ISONITRAMINE – A NEW ALKALOID FROM *Nitraria sibirica*

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By extracting the epigeal part of *Nitraria sibirica* collected in the environs of the settlement of Rybache (KirgSSR), in May 1976, in the budding phase we have obtained 0.25% of total alkaloids.

A benzene solution of the ether-soluble nonphenolic fraction of the combined alkaloids was separated according to basicity with citrate–phosphate buffer solutions having pH values from 8 to 4 at intervals of 1 pH unit. By working up the ethereal fraction with pH 8 we isolated a white crystalline optically active base (I) with $[\alpha]_D$ −30° (c 1.36; chloroform), mp 102-103°C, which we have called isonitramine.

The molecular weight of the alkaloid (169, mass spectrometrically) and elementary analysis gave the composition $C_{10}H_{19}ON$. The UV spectrum of (I) showed no absorption, and the UV spectrum contained absorption bands of active hydrogen at 3288 and 3305 cm^{-1}.

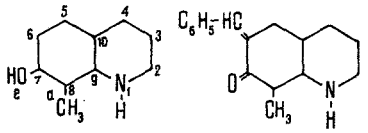
To determine the nature of the active hydrogen, we acetylated (I) with acetic anhydride in the presence of p-toluenesulfonic acid, as a result of which we obtained a O,N-diacetyl derivative of isonitramine (II) in the IR spectrum of which the bands of active hydrogen had disappeared and strong absorption bands of amide and ester carbonyl groups had appeared (1640 and 1735 cm^{-1}, respectively).

In the NMR spectrum of (I) ($CDCl_3$) at 3.87 ppm there is a broadened two-proton singlet apparently due to the protons of the NH and OH groups. In actual fact, this signal is absent from the NMR spectrum of (II). The spectral characteristics of isonitramine are close to and the empirical formula is identical with those of the alkaloid nitramine isolated previously from the plant *Nitraria schoberi* and having the structure of 7-hydroxy-8-methyldecahydroquinoline [1]. The closeness of the structure of these alkaloids was also shown by their mass-spectrometric fragmentation.

The presence of intense peaks of ions with m/e 96 and 110 in the mass spectrum of isonitramine excludes positions 2, 3, 4, 5, and 6 for substituents [2] and, consequently, the hydroxy and methyl groups are present in the C_7 and C_8 positions.

The main product of the condensation of the ketone obtained by the oxidation of (I) with benzaldehyde in an acid medium is the monobenzylidene derivative (III), the mass-spectrometric fragmentation of which coincides completely with that of the analogous derivative of nitramine.

Thus, the positions of the substituents in isonitramine are the same as in nitramine:



I

III

The undoubted difference between these alkaloids is shown by their different states of aggregation and the sign and magnitudes of their optical rotations (for nitramine $[\alpha]_D$ + 16.5°), and the opposite Cotton effects of the ketones from isonitramine and nitramine.

The signal of the proton at C_7 geminal to the hydroxy group, which resonates in the NMR spectrum of isonitramine O,N-diacetate at 4.71 ppm, in the spectrum of N-methylisonitramine at 3.55 ppm, and in the spectrum of the base itself at 3.57 ppm, is informative. The half-width of the signal, 17.5 Hz, shows the axial nature [4] of the proton at C_7 and, consequently, the hydroxy group has the equatorial orientation.

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The nature of the splitting of this signal (quartet, $J_1 = 11$ Hz, $J_2 = 4$ Hz) permits the assumption that the proton at C_8 is equatorial and, consequently, the methyl group is axial.

Analysis of the NMR spectra of nitramine and a number of its derivatives shows a similar orientation of the OH and CH_3 groups, and the difference between the alkaloids is apparently due to the method of linking the rings.

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PRIMARY STRUCTURE OF TRIACETINASE – AN ESTERASE FROM COTTON SEEDS. PEPTIDES FROM CYANOGEN BROMIDE HYDROLYSIS

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The isolation [1] and the quaternary structure [2, 3] of triacetinase – in esterase of cotton seeds [4] – have been reported previously. It has been shown that the esterase consists of four identical polypeptide chains with mol. wt. ~10,000 [1] and the amino-acid composition of a subunit has been determined (moles per mole): Asp, 13.5; Thr, 7.0; Ser, 9.8; Glu, 15; Pro, 4.2; Gly, 14; Ala, 11.1; Val, 3.2; Met, 3.8; Ileu, 3.0; Leu, 5.2; Phe, 3.8; His, 2.0; Lys, 4.2; Arg, 6.8; Tyr, 1.6; 1/2 Cys, 1.8. It has also been established that the N-terminal amino acid is methionine [1] and the C-terminal amino acid is tyrosine.

We now give the results of an investigation of the peptides from the cyanogen bromide hydrolysis of the triacetinase.

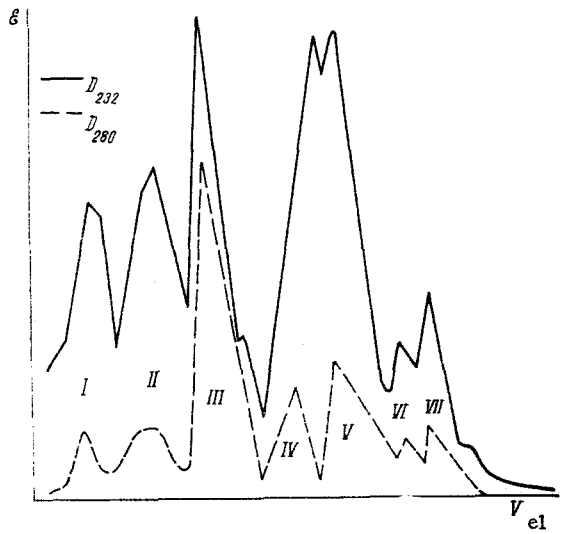

Fig. 1. Gel filtration of the peptides from the BrCN cleavage of triacetinase (column 180 × 1.5 cm equilibrated with 1 M ammonium acetate buffer, pH 7.4, $V_{el} = 3$ ml/h).

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