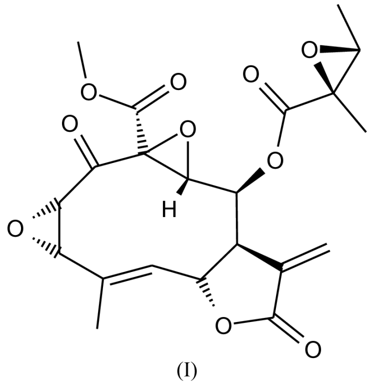
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.090
Data-to-parameter ratio = 11.7

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

Comment

The structure of melampodin A, which differs from the title compound, (I), only by having a *cis*-double bond at C1═C10 and an OH group at C9 instead of the ketone at C1 and epoxide at C9—C10, has been reported, based on X-ray (Watkins *et al.*, 1973) and neutron (Neidle & Rogers, 1972) data. CrO_3 oxidation of melampodin A from *Melampodium leucanthum* has led to the title keto compound (Fischer *et al.*, 1975). The formation of a rearranged ketone at C1 rather than C9 appears to result from a relief of strain in the ten-membered ring, and the structure of (I) was studied in order to determine the ten-ring conformation.



(I)

There are two independent molecules in the asymmetric unit of (I), and their conformations are described by the endocyclic torsion angles in Table 1. The ten-membered rings of the two molecules have very similar conformations, with a mean difference of 2.4° between endocyclic torsion angles, the maximum difference being only 4.0 (4)° for the torsion angle about C1—C10. This conformation differs from the typical melampolide conformation (Fronczek *et al.*, 1986, and references therein) mainly in the portion of the ring near the C1—C2 bond. Typical melampolides tend to have endocyclic torsion angles near zero, −100°, and 70° about C1═C10, C1—C2, and C2—C3, respectively.

The conformations of the epoxyangelate substituents at C8 in the two independent molecules of melampodinone differ by somewhat more than those of the ten-membered rings. The torsion angles about C8—O8 differ by 11.8 (3)°, and those about C17—C18 by 21.7 (4)°.

Cell dimensions at 293 K are a = 7.777 (2), b = 11.681 (4), and c = 23.812 (4) Å, and β = 97.67 (2)°; thus, Z' = 2 is not a result of a phase change on cooling.

Experimental

The preparation of the title compound by epoxidation of melampodin A using CrO_3 in glacial acetic acid has been previously described (Fischer *et al.*, 1975). Crystals were grown from methanol.

Crystal data

$C_{21}H_{22}O_{10}$
M_r = 434.39
Monoclinic, $P2_1$
a = 7.646 (2) Å
b = 11.633 (2) Å
c = 23.709 (4) Å
β = 97.385 (6)°
V = 2091.3 (7) Å^3
Z = 4

D_x = 1.380 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6013 reflections
θ = 2.5–30.5°
μ = 0.11 mm^{-1}
T = 120 K
Fragment, colorless
0.47 × 0.35 × 0.25 mm

Data collection

KappaCCD diffractometer (with Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
23 672 measured reflections
6629 independent reflections

5688 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025
$\theta_{\rm max}$ = 30.5°
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.090
S = 1.05
6629 reflections
568 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.6091P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.26 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0074 (11)

Table 1
Selected geometric parameters (Å, °).

O3—C1	1.201 (3)	O3′—C1′	1.199 (3)
O4—C10	1.442 (2)	O4′—C10′	1.435 (3)
O4—C9	1.442 (3)	O4′—C9′	1.437 (3)
O7—C2	1.434 (3)	O7′—C2′	1.432 (3)
O7—C3	1.435 (3)	O7′—C3′	1.435 (4)
O10—C18	1.436 (3)	O10′—C18′	1.440 (3)
O10—C19	1.449 (3)	O10′—C19′	1.445 (3)
C4—C5	1.338 (3)	C4′—C5′	1.338 (3)
C10—C1—C2—C3	62.6 (3)	C10′—C1′—C2′—C3′	65.8 (3)
C1—C2—C3—C4	−3.4 (3)	C1′—C2′—C3′—C4′	−4.4 (4)
C2—C3—C4—C5	−86.3 (3)	C2′—C3′—C4′—C5′	−87.9 (3)
C3—C4—C5—C6	162.63 (19)	C3′—C4′—C5′—C6′	160.5 (2)
C4—C5—C6—C7	−123.9 (2)	C4′—C5′—C6′—C7′	−121.0 (3)
C5—C6—C7—C8	84.9 (2)	C5′—C6′—C7′—C8′	86.3 (2)
C17—O8—C8—C7	137.91 (17)	C17′—O8′—C8′—C7′	126.12 (19)
C6—C7—C8—C9	−45.4 (2)	C6′—C7′—C8′—C9′	−48.3 (2)
C7—C8—C9—C10	−67.1 (3)	C7′—C8′—C9′—C10′	−71.1 (3)
C8—C9—C10—C1	155.57 (19)	C8′—C9′—C10′—C1′	154.2 (2)
C2—C1—C10—C9	−110.6 (2)	C2′—C1′—C10′—C9′	−106.6 (3)
O8—C17—C18—C20	−42.3 (3)	O8′—C17′—C18′—C20′	−20.6 (3)

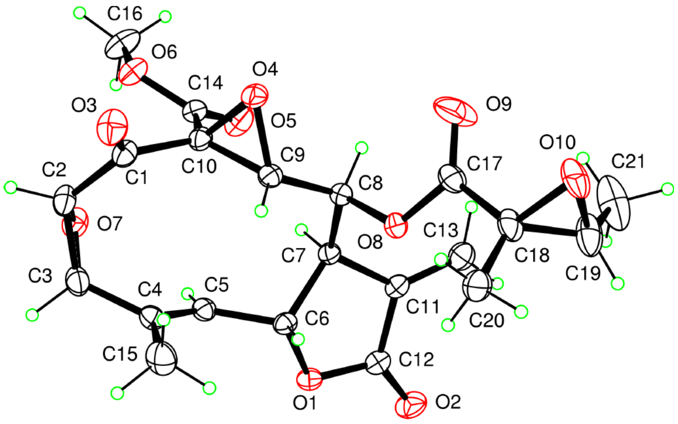


Figure 1
The atom-numbering scheme for the unprimed molecule, with ellipsoids at the 50% probability level.

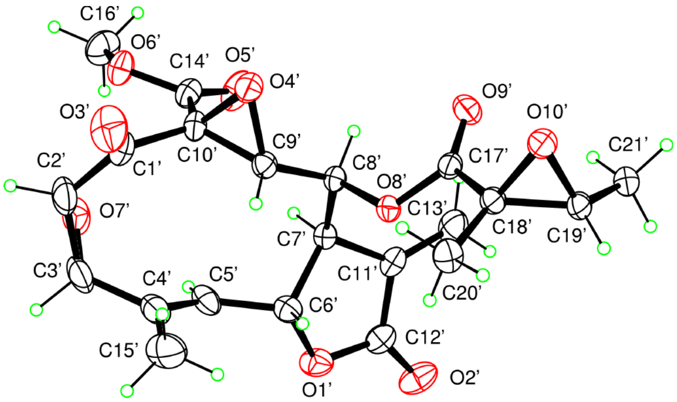


Figure 2
The atom-numbering scheme for the primed molecule, with ellipsoids at the 50% probability level.

Friedel pairs were averaged before refinement. H atoms were placed in calculated positions, with C—H distances in the range 0.95–1.00 Å and $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached atom ($1.5U_{\rm eq}$ for methyl groups), and thereafter treated as riding. A torsional parameter was refined for each methyl group. The absolute configuration could not be determined, and was assigned based on the known configuration of the starting material (Neidle & Rogers, 1972).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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