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The natural diterpenoid kamebacetal A

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Key indicators

Single-crystal X-ray study
T = 289 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.089
Data-to-parameter ratio = 9.8

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

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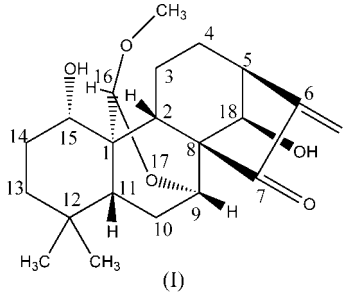
Kamebacetal A, or (1*S**,2*S**,8*S**,9*R**,11*R**,15*S**,16*S**,18*R**)-15,18-dihydroxy-16-methoxy-12,12-dimethyl-6-methylene-17-oxapentacyclo[7.6.2.1^{5,8}.0^{1,11}.0^{2,8}]octadecan-7-one, $C_{21}H_{30}O_5$, is a natural diterpenoid which has cytotoxic and antibacterial activity. The molecule contains five six-membered rings and one five-membered ring. Ring *A* adopts a chair conformation, rings *B*, *C*, *E* and *F* adopt boat conformations, and ring *D* adopts an envelope conformation. The conjugated α-methylenecyclopentanone is the active part of the molecule due to ring strain.

Comment

The natural diterpenoid kamebacetal A, (I), has previously been isolated from *Rabdosia Umbrosa* var. leucantha f. *kameba* (Yoshio *et al.*, 1987) and *Rabdosia Latifolia* var. reniformis (Wang *et al.*, 1986), and its structure was established on the basis of spectroscopic and chemical evidence. Recently, it has also been isolated from *Rabdosia leucophylla*, and its structure has been confirmed by an X-ray diffraction study, the results of which we present here.



(I)

The molecule of (I) (Fig. 1) contains five six-membered rings and one five-membered ring. Ring *A* (C1/C11–C15) adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975) Q = 0.549 (4) Å, θ = 173.6 (4)° and φ = 266 (4)°. Ring *B* (C1/C2/C8–C11) adopts a boat conformation, with Q = 0.866 (3) Å, θ = 93.8 (2)° and φ = 115.7 (2)°. A bridge composed of atoms C16 and O17 links the apex of ring *B* and forms two new six-membered rings, *E* (C9–C10/C1/C16/O17) and *F* (C1/C2/C8/C9/O17/C16), both of which adopt boat conformations, with puckering parameters Q = 0.817 (3) Å, θ = 89.4 (2) and φ = 238.8 (2)° for ring *E*, and Q = 0.797 (3) Å, θ = 88.6 (2) and φ = 66.4 (2)° for ring *F*. Ring *C* (C2–C5/C18/C8) adopts a boat conformation, with Q = 0.829 (3) Å, θ = 79.7 (2) and φ = 296.0 (2)°. The five-membered ring *D* (C5–C8/C18) is a conjugated α-methylenecyclopentanone and adopts an envelope conformation.

Adjacent molecules in (I) are connected by hydrogen bonds running along the *a* direction (Fig. 2 and Table 2).

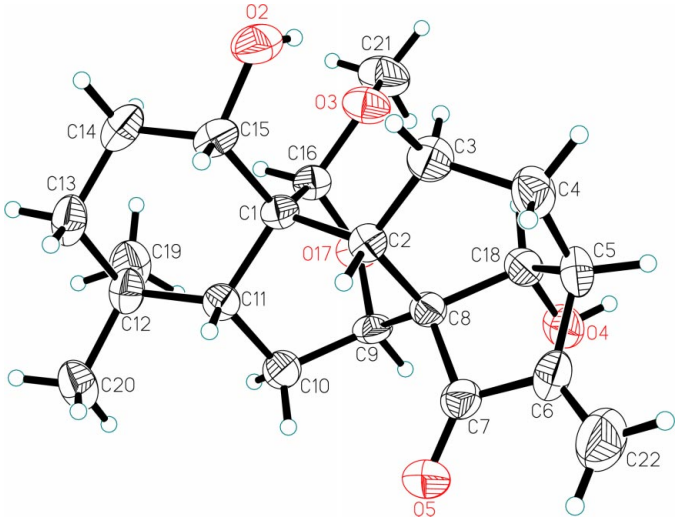


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

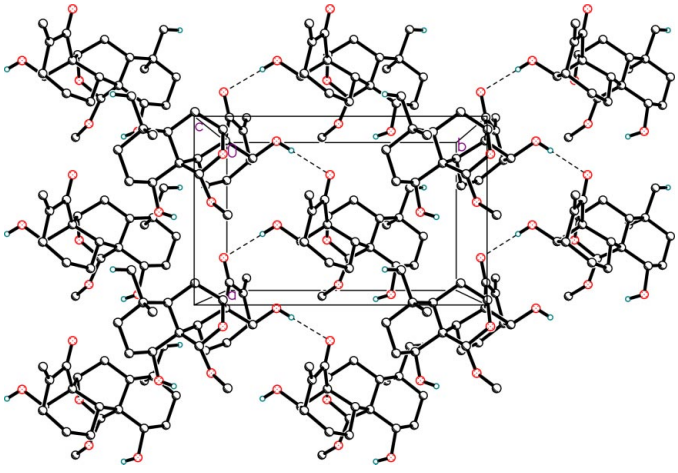


Figure 2
The hydrogen bonding (dashed lines) in (I), viewed normal to the (001) plane. H atoms have been omitted for clarity, except for these involved in hydrogen bonds.

Experimental

Kamebacetal A was isolated from the aerial part of *Rabdosia leucophylla*, which was collected from wild plants growing in the Kangding region, Sichuan province, China. Crystals of (I) suitable for X-ray structure analysis were obtained by slow evaporation at room temperature of a solution in ethyl acetate/methanol (1:1 *v*/*v*).

Crystal data

$C_{21}H_{30}O_5$
M_r = 362.45
Orthorhombic, $P2_12_12_1$
a = 7.8040 (10) Å
b = 12.078 (2) Å
c = 19.007 (3) Å
V = 1791.5 (5) Å^3
Z = 4
D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
θ = 2.8–15.0°
μ = 0.09 mm^{-1}
T = 289 (2) K
Plate, colourless
0.52 × 0.42 × 0.20 mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
2425 measured reflections
2354 independent reflections
1396 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.5°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -1 \rightarrow 24$
3 standard reflections
every 97 reflections
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.089
S = 0.88
2354 reflections
241 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.025
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0096 (10)

Table 1
Selected geometric parameters (Å, °).

O5—C7	1.218 (3)	C6—C7	1.482 (4)
C5—C6	1.505 (4)	C7—C8	1.531 (4)
C5—C18	1.546 (4)	C8—C18	1.543 (4)
C6—C22	1.313 (5)		
C6—C5—C18	101.1 (3)	O5—C7—C8	127.4 (3)
C22—C6—C7	123.2 (3)	C6—C7—C8	107.2 (3)
C22—C6—C5	129.6 (3)	C7—C8—C18	98.4 (3)
C7—C6—C5	107.2 (3)	C8—C18—C5	101.0 (2)
O5—C7—C6	125.3 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O3	0.82	2.08	2.793 (3)	145
O4—H4O···O5^{i}	0.82	2.17	2.990 (3)	177
C20—H20A···O17^{ii}	0.96	2.60	3.505 (4)	158

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

All H atoms were placed in calculated positions and refined in the riding-model approximation, with C—H = 0.96–0.98 Å, O—H = 0.82 Å and U_{iso}(H) = 1.2U_{eq}(carrier atom). Friedel pairs were merged before the final refinement, and only the relative stereochemistry is shown in the scheme and Figs. 1 and 2; the absolute configuration could not be determined.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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