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Key indicators

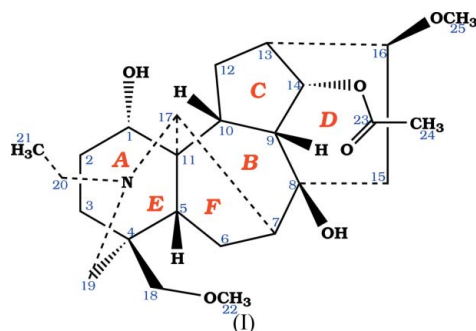
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.034
 wR factor = 0.085
Data-to-parameter ratio = 7.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.14-Acetyl-20-ethyl-1,8-dihydroxy-
16,18-dimethoxylycoctonine

The title compound ($\text{C}_{25}\text{H}_{39}\text{NO}_6$), a polycyclic diterpenoid alkaloid, has been isolated from *Delphinium roylei* Munz. Two *cis*-fused ring junctions are observed between cyclohexane *A* and piperidine *E* rings and between cyclohexane *B* and cyclopentane *C* rings. Two *trans*-fused ring junctions involve cyclohexane *A* and cyclopentane *B* rings and also piperidine *E* and cyclopentane *F* rings. Cyclopentane ring *F* is in a twist conformation, while the other cyclopentane ring, *C*, forms an envelope conformation. Piperidine ring *E* is in a chair conformation, the two cyclohexane rings *A* and *B* adopt twist–boat conformations and cyclohexane ring *D* is in a screw–boat conformation. Of the five substituents, only one is α -oriented. The molecules are packed along the *c* axis in layers parallel to the *ab* plane and stabilized by weak inter- and intramolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds.

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Comment

Delphinium roylei Munz. is a 50–100 cm tall perennial herb found at 2300–2800 m above sea level (Ali & Nasir, 1991). *Delphinium*, an important genus of the family Ranunculaceae, is well known for its medicinal properties (Benn *et al.*, 1984). The genus is recognized by its biologically active and structurally complex diterpenoid and norditerpenoid alkaloids with febrifugal, sedative, cardiotoxic and analgesic activities (Benn *et al.*, 1983). Some species of *Delphinium* are reported to be used as insecticides, antirheumatics and for the treatment of sciatica (Baytop, 1984). Recently, our research group has reported the anti-epileptic activity of aqueous extracts and acetone fractions of *Delphinium denudatum* (Raza, Shaheen, Choudhary, Sombati *et al.*, 2001; Raza, Shaheen, Choudhary, Suria *et al.*, 2001; Raza *et al.*, 2003).



During our ongoing phytochemical investigations, we have reported the single-crystal structure of talatisidine (Shaheen *et al.*, 2004). Here, we report for the first time a single-crystal X-ray crystallographic study of condelfine (I), isolated now from *D. roylei* Munz. and previously isolated from *Aconitum*

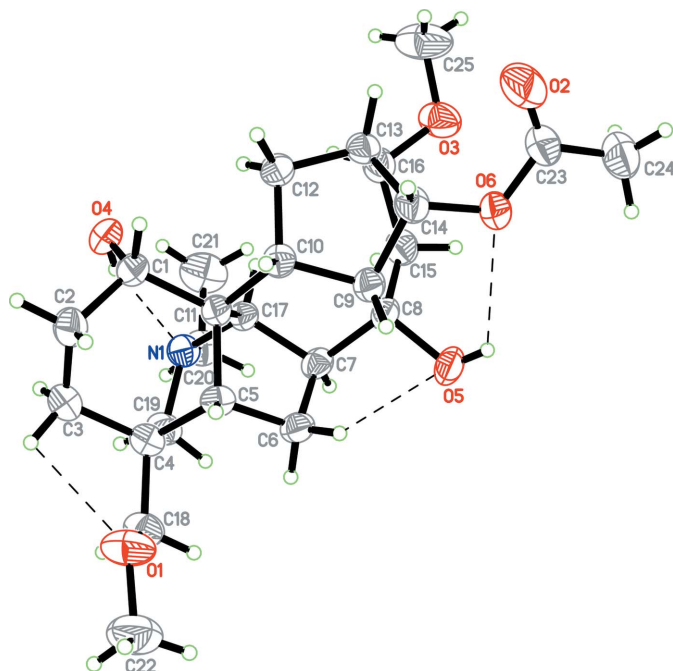


Figure 1
The structure of compound (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate hydrogen bonds.

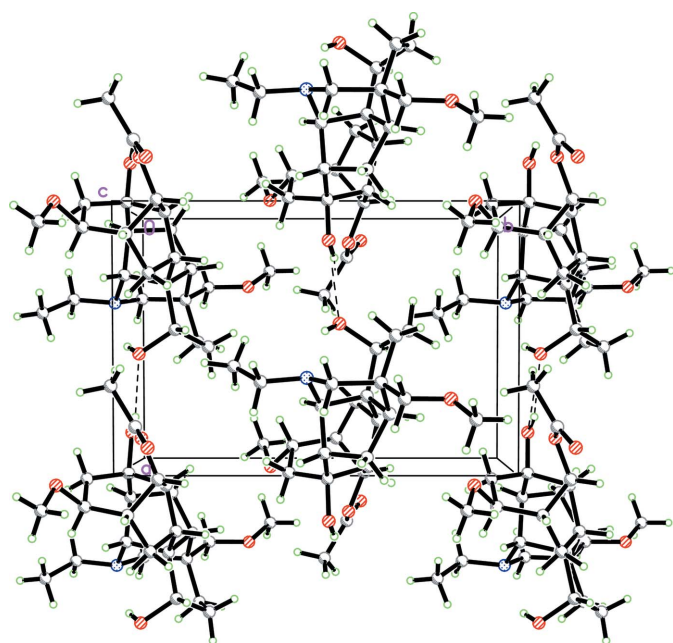


Figure 2
A view of the molecular packing in (I), down the *c* axis. Dashed lines indicate hydrogen bonds.

species (Pelletier *et al.*, 1967; Sultankhodazhaev *et al.*, 1982*a,b*; De la Fuente *et al.*, 1988). The bond lengths in (I) show normal values (Allen *et al.*, 1987). The absolute stereochemistry could not be determined as the anomalous dispersion effects are too weak. However, the absolute configuration of (I) is assumed to be the same as that reported for talatsidine (Pelletier *et al.*, 1967). The molecule of (I) has a highly rigid structure

consisting of six main rings (*A–F*). In the lycocotinine nucleus of (I), the junctions of rings *A/E* [$C4–C5–C11–C17 = -72.7 (2)^\circ$] and rings *B/C* [$C8–C9–C10–C12 = -89.6 (2)^\circ$] are *cis*-fused, while rings *A/B* [$C6–C5–C11–C1 = 167.17 (19)^\circ$] and rings *E/F* [$C4–C5–C11–C10 = 172.52 (18)^\circ$] are *trans*-fused. The five-membered ring *F* is twisted at $C17–C11$, forming a twist conformation, while the other five-membered ring *C* forms an envelope conformation; atom $C14$ deviates from the $C9/C10/C12/C13$ plane by $0.3248 (16) \text{ \AA}$.

The six-membered ring *E* forms a chair conformation. Two six-membered rings (*A* and *B*) are found in the twist-boat form [puckering amplitudes = $0.754 (2)$ and $0.637 (2)^\circ$, respectively], while six-membered ring *D* is in a screw-boat conformation [puckering amplitude = $0.693 (2)^\circ$] (Cremer & Pople, 1975). The title compound, (I), has β -oriented hydroxy, methoxymethyl, hydroxy and methoxy substituents at $C1$, $C4$ and $C16$, respectively. The acetoxy group attached to $C14$ in ring *C* is α -oriented with respect to the β -methoxy group attached to $C16$ in ring *D*. The sp^3 character of N in (I) is supported by the average of all angles at N (112.1°).

The title compound packs along the *c* axis, forming layers parallel to the *ab* plane. The molecules are stabilized by weak intramolecular $O–H \cdots N$, $O–H \cdots O$ and $C–H \cdots O$ and intermolecular $O–H \cdots O$ interactions. A pair of six-membered ring graph-set motifs (*S6*) involving $C1–O4–H1O4 \cdots N1–C17–C11–$ and $C8–O5–H1O5 \cdots O6–C14–C9–$ is generated, while $C3–H3B \cdots O1–C18–C4–$ and $C8–O5 \cdots H6A–C6–C7–$ generate another pair of five-membered ring (*S5*) graph-set motifs (Bernstein *et al.*, 1995).

Experimental

The air-dried and powdered aerial parts (2 kg) of *Delphinium roylei* Munz. were extracted exhaustively with *n*-hexane (3×5 l), followed by ethanol (3×5 l) extraction at room temperature for 10 d (3 times). The ethanol was evaporated *in vacuo*, yielding 166 g of crude extract. The ethanol extract was partitioned between CH_2Cl_2 and water at acidic, basic and neutral pH to obtain CH_2Cl_2 fractions at different pH. The CH_2Cl_2 fraction obtained at pH 10 (12 g) was subjected to silica-gel column chromatography (silica gel, 240 g) using a gradient of *n*-hexane, CH_2Cl_2 and 10% ethanol to yield 15 subfractions (F1–15). Subfraction F14 (2% MeOH, CH_2Cl_2) was purified by silica-gel column chromatography using an *n*-hexane–acetone solvent system (8:2) with 10 drops of diethylamine per 100 ml to afford compound (I) (13 mg) [yield 0.0002%, R_f 0.43, *n*-hexane–acetone (6:4) with 10 drops of diethylamine].

Crystal data

$C_{25}H_{39}NO_6$
 $M_r = 449.57$
 Monoclinic, $P2_1$
 $a = 8.9484 (12) \text{ \AA}$
 $b = 13.2080 (17) \text{ \AA}$
 $c = 9.8945 (13) \text{ \AA}$
 $\beta = 93.553 (2)^\circ$
 $V = 1167.2 (3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.279 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3947 reflections
 $\theta = 2.1–25.0^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Block, colourless
 $0.45 \times 0.20 \times 0.19 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.961$, $T_{\max} = 0.983$
 5883 measured reflections

2152 independent reflections
 2103 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -15 \rightarrow 15$
 $l = -11 \rightarrow 5$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.085$
 $S = 1.10$
 2152 reflections
 297 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.1886P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond and torsion angles ($^\circ$).

C20—N1—C19	110.04 (19)	C19—N1—C17	113.34 (18)
C20—N1—C17	113.0 (2)	C13—C14—C9	102.07 (18)
C7—C8—C9—C10	−40.1 (2)	C6—C5—C11—C1	167.17 (19)
C8—C9—C10—C12	−89.6 (2)	C9—C10—C12—C13	−1.0 (2)
C4—C5—C11—C17	−72.7 (2)	C8—C9—C14—C13	71.2 (2)
C6—C5—C11—C10	−70.0 (2)	C1—C11—C17—C7	−174.34 (17)
C4—C5—C11—C10	172.52 (18)	C17—N1—C20—C21	−65.8 (3)

Table 2

Hydrogen-bond geometry (Å , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H1O4 \cdots N1	0.81	1.9927	2.7166 (19)	148
O5—H1O5 \cdots O4 ⁱ	0.77	2.1445	2.8184 (17)	146
O5—H1O5 \cdots O6	0.77	2.5705	3.0546 (18)	123
C3—H3B \cdots O1	0.97	2.49	2.895 (3)	105
C6—H6A \cdots O5	0.97	2.52	2.868 (2)	101

Symmetry code: (i) $x + 1, y, z$.

H atoms were placed in calculated positions, with C—H distances in the range 0.96–0.98 Å. The U_{iso} values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged before the final refinement.

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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