COMPARISON OF THE SECONDARY-ION AND ELECTRON-IMPACT MASS SPECTRA OF ALKALOIDS

Ya. V. Rashkes, E. G. Mil'grom, and Yu. M. Mil'grom*

An advantage of using secondary-ion spectra for determining the molecular masses of quaternary bases and bases the molecular ions of which are unstable to electron impact is shown. The LSIMS spectra of four groups of diterpene alkaloids include the 100% peaks of the (M + H)$^+$ ions and the peaks of the main fragments present in the EI spectra. The B/E = const. spectra of the key ions obtained by the different methods are compared. The closeness of the values of A of analogous transitions calculated from the B/E and MD spectra is confirmed.

Electron-impact (EI) mass spectrometry has hitherto provided the bulk of structural—analytical information in the field of alkaloid chemistry. An exception is formed by nonvolatile bases unstable to heat and to electron impact. Beginning from the 70s the problem of analyzing such substances have been solved with the aid of "mild" methods of ionization, among which one of the leading positions is occupied by secondary-ion mass spectrometry using liquid matrices (LSIMS). By using bombardment with Ar$^+$ ions and a solid silver support, Benninghoven et al. obtained secondary-ion spectra of polar and unstable compounds of various groups, including the alkaloids ephedrine and atropine, that contained the stable (M + H)$^+$ or M$^+$ ions and some fragments [1, 2]. The same group of workers showed the possibility of performing the quantitative and qualitative analysis of a mixture of opium alkaloids present at the nanogram level in urine extracts [3]. Meyer [4] successfully used the LSIMS method to obtain the spectra of quaternary bases. A number of investigations have been devoted to the search for compositions of liquid matrices for improving the quality of the spectra [5, 6]. However, in recent years, in spite of the wide use of the LSIMS method for analyzing various types of polar compounds, there have been practically no publications describing its application to the investigation of alkaloids. Nevertheless, this method can be used not only as a supplement to EI spectra but also completely independently in the analysis of mixtures of alkaloids in order to confirm the composition of quaternary bases and bases unstable to EI.

In the present paper we give the results of an investigation of various groups of alkaloids by the LSIMS method.
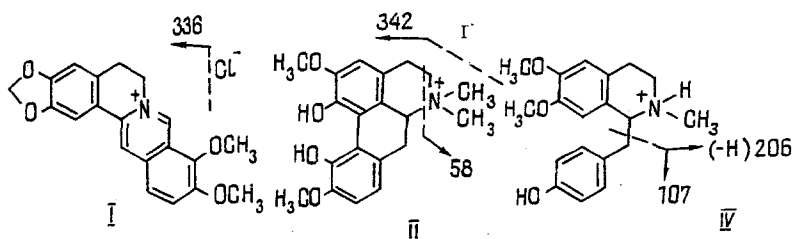
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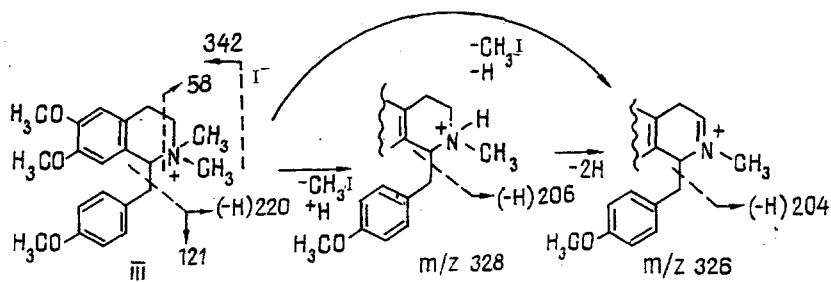
The mass number of the positive ion of the berberine chloride molecule (I) is 336 a.m.u. It is impossible to identify this compound from its EI spectrum (Table 1). In the region of high mass numbers it contains the weak peak of an ion with m/z 351, ions of medium height with m/z 337 and 336, and a triplet of peaks of ions with m/z 322-320. Then a series of homologous peaks with decreasing heights is observed down to the region below 170 m.u., where doubly charged variants of the same ions appear. The maximum peaks in the spectrum are those of the CH_3Cl ions with m/z 50/52. This compound probably undergoes far-reaching thermal decomposition under the inlet conditions ($t = 170°C$). In the LSIMS spectrum the peak of the ion with m/z 336 has a height far exceeding those of the other ions that are characteristic for compounds with methoxy and methylenedioxy groups — $(M - 15)^+$, $(M - 30)^+$, $(M - 44)^+$, and $(M - 58)^+$. In the high-mass region a cluster ion with m/z 428 (336 + 92) is observed.

The quaternary base magnoflorine iodide (II) is, in essence, the methiodide of a tertiary base of the aporphine series. Its EI spectrum is characterized by the properties common to this type of compounds [7]. Together with the peak of an ion with m/z 327 $(M - CH_3I)^+$, the more intense peak of an ion with m/z 341 $(M - HI)^+$ is observed. In the region of low mass numbers there are peaks of ions with m/z 142 $(CH_3I)^+$, 128 $(HI)^+$, and 127 $(I)^+$ and the 100% peak of an ion with m/z 58. The breakdown of the m/z 327 ion by the alternative elimination of CH_3 and CH_2O is recorded.

In the LSIMS spectrum of (II) the ion with m/z 58 is again the maximum ion. But the main characteristic of this spectrum is the presence of the peak of the quaternary magnoflorine ion with m/z 342. The breakdown of this ion with the elimination of CH_4 and CH_2O takes place to an insignificant degree.

In the molecule of O-methylarmepavine methiodide (III) there is an increment analogous to magnoflorine; however, here the $(M - CH_3)^+$ ion with m/z 327 is unstable because of the energetically favorable ejection of a p-methoxybenzyl radical and the stability of the resulting ion with m/z 206 (in the EI regime). In addition to this, the quaternary form of the base is confirmed by the presence in the spectrum of the peaks of ions with m/z 142, 127, and 58. The p-methoxybenzyl moiety appears in the spectrum in the form of an ion with m/z 121.

The LSIMS spectrum of (III) is more complex. In addition to the 100% peak of the cation of this compound with m/z 342, there is the peak of an ion with m/z 328 which can be represented in the form of the $(M + H)^+$ ion of the tertiary O-methylarmepavine formed in the matrix after the elimination of CH_3I. An ion with m/z 326 may be formed by alternative routes. All three quaternary ions have a tendency to split out the substituent at C-1, but in the form of a neutral p-methoxytoluene molecule. This leads to the formation of even-electron fragments with m/z 220, 206, and 204. The ion with m/z 58 is second in intensity in this spectrum. The ion with m/z 342 also breaks down with the elimination of the particles CH_2O, $CH_2O + CH_3$, and $CH_3 + CO$, which is characteristic for methoxy-substituted aromatics. All the above-mentioned transitions are confirmed by metastable peaks. In the low-mass region, the peak of the methoxytropylium cation with m/z 121 is also observed. Among the high masses there is the weak peak of the $(M - H)^+$ ion with m/z 468 and that of a cluster ion with m/z 434 (342 + 92).

The electron-impact spectrum of the tertiary base armepavine (IV) shows a weak M^+ peak (m/z 313, 0.4%), while the maximum peak of an ion with m/z 206, far exceeding all the others in height, arises after the ejection of a p-hydroxybenzyl radical [8]. In the LSIMS spectrum of (IV), the peak of an ion with m/z 314 $(M + H)^+$ stands out by its intensity. Its fragmentation takes place more selectively than that of the methiodide (III), and the height of the peak of the ion with m/z 206, formed by a mechanism analogous to the process leading to the appearance of the ion with m/z 220 (III), amounts to 60% of the height of the peak of the m/z 314 ion. Of ions characterizing the decomposition of the MeO groups it is possible to record only the presence of the peak of the $(MH - CH_2O)^+$ ion with m/z 284. The region of low masses has the peak of the hydroxytropylium ion with m/z 107.

Thus the advantage of LSIMS spectra for determining the molecular masses of quaternary bases and of bases the M^+ ions of which are unstable to EI is obvious.
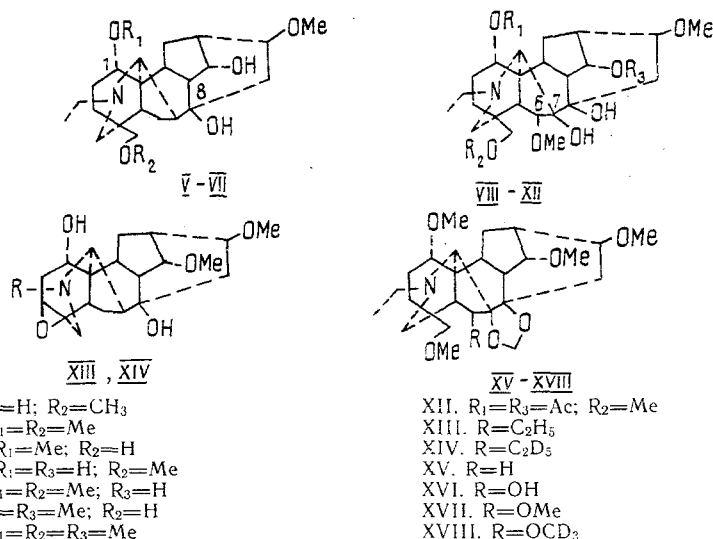
TABLE 1. Mass Numbers (*m/z*) and Relative Intensities (%) of the Main Fragments
in the EI (a) and LSIMS (b) Mass Spectra of Compounds (I)-(IV)

Compound	Mass numbers and relative intensities
I	a) 351(3), 337(21), 336[(M — Cl)$^+$, 14], 322(17), 321(34), 320(20), 308(6), 307(9), 306(13), 304(7), 292(11), 278(20), 52(33), 50(100)
	b) 428 [(M — Cl+Gl.*.)$^+$, 7], 336 [(M — Cl)$^+$, 100], 322(8), 321 (9), 320(11), 306(13), 304(7), 294(4), 292(8), 278(8)
II	a) 341 [(M—HI)$^+$,83], 327(23), 312(8), 310(6), 283(21), 142(35), 128(43), 127(33), 58(100)
	b) 342[(M — I)$^+$, 80], 328(7), 326(7), 312(4), 297(7), 58(100)
III	a) 341[(M — HI)$^+$, 0,7], 327[(M — CH₃I)$^+$, 0,3], 206(100), 142(13), 127(3), 121(2), 58(3)
	b) 468 [(M — H)$^+$, 0,3], 434 [(M — I+$^{Gl.}$)$^+$, 0,3], 342 [(M — I) $^+$, 100], 328(3), 326(2), 312(3), 299(1), 297(2), 220(3), 206(2), 204(1), 121(5), 58(50)
IV	a) 313 (M$^+$, 0,4), 312(0,6), 311(0,4), 206(100), 204(5), 190(9), 162(4), 107(4)
	b) 627 [(2M+H)$^+$, 0,8], 406 [(M+H+ Gl. *)$^+$, 2], 314 [(M+H)$^+$, 100], 312(8), 284(4), 206(60), 107(8)

*Gl.) Glycerol molecule.

Let us now dwell on the characteristics of the LSIMS spectra of diterpene alkaloids with the lycoctonine skeleton. The EI spectra of these bases have been described repeatedly [9-12]. Characteristic for them are M$^+$ ions of medium stability and the predominant formation of stable even-electron fragments as the result of competing reactions involving the ejection of an OR group from C-1 and of a methyl radical from the N—Et group. The appearance potentials of these ions are obviously fairly low since the spectra of the lycoctonine alkaloids scarcely change at energies of the ionizing electrons of 12-14 eV.

To analyze LSIMS spectra we selected samples of representatives of four groups of lycoctonine bases with the following main processes in their EI spectra: 1) 8-monools (V-VII) [predominant formation of the (M — OR$_1$)$^+$ ion] [12]; 2) 6-OMe-7,8-diols (VIII-XII) (competition between the ejection of ÔR$_1$ and ĊH$_3$ from C$_6$—OMe, the proportion of the first process rising in the sequence R$_1$ = H, Me, Ac) [12]; 3) C$_{18}$-bases with a 3,4-epoxy group (XIII)-(XIV) (ejection of ĊH$_3$ from N—Et) [13]; and 4) compounds with a 7,8-methylenedioxy group (XV-XVIII) (predominating elimination of ÔMe from C-1) [14].

V. R₁=H; R₂=CH₃
VI. R₁=R₂=Me
VII. R₁=Me; R₂=H
VIII.R₁=R₃=H; R₂=Me
IX. R₁=R₂=Me; R₃=H
X. R₁=R₃=Me; R₂=H
XI. R₁=R₂=R₃=Me

XII. R₁=R₃=Ac; R₂=Me
XIII. R=C₂H₅
XIV. R=C₂D₅
XV. R=H
XVI. R=OH
XVII. R=OMe
XVIII. R=OCD₃

A high intensity of the peak of the (M + H)$^+$ ion serves as the main characteristic of all the LSIMS spectra of these compounds (Table 2). The stability of the (M + H)$^+$ ion is 2-6 times greater than the W_{M^+} values in the corresponding EI spectra. It is definitely due to the increased proton affinity of the molecules of tertiary amines and the quaternary ammonium structure of the (M + H)$^+$ ions.

Another feature of the LSIMS spectra of the diterpene alkaloids (V)-(XVIII) is the presence of the peaks of ions of all the main even-electron fragments that are characteristic of the EI spectra of these bases. The mass numbers of these fragments

TABLE 2. Relative Intensities (%) of the Key Ions and Stabilities W (%) of the $(M + H)^+$ Ions in the LSIMS Spectra of Compounds (V)-(XVIII)

Compound	$W_{(M+H)^+}$	$(M+H)^+$	$(M-H)^+$	$(M-15)^+$	$(M-17)^+$	$(M-31)^+$	$(M-45)^+$	$(M-47)^+$	$(M-49)^+$	Other ions
V	33	99	42	9	100	12	5	6	14	$(M-33)^+16$
VI	55	100	16	10	23	20	4	3	3	$(M-33)^+5$
VII	61	100	12	4	17	18	3	3	3	$(M-33)^+3$
VIII	40	100	15	16	65	10	4	4	8	$(M-33)^+8$
IX	29	100	38	23	50	36	5	7	9	$(M-33)^+13$
X	15	100	77	35	90	77	6	10	21	$(M-33)^+23$
XI	22	100	60	31	88	65	10	13	19	$(M-33)^+19$
XII	24	100	48	25	82	23	10	7	11	$(M-33)^+13$ $(M-59)^+86$
XIII	38	100	35	13	64	10	2	2	5	$(M-33)^+5$
XIV	35	100	9	4(—CH$_3$) 5(—CD$_3$)	32	4	2	2	2	$(M-2)^+1$
XV	48	100	17	11	4	26	6	4	1	$(M-33)^+2$ $(M-29)^+10$
XVI	60	100	11	7	2	13	3	2	1	$(M-30)^+10$ $(M-29)^+5$
XVII	37	100	36	24	10	36	12	7	2	$(M-30)^+6$ $(M-29)^+26$
XVIII	12	100	97	44(—CH$_3$) 8(—CD$_3$)	11	33(—OCH$_3$) 8(—OCD$_3$)	18 9(M—48)$^+$	8 6(M—50)$^+$		$(M-30)^+14$ $(M-61)^+15$ $(M-64)^+20$

TABLE 3. Percentage Losses of D from the Nitrogen Atom in Various Processes in the Breakdown of the [M + (n + 1)D]⁺ Ions in the Spectra of the Deuteroexchange Products from (VI), (XI), and (XVII)

Initial bases	Daughter ions			
	$(M-1)^+$	$(M-15)^+$	$(M-17)^+$	$(M-31)^+$
VI	30	*	30	0
XI	100	0	50	0
XVII	65	25	*	75

*No calculations were performed in view of the low intensities of the peaks.

TABLE 4. Relative Intensities of the MPs (A) in the B/E = const. Spectra of the $(M + H)^+$, $(M - H)^+$, and $(M - 17)^+$ Ions of Compounds (V)-(XIII) and (XVII) Recorded in the LSIMS Regime

	Parental ion											
	$(M+H)^+$		$(M-H)^+$						$(M-17)^+$			
	daughter ions											
Com-pound	$(M-15)^+$	$(M-OR_i)^+$	$(M-30)^+$	$(M-32)^+$	$(M-17)^+$	$(M-19)^+$	$(M-31)^+$	$(M-33)^+$	$(M-33)^+$	$(M-35)^+$	$(M-47)^+$	$(M-49)^+$
V	0,2	1,1	—	—	2,3	0,8	—	—	0,2	0,2	—	0,2
VI	—	1,0	0,2	0,8	—	—	2,2	0,6	—	—	—	0,1
VII	—	0,7	0,2	0,4	—	—	4,2	0,5	—	—	—	0,2
VIII	0,3	0,4	—	—	1,0	1,9	—	—	0,3	0,2	0,1	0,3
IX	0,5	0,4	0,1	0,2	0,7	0,7	2,8	1,0	0,4	0,2	0,1	0,7
X	0,4	0,3	0,1	0,1	0,7	0,5	3,1	0,7	0,4	0,1	0,1	0,7
XI	0,7	0,7	0,2	0,4	0,8	0,9	3,6	1,1	0,5	0,2	0,2	0,7
XII	0,2	0,5	—	—	2,6	0,5	0,1	0,7	0,5	0,1	0,1	0,4
XIII	0,1	0,3	—	0,1	0,4	0,5	0,1	0,6	—	—	0,1	0,3
XVII	0,1	0,4	0,6	—	0,3	0,1	4,7	0,5	0,8	—	2,0	2,1

Note: XII $A_{(M-H)^+ \rightarrow (M-59)^+}$ = 2.6.

in the LSIMS and EI spectra are identical, but the mechanisms of their formation are different. The parental ions in the LSIMS regime are the $(M + H)^+$ ions, and the neutral fragments that appear on their breakdown are CH_4, H_2O, MeOH, and AcOH molecules, and not the radicals $\dot{C}H_3$, $\dot{O}H$, $CH_3\dot{O}$, and $Ac\dot{O}$ that are split out by the M^+ ions on breakdown under EI.

A characteristic exception in this connection is the ejection of a CH_2O molecule from the compounds with a 7,8-methylenedioxy group (XV-XVIII). This particle is eliminated from the $(M + H)^+$ ions and gives an even-electron fragment, in contrast to the odd-electron $(M - 30)^+$ ions found in the EI regime.

In the LSIMS spectra there is a pronounced redistribution of the contributions of the other even-electron fragments as compared with the EI spectra. Thus, for the compounds of the first, second, and fourth groups, the process of ejection of $\dot{C}H_3$ from the N-ethyl group is sharply suppressed. Among the peaks of the fragmentary ions of delcosine diacetate (XII) the peak of the $(M + H - AcOH)^+$ ion has the greatest intensity. In the spectra of compounds with a 3,4-epoxy group, (XIII) and (XIV), the ejection of $\dot{C}H_3$ from the N-ethyl group has lost its leading role. Among the peaks of the fragmentary ions of compounds of the first three groups [apart from (XII)] the most intense is that of the $(M + H - H_2O)^+$ ion, which is uncharacteristic for the spectra of compounds with a 7,8-methylenedioxy group (XV-XVIII), where the peak of this ion is low even for the hydroxyl-containing delcorine (XVI) (Table 2). This fact shows that the dehydration of the $(M + H)^+$ ion (at least for compounds with R_1 = H) takes place with the predominant participation of the OH groups at C-7 and C-8.

A separate discussion is necessary for the $(M - H)^+$ [$(M + H - H_2)^+$] ions, the heights of which are some of the greatest among the peaks of fragmentary ions and vary, with no definite dependence on structure, between 0.1 of the height of the $(M + H)^+$ peak almost to equality with it. In the EI spectra the peaks of the $(M - H)^+$ ions are also observed, with

TABLE 5. Relative Intensities of the MPs (*A*) in the B/E = const. Spectra of the $(M - 15)^+$ and $(M - OR_1)^+$ Ions of Compounds (V)-(XIII) and (XVII) Recorded in the LSIMS (b) and EI (a) Regimes

Parental ion. Daughter ions under $(M-15)^+$: $(M-33)^+$, $(M-45)^+$, $(M-47)^+$. Daughter ions under $(M-OR_1)^{+\cdot}$: $(M-OR_1-16)^+$, $(M-OR_1-18)^+$, $(M-OR_1-30)^+$, $(M-OR_1-32)^+$.

Compound	$(M-33)^+$		$(M-45)^+$		$(M-47)^+$		$(M-OR_1-16)^+$		$(M-OR_1-18)^+$		$(M-OR_1-30)^+$		$(M-OR_1-32)^+$	
	b	a	b	a	b	a	b	a	b	a	b	a	b	a
V	1,1	0,4	0,2	0,1	0,2	0,04	0,2	0,1	0,2	0,04	—	0,05	0,2	0,05
VI	0,3	0,2	0,5	0,07	1,2	1,4	0,2	—	—	0,05	0,1	0,02	0,2	0,03
VII	0,2		0,1		0,3		0,3		0,1		0,2		0,1	
VIII	3,9	1,9	—	—	0,2	0,05	0,3	3,0	0,2		0,1	0,1	0,3	0,3
IX	3,7	1,8	0,3	0,2	0,3	0,1	0,1	—	0,6	0,08	0,1	0,05	0,6	0,5
X	2,6	8,2	0,2	0,07	0,3	0,2	0,2	—	0,4	0,3	0,1	0,04	0,3	0,4
XI		4,5		0,1		0,1	0,2	0,04	0,5	0,2	0,2	0,04	0,6	0,3
XII	2,4	6,9	0,2	—	0,2	0,2	0,1	0,01	0,3	0,07	0,1	0,01	0,4	0,3
XIII	0,9	0,3	—	0,2	—	0,04	—			—	0,1		0,3	
XVII	0,3	0,4	1,7	3,7	0,5	0,1	0,5	0,2	0,2	0,06	1,2	0,4	0,4	0,1

TABLE 6. Values of *A* for the Transitions $(M + H)^+ \to$ $(M - 15)^+$ and $(M + H)^+ \to (M - OR_1)^+$ Calculated from the B/E and MD (LSIMS) Spectra

| Compound	$(M+H)^+ \to (M-15)^+$ MD	$(M+H)^+ \to (M-15)^+$ B/E	$(M+H)^+ \to (M-OR_1)^+$ MD	$(M+H)^+ \to (M-OR_1)^+$ B/E
V	0,9	0,9	3,4	3,4
VI	0,3	0,4	6,4	6,7
VIII	2,2	1,1	2,6	1,8
IX	1,4	1,3	1,9	2,0
XII	0,4	0,6	1,5	2,2

intensities that are variable but are always far less than those of the M^+ peaks. Their predominant origin through the splitting out of H· from one of the two CH_2 groups adjacent to the nitrogen atom is not a matter of doubt. So far as concerns dissociation in the regime of secondary-ion emission, the nature of the $(M - H)^+$ ions may be a dual one: a) as the result of the occurrence of ion-molecule reactions in the liquid matrix before bombardment with Cs^+ ions; and b) as the result of the ejection of H_2 from the $(M + H)^+$ ions to which the excess energy of the Cs^+ ions has been imparted [15].

To check these alternatives, we measured the heights of the $(M + H)^+$ and $(M - H)^+$ peaks in the spectrum of lycoctonine (X) with energies of the primary ions decreasing from 7 to 2 keV. It was found that the decreases in the yields of the two ions took place disproportionately, and, starting from 3 kV the $(M - H)^+$ peaks became higher than the $(M + H)^+$ peaks. The fact that with a decrease in the energy of the Cs^+ ions the heights of the peaks under consideration fell tenfold cannot be an argument in favor of an insignificant contribution of the first mechanism: according to a known concept, the energy of the primary ions (or atoms in the FAB regime) is used to "spatter" charged particles from the matrix [16]. We may also mention that we were unable to record the ejection of H_2 with the aid of MD and B/E spectra of metastable ions. Thus, the first of the alternatives is more probable.

From the LSIMS spectrum of $N—C_2D_5$-monticamine (XIV) it is possible to make a semiquantitative estimate of the processes involving the detachment of H· from a CH_2 group adjacent to the nitrogen atom. The contribution of the $(M - H)^+$ ion decreases by a factor of 3 in comparison with the spectrum of monticamine (XIII), and the contribution of the $(M - D)^+$ ion is an order of magnitude less again (Table 2). In light of the primary isotope effect, both facts are evidence in favor of the predominant ejection of H· from the N-ethyl group.

We also set ourselves the aim of finding the probability of the presence of daughter ions with the same structure in the EI and LSIMS spectra. An indispensable condition for the formation of ions with the same structure is that the neutral

particles ejected from the (M + H)$^+$ ion should be formed from the hydrogen protonating the nitrogen atom and the radicals participating in the process of fragmentation under EI. The following scheme illustrates this situation:
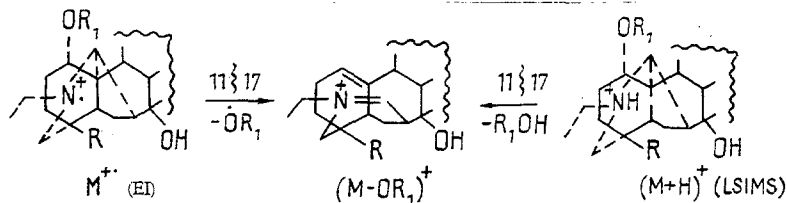
Even without the performance of special experiments it can be predicted with confidence that the realization of this scheme under the LSIMS regime will be restricted by at least three factors: 1) the existence of alternative routes for the formation of daughter ions with the same mass numbers through the splitting out of monotypical substituting groups, which has been established previously [13, 17, 18]; 2) the competing ejection of R$_1$OH with the inclusion of various hydrogen atoms of OH groups; and 3) the redistribution of the contributions of the various processes due to the different stabilities and different reserves of internal energy of the M$^+$ (EI) and (M + H)$^+$ (LSIMS) ions, which is difficult to monitor. On the other hand, a stimulating factor in the formation of such structures may be the stability of the key ions, which is responsible for the fairly high selectivity of the fragmentation of the lycoctonine bases. All considerations relating to the given scheme may also be used in relation to the other characteristic pathways of the breakdown of the compounds under discussion.

In the EI spectrum of N—C$_2$D$_5$-monticamine (XIV), the contribution of the ejection of $\dot{C}$D$_3$ was 2.2 times greater than the contribution of the ejection of the same radical from other positions [13]. In the LSIMS spectrum this ratio fell to 1.2, which indicates some preference for the occurrence of more complex rearrangements in LSIMS.

The intensity of the ejection of $\dot{C}$D$_3$ from 6-OCD$_3$-delcorine under EI conditions is almost 6 times higher than the analogous magnitude characterizing the ejection of $\dot{C}$H$_3$ from N—C$_2$H$_5$ [14]. In the LSIMS spectrum, this ratio changes to the opposite (0.18), which indicates the predominant formation of fragments the precursors of which localize the charge on the nitrogen atom and not on the 7,8-methylenedioxy group, as in the EI spectra [14].

In the spectra of the deuteroexchange products from (VI), (XI), and (XVII) the maximum shift of the polyisotopic peaks of the (M + H)$^+$ ions is equal to the number of mobile hydrogen atoms in the molecule [n plus unity (replacement of the proton at the nitrogen atom by deuterium)]. In order to evaluate the contributions of the alternative processes for the breakdown of the (M + D$_{n+1}$)$^+$ ions (with and without the loss of the D at the nitrogen atom) we used a method developed previously for calculating the relative contents of an isotropic label in parental and daughter ions [19]. On the basis of these calculations we estimated the percentages of the (M — 1)$^+$, (M — 15)$^+$, (M — 17)$^+$, and (M — 31)$^+$ ions formed with the loss of the deuterium at the nitrogen atom. The results are given in Table 3.

It can be seen from Table 3 that not one of the breakdown processes under consideration takes place monotypically in representatives of the three groups of bases. In three cases out of ten there was no loss of the isotopic label, which totally excludes the possibility of the formation of fragments of the same structure as in the breakdown of M$^+$ under EI. Not more than a quarter of the (M — 15)$^+$ ions from 6-OMe-delcorine (VII) arise with the loss of the hydrogen protonating the nitrogen atom. On the other hand, the percentage loss of the same atom on the splitting out of a methanol molecule approximately corresponds to the proportion of (M + H — CH$_3$OH)$^+$ ions calculated from the spectrum of 6-OCD$_3$-delcorine (XVIII); i.e., these ions may have the same structure as the majority of the (M — 31)$^+$ ions in the EI spectrum of the same compound. Judging from the figures of Table 3, the ways in which a H$_2$O molecule is split out from the (M + H)$^+$ ions of talatisamine (VI) and delphatine (XI) are indeterminate.

In spite of the identity of the structures of rings A and of the elements adjacent to the nitrogen atom in the (VI), (XI), and (XVII) molecules, the percentage losses of deuterium on the formation of the (M + 1)$^+$ ions from the deuterated bases are different.

In order to judge the similarity of the structures of the daughter ions in the EI and LSIMS spectra, we made an attempt to use the method of linked scanning, B/E = const. The B/E spectra of the (M + H)$^+$, (M — H)$^+$, (M — 15)$^+$, (M — 17)$^+$, and (M — OR$_1$)$^+$ ions were obtained in the LSIMS regime for ten alkaloids and were compared with the corresponding EI spectra. The relative intensities of the metastable peaks (MPs) of the main transitions are given in Tables 4 and 5.

All the linked-scanning spectra of the compounds of one subgroup with the same R$_1$ are monotypical in the qualitative respect and extremely close in the quantitative respect (for example, the B/E spectra of talatisamine (VI) and of aconoridine

(VII), browniine (IX), lycoctonine (X), and delphatine (XI)). The spectra of the $(M - OR_1)^+$ ions of the bases of one group but with different R_1's are fairly close in the cases of the 8-monools (V)-(VII) and the 7,8-diols (VIII)-(XII).

The spectra of monotypical fragments of compounds of different groups differ considerably from one another; for example, the B/E spectra of the $(M - H)^+$ ions of talatisamine (VI), delphatine (XI), monticamine (XIII) and 6-OCH_3-delcorine (XVII) (see Table 4).

The $(M + H)^+$ ions have no analogues in the EI spectra, while the $(M - H)^+$ ions in the same spectra are insufficiently representative for the performance of measurements. We have therefore compared the B/E spectra of the $(M - 15)^+$, $(M - 17)^+$, and $(M - OR_1)^+$ ions (Table 5). The B/E spectra of the $(M - 15)^+$ ions obtained with the aid of various methods of ionization do not, as a rule, show qualitative and substantial differences within the individual subgroups of alkaloids (Table 5).

The B/E spectra of the $(M - 17)^+$ ions of talatisamine (VI) recorded in the two regimes differ sharply from one another. In the LSIMS regime a single transition with the loss of a methanol molecule is observed (Table 4), while in the EI spectrum there are three main peaks, corresponding to the loss of 16, 30, and 48 a.m.u. [17]. In the analogous EI spectrum of the ions of browniine (IX) there are the peaks of the same transitions but with a different intensity ratio. The B/E spectra of the $(M - 17)^+$ ion (LSIMS) is characterized by the absence of a transition with the loss of 48 a.m.u. and by a redistribution of the intensities of the other peaks. These facts do not contradict the information in Table 3, where the existence of alternative pathways for the appearance of the $(M - 17)^+$ daughter ions is implied.

The B/E spectra of the $(M - 17)^+$ ions of compounds with R_1 = H (V and VIII), coinciding in mass with $(M - OR_1)^+$ (Table 5), have appreciable quantitative differences in the case of EI but differ little in the LSIMS spectra. The B/E spectra of the $(M - 17)^+$ ions of compounds of the first and second groups with R_1 = CH_3 obtained with different methods of ionization differ by the presence in the LSIMS spectra of transitions with the loss of 16 a.m.u. The B/E spectra of the analogous ions of 6-OCH_3-delcorine (XVII) are qualitatively closer. These facts agree with results showing the percentage loss of deuterium on the formation of the $(M - OR_1)^+$ ions (Table 3).

Thus, in spite of the characteristic nature of the B/E (LSIMS) spectra within the various subgroups of diterpene alkaloids, the accumulated facts are insufficient for judging the similarity of the structures of the parental ions because of the low sensitivity of the methods used for revealing alternative methods of fragmentation.

In the development of investigations to measure the parameters of metastable peaks [16], the A values of the transitions $(M + H)^+ \rightarrow (M - 15)^+$ and $(M + H)^+ \rightarrow (M - OR_1)^+$ in the B/E and MD spectra of a series of lycoctonine bases were compared (Table 6). The measurements in the LSIMS regime were close to one another, and so were those on the use of EI [17]. These results confirm the conclusion that the magnitude of A is a measure of the breakdown of the ions in the first field-free space of the mass spectrometer. The parameters given are an order of magnitude smaller than in the spectra of the metastable ions obtained with the aid of EI, which is explained by the high stability of the parental ions $(M + H)^+$.

EXPERIMENTAL

Synoptic spectra and the spectra of metastable ions in the LSIMS regime were recorded on a MKh 1310 instrument with a LSIMS ion source made in the Institute of Analytical Instrument Construction of the Russian Academy of Sciences (St. Petersburg). Ionization was achieved with a beam of accelerated Cs^+ ions having an energy of 7 keV; the accelerating voltage in the recording of the synoptic and B/E spectra was 5 kV, and for the MD spectra 2.5 kV. The samples were dispersed in glycerol and deposited on a steel target for direct sample introduction.

To obtain the results given in Tables 4 and 5, the slit between the magnetic and electrostatic analyzers was made smaller so as to exclude the passage of particles in the neighborhood of the selected parental ion and also the products of the breakdown of these particles. The results given in Tables 1-3 were obtained with a fully opened slit.

The deuteration of the glycerol matrix to give $C_3H_5(OD)_3$ was performed with an excess of deuteromethanol CD_3OD at room temperature for about two hours, and the remains of the solvent were pumped out under vacuum. To obtain the LSIMS spectra, the products of the deuterium exchange of the sample were dispersed in $C_3H_5(OD)_3$.

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