MASS-SPECTROMETRIC STUDY OF ALKALOIDS OF THE LYCORINE TYPE

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We have previously studied the mass spectra of alkaloids of the ungerine type [1]. Continuing our investigation of the mass-spectrometric behavior of alkaloids similar to them in structure, we have considered the mass spectra of six alkaloids of the lycorine type isolated from plants of the family Amaryllidaceae and four derivatives of these alkaloids [2] (Table 1).

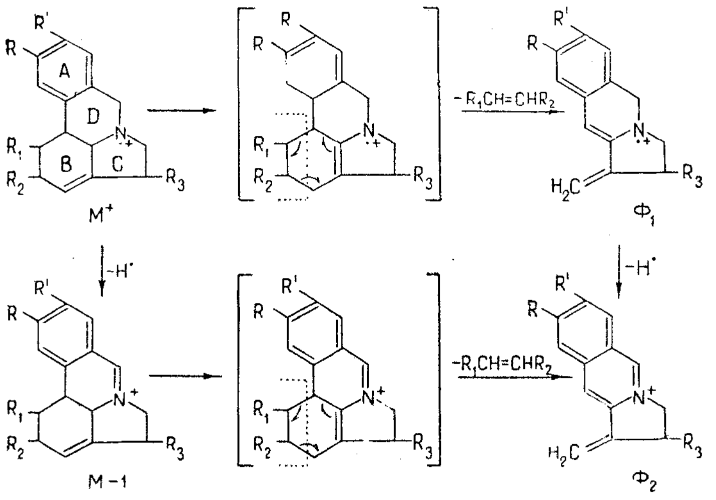
Table 1

Compound	R, R'	R_1	R_2	R_3
(I) Caranine	$-O-CH_2-O-$	OH	H	H
(Ia) Deuterocaranine	$-O-CH_2-O-$	OD	H	H
(II) Pluviine	OCH_3 OCH_3	OH	H	H
(III) Lycorine	$-O-CH_2-O-$	OH	OH	H
(IIIa) Diacetyllycorine	$-O-CH_2-O-$	OAc	OAc	H
(IIIb) Lycorine	$-O-CH_2-O-$	H	H	H
(IV) Methylpseudolycorine	OCH_3 OCH_3	OH	OH	H
(V) Ungminorine	$-O-CH_2-O-$	OH	OCH_3	OH
(Va) Diacetylungminorine	$-O-CH_2-O-$	OAc	OCH_3	OAc
(VI) Galanthine	OCH_3 OCH_3	OH	OCH_3	H

It has been established that the mass spectra of all the compounds of this group are characterized by peaks of very high intensity in the region of high mass numbers and by the absence of strong peaks from the region of low mass numbers. The decomposition of the molecular ions of the alkaloids I–VI and their derivatives begins with the formation of the (M-1) ion due to the detachment of a hydrogen atom from ring D (scheme 1). The energetic suitability of this process is due to its extension of the system of conjugated double bonds.

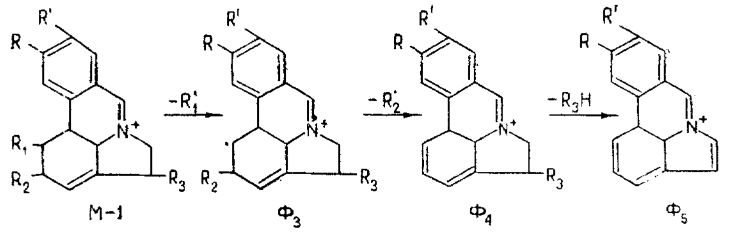
The second characteristic direction of the decomposition of the molecular ions of all the compounds studied is the formation of the ion-radical Φ_1, apparently arising as the result of a retrodiene cleavage of a tautomeric form of the molecular ion in which migration of a double bond from ring B into the position of the linkage of rings B and C takes place. The fragment Φ_2 is formed from the ion (M-1) by a similar mechanism. Another probable route for the origin of the ion Φ_2 is the elimination of a hydrogen atom from ring D of fragment Φ_1. Before the completion of this investigation, two papers [3, 4] appeared which gave the results of a study of the mass spectra of compounds I, III, IIIa, and IV, which were similar to ours.

Scheme 1

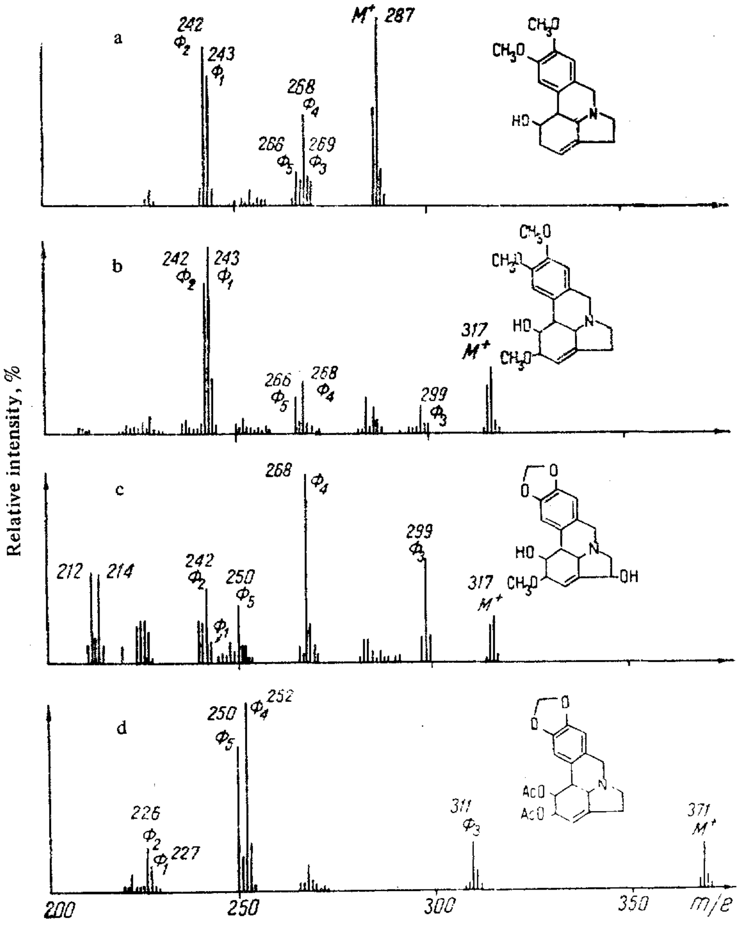


Another characteristic direction of fragmentation of the compounds studied is connected with the successive detachment from the ion (M-1) of the radicals R_1 and R_2 and of the molecule HR_3, leading to an extension of the system of conjugated double bonds (Scheme 2). The elimination of substituents R_1-R_3 in this sequence may also take place directly from the molecular ion, but the peaks of the corresponding fragments have a lower intensity. The values of m/e and the relative intensities of the peaks of the characteristic fragments in the spectra of all the compounds studied are given in Table 2.

Scheme 2



In addition to the general features of the fragmentation mentioned above, some specific features due to the nature of the substituents R_1-R_3 have been found. For example, in the spectra of III, IV, and VI, the elimination of the substituent R_1 = OH from the ion (M-1) takes place predominantly not in the form of an OH radical but in the form of a neutral molecule of water. Consequently, the peak of the ion (M-19) is more intense than that of the ion (M-18) (Φ_3) (figure).



Mass spectra of pluviine (a), galanthine (b), ungminorine (c), and diacetyllycorine (d).

Characteristic for the spectrum of ungminorine is the elimination of the groups of atoms CO and CHOH from the ion Φ_2, leading to the formation of fragments with m/e 214 and 212, respectively (see Scheme 3 and the figure).

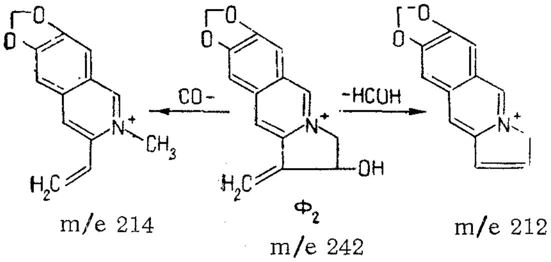
The correctness of the proposed sequence of fragmentation of the compounds studied is confirmed by the mass spectra of deuterocaranine (Ia) and, in a majority of cases, by the presence in the mass spectrum of the corresponding metastable peaks.

The mass spectra were taken on a standard MKh-1303 mass spectrometer fitted with a system for the introduction of the sample directly into the ion source at 100–150° C with an energy of the ionizing electrons of 30–70 eV.

Table 2

Compound	Value of m/e (relative intensity, %)						
	M+	M−1	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5
(I)	271(73)	270(43)	227(62)	226(100)	253(18)	252(70)	250(13)
(Ia)	272(72)	271(45)	227(66)	226(100)	253(22)	252(70)	250(22)
(II)	287(100)	286(52)	243(68)	242(84)	269(15)	268(48)	266(16)
(III)	287(53)	286(27)	227(100)	226(98)	269(10)	252(10)	250(22)
(IIIa)	371(24)	370(3)	227(16)	226(23)	311(25)	252(100)	250(75)
(IIIb)	255(49)	254(100)	227(42)	226(59)	253(8)	252(23)	250(4)
(IV)	303(45)	302(32)	243(100)	242(95)	285(11)	268(10)	266(25)
(V)	317(24)	316(22)	243(13)	242(40)	299(53)	268(100)	250(30)
(Va)	401(7)	400(5)	285(20)	284(13)	341(73)	310(95)	250(100)
(VI)	317(35)	316(26)	243(100)	242(80)	299(5)	268(28)	266(20)

Scheme 3



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Summary

1. The mass spectra of six alkaloids of the lycorine type (caranine, pluviine, lycorine, methylpseudolycorine, ungminorine, and galanthine) and four derivatives of these alkaloids have been studied.

2. Three main directions of fragmentation of the molecular ions of the compounds studied have been established: the formation of the ion (M-1), the cleavage of ring B in the form of a retrodiene reaction, and the successive elimination of the substituents from rings B and C in the ion $(M-1)^+$.

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