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Redetermination of ternifoline-C at 150 K

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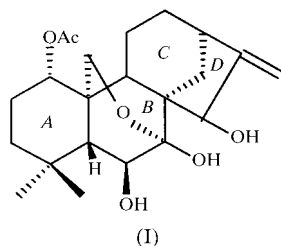
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The relative stereochemistry of ternifoline-C (7,20-epoxy-*ent*-kaur-16-ene-1,6,7,15-tetrol 1-acetate), C₂₂H₃₂O₆, previously reported by Wu [*Fudan Xuebao Zir. Kex.* (1988), **27**, 61–65], has been redetermined at 150 K. The molecular geometry and crystal packing agree well with the previous study.

Comment

The structure of the diterpenoid ternifoline-C, (I), has been reported previously (Wu, 1988) as the *ent*-kaurane but was not included in the Cambridge Structural Database (Allen *et al.*, 1983). We can confirm the structure reported previously, but the cell volume of the present determination is slightly lower [992.4 (3) *versus* 1015 Å³] and hence the calculated density higher (1.313 *versus* 1.284 Mg m⁻³), which indicates that the previous structure was probably determined at room temperature.



From the relative stereochemistry shown in the scheme (the absolute stereochemistry has not been determined in this study), the nine chiral centres present in the *ent*-kaurane (assumed) are: C1 *S*, C5 *R*, C6 *S*, C7 *S*, C8 *S*, C9 *S*, C10 *S*, C13 *R* and C15 *R*. If the relative stereochemistry reported is not the absolute stereochemistry, then all these chiral centres will invert to form the kaurane.

The ring conformations (see sketch) approximate to *A* chair, *B* boat, *C* boat, and *D* half-chair (*A* is the left-most ring in the scheme). Also, the two six-membered rings formed by the C20 and O1 bridging atoms under the *B* ring both adopt approximate boat conformations.

Details of three well defined hydrogen bonds (two inter- and one intramolecular) are shown in Table 2. The C—OH bond lengths are affected by the hydrogen bonds, with C7—O3 being shorter than both C6—O2 and C15—O4, as O3 is only involved in one hydrogen bond, whereas O2 and O4 are each involved in two hydrogen bonds. Endocyclic angle distortions and some torsion angles which help define ring conformations are included in Table 1. Other short non-bonded separations include O2···O3 of 2.772 (4) Å and O4···O3ⁱ of 2.974 (4) Å [symmetry code: (i) $-x, y - \frac{1}{2}, -z$], where the H···O separations are 2.5 Å and the angle subtended by the H atom is less than 120°.

A crystallographic study of a similar fused-ring system has been reported for oridonin (Shi *et al.*, 1992) and similar systems have been studied by NMR (Hou *et al.*, 2000). *ent*-Kauranes (crystalline and amorphous) which lack the C20 and O1 bridging atoms have also been widely reported (Tazaki *et al.*, 1999; Zhao *et al.*, 1999).

Experimental

The diterpene 7,20-epoxy-*ent*-kaur-16-ene-1,6,7,15-tetrol 1-acetate was extracted from the Chinese medicinal plant *Rabdosia serra* (Maxim.) Hara (Labiateae). A previous study (Wu, 1988) had isolated the diterpene from another species of *Rabdosia*.

Crystal data

C₂₂H₃₂O₆
M_r = 392.48
Monoclinic, *P*2₁
a = 10.9870 (16) Å
b = 6.0330 (8) Å
c = 15.429 (3) Å
 β = 103.989 (6)°
V = 992.4 (3) Å³
Z = 2

D_x = 1.313 Mg m⁻³
Mo *K*α radiation
Cell parameters from 3394 reflections
 θ = 1.91–27.54°
 μ = 0.094 mm⁻¹
T = 150 (2) K
Needle, colourless
0.15 × 0.05 × 0.02 mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
 φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
T_{min} = 0.987, *T_{max}* = 0.998
7295 measured reflections

3394 independent reflections
2168 reflections with *I* > 2σ(*I*)
R_{int} = 0.074
 θ_{\max} = 27.54°
h = −14 → 13
k = −5 → 7
l = −18 → 18

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.059
wR (*F*²) = 0.143
S = 0.967
3394 reflections
268 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.214 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.255 \text{ e \AA}^{-3}$
Absolute structure: Flack (1983),
1054 Friedel pairs
Flack parameter = 1.7 (16)

Table 1

Selected geometric parameters (Å, °).

O1—C7	1.442 (4)	O4—C15	1.428 (4)
O1—C20	1.451 (4)	C6—C7	1.519 (5)
O2—C6	1.438 (4)	C8—C9	1.566 (5)
O3—C7	1.403 (4)	C16—C17	1.319 (6)
C7—O1—C20	112.4 (3)	C9—C10—C5	105.7 (3)
C19—C4—C5	114.7 (3)	C12—C11—C9	113.6 (3)
C4—C5—C10	119.0 (3)	C8—C14—C13	100.6 (3)
C14—C8—C15	99.1 (3)	C15—C16—C13	107.7 (3)
C10—C5—C6—C7	11.3 (4)	C11—C12—C13—C14	21.7 (4)
C14—C8—C9—C11	-8.8 (4)	C7—O1—C20—C10	-5.3 (4)
C7—C8—C9—C10	-4.7 (4)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O4 ⁱ	0.76 (6)	2.07 (5)	2.795 (4)	158 (5)
O3—H3...O4 ⁱⁱ	0.92 (4)	1.91 (5)	2.687 (4)	142 (3)
O4—H4...O2	0.87 (5)	1.84 (5)	2.665 (5)	158 (4)

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

The hydroxy H atoms were refined freely and the remaining H atoms were initially placed in calculated positions and thereafter allowed to ride on their attached atoms with common isotropic displacement parameters which converged to 0.034 (2) (non-methyl H atoms) and 0.063 (4) Å² (methyl H atoms). The absolute configuration could not be established by this experiment in view of the X-ray wavelength and the elements present.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *PLATON* (Spek, 1998) and *SHELXL97*.

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