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Natural diterpenoid ludongnin, octahydro-5′-hydroxy-7a-methyl-8′-methylenespiro[isobenzofuran-4(1*H*),-4′(3′*H*)-[1*H*-7,9a]methanocyclohepta[c]pyran]-1′,3,9′(3a*H*,4′a*H*)-trione

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The asymmetric unit of ludongnin consists of two molecules of $C_{20}H_{24}O_6$. The hydroxyl group of each molecule participates in a hydrogen bond with the carbonyl oxygen of the δ-lactone moiety of a translationally related molecule, thus giving rise to the two symmetry-independent sets of infinite chains in the crystal, one of which is stretched along the *c* and another along the *a* axis of the crystal.

Key indicators

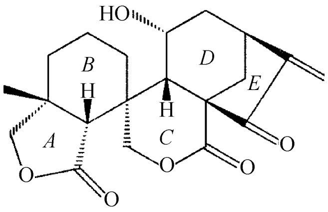
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
R factor = 0.038
wR factor = 0.081
Data-to-parameter ratio = 7.3

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

Comment

The diterpenoid ludongnin, (I), has been previously isolated from *Rabdosia rubescens* Hara (Ruan *et al.*, 1986; Sun *et al.*, 1988; Zheng *et al.*, 1984, 1986) and its structure was established from the spectroscopic and chemical evidence. Recently, it was for the first time isolated from *Rabdosia var lophanthoides* Hara, and its structure was confirmed by an X-ray diffraction study (Fig. 1).

In both molecules, the *B* ring adopts a chair, whereas the *D* ring shows a boat conformation. The isobenzofuran ring system couples orthogonally to the methanocyclohepta[*c*]-pyran moiety through a spiro-C atom. The differences in the geometrical parameters between the two independent molecules are in fact negligible; the most notable discrepancies, as one would expect, concern the values of the torsion angles: C12—C13—C16—C17 −92.1 (5), C12′—C13′—C16′—C17′ −100.1 (5), C14—C13—C16—C17 151.1 (4) and C14′—C13′—C16′—C17′ 143.5 (4)°.



ludongnin

The hydroxyl group of each of the independent molecules participates in a hydrogen bond with the carbonyl oxygen of the δ-lactone moiety of the same molecule as transformed by the *c* or *a* translation [O···O 2.824 (4) and 2.856 (3) Å, respectively]. Thus, two independent molecules give rise to two sets of infinite chains in the crystal, one of which is stretched along the *c* and another along the *a* axis of the crystal (Fig. 2).

Experimental

2 kg of dried powder of the whole herb of *Rabdosia var lophanthoides* were soaked three times with 95% EtOH at room temperature. The

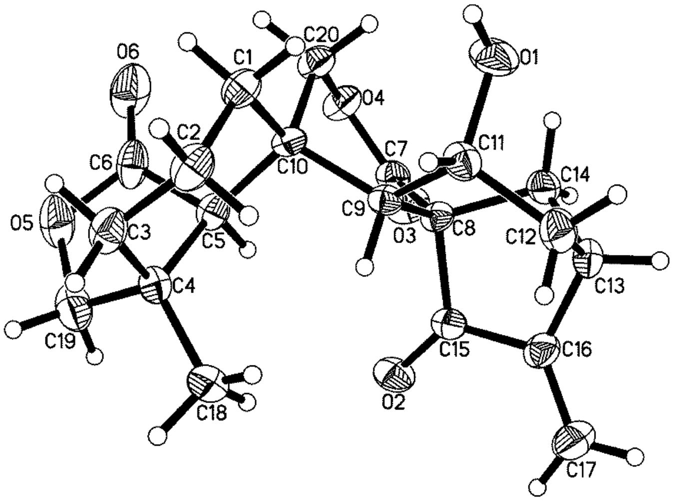


Figure 1
One of the independent molecules of the title compound, shown with 50% probability displacement ellipsoids.

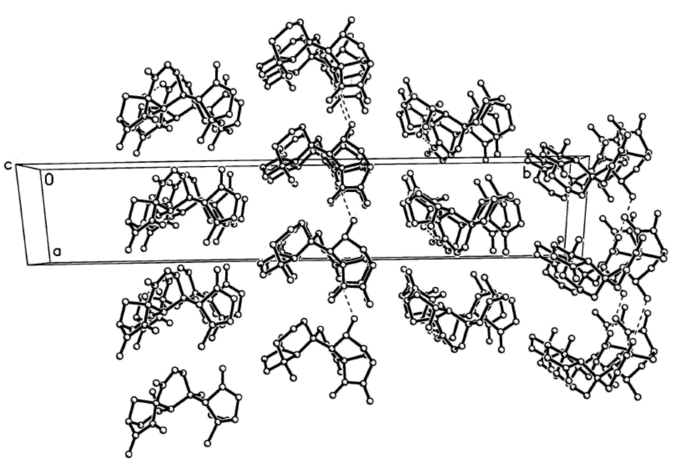


Figure 2
The crystal-packing diagram for the title compound viewed down the *c* axis. H atoms have been omitted for clarity.

ethanolic extracts were evaporated under reduced pressure and the residue was successively fractionated 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; an acetone–chloroform mixture was used for recrystallization of the title compound. Its purity was checked by ^{1}H NMR spectroscopy. α^{D}_{12} −138° (*c* = 1, pyridine); UV λ_{max} (95%EtOH): 230 nm (ε 7130). Crystals suitable for X-ray structure analysis were obtained by slow evaporation from an aqueous solution containing chloroform and methanol in a 1:1 ratio at room temperature.

Crystal data

$C_{20}H_{24}O_6$
M_r = 360.39
Monoclinic, $P2_1$
a = 7.2397 (13) Å
b = 36.724 (8) Å
c = 7.304 (2) Å
β = 115.69 (2)°
V = 1749.9 (7) Å^3
Z = 4

D_x = 1.368 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18 reflections
θ = 3.1–14.2°
μ = 0.10 mm^{-1}
T = 291 (2) K
Prism, colorless
0.52 × 0.44 × 0.42 mm

Data collection

Siemens *P*4 diffractometer
ω scans
3894 measured reflections
3474 independent reflections
2512 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 26.0°

$h = 0 \rightarrow 8$
$k = 0 \rightarrow 45$
$l = -9 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.081
S = 0.91
3474 reflections
474 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0135 (12)
Absolute structure: Flack (1983)
Flack parameter = −0.4 (11)

Table 1
Selected geometric parameters (Å, °).

O2—C15	1.207 (4)	O2′—C15′	1.213 (4)
O3—C7	1.210 (4)	O3′—C7′	1.204 (4)
O6—C6	1.193 (5)	O6′—C6′	1.196 (5)
C16—C17	1.310 (5)	C16′—C17′	1.320 (5)
C20—C10—C9	106.4 (3)	C20′—C10′—C5′	112.3 (3)
C1—C10—C9	113.5 (3)	C1′—C10′—C5′	108.9 (3)
O1—C11—C9	111.7 (3)	O1′—C11′—C9′	113.5 (3)
O2—C15—C16—C17	2.7 (6)	O2′—C15′—C16′—C17′	9.2 (6)
C8—C15—C16—C17	179.2 (4)	C8′—C15′—C16′—C17′	−172.9 (3)
C14—C13—C16—C17	151.1 (4)	C14′—C13′—C16′—C17′	143.5 (4)
C12—C13—C16—C17	−92.1 (5)	C12′—C13′—C16′—C17′	−100.1 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O3^{i}	0.82	2.05	2.824 (4)	157
O1′—H1′*A*···O3′^{ii}	0.82	2.07	2.856 (3)	159

Symmetry codes: (i) $x, y, z - 1$; (ii) $x - 1, y, z$.

H atoms were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation with the displacement parameters U_{iso} set equal to $1.2U_{eq}$ of the corresponding carrier atom. As one would expect, both independent molecules have the same configuration. Lack of anomalous scatterers and, hence, a high s.u. of the Flack parameter, −0.4 (11), do not permit us to make an unambiguous assignment of the absolute configuration of the title compound.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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/PC* (Siemens, 1991); software used to prepare material for publication: *SHELXL*97.

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