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# Paxdaphnine B: a 1,19-bisnor-daphniphyllum alkaloid

**Yong-Bin Lu,[a,b] Ning-Chuan Kong,[c] Yuan-Yuan Feng,[a,b] Xiao-Jiang Hao[c] and Yang Lu[a,b]***

[a]Key Laboratory of Bioactive Substances and Resources Utilization of Chinese Herbal Medicine, Ministry of Education, Institute of Materia Medica, Chinese Academy of Medical Sciences, People's Republic of China, [b]Peking Union Medical College, 1 Xiannong Tan Street, Beijing 100050, People's Republic of China, and [c]State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, Yunnan, People's Republic of China

Correspondence e-mail: luy@imm.ac.cn

**Key indicators**

Single-crystal X-ray study
*T* = 295 K
Mean σ(C–C) = 0.006 Å
*R* factor = 0.052
*wR* factor = 0.137
Data-to-parameter ratio = 7.4

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

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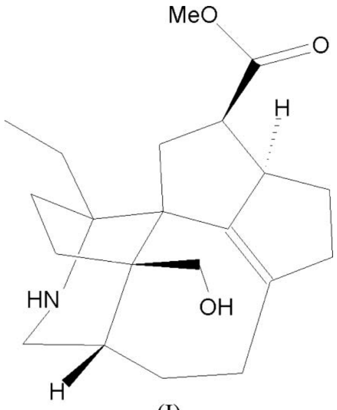
The title compound, methyl 5-ethyl-2-methoxy-6-azapentacyclo[9.5.1.$0^{1,5}$.$0^{2,8}$.$0^{14,17}$]heptadec-11 (17)-ene-15-carboxylate, $C_{21}H_{31}NO_3$, obtained from the fruits of *Daphniphyllum macropodum*, is a newly identified alkaloid with a complex polycyclic skeleton. It crystallizes with two unique molecules in the asymmetric unit that differ in the orientation of the hydroxyl group. The molecules are linked into chains along the *a* axis by intermolecular O—H···N hydrogen bonds.

## Comment

*Daphniphyllum macropodum* is native to southern China, and its fruits have been applied traditionally as anti-inflammatory agents (Zhen & Min, 1980). The structure of paxdaphnine B was previously reported as the first 1,19-bisnor-daphniphyllum alkaloid from spectroscopic investigations (Fan *et al.*, 2007). We have recently crystallized the compound from acetone and its structure is reported here. The compound crystallizes with two unique molecules (1 containing O1 and C23 and 2 containing O1′ and C23′) in the asymmetric unit that differ in the orientation of the C21/O1 and C21′/O1′ hydroxyl groups as indicated by the torsion angles [1: C4—C5—C21—O1= 64.7 (5)°; 2: C4′—C5′—C21′—O1′ = −25.7 (5)°; Figs. 1 and 2].



(I)

The skeleton of the title compound, (I), is composed of three five-membered rings, a six-membered ring and a seven-membered ring. All three five-membered rings have envelope conformations, with atoms C8, C15 and C16 at the flaps of the envelopes in molecule 1. They lie 0.746 (3), 0.461 (3) and 0.452 (3) Å, respectively, from the planes formed by the other four atoms of the individual rings; the corresponding values in molecule 2 are 0.741 (3), 0.428 (3), 0.421 (3) Å, respectively. The resultant puckering causes significant contractions of the C2—C8—C5, C9—C15—C14 and C15—C16—C17 angles.

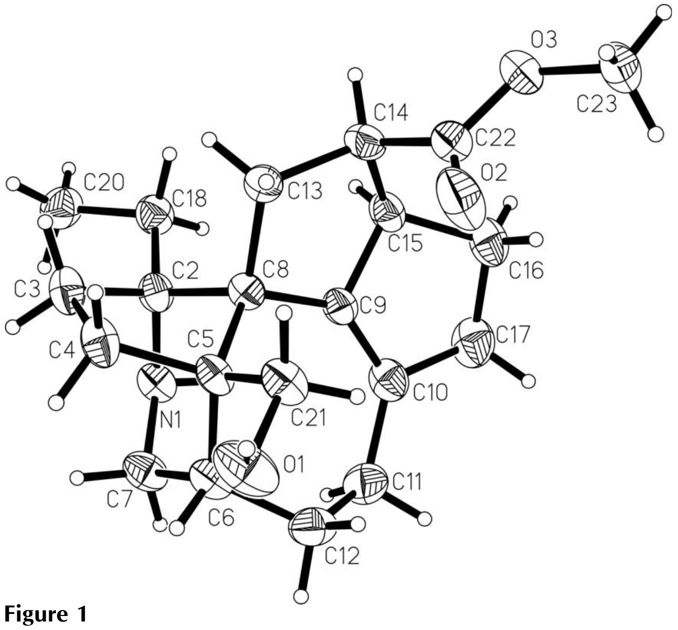


**Figure 1**
The molecular structure of molecule 1, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

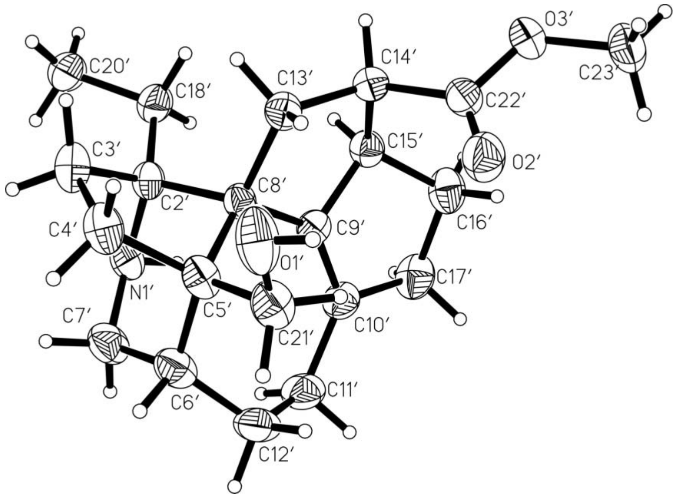


**Figure 2**
The molecular structure of molecule 2, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

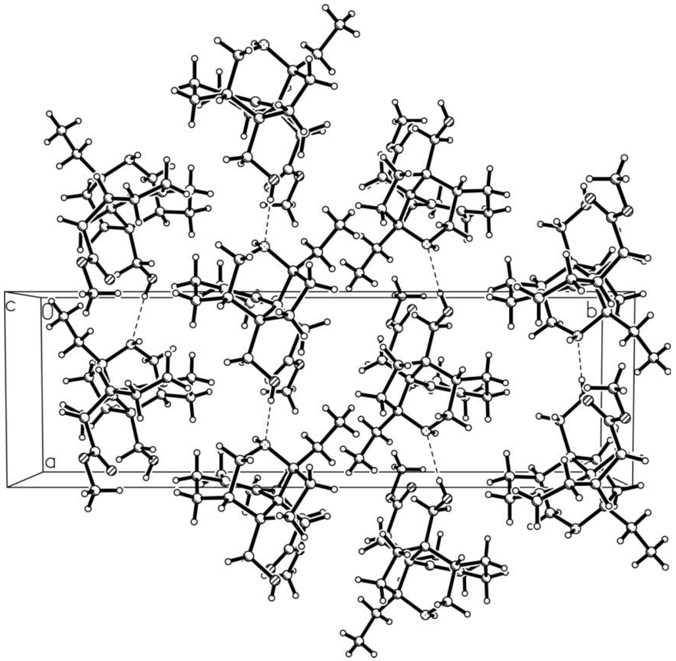


**Figure 3**
The molecular packing of the title compound, viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

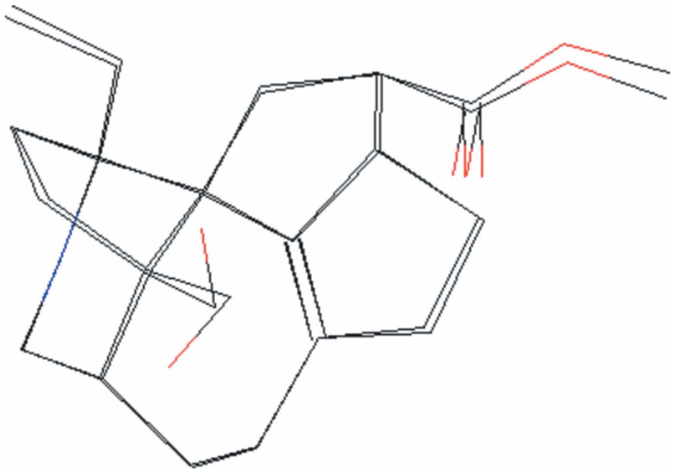


**Figure 4**
Superimposition of the two independent molecules of the title compound. H atoms have been omitted.

The six-membered heterocyclic rings adopt chair conformations. The seven-membered rings have pseudo-chair conformations with C6 above and C9 and C10 below the plane formed by atoms C5, C8, C11 and C12 for molecule 1. In molecule 2, the seven-membered rings adopt the same pseudo-chair conformations.

In the crystal structure, molecules are linked into chains along the *a* axis (Fig. 3), by intermolecular O—H···N hydrogen bonds (Table 1).

## Experimental

The fruits of *D. macropodum* (20 kg) were extracted with 90% EtOH. The crude extract was acidified with tartaric acid to pH 3 then extracted with $CHCl_3$ to remove compounds that are insoluble in water. The pH of the aqueous phase was increased to pH 10 with aqueous ammonia and extracted with $CHCl_3$ to obtain the crude alkaloid (47.0 g). This was chromatographed on silica gel eluting with $CHCl_3/CH_3OH$ (1:0 to 0:1, *v*/*v*) to give five fractions. Fraction 2 was repeatedly chromatographed on silica and further purified with Sephadex LH-20 to yield paxdaphnine B (21 mg).

### *Crystal data*

$C_{21}H_{31}NO_3$
$M_r = 345.47$
Monoclinic, $P2_1$
$a = 7.7500$ (15) Å
$b = 24.717$ (3) Å
$c = 9.605$ (2) Å
$\beta = 94.619$ (7)°
$V = 1833.9$ (5) Å$^3$

$Z = 4$
$D_x = 1.251$ Mg m$^{-3}$
Mo *Kα* radiation
$\mu = 0.08$ mm$^{-1}$
$T = 295$ (2) K
Prism, colourless
0.50 × 0.20 × 0.20 mm

**o590** Lu *et al.* • $C_{21}H_{31}NO_3$ *Acta Cryst.* (2007). E**63**, o589–o591

*Data collection*

| | |
|---|---|
| MAC DIP 2030K diffractometer | 3431 independent reflections |
| $\omega$ scans | 3019 reflections with $I > 2\sigma(I)$ |
| Absorption correction: none | $R_{\rm int} = 0.035$ |
| 10725 measured reflections | $\theta_{\rm max} = 25.4°$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0864P)^2 + 0.2863P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.052$ | $(\Delta/\sigma)_{\rm max} = 0.004$ |
| $wR(F^2) = 0.137$ | $\Delta\rho_{\rm max} = 0.16$ e Å$^{-3}$ |
| $S = 1.04$ | $\Delta\rho_{\rm min} = -0.18$ e Å$^{-3}$ |
| 3431 reflections | Extinction correction: *SHELXL97* |
| 464 parameters | Extinction coefficient: 0.134 (8) |
| H atoms treated by a mixture of independent and constrained refinement | |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$A$···N1$^{\rm i}$ | 0.82 | 2.15 | 2.937 (4) | 160 |
| O1′—H1′$A$···N1′$^{\rm ii}$ | 0.82 | 1.95 | 2.770 (4) | 177 |

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

In the absence of significant anomalous dispersion effects, Friedel pairs were merged. The amine H atoms were located in a difference Fourier map and refined freely with isotropic displacement parameters [N—H = 0.83 (5) and 0.95 (5) Å; $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N)]. All other H atoms were positioned geometrically and refined using a riding model with C—H = 0.98 Å, $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for CH, C—H = 0.97 Å, $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for CH$_2$, C—H = 0.96 Å, $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for CH$_3$ atoms and O—H = 0.82 Å, $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) for the OH groups.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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*Acta Cryst.* (2007). E**63**, o589–o591 Lu *et al.* • $C_{21}H_{31}NO_3$ **o591**