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20-*N*-Ethyl-1,8,14-trihydroxy-16β,18-dimethoxylycoctonine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.063
wR factor = 0.131
Data-to-parameter ratio = 7.8

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

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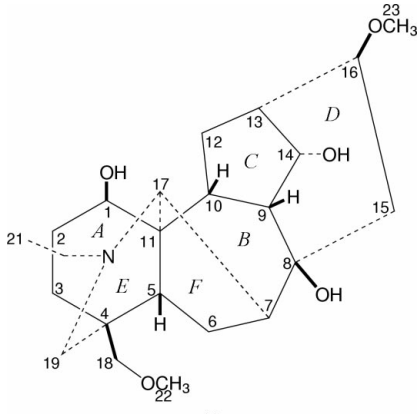
The title compound, $C_{23}H_{47}NO_5$, has been isolated from *Delphinium roylei* for the first time. The molecular architecture comprises six fused rings, *A*–*F*. The six-membered rings, *A* and *E*, are in chair conformations, while ring *D* is in a distorted boat form. The seven-membered ring *B* is in a boat form and the remaining two five-membered rings, *C* and *F*, are in envelope conformations. The crystal structure is stabilized by O—H···O, C—H···O and C—H···N interactions.

Comment

Delphinium roylei Munz. is a 50–100 cm long perennial herb found at an elevation of 2300–2800 m (Ali & Nasir, 1991). *Delphinium* (Larkspur), an important genus of the family *Ranunculaceae*, is well known for its potential uses in medicine. The genus is recognized for its poisonous constitutents, which consist of biologically active and structurally complex diterpenoid and norditerpenoid alkaloids with febrifuge, sedative, cardiotonic and analgesic activities (Benn & Jacyno, 1983, 1984). Some of the species of *Delphinium* are reported to be used as insecticides and anti-rheumatics and for the treatment of sciatica (Baytop, 1984). Recently, our research group has reported anti-epileptic activity in aqueous and acetone fractions of *Delphinium denudatum* (Raza, Shaheen, Choudhary, Rafiq *et al.*, 2001; Raza, Shaheen, Choudhary, Suria *et al.*, 2001; Raza *et al.*, 2003). During our ongoing phytochemical investigations on this plant, we have isolated and performed single-crystal X-ray diffraction studies on the title compound, also known as talatisidine, (I), which has previously been reported as being extracted from other species of the genus *Delphinium* (Pelletier *et al.*, 1967).



(I)

Compound (I) crystallizes in the space group *C*2. The bond lengths and angles in (I) show normal values (Allen *et al.*, 1987). The absolute stereochemistry could not be determined,

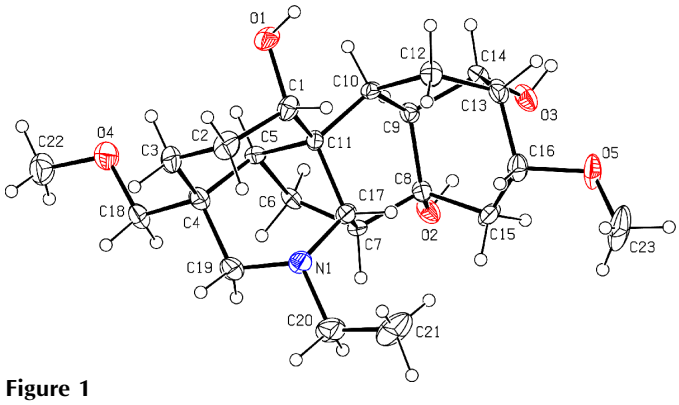


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

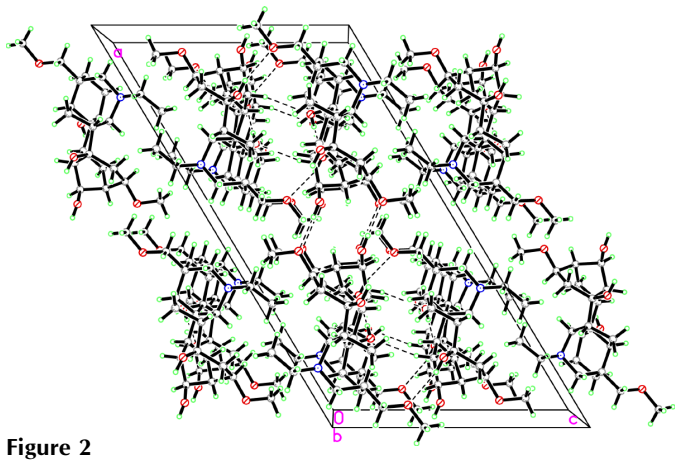


Figure 2
A view, down the *b* axis, of the molecular packing in (I). Dashed lines indicate hydrogen bonds.

as the anomalous dispersion effects are too weak. However, the absolute configuration of (I) is assumed to be the same as that reported for talatisidine by Pelletier *et al.* (1967).

The molecule of (I) has a rigid structure consisting of six main rings, *A*–*F*. In the lycoctonine nucleus of (I), the junctions of the main rings *A*/*E* and *B*/*C* are *cis* [C17—C11—C5—C4 71.8 (4)° and C8—C9—C10—C12 91.9 (4)°], while rings *A*/*B* [C6—C5—C11—C1 −169.6 (4)°] and *E*/*F* [C4—C5—C11—C10 −174.4 (4)°] are *trans* fused. The six-membered rings *A*, *D* and *E* adopt chair, distorted-boat and chair conformations, respectively. The two five-membered rings, *C* and *F*, are in envelope conformations, while the seven-membered ring *B* is found in the twisted-boat form.

Compound (I) contains *β*-oriented hydroxy and methoxymethyl substituents at C1 and C4, respectively. The tertiary hydroxy group situated at the junction of rings *B* and *D* at C8, and the methoxy group at C16 of ring *D*, are also *β*-oriented. However, the third hydroxyl group at C14 in ring *C* is *α*-oriented with respect to the *β*-methoxy substituent at C16. The sum of the angles at N1 (337.9 Å) is indicative of sp^3 character.

The packing of (I) is composed of parallel layers stabilized by four O—H···O, one C—H···N and three C—H···O interactions (Table 1).

Experimental

Air-dried and powdered aerial parts (2.0 kg) of *Delphinium roylei* Munz. were extracted exhaustively with *n*-hexane (3 × 5 l) followed by ethanol (3 × 5 l) over a period of 10 d at room temperature. The ethanolic extract was filtered and concentrated under reduced pressure to afford 166 g of dried mass. The concentrated ethanolic extract was dissolved in distilled water, acidified to pH 2.0 and extracted with dichloromethane to yield a non-alkaloidal mixture (50.0 g). The acidic extract was then basified with 10% KOH (pH 8–10) and extracted with dichloromethane to obtain an alkaloidal fraction (12.0 g). Employment of a repeated column-chromatography procedure using a type 60 (70–230 mesh) silica-gel column (Merck) and a flash (234–300 mesh) silica-gel column (Merck) afforded talatisidine, (I), after elution with petroleum ether–acetone–diethylamine (94:03:1), in 2.31 × 10^{-3}% yield (R_f = 0.43, 40% acetone–hexane + a few drops of diethylamine). Compound (I) was recrystallized from petroleum ether–acetone (1:1) as slab-shaped colourless single crystals. The melting point of (I) is 493 K, similar to the value reported by Pelletier *et al.* (1967).

Crystal data

$C_{23}H_{37}NO_5$
M_r = 407.54
Monoclinic, *C*2
a = 24.189 (7) Å
b = 7.747 (2) Å
c = 13.310 (4) Å
β = 120.943 (5)°
V = 2139.3 (10) Å^3
Z = 4
D_x = 1.265 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7164 reflections
θ = 1.8–25.0°
μ = 0.09 mm^{-1}
T = 293 (2) K
Slab, colourless
0.44 × 0.22 × 0.10 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.962, T_{max} = 0.991
5739 measured reflections
2033 independent reflections
1965 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.0°
h = −27 → 28
k = −9 → 9
l = −15 → 10

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.131
S = 1.28
2033 reflections
261 parameters
H atoms trated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 3.837P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O2^{i}	0.82	2.07	2.889 (6)	179
O2—H2O···O3	0.84 (6)	2.37 (6)	2.945 (6)	126 (1)
O2—H2O···O4^{ii}	0.84 (6)	2.36 (6)	3.130 (5)	151 (1)
O3—H3O···O5^{iii}	0.82	1.96	2.781 (6)	174
C2—H2*A*···N1	0.97	2.41	2.923 (7)	113
C6—H6*B*···O2	0.97	2.57	2.911 (7)	101
C9—H9···O1^{ii}	0.98	2.57	3.512 (7)	159
C10—H10···O1	0.98	2.40	2.770 (7)	101

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

All H atoms in (I), except for H2O, were positioned geometrically in calculated positions [C—H = 0.96–0.98 Å and O—H = 0.82 Å] and treated as riding atoms, with U_{iso}(H) constrained to be $1.5U_{eq}$ of the carrier atom for methyl and hydroxyl H atoms, and $1.2U_{eq}$(parent atom) for the remaining H atoms. Both the positional and isotropic displacement parameters of the hydroxyl H atom, H2O, were refined [O—H = 0.82 (4) Å]. The Friedel reflections were merged before the final refinement because of the absence of significant anomalous scattering effects.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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