THE STRUCTURE OF NITRAMIDINE

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From the combined ether-soluble alkaloids of Nitraria schoberi L., collected in the Kyzylkumy of the Bukhara Oblast' atthe beginning of May, 1971, in the budding period we have isolated the alkaloid nitramidine (I), with the composition $C_{20}H_{23}N_3$, mol. wt. 305 (mass spectrometrically). The free base could not be crystallized, but it formed a hydrochloride (II) – a yellow crystalline substance with mp 251-253°C (ethanol).

In various solvents, (I) behaves differently, the color being bluer in nonpolar solvents (it is yellow in aqueous and methanolic solutions and red in chloroform solutions). Such behavior is characteristic for compounds of the anhydronium base type [1].

The absorption maxima in the UV spectrum of (II) in neutral media ($\lambda_{\max}^{\text{ethanol}}$ 250, 263 nm, log ε 3.95, 4.27) and acid media are close, and on the addition of alkali they undergo some bathochromic shift. This is also typical for the compounds mentioned above.

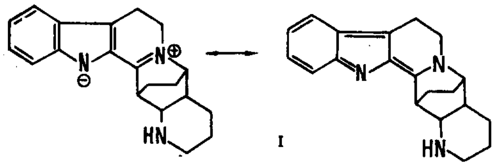
The mass spectrum of (II) has the peaks of ions with m/e 305 (M^+ 100%) 304, 277, 276, 262, 261, 249, 247, 222, 221, 219, 197, 184, 171, 83.

In the Adams hydrogenation of (II) in ethanol over a platinum catalyst, one mole of hydrogen was absorbed and nitrarine [2] in admixture with its isomer was formed. The UV spectrum of the hydrogenation product had the absorption bands $\lambda_{\max}^{\text{ethanol}}$ 226, 280-292 nm (log ε 4.37, 3.61) typical for tetrahydro-β-carboline compounds [3]. Such a large difference in the absorption of nitrarine and nitramidine shows that the double bond in the latter is conjugated with the indole chromophoric group. The presence in the mass spectrum of (II) of intensive peaks of ions with m/e 222 and 221 due to a tetramethylenedihydro-β-carboline fragment confirms the position of the double bond in one of the two possible positions: the third or the fifth.

The PMR spectrum of (II) (CF_3COOH) lacks the one-proton signal at 4.80 δ relating to the proton on the third carbon atom in nitrarine.

For a definitive answer to this question, we dehydrogenated nitrarine with mercuric acetate at 80°C for two hours. The UV spectrum of the product obtained was identical with that of nitramidine, on the one hand, and with 1,3-dehydroyohimbine, which has the form of an anhydronium base, on the other hand [4].

Thus, nitramidine has the structure of 1,3-dehydronitrarine:



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