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ALKALOIDS OF LEONTICE DARVASICA

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From the epigeal part of L. darvasica, family Berberidaceae, collected in the flowering stage in the western Gissars range we have obtained 1.1% of total alkaloids by chloroform extraction. From them we have isolated thaspine [1], and from the mother liquor of the latter in the form of perchlorates N-methylcytisine and a new alkaloid darvasine with mp 145° C (ether) $[\alpha]_D$ −183° (c 1; ethanol), having the composition $C_{15}H_{22}N_2O$. Darvasine forms crystalline mono salts: perchlorate with mp 250° C (ethanol), picrate with mp 231° C (decomp., ethanol), and methiodide with mp 262° C (acetone). The IR spectrum of the alkaloid has absorption bands characteristic for the carbonyl of a six-membered lactam and a double bond (1670 w, 1645 cm^{-1}) and the UV absorption spectrum shows that these groups are conjugated in the form of the $-\overset{|}{C}=\overset{|}{C}-\overset{|}{N}-\overset{|}{C}=O$ chromophore (λ_{max} 244 mμ, log ε 4.3).

A study of the mass spectrum of darvasine (taken on a MKh-1303 mass spectrometer at an energy of the ionizing electrons of 40 V and a temperature of 85° C) has shown that it belongs to the matrine group of alkaloids with one double bond in ring C. The fragments formed by the elimination of the methyl and ethyl radicals from rings A and B are analogous to those of matrine and sophocarpine; however, the ions arising as a result of the degradation of ring C differ markedly from those of matrine and sophocarpine [2]. The peaks of the ions in the region of lower mass numbers are displaced by one or two atomic units, as in leontalbine. The spectra of darvasine and leontalbine differ in the intensity of several peaks, which is explained by steric factors. The dehydrogenation of darvasine using palladized asbestos (260-270° C, 30 min) gave hexadehydrodarvasine, identical with octadehydromatrine [3].

The NMR spectrum of the alkaloid shows, in addition to complex signals of protons of various methylene and methine groups, the signal of an isolated olefinic proton present in the α-position to a heteroatom (τ 3.19), which corresponds to a position of the double bond at C_5-C_{17}. The IR spectrum of darvasine lacks a trans band [4]. Consequently, the base is the first representative of the matrine alkaloids of the cis series and has the structure of 5,17-dehydroisomatrine.

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