

Octahydro-7a,8'-dimethylspiro[isobenzofuran-4(1H),4'(3'H)-[1H-7,9a]methanocyclohepta[c]pyran]-1',3,9'(3aH,4'aH)-trione

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Key indicators

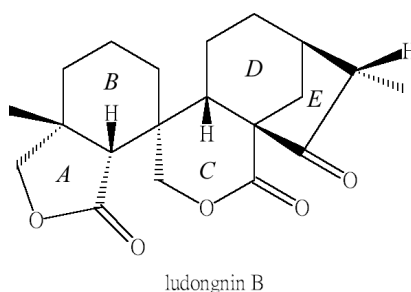
Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.053
wR factor = 0.128
Data-to-parameter ratio = 10.0

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

The title compound, $\text{C}_{20}\text{H}_{26}\text{O}_5$, or ludongnin B, which has been isolated from *Rabdosia* var *lophanthoides*, is composed of three six-membered rings and two five-membered rings. The isobenzofuran ring system couples almost orthogonally to the methanocyclohepta[c]pyran moiety through a spiro-C atom.

Comment

Rabdosia lophanthoides is widely distributed in South and Southeast Asia and has long been used as a folk medicine in China. Its concoctions are used for the treatment of acute icteric hepatitis, acute cholecystitis, enteritis, laryngopharyngitis, gynopathy and lepromatous leprosy (Wu & Li, 1977). As natural diterpenoids isolated from plants which belong to *rabdosia* category usually have antibiotic and antitumor activity (Zhu, 1982), in order to isolate bioactive constituents from this plant, we investigated the whole herb of *Rabdosia* var *lophanthoides*, which led to the isolation of the title compound, (I), the natural diterpenoid ludongnin B. It had previously been isolated from *Rabdosia rubescens* Hara (Sun *et al.*, 1988; Zheng *et al.*, 1986) and its structure was established from IR, ^1H NMR and ^{13}C NMR spectral evidence. This is the first time that ludongnin B has been isolated from *Rabdosia lophanthoides*, and its structure was confirmed by X-ray analysis.



The title compound, (I), is composed of three six-membered rings and two five-membered rings (Fig. 1). The cyclohexane ring *B* (C1–C5/C10) exists in a twist chair conformation owing to the *cis* fusion with ring *A*. This is also indicated by the smaller torsion angles C2–C3–C4–C5 of $36.2(5)^\circ$, C3–C4–C5–C10 of $-34.3(4)^\circ$ and C4–C5–C10–C1 of $45.0(4)^\circ$. Ring *C* (C7–C10/C20/O2) adopts a sofa conformation with the apex at C10, displaced by $0.745(5) \text{ \AA}$ from the mean plane of the remaining five atoms, and ring *D* (C8–C9/C11–C14) adopts a boat conformation. The two five-membered rings, *A* (C4–C6/O1/C19) and *E* (C8/C13–C16),

Received 21 September 2001

Accepted 26 September 2001

Online 6 October 2001

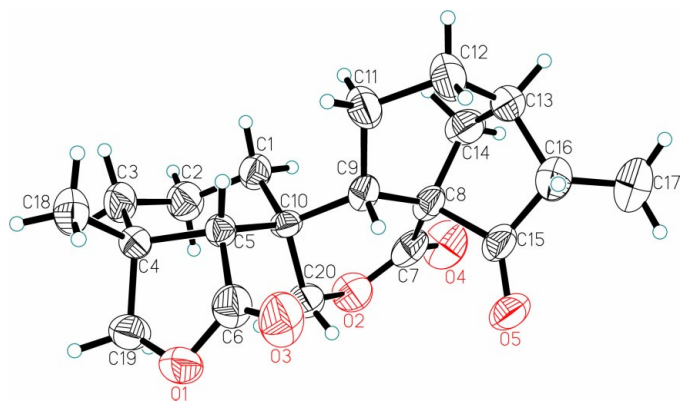


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

adopt envelope conformations, with C4 and C14 displaced by 0.521 (6) and 0.715 (6) Å, respectively, from the mean plane of the remaining four atoms. The C18 methyl group is equatorial to ring *B* and the associated torsion angles are 158.1 (4) (C2–C3–C4–C18) and -156.2 (3)° (C18–C4–C5–C10). The isobenzofuran ring system couples almost orthogonally to the methanocyclohepta[*c*]pyran moiety through a spiro-C atom.

Experimental

The plant was collected in the mountain near Shangqiu City, Shanxi province, People's Republic of China. The identity of the plant was confirmed by Dr Li Bao-Lin of Shanxi Normal University. 2 kg of dried powder of the whole herb of *Rabdosia* var *lophanthoides* were soaked three times with 95% EtOH at room temperature. The ethanolic extracts were evaporated under reduced pressure, 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 and the crude compound was purified by column chromatography on silica gel with an acetone–chloroform mixture to obtain the pure title compound, (I), (m.p. 569–571 K). Crystals of (I) were obtained by slow evaporation from an aqueous solution containing chloroform and methanol in a 1:1 ratio at room temperature.

Crystal data

$C_{20}H_{26}O_5$	$D_x = 1.315 \text{ Mg m}^{-3}$
$M_r = 346.41$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 29 reflections
$a = 7.569$ (2) Å	$\theta = 3.3\text{--}12.2^\circ$
$b = 9.397$ (2) Å	$\mu = 0.09 \text{ mm}^{-1}$
$c = 12.310$ (3) Å	$T = 295$ (2) K
$\beta = 92.62$ (2)°	Prism, colorless
$V = 874.6$ (4) Å ³	$0.42 \times 0.34 \times 0.14 \text{ mm}$
$Z = 2$	

Data collection

Siemens P4 diffractometer	$\theta_{\text{max}} = 28.3^\circ$
ω scans	$h = 0 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 12$
2561 measured reflections	$l = -16 \rightarrow 16$
2291 independent reflections	3 standard reflections
1206 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.023$	intensity decay: 2.9%

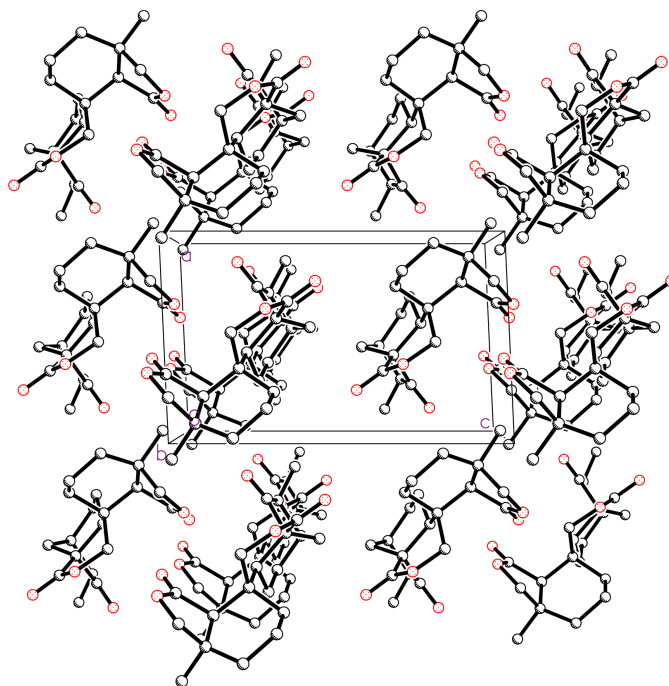


Figure 2
The crystal-packing diagram of (I), viewed down the *b* axis. H atoms have been omitted for clarity.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.87$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
2291 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
228 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.017 (4)
	Absolute structure: see text

Table 1

Selected geometric parameters (Å, °).

C2–C3–C4–C5	36.2 (5)	C18–C4–C5–C10	-156.2 (3)
C2–C3–C4–C18	158.1 (4)	C4–C5–C10–C1	45.0 (4)
C3–C4–C5–C10	-34.3 (4)		

H atoms were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation with U_{iso} values equal to $1.2U_{\text{eq}}$ of the corresponding carrier atom. Since the Flack (1983) parameter was 2 (2), the Friedel reflections were merged before the final refinement; 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: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1991); software used to prepare material for publication: *SHELXTL97*.

This project was supported by the Natural Science Foundation of China.

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