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ALKALOIDS OF THE EPIGEAL PART OF *Aconitum kirinense*

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Lepenine and the new alkaloid lepenine N-oxide have been isolated from the epigeal part of Aconitum kirinense.

The plant *Aconitum kirinense* Nakai grows on dry slopes in the oak forests of the Far East, Amur, and Maritime Territory [1]. The alkaloids lepenine, akirine [2], and 8-acetylexcelsine [3] have previously been isolated from this species. We have continued an investigation of the alkaloid composition of the epigeal part of this species gathered in the villge of Chernyatino, Maritime Territory during the flowering period. The total alkaloids amounted to 1.6% of the weight of the air-dry raw material. By separating the ether-extracted fraction we isolated the known alkaloid lepenine [4] and a new compound with the composition $C_{22}H_{33}NO_4$ (I).

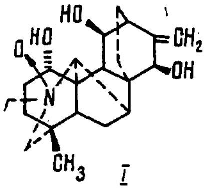
The base dissolved well in water, methanol, and ethanol, and sparingly in chloroform. The spectral characteristics of (I) were close to those of lepenine (II) [4], but the molecule of (I) contained one oxygen atom more than that of lepenine.

The IR spectrum of (I) had absorption bands of hydroxy groups (3390-3340 cm^{-1}) and of a terminal methylene group (3080, 1650, 900 cm^{-1}), and also absorption bands (1597, 1280 cm^{-1}) assigned to a N$\rightarrow$O bond. The PMR spectrum exhibited the signals of a tertiary C-methyl group (0.77 ppm, 3H, s), a N-ethyl group (1.32 ppm, 3H, t, J = 7 Hz), and an exomethyl group (5.15 and 4.91 ppm, 1H each, br.s).

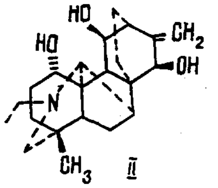
The mass spectrum of (I) contained the triplet of $(M - 16)^+$, $(M - 17)^+$, and $(M - 18)^+$ peaks that is characteristic for N-oxides.

It can be seen from Table 1 that on passing from (I) to (II) downfield shifts of the signals of the N-ethyl and tertiary C-methyl groups and of the C-20 protons, by 0.34, 0.13, and 0.36 ppm, respectively, take place. Analogous shifts have been observed previously for a number of N-oxides [5].

What has been said above permitted the assumption that (I) was lepenine N-oxide. When (I) was reduced with zinc in hydrochloric acid a product identical with lepenine was obtained. Consequently, (I) had the structure of lepenine N-oxide.



I



II

The ^{13}C NMR spectrum of lepenine N-oxide (Table 2) corresponded satisfactorily with its proposed structure. The multiplicities of the signals were determined with the aid of an off-resonance spectrum, and the assignments of the signals were made by comparison with the spectrum of lepenine. The spectrum of (I), like that of lepenine, showed the signals of 22 carbon atoms, with the same multiplicities, which was evidence in favor of the location of the additional oxygen atom at the nitrogen atom. The greatest change of chemical shifts was observed,for carbon atoms close to the nitrogen atom (C-19, C-20, $N-\underline{CH_2}-$, $N-CH_2-\underline{CH_3}$). Base (I) is the first N-oxide among alkaloids of the denudatine type.

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TABLE 1. Chemical Shifts of the Protons of Lepenine N-Oxide (I) (CD_3OD) and of Lepenine (II) ($CDCl_3$ 100 MHz, δ, ppm)

Compound	$C_4—CH_3$	$N—CH_2—CH_3$	$C═CH_2$	H—C-20	H—C-15
Lepenine N-oxide (I)	**0.77** **3H**, s	1.32 3H, t, **J=7** Hz	**5.15** and **4.91** each **1H**, br.s	**3.95 1H**, s	**4.14 1H**, s
Lepenine (II)	**0.64** **3H**, s	**0.98** 3H, t **J=7,5** Hz	**5.14** and **4.93** each **1H**, br.s	**3.59** **1H**, s	**4.15** **1H**, s

TABLE 2. Chemical Shifts of the Carbon Atoms of Lepinine N-Oxide (CD_3OD) and of Lepenine ($CDCl_3$) (δ, ppm)

C-atom	Multiplicity	I	II	C-atom	Multiplicity	I	II
1	d	67.4	70.1	14	t	25.2	25.1
2	t	30.6	31.7	15	d	77.8	77.9
3	t	36.5	39.3	16	s	153.6	155.5
4	s	35.4	33.8	17	t	110.7	108.7
5	d	50.7	52.8	18	d	26.4	26.3
6	t	28.7	28.2	19	t	67.8	51.1
7	d	48.0	47.9	20	d	83.9	68.3
8	s	44.1	44.3	N			
9	d	55.3	54.3	CH_2	t	74.6	57.3
10	s	53.6	51.6	CH_3	q	8.0	13.8
11	d	73.1	73.2				
12	d	45.6	42.4				
13	t	23.0	23.8				

EXPERIMENTAL

For general observations, see [3]. ^{13}C NMR spectra were taken on a Tesla BS 657 A instrument in deuterochloroform (0 — TMS, δ, ppm)

Isolation of the Total Alkaloids. The comminuted air-dry epigeal part of the plant *Aconitum kirinense* (1260 g) was extracted by the procedure described in [3]. In this way hexane (0.73 g), ether (4.0 g), chloroform (4.75 g), butanol (4.62), and washing chloroform (6.15 g) fractions of the total alkaloids were obtained.

Separation of the Ether Fraction. The ether fraction was chromatographed on a column of alumina with elution by benzene with gradually increasing additions of acetone. On elution with benzene–acetone (5:1), fractions 61-69 yielded lepenine (0.22 g). Finally, the column was eluted with methanol. The methanol fraction was rechromatographed on a column of silica gel with gradient elution by benzene and acetone. With the aid of acetone, the fractions eluted by acetone yielded 0.4 g of amorphous lepenine N-oxide.

Lepenine N-oxide $C_{22}H_{33}NO_4$.

IR spectrum (ν_{max}^{KBr}, cm^{-1}): 3390-3340 (OH), 3080, 1650, 900 ($C═CH_2$), 1597, 1280 ($N \rightarrow O$), 1695.

Mass spectrum m/z (%): M^+ 375 (17), 359 (50), 358 (58), 357 (33), 342 (25), 341 (67), 340 (17), 331 (33), 330 (25), 329 (42), 313 (67), 312 (100), 311 (33), 300 (30), 294 (33), 284 (33), 256 (33).

Reduction of Lepenine N-Oxide. At room temperature, zinc dust was added in portions to a solution of 0.02 g of lepenine N-oxide in 2 ml of 10% HCl, and the mixture was shaken for 18 h. The excess of zinc dust was filtered off, the filtrate was made alkaline with sodium carboate, and the reaction product was extracted with ether. After the solvent had been distilled off, 0.006 g of a product identified as lepenine was isolated with the aid of acetone.

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