perature. The reaction mixture was acidified and was again left for 2 days. The acid solution was extracted with chloroform. The residue obtained after the chloroform had been distilled off was shown by TLC in systems 2, 3, 7, and 9, to contain glycoperine.

SUMMARY

The first bioside of the furanoquinoline series – haplosinine, which has the structure of haplopine 7-O-[O-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranoside – has been isolated from the epigeal part of Haplophyllum perforatum.

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SEPACONITINE – A NEW ALKALOID FROM Aconitum septentrionale

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The structure of a new alkaloid sepaconitine isolated from the epigeal part of Aconitum septentrionale has been established on the basis of spectral characteristics.

Aconitum septentrionale Koelle (wolfbane monkshood) is a plant that is widely distributed on the territory of the RSFSR [1].

We have investigated the epigeal part of A. septentrionale gathered before the beginning of budding in the Moscow, Yaroslavl', and Vladimir Oblasts in May, 1983.

The total amount of alkaloids in this period was 0.32% of the weight of the air-dry raw material.

Separation of the mixture of bases yielded lappaconitine [2, 3] and a new base with the composition $C_{30}H_{42}N_2O_8$, mp 250-253°C, $[\alpha]_D^{20}$ +25° (c 0.60; chloroform) which we have called sepaconitine (II).

The IR spectrum of (II) contained absorption bands at (cm^{-1}) 1690 (carbonyl of an aromatic acid ester) and at 1596, 1260, 1247, 1170, and 760 (1,2-substituted aromatic ring).

The PMR spectrum of the base contained the signals of the methyl radical of an ethyl group at 1.08 ppm (3 H, t, J = 7 Hz), of three methoxy groups at 3.27, 3.28, and 3.38 ppm (singlets, 3 H each), and a one-proton doublet at 3.73 ppm (J = 5 Hz), together with the signals of four aromatic protons in the weak-field region at 6.55-7.68 ppm.

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TABLE 1. Chemical Shifts of the Carbon Atoms in the ^{13}C NMR Spectra of Sepaconitine (II), Lappaconitine (I), N-Deacetyllappaconitine (IV), Finaconitine (V), Ranaconitine (VI), and the Amino Alcohol of Sepaconitine (III)

C	II	I	IV	V	VI	III
1	78,1	84,2	83,2	77,1	83,5	78,7
2	26,7	26,2	26,3	26 5	26,5	26,8
3	31,9	31,9	32,1	31,5	31,6	37,3
4	83,1	84,7	84,5	84,6	84,4	71,2
5	44,7	48,6	48,9	44,0	51,5	46,8
6	24,5	26,8	26,9	32,9	32,5	24,0
7	47,1	47,6	47,7	76,6	85,7	47,1
8	74,8	75,6	75,8	84,9	77,9	77,8
9	79,8	78,6	78,7	79,5	78,4	79,9
10	79,1	49,0*	49,1*	78,5	36,6	79,1
11	56,4	51,0	51,0	57,0	51,4	56,3
12	37,6	24,2	24,1	37,1	25,9	37,7
13	34,8	36,4*	36,5*	34,8	49,8	34,7
14	88,0	90,2	90,4	87,7	90,0	88,0
15	44,9	44,9	44,9	37,6	37,8	44,8
16	83,0	82,9	83,1	82,7	82,9	83,0
17	61,6	61,5	61,7	64,3	63,1	61,8
18	—	—	—	—	—	—
19	55,9	55,5	55,8	55,1	55 2	58,0
N—CH_2	48,9	49,9	50,0	51,0	48,7	49,0
CH_3	13,5	13,5	13,6	14,5	14,4	13,5
C-1′	56,2	56,5	56,5	55,9	56,3	56,2
C-14′	58,1	57,9	58,0	57,9	58,0	58,0
C-16′	56,2	56,1	56,2	56,3	56,3	56,2
NHC=O	—	169,5	—	169,3	169,5	—
CH_3	—	25,6	—	25,5	25,6	—
H_4C_6—C=O	167,4	167,7	167,7	167,4	167,7	—
1″	112,1	115,9	112,2	115,8	115,9	—
2″	150,6	141,8	150,7	141,6	141,8	—
3″	116,3	120,4	116,8	129,3	120,4	—
4″	133,9	134,6	134,0	134,4	134,6	—
5″	116,9	122,6	116,4	122,5	122,6	—
6″	131,9	131,3	131,8	131,0	131,3	—

*See [6].

The mass spectrum of sepaconitine was similar to those of diterpene bases of the C-18 series (lappaconitine, N-deacetyllappaconitine, etc.) esterified at a C-4 hydroxy group. In all these cases, the maximum peak corresponded to the ejection of a molecule of the acid from the molecular ion.

In the mass spectrum of (II) the peak of the $(M - 137)^+$ ion was the maximum and corresponded, as in the mass spectrum of N-deacetyllappaconitine, to the ejection of anthranilic acid.

The alkaline hydrolysis of (II) yielded an amino alcohol $C_{23}H_{37}NO_7$ (III), mp 110-112°C, and an acid with mp 144-145°C, which was identified from its IR spectra and by a direct comparison as anthranilic acid.

In the high-mass region, the mass spectrum of (III) was practically identical with that of lappaconine [3], differing from the latter by a displacement of the peaks by 16 mass units. The maximum peak was that of the $(M - 31)^+$ ion resulting from the ejection of a methoxy group from C-1 [4].

The PMR spectrum of (III) contained the signals from the methyl radical of an N-ethyl group at 1.05 ppm (3 H, t, J = 7 Hz) and from three methoxy groups at 3.25 ppm (6 H, s), and 3.36 ppm (3 H, s).

The ^{13}C NMR spectrum of sepaconitine taken in deuterochloroform contained 30 signals. The assignment of the signals was made on the basis of the ^{13}C NMR spectrum under conditions of complete and incomplete suppression of carbon-proton interactions and from a comparison of the results obtained with the ^{13}C NMR spectra of dieterpene alkaloids of the C-18 series: lappaconitine (I), N-deacetyllappaconitine (IV), finaconitine (V), and ranaconitine (VI) [5].

In the off-resonance spectrum of sepaconitine five singlets of quaternary carbon atoms were observed.

The signal of the C-11 quaternary carbon atom, having no oxygen-containing substituents, was present in the 51.0-52.4 ppm region of the ^{13}C NMR spectra of (I), (IV), and (VI). In the spectrum of (II), the same signal was observed at 56.4 ppm, and in the spectrum of (V) at 57.0 ppm. The paramagnetic shift by 6 ppm in the latter case in comparison with the C-11 signals in (I), (IV), and (VI) was caused by a hydroxy group at C-10.

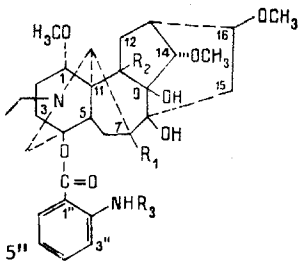
The signal of the C-7 carbon atom in the spectrum of sepaconitine was observed at 47.1 ppm in the form of a dobulet (for (I) it is at 47.6 and for (IV) at 47.7 ppm), while in the spectrum of (VI) it was present at 85.7 ppm in the form of a singlet, and in (V) at 76.6 ppm (s). Consequently, in (II) there was no oxygen-containing substituent at C-7.

The signals of the quaternary carbons at 74.8 and 79.8 ppm in sepaconitine permitted the two hydroxy groups to be located at C-8 and C-9. The presence of a substituent at C-9 was also confirmed by the PMR spectrum of (II) in which a one-proton doublet from H-14 was observed at 3.73 ppm (J = 5 Hz).

In the ^{13}C NMR spectrum of the amino alcohol (III), the signal from the C-11 carbon atom was located at 56.3 ppm. Thus, in sepaconitine and its amino alcohol there is a hydroxy group at C-10.

An analysis of the ^{13}C NMR spectrum of sepaconitine and a comparison of it with the spectra of (I-VI) showed that hydroxy group at C-10 had a considerable influence on the chemical shifts of the neighboring carbon atoms. Thus, the signals of the C-9, C-11, and C-12 carbon atoms in (II) underwent paramagnetic shifts of 1.1, 5.4, and 13.5 ppm, respectively, and the C-1, C-5, C-8, C-13, and C-14 signals diamagnetic shifts by 5.1, 4.2, 1.0, 1.7, and 2.4 ppm, respectively, relative to the signals of the same carbon atoms in the ^{13}C NMR spectrum of N-deacetyllapaconitine.

On the basis of what has been said above, structure (II) is proposed for sepaconitine, which agrees well with all the spectral characteristics.



I.	R_1=H;	R_2=H;	R_3=Ac
II.	R_1=H;	R_2=OH;	R_3=H
IV.	R_1=H;	R_2=H;	R_3=H
V.	R_1=OH;	R_2=OH;	R_3=Ac
VI.	R_1=OH;	R_2=H;	R_3=Ac

We have also isolated sepaconitine in minor amount from the epigeal part of A. leucostonum collected in the prebudding period in the region of the Santash pass (KirgSSR).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrophotometer, mass spectra on a MKh-1310 mass spectrometer fitted with a system for direct introduction into the ion source, and PMR spectra on JNM-4H-100/100 MHz and XL-200 (Varian) instruments in deuterochloroform with HMDS as internal standard (the values are given in δ scale). ^{13}C NMR spectra were taken on BS-567 A (Tesla) and CFT-20 (Varian) spectrometers in deuterochloroform. Chemical shifts are given relative to the internal standard TMS.

Extraction of A. septentrionale. The epigeal part of the plant (55 kg) was extracted with chloroform at room temperature (8 extractions). This yielded a total of 175 g of alkaloids.

Lappaconitine (I). From a total of 143 g of alkaloids (extractions 1-5) was isolated 23 g of lappaconitine hydrobromide containing as an impurity another two, unidentified, bases.

Sepaconitine (II). The mother solution (114 g) after the removal of the mixture of hydrobromides was separated according to basicities. The ethereal fraction (pH 7.5), after treatment with acetone, yielded 5.45 g of compound (II), mp 250-253°C (methanol–chloroform

(3:2)). After similar treatment of the combined alkaloids from extractions 6-8 (19.95 g), another 0.35 g of sepaconitine was isolated. The amount of (II) was 0.01% of the weight of the raw material.

Amino Alcohol of Sepaconitine (III). Sepaconitine (0.5 g) was heated in 5% aqueous methanolic NaOH for 2 h. The solvent was distilled off, the residue was dissolved in water, and the solution was extracted with ether and with chloroform. The yields were 0.27 and 0.06 g, respectively. After purification, 0.2 g of (III) with mp 110-112°C (from ether) was obtained. Then, with cooling, the alkaline solution was made acid by means of 40% sulfuric acid and was extracted with ether. The yield of acid extract was 0.12 g. It was purified by boiling with activated carbon in a mixture of ether and chloroform for 15 min. After the solvents had been distilled off, 0.08 g of an acid with mp 145-147°C was isolated.

Separation of the Mother Solution from the Combined Alkaloids of A. leucostonum. The mother solution (100 g), after the removal of lappaconitine, was separated according to the basicities at pH 6, 7.5, and 10. An ethereal fraction (pH 7.5; 4.47 g) was chromatographed on type KSK silica gel (1:60) using chloroform–methanol (1%) as eluent. Fractions 22-24 (0.15 g) yielded a base with mp 248-250°C (hexane–acetone), which was identical according to TLC and a direct comparison of samples and on the basis of spectral characteristics with the sepaconitine (II) from A. septentrionale.

SUMMARY

A new alkaloid sepaconitine has been isolated from the epigeal parts of Aconitum septentrionale and A. leucostonum, and its structure has been established.

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