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4-Hydroxy-3,4a,8-trimethyl-3,3a,4,4a,-7a,8,9,9a-octahydroazuleno[6,5-*b*]furan-2,5-dione

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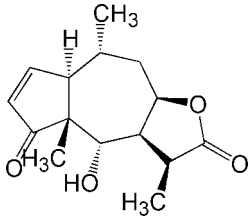
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.077; data-to-parameter ratio = 9.0.

The title compound, $C_{15}H_{20}O_4$, also known as dihydrohelenalin, is a drug obtained from a Chinese plant. It contains a seven-membered ring in a chair conformation and two five-membered rings in twist conformations. The crystal packing involves O—H···O hydrogen bonds.

Related literature

For background, see: Bohlmann & Chen (1980); for similar compounds, see: Giordano *et al.* (1992).



Experimental

Crystal data

$C_{15}H_{20}O_4$
M_r = 264.31
Monoclinic, $P2_1$
a = 6.3634 (13) Å
b = 12.608 (3) Å
c = 8.1146 (16) Å
β = 95.59 (3)°
V = 647.9 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 113 (2) K
0.10 × 0.06 × 0.04 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.982, T_{max} = 0.996
4971 measured reflections
1605 independent reflections
1508 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.077
S = 1.07
1605 reflections
178 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O4^{i}	0.80 (3)	2.09 (3)	2.8792 (19)	173 (2)

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2557).

References

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supplementary materials

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4-Hydroxy-3,4a,8-trimethyl-3,3a,4,4a,7a,8,9,9a-octahydroazuleno[6,5-*b*]furan-2,5-dione

S.-C. Pu, C.-L. Tu and Y. Deng

Comment

Dihydrohelenalin is one of the active components isolated from the traditional Chinese medicinal herb, Centipeda minima (*L*.), which has been found in moisty places throughout China and India. It is used to treat rhinitis, sinusitis and nasopharyngal tumors (Bohlmann & Chen, 1980). We report here the crystal structure (Fig. 1).

The crystal structure of (I) illustrated in Fig. 1 shows that seven-ring is chair conformation. Intermolecular O—H···O hydrogen bonds stabilize the crysta structure.

Experimental

The air-dried plant of Centipeda minima (*L*.) was exacted with EtOH (95%) and the extract was concentrated *in vacuo*. The residue was subjected to silical-gel column chromatography. Elution with chloroform-methanol (95:5 *v*/*v*) yielded the title compound. The identity of the title compound was confirmed by NMR spectroscopy. ^{1}H NMR in $CDCl_3$ (500 MHz): 0.9(3*H*, 8, H-15), 1.22 (3*H*, d, J=7 Hz, H-14), 1.35 (3*H*, d, J=7 Hz, H-13), 1.75 (1*H*, ddd, H-9a), 2.18 (1*H*, m, H-10), 2.2 (1*H*, ddd, H-9 b), 4.36 (1*H*, s, H-6), 4.78 (1*H*, m, H-8), 6.1 (1*H*, dd, J=8, 4 Hz, H-3), 7.7 (1*H*, dd, J=8, 2 Hz, H-2).

Refinement

In the absence ob anomalous scatterers Friedel pairs had been merged. The absolute configuration was set to be identical with the naturally occurring compound. All H atoms were positioned geometrically and refined using a riding model, with C—H in the range of 0.93 to 0.98Å and with U_{iso}(H) = 1.2U_{eq}(C,*O*) or U_{iso}(H) = 1.5U_{eq}(methyl C). The coordinates of the hydroxyl H atom were refined.

Figures

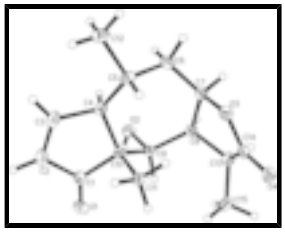

Fig. 1. A view of the molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

4-Hydroxy-3,4a,8-trimethyl-3,3a,4,4a,7a,8,9,9a- octahydroazuleno[6,5-*b*]furan-2,5-dione

Crystal data

$C_{15}H_{20}O_4$ $D_x = 1.355$ Mg m^{-3}

M_r = 264.31	Melting point: 222.0-224.0 K
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 6.3634 (13) Å	Cell parameters from 1887 reflections
b = 12.608 (3) Å	θ = 2.5–27.8º
c = 8.1146 (16) Å	μ = 0.10 mm^{-1}
β = 95.59 (3)º	T = 113 (2) K
V = 647.9 (2) $Å^3$	Block, colorless
Z = 2	0.10 × 0.06 × 0.04 mm
F_{000} = 284	

Data collection

Rigaku Saturn diffractometer	1605 independent reflections
Radiation source: rotating anode	1508 reflections with $I > 2\sigma(I)$
Monochromator: confocal	R_{int} = 0.033
T = 113(2) K	θ_{max} = 27.8º
ω and φ scans	θ_{min} = 2.5º
Absorption correction: multi-scan (Crystalclear; Rigaku/MSC, 2005)	h = −8→8
T_{min} = 0.982, T_{max} = 0.996	k = −16→14
4971 measured reflections	l = −10→9

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.030	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.077	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.0251P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
1605 reflections	$\Delta\rho_{max}$ = 0.22 e $Å^{-3}$
178 parameters	$\Delta\rho_{min}$ = −0.18 e $Å^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4530 (2)	0.75516 (10)	0.67372 (18)	0.0228 (3)
O2	0.11462 (19)	0.62013 (10)	0.85849 (17)	0.0172 (3)
H2	0.122 (4)	0.680 (2)	0.891 (3)	0.026*
O3	0.49752 (19)	0.31461 (9)	0.89731 (16)	0.0180 (3)
O4	0.8182 (2)	0.33531 (11)	1.02981 (18)	0.0222 (3)
C1	0.3892 (3)	0.67410 (14)	0.6056 (2)	0.0173 (4)
C2	0.3093 (3)	0.65984 (15)	0.4304 (2)	0.0219 (4)
H2A	0.3193	0.7104	0.3447	0.026*
C3	0.2207 (3)	0.56410 (15)	0.4119 (2)	0.0205 (4)
H3	0.1659	0.5361	0.3078	0.025*
C4	0.2164 (3)	0.50487 (13)	0.5728 (2)	0.0151 (3)
H4	0.0773	0.5224	0.6139	0.018*
C5	0.2305 (3)	0.38352 (14)	0.5744 (2)	0.0177 (4)
H5	0.3802	0.3617	0.5658	0.021*
C6	0.1580 (3)	0.34060 (14)	0.7367 (2)	0.0184 (4)
H6A	0.0139	0.3682	0.7455	0.022*
H6B	0.1454	0.2626	0.7250	0.022*
C7	0.2865 (3)	0.36248 (13)	0.9015 (2)	0.0167 (4)
H7	0.2163	0.3217	0.9864	0.020*
C8	0.3262 (3)	0.47520 (13)	0.9748 (2)	0.0146 (3)
H8	0.2140	0.4866	1.0511	0.018*
C9	0.3241 (3)	0.57586 (12)	0.8658 (2)	0.0137 (3)
H9	0.4232	0.6283	0.9241	0.016*
C10	0.3840 (3)	0.56456 (12)	0.6887 (2)	0.0137 (3)
C11	0.6100 (3)	0.52231 (14)	0.6802 (2)	0.0162 (3)
H11A	0.6195	0.4496	0.7228	0.024*
H11B	0.7102	0.5675	0.7475	0.024*
H11C	0.6441	0.5230	0.5650	0.024*
C12	0.0888 (3)	0.33500 (16)	0.4300 (3)	0.0244 (4)
H12A	0.1353	0.3597	0.3249	0.037*
H12B	−0.0578	0.3569	0.4373	0.037*
H12C	0.0984	0.2575	0.4355	0.037*
C13	0.5314 (3)	0.45433 (14)	1.0879 (2)	0.0194 (4)
H13	0.4850	0.4244	1.1926	0.023*
C14	0.6371 (3)	0.36407 (13)	1.0068 (2)	0.0170 (4)
C15	0.6810 (3)	0.54405 (15)	1.1414 (3)	0.0233 (4)
H15A	0.7498	0.5693	1.0459	0.035*
H15B	0.7883	0.5185	1.2271	0.035*
H15C	0.6016	0.6023	1.1859	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0248 (7)	0.0170 (6)	0.0273 (8)	−0.0031 (5)	0.0055 (6)	0.0005 (5)
O2	0.0140 (6)	0.0137 (5)	0.0239 (7)	0.0030 (5)	0.0020 (5)	−0.0020 (5)
O3	0.0169 (6)	0.0154 (6)	0.0218 (7)	0.0025 (4)	0.0023 (5)	0.0001 (5)
O4	0.0165 (6)	0.0228 (6)	0.0272 (8)	0.0035 (5)	0.0023 (5)	0.0071 (5)
C1	0.0142 (8)	0.0175 (8)	0.0207 (10)	0.0027 (6)	0.0041 (7)	0.0037 (7)
C2	0.0218 (9)	0.0265 (9)	0.0177 (10)	0.0051 (7)	0.0032 (7)	0.0060 (7)
C3	0.0174 (9)	0.0290 (9)	0.0150 (9)	0.0047 (7)	0.0003 (7)	0.0006 (7)
C4	0.0128 (8)	0.0187 (8)	0.0138 (9)	0.0000 (6)	0.0011 (6)	−0.0021 (7)
C5	0.0153 (8)	0.0185 (8)	0.0191 (10)	0.0001 (6)	0.0003 (7)	−0.0054 (7)
C6	0.0172 (8)	0.0153 (7)	0.0223 (10)	−0.0023 (6)	0.0007 (7)	−0.0003 (7)
C7	0.0157 (8)	0.0149 (8)	0.0196 (9)	0.0002 (6)	0.0020 (7)	0.0018 (7)
C8	0.0175 (8)	0.0141 (7)	0.0122 (8)	0.0007 (6)	0.0013 (6)	−0.0008 (6)
C9	0.0116 (8)	0.0124 (7)	0.0171 (9)	0.0011 (6)	0.0007 (6)	−0.0008 (6)
C10	0.0116 (8)	0.0148 (7)	0.0147 (9)	−0.0004 (6)	0.0013 (6)	0.0000 (6)
C11	0.0120 (8)	0.0191 (8)	0.0177 (9)	0.0004 (6)	0.0025 (6)	0.0004 (7)
C12	0.0240 (9)	0.0244 (9)	0.0243 (11)	−0.0057 (7)	−0.0001 (7)	−0.0078 (8)
C13	0.0191 (9)	0.0191 (8)	0.0192 (10)	0.0021 (7)	−0.0021 (7)	0.0007 (7)
C14	0.0170 (8)	0.0166 (8)	0.0176 (9)	0.0013 (6)	0.0023 (7)	0.0056 (7)
C15	0.0200 (9)	0.0255 (9)	0.0228 (11)	−0.0001 (7)	−0.0058 (7)	−0.0026 (8)

Geometric parameters (Å, °)

O1—C1	1.213 (2)	C7—C8	1.552 (2)
O2—C9	1.441 (2)	C7—H7	1.0000
O2—H2	0.80 (3)	C8—C13	1.544 (2)
O3—C14	1.347 (2)	C8—C9	1.546 (2)
O3—C7	1.475 (2)	C8—H8	1.0000
O4—C14	1.205 (2)	C9—C10	1.529 (2)
C1—C2	1.473 (3)	C9—H9	1.0000
C1—C10	1.539 (2)	C10—C11	1.541 (2)
C2—C3	1.335 (3)	C11—H11A	0.9800
C2—H2A	0.9500	C11—H11B	0.9800
C3—C4	1.507 (3)	C11—H11C	0.9800
C3—H3	0.9500	C12—H12A	0.9800
C4—C5	1.533 (2)	C12—H12B	0.9800
C4—C10	1.547 (2)	C12—H12C	0.9800
C4—H4	1.0000	C13—C14	1.506 (3)
C5—C12	1.535 (3)	C13—C15	1.515 (3)
C5—C6	1.536 (3)	C13—H13	1.0000
C5—H5	1.0000	C15—H15A	0.9800
C6—C7	1.523 (3)	C15—H15B	0.9800
C6—H6A	0.9900	C15—H15C	0.9800
C6—H6B	0.9900		
C9—O2—H2	109.2 (17)	C7—C8—H8	105.6

C14—O3—C7	109.80 (13)	O2—C9—C10	108.17 (14)
O1—C1—C2	127.68 (17)	O2—C9—C8	107.35 (13)
O1—C1—C10	125.24 (17)	C10—C9—C8	118.16 (13)
C2—C1—C10	107.06 (15)	O2—C9—H9	107.6
C3—C2—C1	108.70 (17)	C10—C9—H9	107.6
C3—C2—H2A	125.6	C8—C9—H9	107.6
C1—C2—H2A	125.6	C9—C10—C1	110.26 (13)
C2—C3—C4	113.23 (17)	C9—C10—C11	113.15 (14)
C2—C3—H3	123.4	C1—C10—C11	103.35 (13)
C4—C3—H3	123.4	C9—C10—C4	113.33 (14)
C3—C4—C5	119.72 (16)	C1—C10—C4	102.31 (14)
C3—C4—C10	102.46 (14)	C11—C10—C4	113.33 (14)
C5—C4—C10	116.38 (14)	C10—C11—H11A	109.5
C3—C4—H4	105.7	C10—C11—H11B	109.5
C5—C4—H4	105.7	H11A—C11—H11B	109.5
C10—C4—H4	105.7	C10—C11—H11C	109.5
C4—C5—C12	111.23 (16)	H11A—C11—H11C	109.5
C4—C5—C6	109.65 (15)	H11B—C11—H11C	109.5
C12—C5—C6	108.12 (15)	C5—C12—H12A	109.5
C4—C5—H5	109.3	C5—C12—H12B	109.5
C12—C5—H5	109.3	H12A—C12—H12B	109.5
C6—C5—H5	109.3	C5—C12—H12C	109.5
C7—C6—C5	120.55 (15)	H12A—C12—H12C	109.5
C7—C6—H6A	107.2	H12B—C12—H12C	109.5
C5—C6—H6A	107.2	C14—C13—C15	113.24 (16)
C7—C6—H6B	107.2	C14—C13—C8	104.89 (15)
C5—C6—H6B	107.2	C15—C13—C8	120.98 (15)
H6A—C6—H6B	106.8	C14—C13—H13	105.5
O3—C7—C6	108.55 (14)	C15—C13—H13	105.5
O3—C7—C8	105.59 (13)	C8—C13—H13	105.5
C6—C7—C8	123.76 (14)	O4—C14—O3	121.47 (16)
O3—C7—H7	105.9	O4—C14—C13	128.40 (17)
C6—C7—H7	105.9	O3—C14—C13	110.13 (15)
C8—C7—H7	105.9	C13—C15—H15A	109.5
C13—C8—C9	116.10 (14)	C13—C15—H15B	109.5
C13—C8—C7	99.70 (13)	H15A—C15—H15B	109.5
C9—C8—C7	122.73 (15)	C13—C15—H15C	109.5
C13—C8—H8	105.6	H15A—C15—H15C	109.5
C9—C8—H8	105.6	H15B—C15—H15C	109.5
O1—C1—C2—C3	−169.13 (19)	C8—C9—C10—C11	−60.42 (18)
C10—C1—C2—C3	12.6 (2)	O2—C9—C10—C4	−51.72 (17)
C1—C2—C3—C4	3.8 (2)	C8—C9—C10—C4	70.39 (18)
C2—C3—C4—C5	−148.81 (17)	O1—C1—C10—C9	38.0 (2)
C2—C3—C4—C10	−18.3 (2)	C2—C1—C10—C9	−143.68 (14)
C3—C4—C5—C12	−43.8 (2)	O1—C1—C10—C11	−83.2 (2)
C10—C4—C5—C12	−167.85 (15)	C2—C1—C10—C11	95.10 (16)
C3—C4—C5—C6	−163.30 (15)	O1—C1—C10—C4	158.87 (18)
C10—C4—C5—C6	72.62 (18)	C2—C1—C10—C4	−22.84 (17)
C4—C5—C6—C7	−66.9 (2)	C3—C4—C10—C9	142.38 (14)

C12—C5—C6—C7	171.70 (15)	C5—C4—C10—C9	−85.06 (18)
C14—O3—C7—C6	156.60 (14)	C3—C4—C10—C1	23.69 (16)
C14—O3—C7—C8	21.99 (17)	C5—C4—C10—C1	156.25 (15)
C5—C6—C7—O3	−61.67 (19)	C3—C4—C10—C11	−86.89 (17)
C5—C6—C7—C8	62.8 (2)	C5—C4—C10—C11	45.7 (2)
O3—C7—C8—C13	−30.25 (17)	C9—C8—C13—C14	−105.84 (17)
C6—C7—C8—C13	−155.97 (17)	C7—C8—C13—C14	28.15 (18)
O3—C7—C8—C9	99.57 (17)	C9—C8—C13—C15	23.6 (2)
C6—C7—C8—C9	−26.2 (3)	C7—C8—C13—C15	157.62 (18)
C13—C8—C9—O2	−143.00 (15)	C7—O3—C14—O4	176.85 (16)
C7—C8—C9—O2	94.45 (18)	C7—O3—C14—C13	−3.05 (19)
C13—C8—C9—C10	94.47 (18)	C15—C13—C14—O4	29.1 (3)
C7—C8—C9—C10	−28.1 (2)	C8—C13—C14—O4	162.99 (18)
O2—C9—C10—C1	62.28 (16)	C15—C13—C14—O3	−151.05 (15)
C8—C9—C10—C1	−175.61 (14)	C8—C13—C14—O3	−17.1 (2)
O2—C9—C10—C11	177.47 (13)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O4^{i}	0.80 (3)	2.09 (3)	2.8792 (19)	173 (2)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+2.

Fig. 1