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Macrocalyxin I

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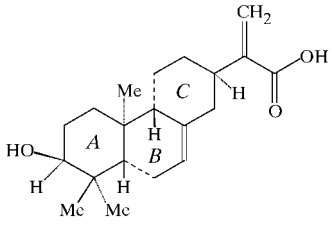
The title compound, 2-[1,2,3,4,4a,4b,5,6,7,8,8a,9-dodecahydro-7-hydroxy-4b,8,8-trimethylphenanthren-2-yl]propenoic acid, $C_{20}H_{30}O_3$, is a naturally occurring diterpenoid which was isolated from *Rabdosia macrocalyx*. The hydroxy and carboxy groups, which are located at the two ends of the molecule, both serve as simultaneous hydrogen-bond donors and acceptors. Two intermolecular O—H···O hydrogen bonds are present and link each molecule to four neighbours, thus forming an extensive hydrogen-bond network within the crystal.

Comment

Rabdosia macrocalyx is widely distributed in Anhui, Jiangsu, Zhejiang, Jiangxi, Fujian, Hunan, Guangdong, Guangxi and Taiwan provinces, China, where it has been used as a folk medicine. Its decoctions are used as antibiotics and for anti-tumor treatment. Macrocalyxins A, B (Cheng *et al.*, 1984), C (Wang *et al.*, 1984), D (Wang *et al.*, 1985), E (Wang *et al.*, 1986), F, G and H (Wang *et al.*, 1995) have been isolated previously from this plant. In order to isolate more bioactive constituents, we investigated the whole herb of *Rabdosia macrocalyx*, which led to the isolation of the title compound, the natural diterpenoid macrocalyxin I, (1), which was isolated from *Rabdosia macrocalyx* Hara for the first time. Its structure was established from spectral evidence and was confirmed by the present X-ray diffraction study.



(1)

The molecule of (1) (Fig. 1) is composed of three six-membered rings. Rings *A* (C1–C5/C10) and *C* (C8/C9/C12–C14) adopt a chair conformation, with mean torsion angles of 51.4 and 52.4°, respectively. Ring *B* (C5–C9/C10) adopts a half-chair conformation owing to the double bond between C7 and C8. The stereochemistry of the *A*/*B* ring junction is *trans*, and the dihedral angle between rings *A* and *B* is 17.60 (5)°; the

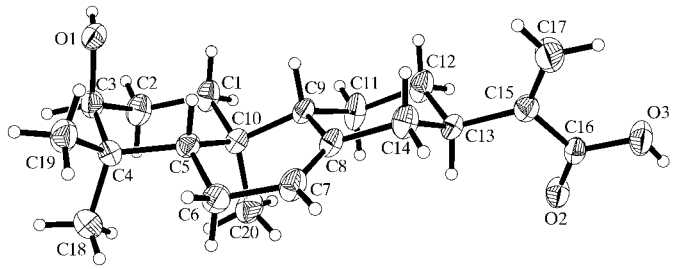


Figure 1
View of the title molecule showing the atomic numbering scheme and 50% probability displacement ellipsoids.

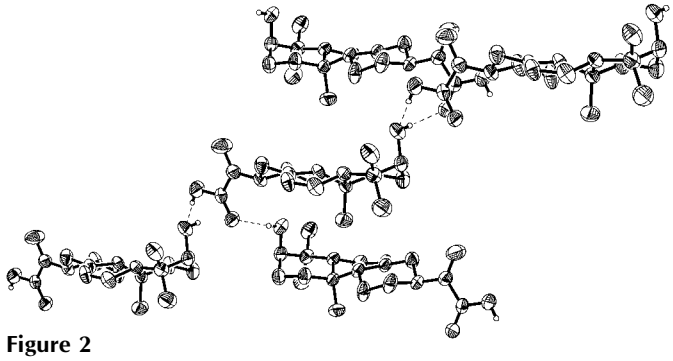


Figure 2
The intermoleculer hydrogen bonding in (1) viewed normal to the (001) plane. H atoms have been omitted for clarity, except for those involved in hydrogen bonds, which are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

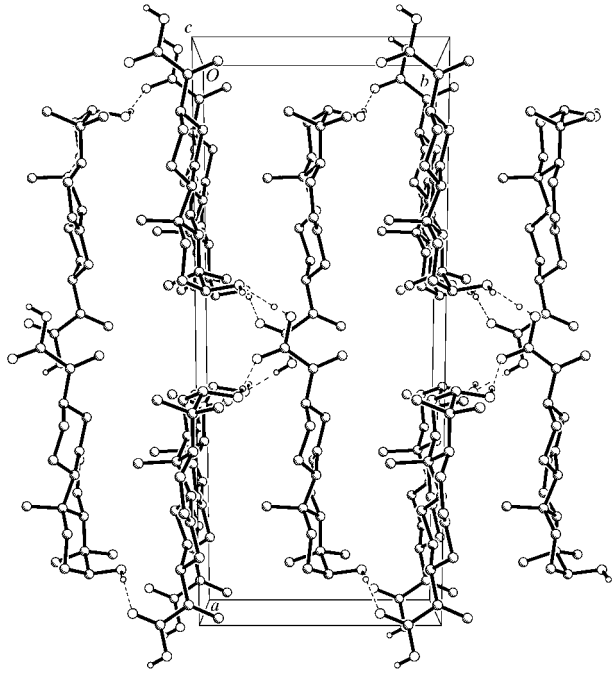


Figure 3
The crystal-packing diagram for the title compound viewed down the *c* axis. H atoms have been omitted for clarity, except for these involved in hydrogen bonds.

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dihedral angle between rings *B* and *C* is 14.92 (7)°. The configurations at the other chiral centers are as follows: C3–OH, C10–Me, C9–H and C13–H are axial and the 1-carboxyethenyl group at C13 is equatorial.

The C17—C15—C16—O2 torsion angle has a value of 172.4 (3)° because of the conjugated double bound. The best least-squares plane formed by atoms C17/C15/C16/O2/O3 has a maximum deviation of 0.0592 Å, and the dihedral angle between this plane and ring *C* is 114.22 (11)°. The hydroxy group located at C3 and the carboxy group located at C15 participate in hydrogen bonding. Both groups serve as simultaneous hydrogen-bond donors and acceptors. Two intermolecular O—H···O hydrogen bonds (Table 2) are present and link each molecule to four adjacent neighbours (Fig. 2). The overall result is an extended hydrogen-bonding network throughout the structure (Fig. 3).

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.432 (3)	C13—C15	1.512 (3)
O2—C16	1.217 (3)	C15—C17	1.310 (4)
O3—C16	1.320 (3)	C15—C16	1.479 (3)
C7—C8	1.320 (3)		
O1—C3—C2	109.2 (2)	O2—C16—O3	121.8 (2)
O1—C3—C4	108.4 (2)	O2—C16—C15	123.2 (2)
C17—C15—C16	119.4 (2)	O3—C16—C15	115.0 (2)
C17—C15—C13	124.9 (2)		
C17—C15—C16—O2	172.4 (3)	C17—C15—C16—O3	−7.8 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O1^{i}	0.82	1.85	2.662 (3)	169
O1—H1O···O2^{ii}	0.82	1.97	2.771 (3)	164

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, 2-z$.

Experimental

Dried powder (7.5 kg) of the whole herb of *Rabdosia macrocalyx* was soaked three times with 95% EtOH at room temperature. The solvent was removed by evaporation at reduced pressure, and the residue was successively fractioned with petroleum ether, EtOAc and *n*-BuOH. The residue of the EtOAc fraction was subjected to column chromatography over silica gel. The column was eluted with a petroleum ether–EtOAc mixture. The crude compound was purified by column chromatography on silica gel with an acetone–chloroform mixture, producing 210 mg of macrocalyxin A and 60 mg of the pure title compound, (1) [m.p.: 490.5–492.5 K ($CHCl_3$/CH_3COCH_3)]. ^{13}C NMR (125 MHz, pyridine): δ (p.p.m.) 169.8 (C16), 147.5 (C15), 137.2 (C8), 121.7 (C17), 121.2 (C7), 75.1 (C3), 52.4 (C9), 44.3 (C5), 41.7 (C6), 39.7 (C13), 37.5 (C4), 35.3 (C10), 32.3 (C14), 32.2 (C12), 29.3 (C19), 26.4 (C11), 25.7 (C1), 23.3 (C2), 23.1 (C18), 15.3 (C20). Crystals suitable for X-ray structure analysis were obtained by slow evaporation from an aqueous solution in chloroform and methanol (1:1) at room temperature.

Crystal data

$C_{20}H_{30}O_3$
M_r = 318.44
Monoclinic, *C*2
a = 24.066 (2) Å
b = 10.017 (1) Å
c = 7.608 (1) Å
β = 101.35 (1)°
V = 1798.2 (3) Å^3
Z = 4
D_x = 1.176 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 25 reflections
θ = 3.3–12.3°
μ = 0.08 mm^{-1}
T = 295 (2) K
Prism, colorless
0.50 × 0.50 × 0.40 mm

Data collection

Siemens *P*4 diffractometer
ω scans
2311 measured reflections
2178 independent reflections
1605 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.5°
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 13$
$l = -9 \rightarrow 9$
3 standard reflections
every 97 reflections
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.097
S = 0.98
2178 reflections
214 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.035 (2)

H atoms were placed in geometrically calculated positions and included in the final refinement as riding, with U_{iso} values equal to $1.2U_{eq}$ of the carrier atom. An attempt to establish the absolute configuration failed. The Flack (1983) parameter obtained was −0.9 (16). The Friedel pairs were merged before the final refinement and only the relative stereochemistry is shown in the Scheme and figures.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Siemens, 1991); software used to prepare material for publication: *SHELXTL*/*PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1347). Services for accessing these data are described at the back of the journal.

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