NORDITERPENOID ALKALOIDS FROM *Delphinium cinereum*

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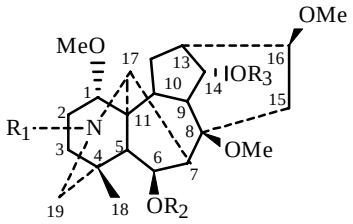
The genus *Delphinium* (Ranunculaceae) is represented by 26 species in the Flora of Turkey [1, 2].

In continuation of our investigations on Turkish *Aconitum*, *Delphinium*, and *Consolida* species [3–7] we have now studied an endemic species, *Delphinium cinereum* Boiss. There is no publication on the diterpenoid alkaloids of *D. cinereum.*

Delphinium cinereum Boiss. (Ranunculaceae) was collected near fields and roadsides in Antalya-Akseki, Turkey at an altitude 600–800 m in August 1999 and identified by one of us (H.O.) A voucher specimen is deposited in the Herbarium of Science and Literature Faculty of Suleyman Demirel University (Ozcelik 8194).

Dried and powdered aerial parts of *D. cinereum* (2.100 kg) were extracted with 90% EtOH by percolation at room temparature and the extract obtained evaporated to dryness *in vacuo*. The residue was treated with 0.5 N H_2SO_4 and extracted with $CHCl_3$. NaOH (5%) was then added to the aqueous solution (cooled in ice) to bring it to pH 10. The solution was again extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated to dryness, yielding 10 g of crude alkaloid mixture. The crude alkaloid extract was first separated by VLC on a basic Al_2O_3 (EM 1085) column with petroleum ether–$CHCl_3$–MeOH mixtures to give 26 fractions. VLC fractions 19–21 ($CHCl_3$–MeOH 99:1) were combined and chromatographed by chromatotron chromatographic separations on a Chromatotron, which were carried out on rotors coated with a 1 mm thick layer of Merck Al_2O_3 60 GF-254 (1092) or SiO_2 PF-254 (7749) on a SiO_2 rotor with petroleum ether–$CHCl_3$–MeOH mixtures, giving 64 fractions. Chromatotron fractions 33–37 (petroleum ether–$CHCl_3$ 50:50) were combined and 14-acetyl peregrine (**1**) (12 mg) and 14-methyl peregrine (**2**) (8 mg) were obtained by preparative chromatography (Si-gel; toluene–EtOAc–DEA 10:2:1).

Chromatotron fractions 38–43 (petroleum ether–$CHCl_3$ 40:60) were combined, and rechromatographed over a Si-gel column with petroleum ether–$CHCl_3$ mixtures to give peregrine (**3**) (35 mg). Chromatotron fractions 56–60 ($CHCl_3$–MeOH 98:2) were combined and peregrine alcohol (**4**) (31 mg) and *N*-deethylperegrine alcohol (**5**) (10 mg) were obtained by preparative chromatography (Si-gel; toluene–EtOAc–DEA 10:4:1).



1 - 5

1: R_1 = Et, R_2 = R_3 = Ac; **2:** R_1 = Et, R_2 = Ac, R_3 = Me
3: R_1 = Et, R_2 = Ac, R_3 = H; **4:** R_1 = Et, R_2 = R_3 = H
5: R_1 = R_2 = R_3 = H

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TABLE 1. ^{13}C NMR Data of *Delphinium cinereum* Alkaloids

Position	**1**	**2**	**3**	**4**	**5**
1	84.3 d	84.4 d	84.5 d	85.2 d	83.0 d
2	27.0 t	26.8 t	26.5 t	26.5 t	25.5 t
3	37.2 t	36.9 t	37.3 t	37.2 t	34.9 t
4	34.2 s	34.1 s	34.5 s	34.6 s	34.3 s
5	56.3 d	56.1 d	56.4 d	59.0 d	58.8 d
6	73.1 d	73.3 d	73.4 d	73.0 d	72.8 d
7	42.1 d	42.1 d	42.7 d	45.7 d	45.6 d
8	78.7 s	78.0 s	79.0 s	80.7 s	77.4 s
9	41.5 d	41.8 d	44.5 d	44.0 d	45.1 d
10	46.0 d	46.2 d	46.0 d	46.2 d	49.0 d
11	48.5 s	48.4 s	48.3 s	48.3 s	48.4 s
12	28.7 t	28.6 t	28.8 t	28.5 t	28.1 t
13	39.0 d	39.1 d	38.6 d	37.9 d	39.0 d
14	76.0 d	84.1 d	75.5 d	75.4 d	75.2 d
15	35.5 t	35.3 t	33.2 t	33.1 t	33.7 t
16	83.6 d	83.6 d	82.4 d	82.4 d	82.2 d
17	64.2 d	63.8 d	64.8 d	64.4 d	77.0 d
18	25.9 q	26.0 q	25.9 q	26.0 q	26.3 q
19	57.5 t	57.5 t	57.5 t	58.0 t	52.0 t
N-$\underline{CH_2}$-CH_3	48.9 t	49.2 t	49.5 t	49.6 t	-
N-CH_2-$\underline{CH_3}$	13.6 q	13.4 q	13.5 q	13.7 q	-
OCH_3-1	56.1 q	55.8 q	56.2 q	56.3 q	55.5 q
OCH_3-8	48.0 q	47.8 q	48.5 q	48.6 q	48.3 q
OCH_3-14	-	57.5 q	-	-	-
OCH_3-16	56.5 q	56.2 q	56.5 q	56.5 q	56.4 q
Ac-6	171.5 s	170.8 s	170.2 s	-	-
	21.7 q	21.7 q	21.5 q	-	-
Ac-14	171.5 s	-	-	-	-
	21.5 q	-	-	-	-

All the alkaloids were identified by comparison of their ^1H and ^{13}C, DEPT, and NMR data [7–11] and in some cases by Co-TLC behavior with those of authentic samples [7–10].

This is the second report for the occurrence of *N*-deethylperegrine alcohol in a plant [7]. The ^{13}C NMR data of the isolated alkaloids are shown in Table 1.

NMR spectra were recorded on a Bruker 500 MHz spectrometer. MS were determined on a Finnigan MAT 90 spectrometer.

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