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DITERPENOID ALKALOIDS OF *Delphinium schmalhausenii*

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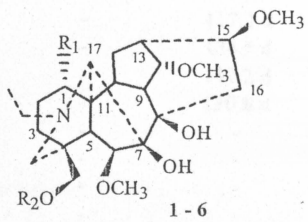
From the aerial parts of Delphinium schmalhausenii *six norditerpenoid alkaloids gigactonine, lycoctonine, anthranoyllycoctonine, delsemine A, delsemine B,* N*-acetyldelectine and a diterpenoid alkaloid septatisine were isolated.*

Key words: *Delphinium schmalhausenii*, Ranunculaceae, diterpenoid alkaloids.

Diterpenoid alkaloids are neurotoxic agents, causing bradycardia, muscle failure, hypotension, and death by respiratory arrest [1–3].

In continiation of our investigations on Turkish *Aconitum*, *Delphinium,* and *Consolida* species [4–8] we have now studied *Delphinium schmalhausenii* Alb. There is no publication on the diterpenoid alkaloids of *D. schmalhausenii* except the presence of methyllycaconitine in a sample of North Caucasus origin [9].



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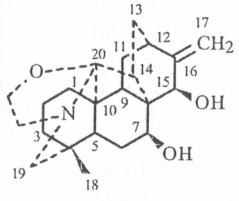

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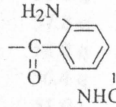
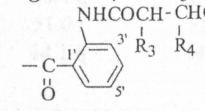
1: $R_1 = OH$, $R_2 = H$
2: $R_1 = OCH_3$, $R_2 = H$

3: $R_1 = OCH_3$, $R_2 =$



4, 5: $R_1 = OCH_3$, $R_2 =$



4: $R_3 = CH_3$, $R_4 = H$
5: $R_3 = H$, $R_4 = CH_3$

6: $R_1 = OCH_3$, $R_2 =$

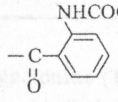


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TABLE 1. ^{13}C NMR Data of the *Delphinium schmalhausenii* Alkaloids

C atom	1	2	3	4	5	6	7
1	72.5 d	82.8 d	84.0 d	83.8 d	83.8 d	85.0 d	30.5 t
2	29.2 t	28.8 t	26.2 t	25.9 t	26.0 t	25.5 t	19.5 t
3	30.5 t	31.5 t	32.5 t	32.2 t	32.2 t	32.5 t	41.5 t
4	38.0 s	38.4 s	37.8 s	37.6 s	37.6 s	38.4 s	34.8 s
5	48.5 d	49.0 d	50.4 d	50.5 d	50.5 d	49.6 d	46.7 d
6	90.4 d	90.5 d	91.0 d	90.8 d	90.8 d	90.1 d	23.3 t
7	87.5 s	88.3 s	88.7 s	88.2 s	88.5 s	89.1 s	70.0 d
8	78.2 s	77.6 s	77.6 s	77.5 s	77.5 s	76.5 s	50.1 s
9	43.5 d	43.3 d	43.5 d	43.4 d	43.4 d	45.1 d	44.2 d
10	44.0 d	48.5 d	46.2 d	46.2 d	46.2 d	46.1 d	47.1 s
11	49.4 s	48.8 s	49.1 s	49.2 s	49.2 s	48.2 s	29.2 t
12	26.7 t	26.2 t	28.8 t	28.8 t	28.8 t	27.5 t	34.5 d
13	37.8 d	38.1 d	38.4 d	38.0 d	38.0 d	36.4 d	27.4 t
14	84.3 d	84.3 d	84.2 d	83.8 d	83.8 d	75.3 d	49.6 d
15	33.5 t	33.6 t	33.7 t	33.5 t	33.7 t	33.1 t	68.7 d
16	83.0 d	83.7 d	82.6 d	82.4 d	82.5 d	81.7 d	157.8 s
17	66.0 d	65.2 d	64.5 t	64.8 d	64.6 d	65.4 d	103.7 t
18	66.8 t	67.5 t	68.8 t	70.0 t	70.0 t	69.5 t	28.6 q
19	57.1 t	52.5 t	52.6 t	52.1 t	52.1 t	52.5 t	57.3 t
20	-	-	-	-	-	-	104.6 s
1′	-	-	110.5 s	114.8 s	114.8 s	115.1 s	-
2′	-	-	150.8 s	141.7 s	141.7 s	141.2 s	-
3′	-	-	117.2 d	120.3 d	120.5 d	120.2 d	-
4′	-	-	134.5 d	135.0 d	135.0 d	134.6 d	-
5′	-	-	117.2 d	122.5 d	122.6 d	122.5 d	-
6′	-	-	130.8 d	130.0 d	130.2 d	131.3 d	-
1″	-	-	-	173.8 s	171.0 s	169.3 s	-
2″	-	-	-	39.5 d	42.2 t	25.6 q	-
3″	-	-	-	39.1 t	36.4 d	-	-
4″	-	-	-	175.0 s	177.5 s	-	-
2″ (CH_3)	-	-	-	18.2 q		-	-
3″ (CH_3)	-	-	-	-	17.8 q	-	-
Ar-CO	-	-	167.9 s	167.8 s	168.0 s	169.2	-
OCH_3-1	-	55.8 q	55.8 q	56.0 q	55.7 q	56.0 q	-
OCH_3-6	57.3 q	57.5 q	57.8 q	57.6 q	57.9 q	57.5 q	-
OCH_3-14	57.5 q	57.8 q	58.0 q	58.2 q	58.2 q	-	-
OCH_3-16	56.5 q	56.2 q	56.4 q	56.8 q	56.4 q	56.5 q	-
N-$\underline{CH_2}$-CH_3	50.6 t	51.4 t	51.0 t	51.0 t	51.0 t	51.3 t	-
N-CH_2-$\underline{CH_3}$	13.8 q	14.2 q	14.1 q	14.1 q	14.1 q	14.3 q	-
N-$\underline{CH_2}$-CH_2-O-	-	-	-	-	-	-	51.5 t
N-CH_2-$\underline{CH_2}$-O-	-	-	-	-	-	-	61.7 t

As a result, norditerpenoid alkaloids gigactonine (**1**), lycoctonine (**2**), anthranoyllycoctonine (**3**), delsemine A (**4**), delsemine B (**5**), *N*-acetyldelectine (**6**), and diterpenoid alkaloid septatisine (**7**) were isolated from the aerial parts of *Delphinium schmalhausenii*. Methyllycaconitine could not have been isolated from this Turkish sample. The ^{13}C NMR data of the isolated alkaloids are shown in Table 1.

EXPERIMENTAL

General. NMR spectra were recorded on a Bruker, 500 MHz spectrometer. MS were determined on a Finnigan MAT 90 spectrometer. VLC was carried out with Merck Al_2O_3 (EM 1085) and SiO_2 60 G (7731). Chromatographic separations on

a Chromatotron 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). Thin layer chromatograms were run using the solvent system toluene–EtOAC–DEA (7:4:1) and $CHCl_3$–MeOH–NH_4OH (97:3:0.5or 96:4:0.5).

Plant Material. *Delphinium schmalhausenii* Alb. (Ranunculaceae) was collected on Yanlizcam mountain between Ardahan-Savsat, Turkey at an altitude 2800 m in 20.06.2002 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 9862).

Extraction and Isolation. The crude alkaloid extract (6 g) obtained from 2.250 g aerial parts was first separated by VLC on a basic Al_2O_3 column with petroleum ether–$CHCl_3$–MeOH mixtures. Gigactonine (**1**) (10 mg) was isolated from VLC fraction 17 [$CHCl_3$–MeOH (99:1)] by preparative chromatography. VLC fractions 11–12 [petroleum ether–$CHCl_3$ (50:50 to 40:60)] (420 mg) were combined and rechromatographed on a SiO_2 rotor with petroleum ether–$CHCl_3$–MeOH mixtures to give lycoctonine (**2**) (3 mg), anthranoyllycoctonine (**3**) (2 mg), *N*-acetyldelectine (**4**) (5 mg), and delsemine A (**5**) and B (**6**) in a mixture (15 mg). VLC fraction 13 [petroleum ether–$CHCl_3$ [30:70)] (476 mg) was chromatographed on a SiO_2 rotor with petroleum ether $CHCl_3$–MeOH mixtures to give septatisine (**7**) (17 mg).

All the alkaloids were identified by comparison of their ^1H and ^{13}C, DEPT NMR data, and in some cases (**1–3,7**) [10, 11] by Co-TLC behavior with those of authentic samples.

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