LEUCONINE — A NEW ALKALOID FROM Aconitum leucostomum AND A. septentrionale

V. A. Tel'nov and S. K. Usmanova

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A new alkaloid — leuconine — has been isolated from the epigeal parts of Aconitum leucostomum and A. septentrionale, and its structure has been established on the basis of spectral characteristics.

Continuing an investigation of the alkaloids of Aconitum leucostomum [1] and A. septentrionale (A. lycoctonum) [2], we have isolated a new alkaloid with the composition $C_{23}H_{35}NO_5$, mp 195-197°C, which we have called leuconine (I).

The IR spectrum of (I) showed absorption bands of a hydroxy group at 3460 cm^{-1} and of a carbonyl in a five-membered ring at 1740 cm^{-1}.

The PMR spectrum of leuconine contained the signals of the following protons: of the methyl of an N-ethyl group at 1.01 ppm (3H, t, J = 7.5 Hz), of three methoxy groups at 3.25 and 3.32 ppm (singlets, 6H and 3H, respectively), and of a single proton at 3.65 ppm (1H, t, J = 4.5 Hz).

The mass spectrum of (I) was characteristic for norditerpene alkaloids. The maximum peak was that of the $(M - 31)^+$ ion resulting from the splitting out of a methoxy group from C-1 [3].

The ^{13}C NMR spectrum of leuconine contained 22 signals: 3 singlets, 9 doublets, 6 triplets, and 4 quartets. The assignment of the signals was made on the basis of the ^{13}C NMR spectrum of (I) under the conditions of complete and incomplete suppression of carbon-proton interactions and a comparison of the results obtained with literature information on the ^{13}C NMR spectra of norditerpene alkaloids.

The presence in the mass spectrum of leuconine of $(M - 31)^+$ as the maximum peak and also that of a one-proton signal at 3.65 ppm with a SSCC of 4.5 Hz (βH—C-14) in its PMR spectrum permitted two of the methoxy groups to be placed at C-1 and C-14 [3, 4]. In the ^{13}C NMR spectrum of leuconine these carbon atoms were revealed in the form of a doublet at 84.9 ppm.

As mentioned above, the alkaloid contained a carbonyl group in a five-membered ring, which must have been located at C-6. This was confirmed by the ^{13}C NMR spectrum of (I), where a signal was seen in the form of a doublet at 56.8 ppm from the C-5 carbon atom, which resonates in this region when there is a carbonyl group in the α-position with respect to it [5].

In the ^{13}C NMR spectra of the norditerpene alkaloids a cyclic ketone usually resonates in the 211-217 ppm region. In the ^{13}C NMR of leuconine this signal was observed at 222.6 ppm, and there was the signal of a quaternary carbon atom in the form of a singlet at 85.0 ppm. Such a downfield shift of the carbonyl signal could be explained if there was a hydroxy group in a vicinal position to it. In its turn, the C-7 carbon atom experienced an upfield shift. The presence of the signal in the form of a singlet at 85.0 ppm excludes the presence of the hydroxy group at C-4, C-8, C-9, C-10, or C-13 [5].

The presence in the ^{13}C NMR spectrum of signals at 83.2 and 56.3 ppm permitted the remaining methoxy group to be placed at C-16. It followed from what has been said above that there was no carbon- or oxygen-containing substituent at C-4, but there was hydrogen, as was confirmed by a comparison of the ^{13}C NMR spectrum with the ^{13}C NMR spectra of aconosine and of episcopalitine [5].

Institute of Chemistry of Plant Substances, Uzbekistan Academy of Sciences, Tashkent.
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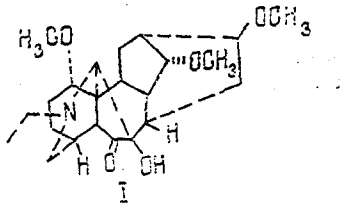
Leuconine is the third norditerpene alkaloid in which there is no oxygen substituent at C-8 [6], and it has the structure (I).



I

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument (KBr tablets), mass spectra on a MKh-1310 mass spectrometer fitted with a system for direct introduction into the ion source, and PMR spectra on a JNH-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard (values given on the δ scale). ^{13}C NMR spectra were taken on a CFT-20 spectrometer (Varian) in deuterochloroform. Chemical shifts are given relative to the internal standard TMS.

For TLC we used KSK silica gel (0–45 mesh) and alumina "for chromatography" (0-80 mesh). Solvent systems: chloroform–methanol (20:1), and chloroform–benzene–methanol (15:5:0.5).

For column chromatography we used deactivated alumina "for chromatography" and KSKG silica gel.

Melting points are uncorrected.

Leuconine from the Epigeal Part of Aconitum leucostomum). The mother solution (63.4 g) after the isolation of lappaconitine was separated according to basicity. Fractions 1-3 [4.15 g, pH 7, hexane–ether (1:1)] were chromatographed on deactivated alumina (1:50) with elution by ether and the collection of 25-ml fractions. Fractions 5-9 (0.58 g), identical according to TLC, were rechromatographed on KSKG silica gel with elution by hexane–acetone (4:1, 3:1, and 2:1). Fractions 11-15 yielded base (I) with mp 192-194°C which, after recrystallization from hexane–acetone (4:1) had mp 195-197°C. Yield 0.21 g.

Mass spectrum, m/z (I, %): M^+ 405 (22%), 390 (5.6), 374 (100), 362 (26.8), 346 (32.1). M(HRMS): 405.1207.

^{13}C NMR spectrum, ppm: C_1 – 84.9, C_2 – 26.3, C_3 – 30.0, C_4 – 35.0, C_5 – 56.8, C_6 – 222.6, C_7 – 85.0, C_8 – 39.1, C_9 – 40.2, C_{10} – 46.0, C_{11} – 44.8, C_{12} – 29.0, C_{13} – 35.8, C_{14} – 84.9, C_{15} – 23.0, C_{16} – 83.2, C_{17} – 62.4, C_{19} – 51.1, $N–CH_2–CH_3$ – 49.5 and 14.1, C_1' – 56.2, C_{14}' – 57.6, C_{16}' – 56.3.

Leuconine from Wolfbane Aconite (A. septentrionale or lycoctonum). A similar treatment of the mother solution (114 g) of the total alkaloids of wolfbane aconite after the isolation of lappaconitine gave a base with mp 193-195°C (0.3 g) which was identified as leuconine on the basis of spectral characteristics (IR, mass, PMR) and a direct comparison.

LITERATURE CITED

1. V. A. Tel'nov, M. S. Yunusov, N. D. Abdullaev, and M. G. Zhamierashvili, Khim. Prir. Soedin., 556 (1988).
2. S. K. Usmanov, V. A. Tel'nov, M. S. Yunusov, N. D. Abdullaev, A. I. Shreter, and G. B. Filippova, Khim. Prir. Soedin., 879 (1987).
3. M. S. Yunusov, Ya. V. Rashkes, V. A. Tel'nov, and S. Yu. Yunusov, Khim. Prir. Soedin., 515 (1969).
4. M. S. Yunusov and S. Yu. Yunusov, Khim. Prir. Soedin., 90 (1970).
5. S. W. Pelleter, Alkaloids: Chemical and Biological Perspectives, Wiley Interscience, New York, Vol. II (1984), pp. 209-213, 271, 362.
6. V. Liang, H. K. Desai, B. S. Joshi, and S. W. Pelletier, Heterocycles, 31, 1889 (1990).