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ALKALOIDS FROM TWO SPECIES OF THE GENUS *Aconitum*

S. K. Usmanova,[1,2*] Chen Li,[1] H. A. Aisa,[1] and R. Shakirov[2]

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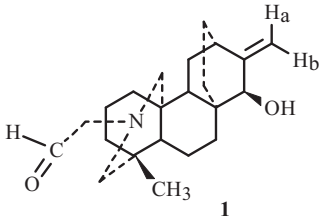
We investigated the aerial part of *Aconitum leucostomum* Worosch collected in the Altai Mountains of Xinjiang–Uyghur Autonomous Region of the PRC. Extraction by $CHCl_3$ of the aerial part of the plant (2.9 kg) afforded total bases (13.26 g, 0.45%). Part of the total alkaloids (6.7 g, pH 6) was chromatographed over a column of Al_2O_3 with elution by hexane:acetone (5:1, 1:1), $CHCl_3$, and $CHCl_3$:MeOH (5:1, 1:1). The first hexane:acetone effluents afforded lappaconitine (2.09 g) and *N*-deacetyllappaconitine (0.13 g). Part of the total bases (6.36 g, pH 10) was chromatographed over a column of Al_2O_3 with elution by hexane:acetone (5:1, 1:1), acetone, and acetone:MeOH (10:1, 5:1, 1:1). The hexane:acetone effluents afforded lappaconitine (1.16 g) and ranaconitine (0.06 g). Base **1** (0.04 g), mp 234°C, was isolated from the acetone fractions.

In continuation of the investigation of the alkaloid composition of *A. septentrionale* (Ranunculaceae) roots collected in the Russian Federation in the Republic of Bashkortostan, we chromatographed the mother liquor of lappaconitine (64 g) over a column of silica gel (290 g) [1]. The column was eluted with $CHCl_3$ and $CHCl_3$:MeOH (100:1, 50:1, 25:1) A total of 460 100-mL fractions was collected.

Work up of the initial $CHCl_3$ effluents (fractions 1–5) with acetone separated lappaconitine (2.66 g), mp 216–218°C; of subsequent fractions (6–35), *N*-deacetyllappaconitine (0.18 g), mp 208–211°C. The $CHCl_3$:MeOH effluents (100:1) (fractions 131–151) were worked up with acetone:EtOH to afford sepaconitine (0.06 g), mp 253–255°C. The $CHCl_3$:MeOH effluents (50:1) (fractions 190–206) were rechromatographed over a column of silica gel. Elution by $CHCl_3$ and $CHCl_3$:MeOH (50:1) isolated songorine (0.02 g), mp 201–203°C. Then, $CHCl_3$:MeOH (25:1) gave fractions 385–425 that were rechromatographed over a column of silica gel with elution by $CHCl_3$:MeOH (50:1 and 25:1). Fractions of 10 mL were collected. Fractions that were identical with respect to R_f were combined and worked up with EtOH to isolate **1**, $C_{22}H_{33}NO_2$, mp 236°C (EtOH).



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Base **1** was insoluble in acetone, MeOH, and EtOH; slightly soluble in $CHCl_3$ and Py; and soluble in DMSO. Its IR spectrum (mineral oil) exhibited absorption bands at 3375 (OH), 3066, 1651, 893 (=CH_2), 2910 and 1678 cm^{-1} (CHO). The mass spectrum (EI-MS) showed peaks for ions with *m*/*z* 343 (72%) $[M]^+$, 342 (100) $[M - 1]^+$, 328 (12.8) $[M - CH_3]^+$, 314 (6.4) $[M - CHO]^+$, 300 (12.8) $[M - COCH_3]^+$, 257 (12.80), 241 (28), 186 (34), 159 (19.4), 105 (21), 91 (29), 55 (32), 41 (38). The mass spectral fragmentation of **1** was identical to that of chellespontine [2] with the exception of the intensity of several peaks. Because a sample of chellespontine was not available for direct comparison with **1**, we used its spectral data (PMR, ^{13}C NMR, HSQC, HMBC) (Table 1). According to the data, **1** did not contain resonances for methoxyls and acetoxyls characteristic of norditerpenoid alkaloids. The data indicated that **1** was a C_{20} atisane-type diterpenoid alkaloid [2]. The ^{13}C NMR spectrum exhibited resonances for 22 C atoms. Of these, three were quaternary methyl, formyl, and terminal methylene groups. The PMR spectrum of **1** had a resonance at δ 3.53 ppm for a proton geminal to a secondary hydroxyl. The resonance of this proton in the HSQC spectrum correlated with the resonance of the C atom at 73.65 (C-15).

1) Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences of the P. R. of China, No. 40-1, Beijing South Road, Urumqi, China, 830011, e-mail: haji@ms.xjb.ac.cn; 2) S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax: (99871) 120 64 75; e-mail: skusmanova@mail.ru. Translated from *Khimiya Prirodnykh Soedinenii*, No. 1, pp. 135–136, January–February, 2011. Original article submitted June 14, 2010.

Table 1. PMR (599.95 MHz), ^{13}C NMR (150.87 MHz), and HMBC Spectra of Base **1** (DMSO-d_6, δ, ppm, TMS, J/Hz) and ^{13}C NMR Spectrum of Chellespontine (C_5D_5N) [2]

C atom	Chellespontine	Base **1**		
	δ_C	δ_C	δ_H	HMBC
1	25.9	24.7	1.42 (1H, m)	
2	19.8	18.5	1.54 (1H, m)	
3	41.4	40.0	1.61 (1H, m)	
4	33.4	32.7		
5	44.9	43.9	1.25 (1H, d, J = 12.6)	C-4, C-7, C-10
6	19.4	18.8	1.04 (1H, m)	C-10, C-4, C-7, C-8
			1.61 (1H, m)	
7	35.0	34.0	1.47 (1H, m)	
			1.86 (1H, br.d, J = 12.6)	
8	38.1	36.8		
9	40.1	38.8	2.07 (1H, t, J = 8.7)	C-22, C-10, C-8, C-1, C-13
10	46.4	45.2		
11	31.0	30.1	1.02 (1H, t, J = 3.6)	C-10, C-5, C-8, C-13, C-15
			1.77 (1H, dt, J = 14.4, 3.6)	
12	36.3	35.0	2.32 (1H, br.s)	
13	25.9	24.8	1.42 (1H, m)	
14	28.1	26.9	1.72 (1H, d, J = 9.0)	C-10, C-12, C-13, C-8, C-15, C-16
15	75.0	73.6	3.53 (1H, d, J = 6.0)	C-16, C-17, C-10,C-8, C-11, C-13
16	156.4	155.2		
17	109.5	108.9	4.99, 4.95 (1H each, s)	C-12, C-15, C-16
18	24.7	24.2	0.96 (3H, s)	C-20, C-5, C-3, C-4
19	59.5	56.8	3.88, 3.79 (1H each, m)	
20	58.3	58.1	3.73 (2H, br.s)	C-22, C-10, C-5, C-3, C-4, C-7
21	64.5	63.1	4.17 (2H, t, J = 4.5)	C-22, C-20, C-19,
22	183.5	181.4	8.76 (1H, br.s)	C-21, C-20, C-10

The resonance of H-15 in the HMBC spectrum indicated through-space ^1H–^{13}C coupling with resonances for atoms at 155.2 (C-16), 108.93 (C-17), 36.86 (C-8), 38.79 (C-9), 45.20 (C-10), 30.11 (C-11), and 24.8 (C-13). A group of resonances at 155.2 (C-16) and 108.9 (C-17) was characteristic of a 17-exomethylene. Moreover, the chemical shift of the resonance at 155.2 ppm (C-16) was indicative of the presence of a hydroxyl on C-15 [3]. Based on these data, the hydroxyl was located on C-15 and had the β-orientation.

The resonance for H-22 (CHO group) at 8.76 ppm in the HSQC spectrum correlated with the resonance of the C atom at 181.4 (C-22) and showed through-space ^1H–^{13}C coupling with resonances for atoms at 63.11 (C-21), 58.1 (C-20), and 45.20 (C-10). This was consistent with the presence of an N–CH_2–CHO group [4, 5]. Through-space ^1H–^{13}C coupling of the resonance for the tertiary methyl protons at 0.96 (3H, s) and resonances for atoms at 32.7 (C-4), 40.0 (C-3), 43.9 (C-5), and 58.1 (C-20) confirmed that an 18-methyl was present.

Thus, based on the presented spectral data (IR, mass, PMR, ^{13}C NMR, HSQC, HMBC), base **1** had the same structure as chellespontine, which was isolated previously from *Consolida hellespontica* (Boiss.) [2]. Chellespontine was isolated for the first time from the studied plant species.

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