DARVASAMINE – A NEW ALKALOID FROM Leontice darvasica

A. Zunnunzhanov, S. Iskandarov, and S. Yu. Yunusov

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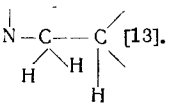
Continuing the separation of the mixture of alkaloids from the epigeal part of L. darvasica, we have separated the mother solutions after the isolation of thaspine, N-methylcytisine, and darvasine [1] into ethereal and chloroformic fractions, from which *l*-lupanine and leontine, respectively, have been obtained. The acid aqueous mother liquor from *l*-lupanine perchlorate was extracted with chloroform. The material not passing into the chloroform was extracted, after being made alkaline, first with ether and then with chloroform. When the ethereal fraction was separated in accordance with the strengths of the bases, the new alkaloid darvasamine was isolated with mp 102°C (ether), $C_{15}H_{24}N_2O$, $[\alpha]_D$ +72° (c 0.4; ethanol), giving a crystalline monoperchlorate with mp 265°C (decomp., acetone), and a monomethiodide with mp 303-305°C (decomp., acetone).

The IR spectrum of darvasamine showed the absorption band of an amide carbonyl at 1645 cm^{-1} and a "fingerprint" region close to that of the quinolizidine alkaloids. The mass spectrum had, in addition to the peak of the molecular ion (M^+ 248), confirming the composition of the alkaloid, the peaks of ions with m/e 219, 205, 191, 177, 162, 150, 138, 136, 96, 83, the intensities of which recalled those of alkaloids of the matrine series [2].

The NMR spectrum was characterized by a quartet at δ 4.45 showing the presence in the substance of the grouping  [13].

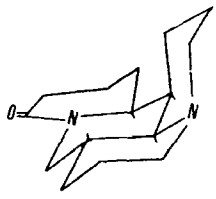
When darvasamine was dehydrogenated in the presence of 45% palladized asbestos at 300-320°C for 30 min, an octadehydro product identical with octadehydromatrine [4] was obtained.

Under the conditions for the dehydrogenation of matrine, leontine, and sophoridine with mercury acetate, darvasamine underwent no change.

When the alkaloid was reduced with lithium tetrahydroaluminate in absolute ether, deoxodarvasamine precipitated; it is a liquid optically active base with $[\alpha]_D$ –12° (c 0.5; ethanol) giving a perchlorate with mp 270°C, a hydriodide with mp 310°C, and a methiodide with mp 310°C.

The IR spectrum of the deoxo base, unlike that of darvasamine, lacked the absorption band of an amide carbonyl and showed a group of bands between 2800 and 2600 cm^{-1} indicating the trans-linkage of rings C and D [5].

Consequently, darvasamine is the first natural isomer of matrine of the cis series.



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