ALKALOIDS OF Nitraria komarovii

XII. TETRAMETHYLENETETRAHYDRO-β-CARBOLINE N-OXIDE

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The plant Nitraria komarovii Iljin et Lava, assigned to the family Zygophyllaceae, is extremely close to Nitraria schoberi L. but, as compared with the latter, forms a less spreading and better-proportioned and more graceful bush with narrower and longer linear-spatulate leaves gradually tapering to the base, and with more delicate inflorescences [1]. It is found in saline clayey and sandy-clayey wastes near the sea (in the western maritime territory of Turkmenia and on Apsheron). We have made a study of N. komarovii growing in the environs of Krasnovodsk, Turkmen SSR [2].

The finely comminuted epigeal part of the plant gathered in May, 1987 (20 kg) was wetted with an 8% solution of ammonia, left for 2 h, and extracted with chloroform 13 times. The bases were extracted from the concentrated chloroform extracts with 10% sulfuric acid. The acid extract was made alkaline with 10% caustic soda and was extracted with benzene and ether and then with chloroform. After the addition of NH_4Cl the phenolic fraction was extracted. In this way, 36.46 g of the benzene fraction, 2.24 g of the ethereal fraction, and 43.21 g of the chloroform fraction of the total bases, and also 1.13 g of the phenolic bases, were obtained.

The benzene fraction of the bases (36.46 g) was chromatographed on a column of silica gel. Elution was performed with chloroform, 450- to 500-ml fractions being collected.

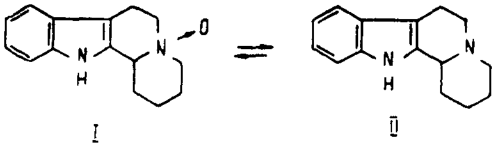
Fractions 4-7 yielded 57 mg of a base with mp 213-214°C (acetone), composition $C_{15}H_{18}N_2O$ (I), $[\alpha]_D$ ±0°. The mass spectrum of (I) contained the peaks of ions with m/z 242 M^+ (2%), 226.1485 (80), 225 (100), 224 (5), 197 (22), 185 (15), 184 (10), 174 (16), 170 (13), 169 (17), 156 (9), and others. The IR spectrum had absorption bands at 745, 1325, 1455, 1630, 1680, 2400-2760, 2860, 2940, and 3150 cm^{-1}.

In the UV spectrum there were the following absorption maxima: $\lambda_{max}^{C_2H_5OH}$ 223, 270-276, 290 nm (log ε 4.86; 3.87; 3.57). On alkalinization, a bathochromic shift was observed: $\lambda_{max}^{C_2H_5OH+OH^-}$ 228, 270-275, 292 nm. The PMR spectrum of (I) exhibited the signals of protons at 1.75-2.12, 2.12-2.75, 3.0-3.60, 4.0, 5.0 (t, 1H), 7.0, 7.25-7.50, 7.62, 8.12 ppm.

The spectral characteristics and also the solubility of the alkaloid in polar solvents (in ethanol, methanol, and water) permitted the assumption that the base was an N-oxide.

When (I) was reduced with zinc in hydrochloric acid, base (II) with mp 151-152°C was obtained. The melting point [3], and the IR, UV, and mass spectra of (II) coincided with those for tetramethylenetetrahydro-β-carboline.

On the oxidation of 3 mg of tetramethylenetetrahydro-β-carboline (II) with perhydrol in ethanol a chromatographic spot identical with that of the base (I) was obtained.



I II

Thus, the new base isolated had structure (I) and was tetramethylenetetrahydro-β-carboline N-oxide, isolated from this plant for the first time.

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LITERATURE CITED

1. Flora of the USSR [in Russian], Izd. Akad. Nauk SSSR, Moscow–Leningrad, Vol. XIV (1949), p. 196.
2. T. S. Tulyaganov and S. Yu. Yunusov, Khim. Prir. Soedin., No. 1, 61 (1990).
3. G. W. Gribble, J. Org. Chem., 37, No. 11, 1833 (1972).

ALKALOIDS OF Aconitum coreanum

V. 13-ACETYL-14-HYDROXY-2-ISOBUTYRYLHETISINE

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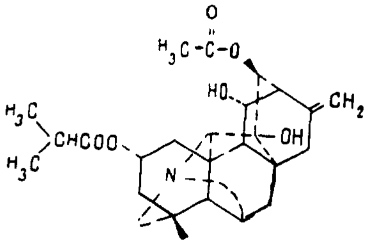
The isolation from the epigeal part of Aconitum coreanum (Levl.) Rapaics of a number of alkaloids of the hetisine and atisine types has been reported previously [1, 2].

Continuing the chromatographic separation of the hexane–ether fractions, we have isolated a base with the composition $C_{26}H_{35}NO_6$, mp 181-182°C (from acetone), $[\alpha]_D$ +58° ($CHCl_3$) (I). The IR spectrum of (I) had absorption bands of hydroxy (3555-3430 cm^{-1}), ester (1745, 1735 cm^{-1}), and exomethylene (1680 cm^{-1}) groups. The following were the main peaks in the mass spectrum of (I), m/z (%): 457 (M^+, 52); 415 [$(M - 42)^+$, 28], 414 [$(M - 43)^+$, 100], 398 [$(M - 59)^+$, 49], 370 [$(M - 87)^+$, 2]. These facts, and also the presence in the PMR spectrum of the signals of the protons of exomethylene, 18-methyl, isobutyryl, and acetyl groups and its close similarity to the PMR spectrum of 14-hydroxy-2-isobutyrylhetisine (Guan-Fu base Z) [3] permitted the assumption that the compound isolated was an acyl derivative of 14-hydroxy-2-isobutyrylhetisine.

A comparative analysis of the PMR spectra of (I) and (II) [3, 4] enabled an assignment to be made of the signals in the PMR spectrum of (I) (Tesla 567 A, 100 MHz, $CDCl_3$, O–HMDS, δ, ppm): 5.12 (br.s, H-2); 4.99 (br.s, H-13); 4.89 and 4.68 (br.s, 1H each, 2H-17); 4.19 (d, J = 9 Hz, H-11); 3.32 (s, H-20), 3.07 (br.s, H-6), 2.88 (d, J = 16 Hz, H-1α); 2.83 and 2.47 (d, 1H each, J = 12 Hz, H-19β and H-19α); 2.55 (d, J = 4 Hz, H-12); 2.40 (m, H-2'); 2.06-1.64 (m, 2H-15, H-9, H-1β, H-7α, H-3α); 1.97 (s, CH_3CO), 1.56 (d.d, J = 15.5; 4 Hz, H-3β); 1.49 (s, H-5), 1.33 (d.d, J = 14, 2 Hz, H-7β); 1.13 and 1.09 (d, 3H each, J = 6.5 Hz, $-C(CH_3)_2$); 0.96 (s, 3H, CH_3) – and on this basis to conclude that (I) had the structure of 13-acetyl-14-hydroxy-2-isobutyrylhetisine.



A direct chromatographic comparison with an authentic sample of 13-acetyl-14-hydroxy-2-isobutyrylhetisine (Guan-Fu base F) isolated from the plant Aconitum coreanum growing in China showed their identity. We thank Jinghan Liu for the information sent [5] and for a sample of Guan-Fu base F.

LITERATURE CITED

1. I. A. Bessonova, M. S. Yunusov, V. G. Kondrat'ev, and A. I. Shreter, Khim. Prir. Soedin., 623 (1987).

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