MASS SPECTROMETRIC INVESTIGATION OF THE ALKALOIDS UNGERINE, UNSEVINE, AND HIPPEASTRINE

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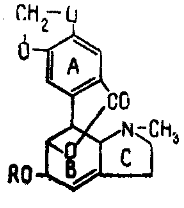
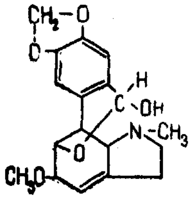
From six species of Ungernia we have isolated 16 alkaloids [1-3] of which six proved to be new. The structure of the new alkaloids has been established by means of a study of their chemical and physical properties [4-6].

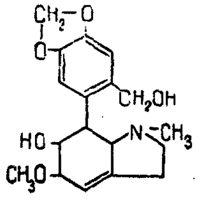
Continuing our systematic investigation of the alkaloids of Ungernia we have for the first time determined the mass spectra of ungerine (I), unsevine (II), hippeastrine (III) and some products of the hydrogenation of substance (I).



I R = CH$_3$
III R = H

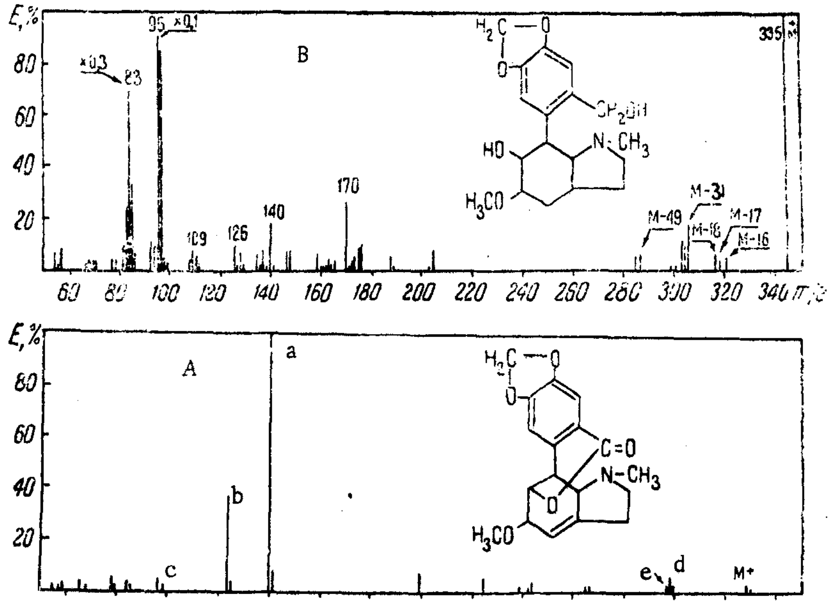


II



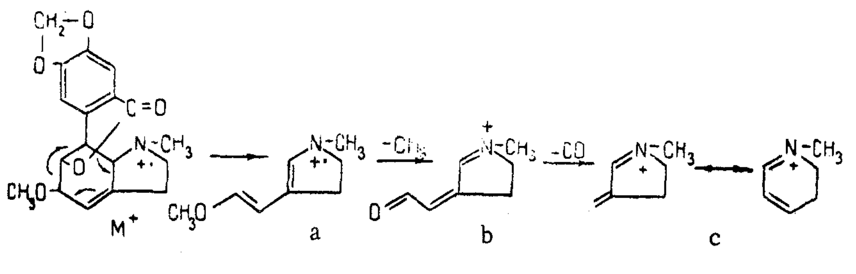
IV

The structural similarity of the alkaloids (I)-(III) is clearly shown in their mass spectra. A characteristic feature of these substances is the low intensity of the peaks of the molecular ions and the small number of peaks, particularly in the region of high mass numbers, for example in the spectrum of ungerine (figure, A).



Mass spectra. A) Ungerine; B) hexahydroungerine.

The main direction of the fragmentation of the molecular ion is its retrodiene decomposition leading to the formulation of fragment *a* giving the most intense peak in the spectra of (I)-(III) (table). The ion radical *a* then loses a methyl group in the case of substances (I) and (III) or a hydrogen atom in the case of substance (II), being converted into the ion b, which eliminates a CO group with the formation of ion c, as can be shown as follows for ungerine [1]:



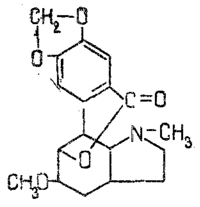
The a → b transition is confirmed by the presence in the mass spectra of substances (I) and (II) of metastable peaks with m/e 110.6 (calculated 110.6), and the b → c transition by the presence in the mass spectrum of (III) of a metastable peak with m/e 73.7 (calculated 73.7). The decomposition of the molecular ion of tetrahydroungerine (IV) in the molecule of which ring B is unaffected by hydrogenation, takes place similarly (see table).

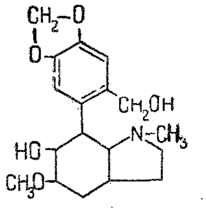
Mass Spectra of Substances (I)–(IV)

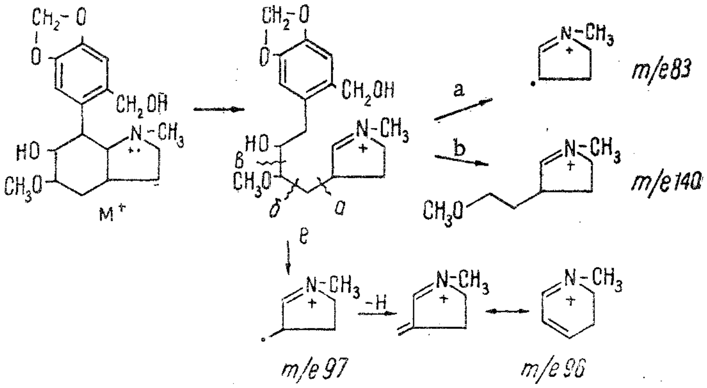
Substance	m/e (relative intensities)					
	M^+	a	b	c	d	e
(I)	329 (2)	139 (100)	124 (38)	96 (6)	298 (6)	297 (3)
(II)	331 (2)	139 (100)	124 (35)	96 (3)	300 (1)	299 (2)
(III)	315 (0.7)	125 (100)	124 (13)	96 (19)	298 (1)	297 (2.3)
(IV)	333 (9)	139 (100)	124 (40)	96 (10)	302 (3)	—

In the region of high mass numbers, the mass spectra of (I), (II), and (IV) have the low-intensity peaks $M-OCH_3$ (d) and $M-CH_3OH$ (e), corresponding to the peaks $M-OH$ and $M-H_2O$ in the mass spectrum of (III).

The pattern of the mass spectra changes sharply on passing to derivatives of substance (I) containing a hydrogenated ring B. Thus, in the mass spectra of dihydroungerine (V) and hexahydroungerine (VI) (figure, B) there are peaks of the molecular ions with a somewhat greater intensity than in substances (I)–(IV) (relative intensity 10–15%). The first act of fragmentation of the molecular ion is apparently a simple α-cleavage leading to the formation of the isometric ion *f*. The further decomposition of the ion *f* gives fragments with m/e 140, 97, 96, and 83. The peaks of the two latter fragments have the greatest intensities. For example, this can be seen in hexahydroungerine (VI):


V


VI



In the region of high mass numbers the mass spectra of substances (V) and (VI) show the peaks of the ions $M-CH_3$ and $M-OCH_3$ [m/e 316 and 300 for (V) and 320 and 304 for (VI)]. The mass spectrometric data obtained once more confirm the structures that we have proposed for compounds (I)–(III).

The mass spectra were taken on a standard MKh-1303 instrument fitted with a thermostatted glass system for introducing the sample into the ion source adjacent to the ionization chamber; the energy of the ionizing electrons was 25–35 eV, the temperature 100–150° C, and the reading accuracy ±1%.

Summary

1. The mass spectra of ungerine, unsevine, hippeastrine, and some products of the hydrogenation of ungerine have been studied.

2. The existence of an influence of an isolated double bond in ring B on the direction of decomposition of the molecular ion has been shown.

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