UDC 543.42

MASS SPECTROMETRY OF THE ALKALOIDS OF <u>LEONTICE</u>

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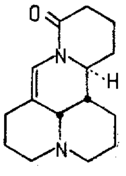
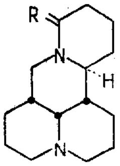
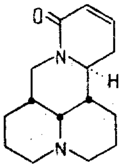
We have studied the mass spectra of leontalbine (I), matrine (II), and the products of the reduction of the latter with lithium aluminum hydride and lithium aluminum deuteride–matridine (III) and matridine-15, 15-d_2 (IV) [1]. For comparison, we have also recorded the mass spectrum of sophocarpine (V) [2].



I



II R = O
III R = H_2
IV R = D_2



V

In the compounds considered, the spatial arrangement of the hydrogen atoms at the asymmetric carbons is the same and therefore no differences due to these factors should be observed in the direction of decomposition.

For these alkaloids, high intensities of the peaks of the molecular ions are characteristic (see table). In the spectra of the alkaloids I, II, and V, the peaks of the ions M - 1 (a) predominate. This is due to the fact that the most favorable process for the decomposition of the molecular ions is the loss of a hydrogen atom at the C_6 tertiary carbon and the stabilization of the positive charge on the N_1 nitrogen atom.

Substance	m/e (% intensity)								
	M^+	a	b	c	d	e	f	g	h
I	246 (52.3)	245 (100)	231 (1.3)	[218] (14.1)	[204] (5.8)	190 (3.8)	[189] 2,3	175 (5.0)	[161] (2,2)
II	248 (100)	247 (98.7)	233 (2.6)	219 (19.1)	205 (77.6)	192 (20.0)	190 7.8	177 (23.5)	162 (27.5)
III	234 (33.3)	233 (11.8)	219 (1.1)	205 (3.6)	191 (8.0)	178 (4.6)	176 (6.1)	177 (5.2)	162 (27,2)
IV	236 (25.7)	235 (10.1)	221 (0.8)	207 (2,5)	193 (6.3)	180 (3.3)	178 (5.2)	177 (4.7)	162 (21.5)
V	246 (72.8)	245 (100)	231 (2.7)	217 (8.9)	203 (19.5)	192 (4.8)	188 (5.6)	177 (14.4)	160 (12.3)

Substance	m/e (% intensity)								
	i	j	k	l	m	n	o	p	q
I	148 (3.4)	134 (2.0)	120 (2.2)	108 (0.7)	97 (0.5)	96 (0.4)	95 (0.8)	83 (79.0)	55 (8.0)
II	150 (60.7)	137 (36.0)	122 (21.7)	110 (13.2)	98 (45.3)	97 (11.2)	96 (48.7)	83 (34,1)	55 (33.7)
III	150 (14.6)	137 (100)	122 (14.4)	110 (8.4)	98 (54.9)	97 (12.0)	96 (32.5)	84 (7.5)	55 (4.8)
IV	150 (17.0)	137 (100)	122 (12.0)	110 (5.1)	98 (48.7)	97 (8.0)	96 (30.8)	86 (5.8)	57 (11.3)
V	150 (44.0)	137 (22,5)	122 (20.3)	110 (12.8)	98 (28.0)	97 (9.2)	96 (47.3)	83 (28,3)	55 (19,1)

Also characteristic is the presence of the peaks of ions arising by the elimination of methyl and ethyl radicals from the molecular ions, these being formed mainly by the splitting of ring A or ring B. The peak corresponding to the ion M - 43 (d) is found in the spectra of all the compounds with the exception of leontalbine. Consequently, the ion **d** arises by the elimination of a C_3H_7 radical from rings A and C. This direction of the decomposition is confirmed by the displacement of this peak in the spectrum of matridine-15, 15-d_2 and the appearance in the spectrum of leontalbine of the peak of the ion M - 42, instead of M - 43, because of the presence of a double bond between C_5 and C_{17}.

A comparative study of the spectra of (I), (II), and (V) has shown that the ions **e** and **g** are formed by the elimination of the neutral particles C_3H_4O and C_4H_7O from the molecular ion.

A distinctive feature of the spectrum of matridine is the presence of peaks with m/e 176 (f) and 177 (g), while in the spectrum of matridine-15, 15-d_2 the peak of an ion with m/e 178 appears in place of that for m/e 176, and the peak with m/e 177 is unchanged. Consequently, the ion **f** arises by the degradation of rings A and C and the ion g by the elimination of a $C_4H_9^{\bullet}$ radical from ring D.

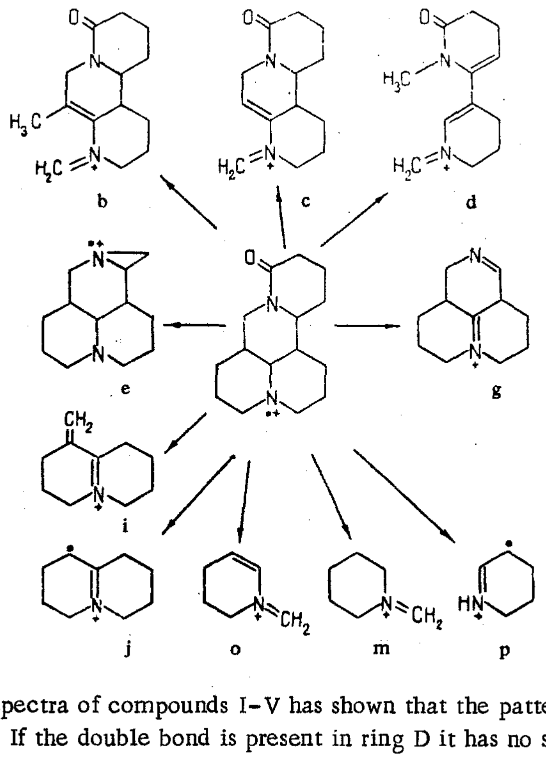
In all the compounds the ion **e** may be formed by the loss of the neutral fragment C_4H_8 from rings B and C. The ion **h** in the alkaloids I, II, and V probably arises from rings C and D and corresponds to the composition $C_{10}H_{10-12}NO$, while in compounds III and IV it arises from rings A and B and has the composition $C_{11}H_{16}N$.

In view of the absence of a double bond from ring C, the spectra of the matrine alkaloids have, regardless of the substituents in ring D, an intense peak of an ion with m/e 150, which arises from rings A and B.

The spectra of compounds II-V, like the spectra of the sparteine alkaloids [3] have a strong peak of an ion with m/e 137, while in the spectrum of leontalbine this direction of decomposition is markedly opposed by the presence of a double bond and it is displaced by three mass numbers. On further decomposition, the ion **j** may undergo fragmentation into ions with m/e 120 and 110.

When there is no double bond in ring C, the spectra of the alkaloids of the matridine series, unlike those of the sparteine series, show strong peaks of ions with m/e 98 and 96, which are formed from ring A.

In the alkaloids I, II, and V the ion **p** apparently arises from ring B and is the ion of a piperideine radical, while in the case of matridine it arises from ring D and has m/e 84.



Thus, our study of the mass spectra of compounds I-V has shown that the pattern of decomposition depends greatly on the position of the double bond. If the double bond is present in ring D it has no substantial influence on the direction of fragmentation.

Characteristic is the presence of peaks of doubly charged ions when both nitrogen atoms in the fragment formed are basic in nature.

The spectra of the alkaloids of the matridine series differ from those of the alkaloids of the sparteine series by the high intensity of the ions (M - 1) and (M - R) and by the presence of strong peaks of an ion with m/e 98, 96.

The mass spectra were recorded on a standard MH-1303 instrument at a temperature of 150–175° C with an energy of the ionizing electrons of 34–36 eV.

Summary

A study of the mass spectra of matrine, leontalbine, sophocarpine, and their reduction products has shown the influence of the basicity of the nitrogen atom and of the double bond on the fragmentation process.

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