STRUCTURE AND SYNTHESIS OF LEONTIDINE

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The epigeal part of Leontice Albertii is rich in alkaloids, the qualitative and quantitative composition of which depends on the growth site [1, 2]. These alkaloids belong to the pyridine, cytisine, biphenyl, matrine, and leontidine groups. On separating the combined alkaloids of the epigeal part collected in the flowering stage in the environs of the village of Sidzhak, Tashkent oblast, we isolated leontidine, which has been found previously in the epigeal part and tubers of Leontice Ewersmannii [3-5]. Some reactions of leontidine have been studied, but its structure has not been determined [6, 7].

The presence in the IR spectrum of leontidine of a trans band, especially absorption in the fingerprint region, shows that it is similar to the alkaloid thermopsine. The NMR spectrum shows the signals of three protons of α-pyridone (βH quartet at 7.04 ppm, γH doublet at 6.12 ppm, αH doublet at 5.75 ppm) and the multiplet of the proton of a methylene group attached to nitrogen, forming part of the α-pyridone system (δ = 4.03 ppm).

The mass spectra of leontidine and its hydrogenation products (Fig. 1) have a number of features, and also peaks, characteristic for the quinolizidine alkaloids [8-10].

![Mass spectra of leontidine (a) and tetrahydroleontidine (b).](image)


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In addition to the peak of the molecular ion \((M^+ 230)\), confirming the composition \(C_{14}H_{18}N_2O\), the spectrum of leontidine has strong peaks of ions with \(m/e 160\) and 146, which are characteristic of quinolizidine alkaloids containing a 1,3-condensed tetrahydroquinolizone fragment connected with at least one methylene group [11].

Peaks of ions with \(m/e 96\) and 84 show the presence of a saturated ortho-substituted six- or five-membered heterocycle, but the high intensity of the latter is in favor of the presence of a terminal pyrrolidine ring. Taking into account the tetracyclic structure of leontidine, we may ascribe to it structure (I), which agrees with the production of tetradehydroleontidine (II) on dehydrogenation over palladium and of oxooleontidine (III) on oxidation with potassium permanganate.

A comparison of the spectra of tetradehydroleontidine (IV) and of \([3,3-D_2]\)tetrahydroleontidine (IV) confirmed the conclusion concerning the formation of the ions with \(m/e 160\) and 146 from rings AB in the decomposition of (I), since in (IV) these peaks are displaced by 4, and in (V) by 6, atomic mass units.

The high intensities of the peaks of the ions with \(m/e 136\) and 122 in (IV) are explained by the disappearance of the conjugated system of double bonds favoring the localization of the positive charge in rings AB. Consequently, in (IV) and (V) fragmentation accompanied by the cleavage of ring C becomes favored. In the mass spectrum of (V) there are also partial shifts of the peaks mentioned, which shows that they arise from rings AB.

The spectrum of hexahydrodes-N-methylleontidine (VII)* obtained by the catalytic hydrogenation of des-N-methylleontidine (VI) is characterized by the presence of the maximum peak of an ion with \(m/e 58\) and by the low intensities of the peaks of the ions formed from the indolizidine part of the molecule. This is due to the cleavage of the \(C_{11}-N_{10}\) bond in (I) (stage of Hofmann degradation).

In the spectrum of leontidane (VIII), the peaks of the molecular ion and of the fragment arising from the elimination of a hydrocarbon particle in the form of an allyl radical from ring A have the highest intensities. This is confirmed by a comparison with the spectrum of \([2,2-D_2]\)leontidane (IX), where the peak of the ion with \(m/e 179\) is also shifted and has the lowest intensity in the spectra of (I) and (IV). A comparison of the spectra of (VIII) and (IX) shows that the low-molecular-weight fragments are formed from rings AB and CD equally, which is explained by the closeness in space of the two linkages. In contrast to

* As in Russian original – Publisher.