NITRARAMINE – A NEW ALKALOID FROM Nitraria schoberi

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UDC 547.944/945

From the combined ether-soluble alkaloids of the epigeal part of Nitraria schoberi L. we have isolated the alkaloid nitraramine (I) – a crystalline, inactive, base with mp 85-86° C and the composition $C_{15}H_{24}ON_2$.

The base does not absorb in the UV region. The IR spectrum (KBr) shows absorption bands of active hydrogen at 3280 and 3530 cm^{-1} and a band of low intensity at 1660 cm^{-1} (double band). In the mass spectrum there is the peak of the molecular ion M^+ 248 (100 %), confirming the composition of the base, and also the peaks of ions with c m/e 231 $(M-17)^+$ (5 %), 219, 204, 190, 176, 162, 150, 136, 122, 109, 98, 96, 83, and 55. The NMR spectrum of (I) ($CDCl_3$, δ scale) is complex. It contains multiplets from methylene and methine protons and in addition it is possible to isolate three one-proton singlets at 4.38 ppm (broadened singlet), 3.88 ppm, and 2.43 ppm, the last two disappearing on the addition of CF_3COOH and possibly being due to the protons of NH and OH groups.

The acetylation of nitraramine gave a N-acetyl derivative (II) (M^+ 290; IR: 1620 cm^{-1}) and a O,N-diacetyl derivative (M^+ 332; IR: 1640 and 1740 cm^{-1}).

When (I) was subjected to Adams hydrogenation in acetic acid, two bases were obtained: (IV) and (V). The mass spectrum of (IV) showed the peaks of ions with m/e 250 (M^+) (21 %), 233 $(M-17)^+$ (7 %), 220, 206, 192, 190, 178, 165, 152, 150, 138, 126, 109, 98, 96, 84, and 57. The mass spectrum of (V) corresponded to a dihydrodeoxynitraramine and contained peaks with m/e 234 (M^+) (100 %), 233 (83 %), 218, 205, 192, 191, 190, 176, 137, 122, 110, 98, 96 and 55. The IR spectrum (V) had strong bands at 2805 and 2755 cm^{-1} (Bohlmann bands) [1].

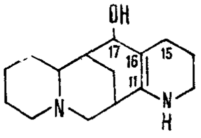
The mass spectra of (I), (IV), and (V), which are characteristic for the quinolizidine alkaloids [2] and the presence of NH groups in these bases suggested a modified sparteine skeleton for nitraramine [3]. The formation under hydrogenation conditions of dihydrodeoxynitraramine (V) suggested the presence in (I) of an allyl alcohol grouping [4], and this was confirmed by the formation of the corresponding ketone (VI) when (I) was oxidized by the procedure for oxidizing allyl alcohols [5]. The IR spectrum of (VI) had strong bands at 1650 and 1580 cm^{-1}, which are characteristic of a conjugated $O=C-C=C-N$ system [6]. The absence from the NMR spectrum of nitraramine of signals from olefinic protons shows that the double bond must be located at C_{16}-C_{11} and the hydroxy group at C_{15} or C_{17}.

The dehydrogenation of nitraramine with Pd/C gave a bright yellow dehydro base (VII) with mp 188-190° C. UV spectrum: $\lambda_{max}^{ethanol}$ 234, 262, 296, 400, 412 nm (log ε 4.15, 4.29, 3.57, 3.47, 3.46).

IR spectrum: 3000, 3040, 1585, 1505, 745 cm^{-1} (aromatic $C=C$ and $C-H$ bonds), 1640 cm^{-1} (quinoid carbonyl or terminal methylene group). In the mass spectrum of (VII) the main peaks are those with m/e 236 (M^+) and 235. The NMR spectrum (CCl_4) shows signals from α-protons of pyridine rings in the form of a two-proton multiplet at 8.49 ppm and a multiplet with its center at 7.04 ppm (5 H, Ar–H). Because of coupling with the axial proton at C_8 [7], the protons of the terminal methylene group form two one-proton triplets at 4.48 and 4.13 ppm ($J \approx 4$ Hz). A quartet (2 H) at 2.98 ppm can be assigned to the protons at C_8 and a multiplet at 2.13 ppm to the proton at C_7.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 435-437, May-June, 1975. Original article submitted February 11, 1975.

On the basis of a study of the UV, IR, NMR, and mass spectra of the hydro base we propose structure (VII) for it. Consequently, nitraramine has the most probable structure (I).



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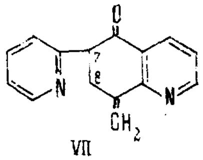

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