

NORDITERPENOID ALKALOIDS FROM *DELPHINIUM FORMOSUM*

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Key Word Index—*Delphinium formosum*; Ranunculaceae; norditerpenoid alkaloids; *N*-acetyldelectine (14-demethylajacine).

Abstract—From the aerial parts of *Delphinium formosum*, a new norditerpenoid alkaloid, *N*-acetyldelectine (14-demethylajacine), was isolated, in addition to six known compounds, lycoctonine, delsemine A, delsemine B, delectine, delcosine and anthranoyllycoctonine. The structures of the compounds were determined by spectroscopic methods.

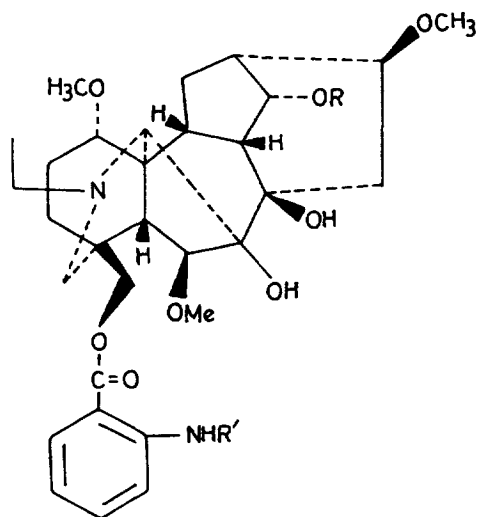
INTRODUCTION

In continuation of our studies of Turkish *Delphinium* species [1–5], we have now studied an endemic plant, *D. formosum* Boiss. et Huet. In a previous study, lycoctonine and delsemine were isolated by two of us [6]. In the present investigation, with a new collection of the plant, we have obtained one new and six known norditerpenoid alkaloids. The known compounds were established as lycoctonine, delsemine A, delsemine B, delectine (**3**) delcosine and anthranoyllycoctonine by comparing their ^1H and ^{13}C NMR data and mass spectra with those in the literature. Since the ^{13}C NMR spectrum of **3** is unpublished, it is given in Table 1, together with those of the new compound and ajacine.

RESULTS AND DISCUSSION

The ^1H NMR spectrum of the new compound (**1**) indicated a norditerpenoid alkaloid with an *N*-acetyl-anthranoyl group. Typical signals were at δ 1.07 (3H, *t*, $J = 7$ Hz, NCH_2CH_3), 3.27, 3.37 and 3.42 (each 3H, *s*, $3 \times \text{OCH}_3$) and the aromatic signals at δ 8.75 (1H, *dd*, $J = 2$ and 8 Hz, H-5'), 7.96 (1H, *br, d*, $J = 8$ Hz, H-4'), 7.48 (1H, *dt*, $J = 2$ and 8 Hz, H-3') and 7.12 (1H, *dt*, $J = 2$ and 8 Hz, H-6'). The broad singlet at δ 11.0 indicated the amide proton. The acetyl signal was at δ 2.23 (3H, *s*) and the signals at δ 4.15 (1H, *d*, $J = 11$ Hz) and 4.22 (1H, *d*, $J = 11$ Hz) (CH_2 -18) were typical of a C-18 ester residue, such as found in ajacine [7]. The HREI mass spectrum of **1** showed a molecular formula $\text{C}_{33}\text{H}_{46}\text{N}_2\text{O}_9$ (m/z 614.3339; calc. 614.3343) 14 mu less than that of ajacine, indicating a

hydroxyl group instead of a methoxyl in one of the following positions: C-1, C-6, C-14 or C-16. A literature survey showed that when there is a hydroxyl group at C-1 or C-16 the chemical shift of the methine should be *ca* δ 72–73 [8–10]. When it is placed at C-6 β it should appear at δ 77–80 and in the case of C-6 α at δ 70–71, while at C-14 the chemical shift of the methine group is at δ 75–76. The ^{13}C NMR spectrum of **1** showed the presence of a methine signal at δ 75.3,



- | | |
|---|---------------------------|
| 1 $\text{R} = \text{H}$; $\text{R}' = \text{COCH}_3$ | <i>N</i> -Acetyldelectine |
| 2 $\text{R} = \text{Me}$; $\text{R}' = \text{COCH}_3$ | Ajacine |
| 3 $\text{R} = \text{R}' = \text{H}$ | Delectine |

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Table 1. ^{13}C NMR data for compounds **1**–**3**

C	1		2	3
	^1H	^{13}C	(^{13}C NMR)	(^{13}C NMR)
1	3.06	84.0	83.9	85.0
2	2.20	26.0	26.1	25.5
3	2.50	32.3	32.2	32.3
4	—	37.8	38.2	37.9
5	2.62	43.0	43.3	42.8
6	3.96	90.6	91.0	90.4
7	—	89.0	88.6	90.5
8	—	78.0	77.5	77.3
9	1.75	50.5	50.5	50.3
10	—	43.0	37.6	36.4
11	—	50.4	49.1	48.4
12	1.50	28.9	28.6	27.5
13	3.20	46.1	46.1	45.1
14	4.02	75.3	83.9	75.3
15	2.60	33.6	33.8	33.1
16	3.20	82.6	82.6	81.8
17	4.70	65.1	64.5	65.2
18	4.15, 4.22	69.7	69.8	68.6
19	2.70, 2.80	52.2	52.5	52.5
N-CH ₂	2.70	51.1	51.0	51.2
CH ₃	1.07	14.1	14.0	14.3
Ar-CO	—	168.1	168.1	167.9
C=O	—	169.0	169.0	—
CH ₃	2.23	25.6	25.5	—
1-OMe	3.27	55.9	55.8	55.9
6-OMe	3.37	57.9	57.8	58.2
14-OMe	—	—	58.1	—
16-OMe	3.42	56.3	56.3	56.4
C-1'	—	114.6	114.5	110.4
C-2'	—	141.9	141.9	150.9
C-3'	7.58	134.9	135.0	134.4
C-4'	7.96	130.3	130.3	130.8
C-5'	8.75	120.6	120.6	116.4
C-6'	7.12	122.5	122.5	116.9

indicating that the hydroxyl group should be at C-14. The doublet signal at δ 4.02 is indicative of this group; it became a triplet ($J = 4.5$ Hz) after D_2O exchange. Other ^1H NMR signals correlated with this structure at δ 3.06 (1H, *dd*, $J = 4$ and 8 Hz, H-1 α), 3.20 (1H, *m*, H-16), 2.70 and 2.80 (each 1H, *m*, H₂-19), 3.96 (1H, *s*, H-6 α) and 2.62 (1H, *s*, H-5). The ^{13}C NMR (DEPT) spect, was also consistent with the suggested structure. When the spectral data were compared with those of ajacine (**2**) (Table 1), they were alike, but with the difference at C-14 and a small difference at C-10 due to the effect of the hydroxyl group at C-14 [11, 12]. The protons and carbons were assigned on the basis of ^1H - ^1H COSY and ^1H - ^{13}C HETCOR correlations (Table 1). Extensive NOESY spectra showed that the stereochemistry of the molecule was similar to that of **2**. Compound **1** was, therefore, *N*-acetyldelectine (14-demethylajacine).

EXPERIMENTAL

General. ^1H and ^{13}C NMR spectra were recorded on

a Bruker AM 400; 2D expts were recorded at 500 MHz. Silica gel (Merck) prep. plates were used for final purification.

Plant material. The plant was collected from the eastern Black Sea area at Trabzon-Sürmene in the Santa highlands at an altitude of 1500 m, in August 1993. A voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Marmara (Istanbul) MARE 4157.

Extraction and isolation. Dried and powdered aerial parts (1.5 kg) were extracted with EtOH by percolation and the extract evapd to dryness at 35° *in vacuo*. The residue was treated with 0.5 N H_2SO_4 and extracted with CHCl_3 . The acid soln was basified with NaOH to pH 10, extracted with CHCl_3 and the CHCl_3 extract was evapd to dryness. The crude alkaloids (1.5 g) obtained were chromatographed over basic alumina (act.1). Alkaloid mixts were further sep'd and/or purified by prep. TLC. The following compounds were isolated: lycocotnine (25 mg), delsemine A (32 mg), delsemine B (12 mg), **3** (12 mg) [13, 14], delcosine (7 mg), anthranoyllycotoxine (10 mg) and **1** (14 mg).

N-Acetyldelectine (14-demethylajacine) (1). Amorphous. $[\alpha]_D^{25} +8^\circ$ (*c* 1.0, CHCl_3). IR $\lambda^{\text{CHCl}_3} \text{ cm}^{-1}$: 3454, 2934, 2824, 1687, 1622, 1589, 1526, 1450, 1367, 1296, 1260, 1164, 1140, 1090, 948, 882, 754. ^1H and ^{13}C NMR in text and Table 1. HREIMS m/z (rel. int.): 614.3339[M]⁺ ($\text{C}_{33}\text{H}_{46}\text{N}_2\text{O}_9$) (47), 597 [M - OH]⁺ (100), 569 [597-CO]⁺ (38); 450 [M - $\text{C}_9\text{H}_8\text{O}_3$]⁺ (30), 420 [450-OMe]⁺ (25), 358 (8), 234 (10), 180 (70), 162 (98), 138 (7), 120 (8).

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