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ent-3β,16-Dihydroxyisopimar-7-ene-2,15-dione: a new tricyclic diterpenoid from the roots of *Euphorbia wallichii*

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Key indicators

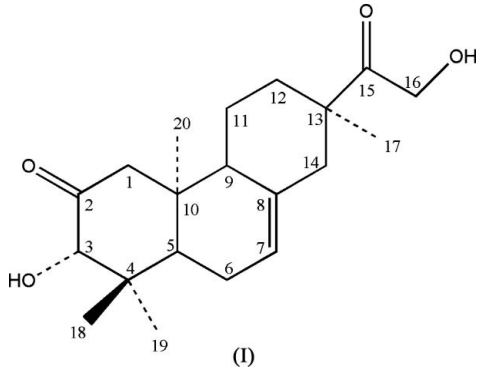
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.101
Data-to-parameter ratio = 9.0

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

The title compound, $C_{20}H_{30}O_4$, is an *ent*-isopimarane diterpenoid which was isolated from the roots of *Euphorbia wallichii*. The molecule contains three six-membered rings, which adopt chair and half-chair conformations. In addition to an intramolecular O—H···O hydrogen bond, an intermolecular O—H···O hydrogen bond connects the molecules into chains.

Comment

Many plants in the family Euphorbiaceae have been the subject of chemical and pharmacological investigation because of their skin-irritant, tumor-promoting and anti-tumor activities. These biological properties have been traced back in many cases to the presence of certain types of diterpenes (Evance & Soper, 1978; Jiao *et al.*, 1990). *Euphorbia wallichii* Hook. f. Fl., a perennial plant distributed mainly in Qinghai-Tibetan Plateau and the surrounding area, has a long history in Tibetan folk medicine as a herbal remedy for curing many skin diseases such as furuncle, exanthema and cutaneous anthrax (Northwest Plateau Institute of Biology, 1991). Our present investigation of the roots of this plant led to the isolation of *ent*-3β,16-dihydroxyisopimar-7-ene-2,15-dione, (I). It is the first time *ent*-isopimarane been obtained from *E. wallichii*. The structure of (I) was elucidated by comprehensive spectroscopic analysis, and was confirmed by single-crystal X-ray diffraction analysis.



(I)

The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. The molecule contains three six-membered rings (*A* = atoms C1–C5/C10, *B* = C5–C10 and *C* = C8/C9/C11–C14). Ring *A* adopts a chair conformation, while ring *B* adopt a slightly distorted half-chair conformation, and ring *C* a slightly distorted chair conformation as a result of the C7═C8 double bond. There is an intramolecular O—H···O hydrogen bond. The molecules are linked by intermolecular O–H···O hydrogen bonds, forming chains running along [011] and [0$\bar{1}$1].

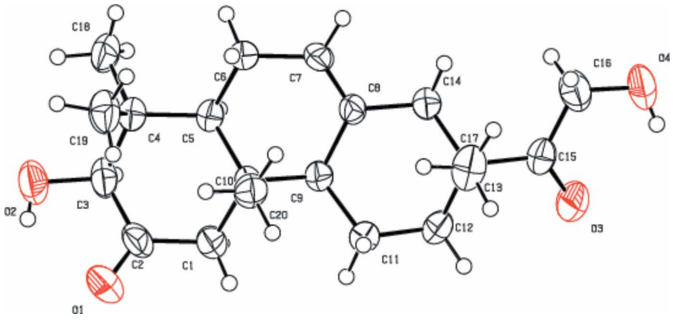


Figure 1
View of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Fresh roots of *E. wallichii* (30 kg) were collected in Lulang at an altitude of 3600–4000 m in the Tibet Autonomous area, People's Republic of China, in July 2003. The extract (600 g) of 90% EtOH was suspended in water (3.0 l) and partitioned successively with EtOAc and *n*-butanol. An aliquot (180 g) of the EtOAc extract was subjected to silica-gel column chromatography (160–200 mesh, 2 kg) and eluted with $CHCl_3$/acetone in increasing polarity. The column chromatographic fractions (500 ml each) were combined according to thin-layer chromatography monitoring into 10 fractions. Fraction 4 (8 g) was applied to an ODS silica-gel column and eluted with MeOH/H_2O (6:4) to yield five fractions. Fraction 4.1 (400 mg) was subjected to silica-gel column chromatography and eluted with $CHCl_3$/acetone (10:1) to afford the pure title compound (I) (m.p. 529–531 K) and was further crystallized at room temperature from acetone to afford prismatic crytals. ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.7 (C15), 210.6 (C2), 132.97 (C8), 123.5 (C7), 115.1 (C7), 82.4 (C3), 64.0 (C16), 51.8 (C9), 51.5 (C1), 48.9 (C5), 45.7 (C13), 45.1 (C10), 42.9 (C4), 32.2 (C12), 28.7 (C18), 23.4 (C6), 19.4 (C11), 18.9 (C17), 16.4 (C19), 15.5 (C20).

Crystal data

$C_{20}H_{30}O_4$
M_r = 334.44
Monoclinic, $P2_1$
a = 9.238 (2) Å
b = 10.124 (3) Å
c = 9.696 (2) Å
β = 97.03 (2)°
V = 900.0 (4) Å^3
Z = 2
D_x = 1.234 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 29 reflections
θ = 3.5–14.5°
μ = 0.08 mm^{-1}
T = 296 (2) K
Prism, colourless
0.60 × 0.54 × 0.24 mm

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: none
2281 measured reflections
2077 independent reflections
1419 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.0°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.102
S = 0.93
2077 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.011 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.211 (4)	O4—C16	1.374 (4)
O2—C3	1.413 (4)	C7—C8	1.312 (4)
O3—C15	1.199 (3)		
C2—C1—C10	112.9 (2)	C8—C9—C10	112.1 (2)
O1—C2—C3	120.6 (3)	C20—C10—C5	112.2 (2)
C1—C2—C3	114.6 (3)	C12—C11—H11*A*	108.9
O2—C3—C4	112.0 (2)	C12—C13—C14	108.4 (2)
C18—C4—C19	108.5 (2)	C17—C13—C15	107.1 (2)
C4—C5—C10	118.5 (2)	O3—C15—C13	122.6 (3)
C7—C6—C5	111.8 (2)	C16—C15—C13	118.2 (3)
C7—C8—C14	120.5 (3)	O4—C16—C15	116.4 (3)
C10—C1—C2—O1	−123.8 (4)	C6—C5—C10—C1	176.6 (2)
O1—C2—C3—O2	−4.2 (4)	C8—C9—C11—C12	−43.6 (4)
O2—C3—C4—C18	−65.5 (4)	C7—C8—C14—C13	139.4 (3)
O2—C3—C4—C19	51.5 (4)	C17—C13—C15—O3	106.3 (4)
C5—C6—C7—C8	−13.1 (4)	C17—C13—C15—C16	−72.1 (4)
C11—C9—C10—C20	56.0 (3)	O3—C15—C16—O4	−3.2 (5)
C4—C5—C10—C9	163.2 (2)	C13—C15—C16—O4	175.3 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*O*···O2^{i}	0.82 (1)	2.18 (3)	2.936 (4)	153 (5)

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

H atoms were positioned geometrically (C—H = 0.93–0.98 Å and O—H = 0.82 Å). H atoms bonded to O atoms were refined freely. H atoms bonded to C atoms were refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). The methyl groups were allowed to rotate but not to tip. The absolute configuration could not be determined from the X-ray analysis because of the absence of strong anomalous scatterers. Friedel pairs were therefore merged before refinement. However, the absolute configuration can be suggested on a biogenetic basis (Wang *et al.*, 2003, 2004).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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