

NORDITERPENE ALKALOIDS FROM *Delphinium cuneatum*E. D. Khairitdinova,<sup>1</sup> E. M. Tsyrlina,<sup>1</sup> L. V. Spirikhin,<sup>1</sup>  
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UDC 547.944/945

A mixture of two new norditerpene alkaloids consisting of two regioisomers was isolated from the total alkaloids of *Delphinium cuneatum* roots. Their structures were proposed as 16-demethoxydelavaine (**2a** and **b**) on the basis of PMR, <sup>13</sup>C NMR, IR, and mass spectra.

**Key words:** *Delphinium cuneatum*, roots, norditerpene alkaloids.

Roots of *Delphinium cuneatum* collected on Belebeev plateau (Bashkortostan, Aslykul/Kandrykul area, flowering phase) were studied. We have previously reported the isolation from this plant of the new alkaloid 16-demethoxymethyllycaconitine (**1**) [1].

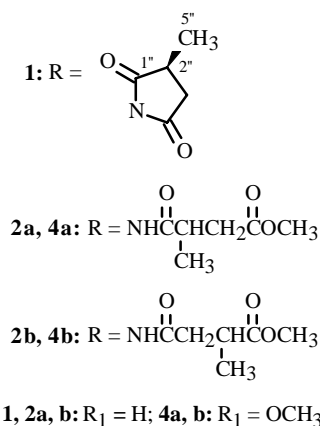
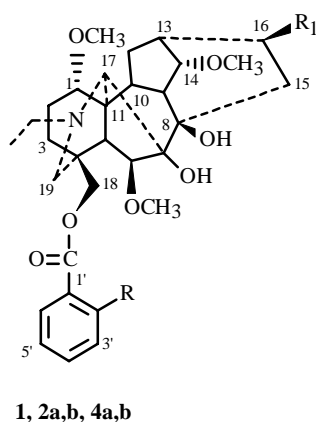
A second base (**2**) that has not been previously described in the literature was isolated during further work on alkaloid separation. The mass spectrum of **2** gave a peak for the molecular ion at 684 [M]<sup>+</sup>. According to IR spectra, **2** contains an ester (1720 cm<sup>-1</sup>) and amides (1540 and 1590 cm<sup>-1</sup>). Alkaline hydrolysis of **2** produced aminoalcohol **3**, the spectral properties (PMR and <sup>13</sup>C NMR) of which were identical to those described earlier for 16-demethoxylycoctonine, the product of alkaline hydrolysis of **1** [1].

Thus, **1** and **2** differed by the substituent on C18.

The PMR spectrum of **2** exhibited two doublets at 1.29 and 1.35 ppm (*J* = 6.9 Hz) and singlets for two ester methoxyls at 3.69 and 3.72 ppm. The aromatic protons resonated at 7.12–8.74. Signals that could be assigned to NHCO protons appeared at very weak field (11.05 and 11.18 ppm).

The <sup>13</sup>C NMR spectrum using JMODCH for **2** gave signals belonging to the C-18 substituent, some of which were doubled such as 114.6/114.7, 141.6/141.8, 51.8/52.0, and 17.9/17.1 ppm. The region characteristic of carbonyl C contained four singlets at 169.9, 172.5, 174.1, and 176.0 ppm (Table 1).

The spectral data suggested that **2** was a pair of isomers **2a** and **2b**, which could be formed from **1** by cleavage of N–C(1'') and N–C(4'') bonds of the succinimide ring with further methoxylation of the corresponding decomposition products. Base **2** might have been formed also from **1** during isolation of the alkaloids.



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TABLE 1. Chemical Shifts in  $^{13}\text{C}$  NMR Spectra of 16-Demethoxymethyllycaconitine (**1**), 16-Demethoxydelavaine (**2**), and Delavaine (**4**) [2] ( $\delta$ , ppm)

Atom	$\delta$ , ppm			Atom	$\delta$ , ppm		
	1	2 (a, b)	4 (a, b)		1	2 (a, b)	4 (a, b)
C-1	83.1	83.0	83.9	$\underline{\text{CH}_3}\text{-CH}_2\text{-N}$	14.2	14.2	14.0
C-2	25.5	25.5	26.1	$\text{CH}_3\text{-}\underline{\text{CH}_2}\text{-N}$	51.1	51.1	50.9
C-3	32.2	32.2	32.3	$\text{C}_1\text{-OCH}_3$	56.0	56.1	55.7
C-4	37.8	37.9	37.7	$\text{C}_{14}\text{-OCH}_3$	58.5	58.5	58.1
C-5	43.0	43.1	43.4	$\text{C}_{16}\text{-OCH}_3$			56.3
C-6	90.9	90.9	91.1	$\text{C}_6\text{-OCH}_3$	57.3	57.3	57.8
C-7	89.8	89.9	88.6	$\text{C=O}$	164.2	168.1	168.1
C-8	77.6	77.6	77.5	C-1'	127.1	114.6/114.7	114.7/114.8
C-9	50.7	50.8	50.7	C-2'	133.0	141.6/141.8	141.7/141.9
C-10	46.3*	46.3	46.2	C-3'	129.3	120.6	120.8
C-11	48.9	48.9	49.1	C-4'	133.6	134.9	134.9
C-12	29.1	29.1	28.8	C-5'	131.1	122.5	122.6
C-13	31.9	31.8	38.2	C-6'	130.0	130.4	130.3
C-14	84.9	84.4	84.0	C-1''	179.8	172.5/176.0	172.4/175.9
C-15	25.4	25.4	33.9	C-2''	35.3	39.0/35.8	39.1/35.9
C-16	22.6	22.6	84.6	C-3''	37.0	37.5/41.4	37.5/41.5
C-17	64.9	64.9	64.6	C-4''	175.8	174.1/169.9	174.1/169.9
C-18	69.6	69.7	69.9	C-5''	16.4	17.9/17.1	17.9/17.1
C-19	52.5	52.5	52.5	$\text{OCH}_3$		51.8/52.0	51.7/51.9

The alkaloid delavaine (**4**) has been reported [2]. It is also a mixture of two isomers that differ from **2** by the presence of a C16 methoxy. Thus, **2** is 16-demethoxydelavaine.

## EXPERIMENTAL

IR spectra were recorded on UR-20 and Specord M80 spectrometers in mineral oil. Mass spectra were obtained on Varian Mat-CH5 and MX-1310 mass spectrometers by matching peaks with ionization energy 70 eV. PMR and  $^{13}\text{C}$  NMR spectra were recorded in Bruker AM-300 and Bruker AMX-III 300 instruments in  $\text{CDCl}_3$  with TMS internal standard.

Total alkaloids isolated by aqueous acetone extraction were divided by base strength into two large fractions: moderately basic (**A**, pH 10) and strongly basic (**B**, pH 12), which in turn were separated into narrower fractions: **A**, pH 6, 7, 9, 12; **B**, pH 6, 7, 9, 12.

**16-Demethoxydelavaine (2a and 2b).** Part of the strongly basic total alkaloids pH 6 (**B**) (0.3 g) was chromatographed over an  $\text{SiO}_2$  column (40/100) with elution by benzene:methanol with methanol concentration increasing from 0.5 to 10% by volume. Effluents containing 3% methanol isolated **2** (0.011 g). Mass spectrum (EI, 70 eV,  $m/z$ ,  $I_{\text{rel}}$ , %): 684 (23)  $[\text{M}]^+$ , 669 (25), 653 (100).

PMR spectrum ( $\text{CDCl}_3$ ,  $\delta$ , ppm, J/Hz): 1.09 (3H, t,  $J = 7.0$ ,  $\underline{\text{CH}_3}\text{-CH}_2\text{-N}$ ), 1.29 and 1.35 (3H, both d,  $J = 6.9$ , H-5''), 3.30, 3.40, 3.43 (3H each, all s,  $3\times\text{OMe}$ ), 3.48 (1H, t,  $J = 4.2$ , H-14), 3.69 and 3.72 (3H, both s,  $2\times\text{OMe}$ ), 3.88 (1H, s, H-6), 4.19 (2H, s, H<sub>2</sub>-18), 7.12, 7.57 (1H each, both d,  $^3J = 7.6$ , H-3', H-6'), 8.00, 8.74 (1H each, both t,  $^3J = 7.6$ , H-4', H-5'), 11.05 and 11.18 (1H, both s, NHCO).

**16-Demethoxylycoctonine (3).** A solution of **2** (0.011 g) in methanol (5 mL) was treated with KOH in methanol (5 mL, 5%) with heating (50°C) on a magnetic stirrer for 2 h until starting **2** disappeared (TLC monitoring). Methanol was removed in a rotary evaporator. The solid was treated with water and extracted with benzene (6 $\times$ 5 mL). The extract was evaporated to afford **3** (0.006 g, quantitative yield).

## ACKNOWLEDGMENT

The work was supported financially by the Foundation for Individual Support of Leading Scientists and Science Schools (grant No. 00-15-97325).

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