B/E LINKED SCANNING SPECTRA OF THE MOLECULAR AND FRAGMENTARY IONS OF LYCOCTONINE BASES

E. G. Sirotenko, Ya. V. Rashkes,
B. V. Fridlyanskii, and B. M. Voronin

UDC 543.51+547.944/945

The B/E linked scanning spectra of the M^+, $(M-15)^+$, and $(M-OR_1)^+$ ions and those of some other series have been investigated. The characteristic nature of the individual intensities of the metastable peaks (the magnitudes A) with the same R_1 radicals for different groups of alkaloids has been shown for the spectra of the M^+ and $(M-15)^+$ ions. The reason for the quantitative differences of the B/E spectra of the $(M-OH)^+$ ions from the spectra of the $(M-OCH_3)^+$ and $(M-OAc)^+$ ions, consisting in the influence of alternative methods of eliminating an OH radical, has been found. It has been confirmed that the values of A of analogous transitions calculated from the B/E and MD spectra are close to one another. On the other hand, the values of the energy of the metastable transitions obtained by these two methods differ from one another by two orders of magnitude.

As is known, the complete interpretation of the mass spectra of the majority of diterpene alkaloids with the lycoctine skeleton is complicated by virtue of the fact that in addition to the reflection of the two or three completely obvious competing directions of breakdown taking place in them there is a whole series of alternative fragmentation processes leading to ions with the same elementary composition [1, 2]. This is due mainly to the presence of several monotypical substituents in the molecules of these bases. The selective introduction of a chemical or isotopic label in such cases requires multistage transformations, while, at the same time, the replacement in some positions of the skeleton of, for example, OH by OMe, can redistribute the contributions of the different processes to such an extent that this makes the fulfillment of the initial task unrealistic [3].

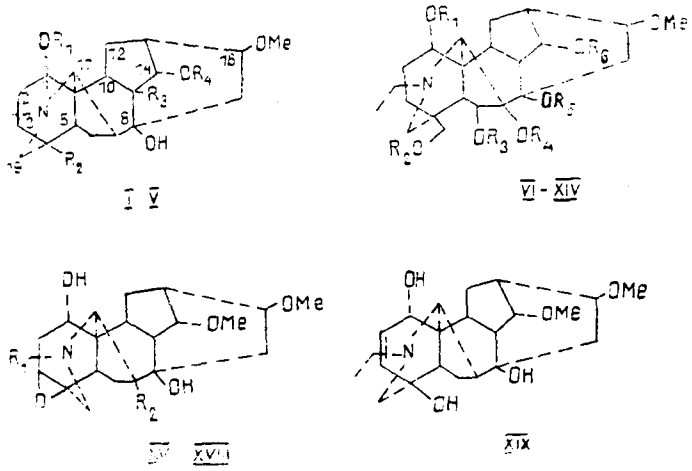
We have shown the basic possibility of differentiating methods of splitting out of identical substituents by different mechanisms through a comparison of the parameters of the metastable peaks (MPs) in the metastable defocusing (MD) spectra: the relative intensity of the MPs (the magnitude A) and the energies of the metastable transitions (T). Thus, differences have been found between the parameters of the MPs on the splitting out of a methyl radical from a N–Et group as the result of simple bond cleavage and on the splitting out of the same particle from a methoxy group at C-6 [1, 4], C-14, or C-16 [5] as the result of more complex breakdown processes. With the aid of the same experimental methods, criteria of the common nature of the mechanism of the splitting out of a substituent at C-1 that is practically universal for the lycoctonine bases have been established and characteristics of the MD spectra indicating the similarity of two- and three-stage fragmentation reactions have been revealed [1, 4].

However, a more strictly based answer to the latter question is hindered by the low resolving capacity (R) of the MD spectra, which does not permit the identification of metastable transitions from parental ions differing from one another by 1-3 m.u. The identification of MD spectra must therefore be linked with the results from the spectra of metastable parental ions, MIKE (DADI) [6], B/E [7], and MS–MS [8]. The first two methods have R ~ 100 and 500 [9] with respect to the daughter ions and permit the calculation of the m/z factors of the ions with an accuracy of 1 unit, while the MS–MS methods, thanks to the action on the ions of neutral particles, permits more multilinear spectra to be obtained.

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Special Design Bureau of Analytical Instrument Construction, Scientific and Technical Branch, Academy of Sciences of the USSR, Leningrad. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 72-84, January-February, 1991. Original article submitted February 26, 1990.

 0009-3130/91/2701-0062$12.50

To confirm the laws of the fragmentation of the lycoctonine bases under EI established previously [1, 2, 4, 5, 10, 11] and to obtain new information on alternative methods for the formation of ions with the same m/z value and on the structures of some daughter ions, we have investigated the B/E = const spectra of the M^+ and $(M-15)^+$ ions of the alkaloids (I-XIX) and the $(M-OR_1)^+$ ions of (I-XV), and also the B/E spectra of a number of other fragmentary ions. In the center of attention were not only the qualitative features of the spectra of the different subgroups of compounds but also the parameters of the MPs.



I. $R_1=R_3=R_4=H$; $R_2=CH_2OMe$ (C_1—α-OH)
II. $R_1=R_3=R_4=H$; $R_2=CH_2OMe$ (C_1—β-OH)
III. $R_1=Me$; $R_2=CH_2OMe$; $R_3=R_4=H$ (C_1—α-OMe)
IV. $R_1=H$; $R_2=R_3=OH$; $R_4=Me$ (C_1—α-OH)
V. $R_1=R_4=Me$; $R_2=R_3=OH$ (C_1—α-OMe)
VI. $R_1=R_4=R_5=R_6=H$; $R_2=R_3=Me$
VII. $R_1=R_2=R_3=Me$; $R_4=R_5=R_6=H$
VIII. $R_1=R_3=R_6=Me$; $R_2=R_4=R_5=H$
IX. $R_1=R_6=Ac$; $R_2=R_3=Me$; $R_4=R_5=H$
X. $R_1=R_4=R_5=H$; $R_2=R_3=R_6=Me$
XI. $R_1=R_2=R_3=R_6=Me$; $R_4=R_5=H$
XII. $R_1=Ac$; $R_4=R_5=H$; $R_2=R_3=R_6=Me$
XIII. $R_1=R_2=R_3=R_6=Me$; $R_4+R_5=>CH_2$
XIV. $R_1=R_2=R_3=Me$; $R_4=CD_3$; $R_4+R_5=>CH_2$
XV. $R_1=C_2H_5$; $R_2=H$
XVI. $R_1=C_2D_5$; $R_2=H$
XVII. $R_1=R_2=H$
XVIII. $R_1=C_2H_5$; $R_2=OH$

Tables 1-3 give the heights of the MPs of all the transitions recorded, normalized relative to the height of the daughter ion, taken as 100%, i.e., in essence, the A values of these transitions. However, it must be borne in mind that the B/E spectra were recorded in two different regimes. To obtain the results presented in Tables 1-3, the slit between the magnetic and the electrostatic analyzers was narrowed in order to exclude the passage of the breakdown products of the ions accompanying the selected daughter ion. The A values of Table 4, calculated for comparison with those of the MD spectra, were obtained with full opening of the slit. The values of A of analogous transitions given in Tables 1-3 and in 4 therefore do not coincide.

Compounds (I-XVIII) can be arbitrarily divided into three groups: the molecules of (I-V) are 8-ols, (I) and (II) being stereoisomers at C-1; each of (VI-XIV) contains a 6-Ome (or, for (XIV) a 6-OCD_3) group and in the 7,8-position have a diol chain (VI-XII) or a methylenedioxy group (MDOG) (XII-XIV); (XV-XVIII) contain 3,4-epoxy groups; and compound (XIX) is isomeric with compound (XV).

B/E Spectra of the Molecular Ions. All the spectra of the compounds of the first two groups (I-XIV) have, with two exceptions, MPs corresponding to transitions to the following daughter ions: $(M-15)^+$, $(M-18)^+$, $(M-30)^+$, $(M-OR_1)^+$, and $(M-32)^+$ (Table 1). Only in the spectra of the bases containing no OH groups (XIII and XIV) is there no peak of a transition to the $(M-18)^+$ ion. So far as concerns the presence in these spectra of other MPs, this depends on the nature of R_1 and the particular group to which the compound belongs. Thus, in the spectra of all the bases with a C_1—αOH group there are MPs of transitions to the $(M-55)^+$ and $(M-56)^+$ ions [2]. When R_1 = Me, a $M^+ \rightarrow (M-33)^+$ two-stage transition is observed,

TABLE 1. Relative Intensities of the MPs (A, %) in the B/E = const Spectra of the Molecular and Fragmentary Ions of Compounds (I-XIV)

Compound	Parental ion												
	M^+						$(M-15)^+$				$(M-OR_1)^+$		
	daughter ions												
	$(M-15)^+$	$(M-13)^+$	$(M-30)^+$	$(M-OR_1)^+$	$(M-31)^+$	other ions	$(M-31)^+$	$(M-15)^+$	$(M-17)^+$	$(M-OR_1-16)^+$	$(M-OR_1-17)^+$	$(M-OR_1-30)^+$	$(M-OR_1-31)^+$
I. Isotalatisidine	3,6	2,1	0,3	11	0,1	$(M-28)^+$ 0,6 $(M-55)^+$ 0,3 $(M-56)^+$ 0,2	0,4	0,1	0,04	0,1	0,04	0,05	0,05
II. Talatisidine	3,3	0,1	0,07	1,7	0,02	$(M-31)^+$ 0,01	0,2	—	0,1	0,1	0,07	0,1	0,07
III. Talatisamine	0,06	0,04	5,8	5,6	0,08	$(M-31)^+$ 0,08	0,2	0,07	1,4	—	0,05	0,02	0,03
IV. Lappaconidine	1,4	0,8	0,04	2,3	0,03	$(M-28)^+$ 0,2 $(M-55)^+$ 0,4 $(M-55)^+$ 0,3	0,2	—	—	0,1	0,2	0,01	0,05
V. Lappaconine	0,1	0,2	10	19	0,2	$(M-31)^+$ 0,2	0,5	0,1	0,9	0,01	0,2	0,02	—
VI. Delcosine	10	0,2	0,4	1,8	0,2	$(M-31)^+$ 0,6 $(M-57)^+$ 0,3 $(M-56)^+$ 0,3	1,9	—	0,05	3,0	0,2	0,1	0,3
VII. Browniine	5,7	0,2	4,7	10	0,3	$(M-39)^+$ 0,3	1,8	0,2	0,1	—	0,08	0,05	0,5
VIII Lycoctonine	15	2,1	1,9	30	0,8	$(M-33)^+$ 2,9	8,2	0,07	0,2	—	0,3	0,04	0,4
IX. Delcosine diacetate	1,6	0,3	0,2	6,1	0,2	$(M-31)^+$ 0,2 $(M-58)^+$ 4,9	6,9	—	0,2	0,01	0,07	0,01	0,3
X. Delsoline	9,4	0,3	0,3	3,3	0,1	$(M-31)^+$ 0,6 $(M-55)^+$ 0,3 $(M-56)^+$ 0,4	3,8	—	0,1	3,1	0,2	0,2	0,4
XI. Delphatine	3,9	0,1	5,7	13	0,1	$(M-31)^+$ 0,1	4,5	0,1	0,1	0,04	0,2	0,04	0,3
XII. Delsoline acetate	0,9	0,03	0,2	2,1	0,2	$(M-31)^+$ 0,1 $(M-59)^+$ 1,8	6,2	—	0,1	0,01	0,07	0,01	0,3
XIII 6-OHC_3-Delcorine	0,9	—	5,8	12	0,04	—	0,4	3,7	0,1	—	—	0,3	0,06
XIV. 6-OCD_3-Delcorine	0,2	—	7,5	9,5	0,05	$(M-CD_3)^+$ 1,8 $(M-OCD_3)^+$ 0,06	3,2	12	0,3	—	—	0,2	0,03
							$(M-CD_3)^+$				$(M-OCD_3)^+$		
							0,3	3,4	0,1	—	—	0,9	0,2

The values of A for the transitions $(M-31)^+ \rightarrow (M-59)^+$ and $(M-34)^+ \rightarrow (M-62)^+$ of (XIV) were 0.02 and 0.8, respectively.

TABLE 2. Values of A in the B/E = const Spectra of the M^+ and $(M-15)^+$ Ions of Compounds (XV-XIX)

Compounds	Parental ions					
	M^+					
	daughter ions					
	$(M-15)^+$	$(M-17)^+$	$(M-18)^+$	$(M-28)^+$	$(M-30)^+$	$(M-31)^+$
XV. Monticamine	1,4	0,2	0,2	0,4	0,2	0,4
XVI. N-C_2D_5-Monticamine	0,5 ($-CH_3$) 2,9 ($-CD_3$)	0,8	—	0,4	0,3	0,8
XVII. Normonticamine	0,4	0,5	1,6	0,3	0,2	0,4
XVIII. Monticoline	2,9	0,3	0,4	0,3	0,03	0,08
XIX. Δ^2-Dihydromonticamine	8,7	1,4	1,8	0,3	0,4	0,9

Compounds	Parental ions						
	M^+				$(M-15)^+$		
	daughter ions						
	$(M-32)^+$	$M-43)^+$	$(M-55)^+$	$(M-56)^+$	$(M-73)^+$	$(M-15)^+$	$(M-47)^+$
XV. Monticamine	0,04	0,2	0,2	0,2	0,3	0,02	0,04
XVI. N-C_2D_5-Monticamine	0,1	0,2	0,2	0,2	1,3 0,2*	0,1 0,2*	0,1 0,02*
XVII. Normonticamine	—	—	—	—			
XVIII. Monticoline	0,08	0,2	0,08	0,08	0,3	0,01	0,03
XIX. Δ^2-Dihydromonticamine	0,05	0,2	—	—	1,1	0,01	0,05

The values of A for the Mps of transitions from the $(M-CD_3)^+$ ions are marked by asterisks.

and when R_1 = Ac (IX and XII), the $M^+ \rightarrow (M-58)^+$ transition is recorded, its peaks competing in height with those of the $M^+ \rightarrow (M-OAc)^+$ transition. Delcosine (VI) and delsoline (X), in the synoptic spectra of which the peaks of the $(M-OMe)^+$ ions due to the splitting out of the substituent at C-6 are of considerable magnitude, show the corresponding transition in the B/E spectra of the MPs; the peaks of the analogous transition in the spectra of their acetates (IX) and (XII) are weaker.

If the bases belong to a single group, then with the same R_1 radicals the values of A of the majority of analogous transitions are of the same order or are close to one another. This relates in the highest degree to the compounds (VI) and (X), and (VIII) and (XI). If the differences in the set of substituents in one group of compounds is greater, as in the case of isotalatisidine and lappaconidine, the values of A for the analogous transitions differ more considerably from one another, which shows the influence of side processes of the splitting out of monotypical substituents. In a number of cases, the B/E spectra are more sensitive to structural changes that are scarcely reflected in the synoptic spectra. Thus, the replacement of an OMe group in the acetate (XII) by OAc (IX) leads to a substantial change in the values of A in transitions to the $(M-18)^+$, $(M-OR_1)^+$, and $(M-58)^+$ ions (Table 1). The difference between the B/E spectra of the M^+ ions of position isomers (browniine (VII) and lycoctonine (VIII)) is very large, while their synoptic spectra differ little. In the spectra of the stereoisomers (I) and (II), in addition to the differences recorded with the aid of the synoptic spectra for the $(M-15)^+$, $(M-OR_1)^+$ [12], and $(M-56)^+$ [1] ions, the following are observed: in the B/E spectrum of the M^+ ion of (I) there is the peak of a transition to the $(M-28)^+$ ion [as also in the case of lappaconidine (XII)], which is absent from the corresponding spectrum of the stereoisomer (II); the values of A for the transitions $M^+ \rightarrow$ [$(M-18)^+$, $(M-30)^+$, $(M-32)^+$, and $(M-33)^+$] for (I) are many times higher than for (II). On the other hand, a closeness of these values is characteristic for the $M^+ \rightarrow (M-15)^+$ transitions: 3.6% (I) and 3.3% (II). In spite of the great difference in the stabilities of the $(M-15)^+$ ions in the synoptic spectra of (I) and (II), their ratios to the stabilities of the corresponding M^+ ions are also close. However, it is difficult to regard this fact as a criterion of the common nature of the mechanism of the formation of the $(M-15)^+$ ions, since we had no other pairs of stereoisomers at our disposal.

The increased intensity of the $M^+ \rightarrow (M-30)^+$ transition must be assigned to the common features of the B/E spectra of the M^+ ions of compounds (I-XIV). A comparison of the values for browniine, delphatine, talatisamine, and lappaconine with those of lycoctonine and lappaconidine permits the conclusion that the elimination of a CH_2O molecule takes place predominantly at the expense of a OMe group at C-1 or C-18. The closeness of the values of A for delphatine and for 6-OMe-delcorine confirms the insignificance of the contribution of the fragmentation of the 7,8-MDO group to this stage [11]. The low intensity of the MP of the $M^+ \rightarrow (M-CD_2O)^+$ in 6-OCD_3-delcorine reflects the weak role of this substituent, too, in the process under consideration. So far as concerns the $M^+ \rightarrow (M-CD_3)^+$ process, in the B/E spectrum of the latter compound its advantage over the splitting out of CH_3 from the N-Et group can well be seen.

The B/E spectra of the molecular ions of the 3,4-epoxy compounds (XV-XVIII) and of Δ^2-dihydromonticamine (XIX) contain the MPs of nine transitions, one of them – $M^+ \rightarrow (M-43)^+$ – being two-stage [5]. The main feature of each of the five spectra consists in the fact that the values of A of the main transitions are, with a few exceptions, related to one another in the same way as the relative intensities of th epeaks of the corresponding daughter ions in the synoptic spectra of (XV-XIX). In all cases, apart from N-normonticamine (XVII), the MP of the $M^+ \rightarrow [M-CH_3(CD_3)]$ transition has the greatest value of A. In the B/E spectrum of (XVII), the peak of the $M^+ \rightarrow (M-H_2O)^+$ transition is the maximum, which also agrees with the synoptic spectrum of this compound. Table 2 clearly shows the appreciable increase in the selectivity of fragmentation in the direction of the splitting out of CH_3 on passing from monticamine (V) and its d_5-analogue (XVI) to monticoline (XVIII) and Δ^2-dihydromonticamine (XIX).

The values of A of only two transitions are nonproportional in comparison with the roles of the corresponding daughter ions in the synoptic spectra. These are the $M^+ \rightarrow (M-H_2O)^+$ and $M^+ \rightarrow (M-CO)^+$ transitions. As can be seen from Table 2, the values of A for the first of the transitions compete with the values of A of the $M^+ \rightarrow (M-17)^+$ transition for monticamine, monticoline, and Δ^2-dihydromonticamine, although the heights of the peaks of the $(M-H_2O)^+$ ions in the synoptic spectra of these compounds are small in comparison with $I_{(M-17)^+}$ [5]. The $(M-CO)^+$ ions are formed as the result of a complex rearrangement [5], and this explains the increase in the value of A for the $M^+ \rightarrow (M-28)^+$ transition [1]. However, taking d_5-monticamine as an example, Table 2 shows that a relative increase in the values of A in rearrangement processes in comparison with processes of simple bond cleavage does not take place in all cases. Thus, in the synoptic spectrum of (VI) $I_{(M-CH_3)^+}/I_{(M-CD_3)^+} = 5:11$ [5], while in the B/E spectrum the values of A of the transitions in the corresponding daughter ions are in a ratio of 1:6 (Table 2). This lack of correspondence can be explained by the triangular form of the MP of the $M^+ \rightarrow (M-CH_3)^+$ transition. On constriction of the slit, its height falls rapidly and not in proportion to the peak of the $M^+ \rightarrow (M-CD_3)^+$ transition, which has a Gaussian form [1].

The MPs of the $M^+ \rightarrow (M-55)^+$ and $M^+ \rightarrow (M-56)^+$ transitions have been recorded in the B/E spectra of compounds (XV), (XVI), and (XVIII). In the corresponding synoptic spectra the peaks of the $(M-C_3H_3O)^+$ ions are observed with medium intensity, these probably being formed by rearrangement with the participation of the C-1–C-3 chain. The peaks of the $(M-56)^+$ ions in the synoptic spectra of these compounds have low intensities but, judging from the presence of the MP of the $M^+ \rightarrow (M-56)^+$ in each B/E spectrum the elimination of an acrolein molecule takes place here, as in other 1α-hydroxy bases [2].

The B/E spectra of the $(M-15)^+$ ions of all the compounds, with a few exceptions, contain the MPs of three transitions corresponding to the loss of H_2O, CH_2O, and CH_3OH molecules (Tables 1 and 2). The spectra of some compounds (talatisamine (III), lappaconine (V), and 6-OCH_3-delcorine (XIII)) have the peaks of transitions indicating the splitting out of 16-m.u. fragments (values of A, respectively, 0.3, 0.3, and 0.4). Since among the $(M-31)^+$ ions of these compounds there is no component corresponding to the loss by the molecular ion of a C_2H_7 particle, one must assume the existence of a specific fragmentation mechanism including the loss of an O atom after the splitting out of a methyl radical. However, from the facts presented it does not appear possible to determine the substituent of the lycoctonine skeleton breaking down in this way.

The values of A for the $(M-15)^+ \rightarrow (M-33)^+$ transition depends on the mechanism by which the parental ion was formed. In the case of the predominant fragmentation of the N-Et group

TABLE 3. Values of A in the B/E = const Spectra of the $(M-17)^+$ Ions (compounds (I) and (III-VII)), the $(M-33)^+$ Ions (I, IV, and VI), and the $(M-47)^+$ Ions (III, V, and VII)

Compound	Parental ion					
	$(M-17)^+$					$[M-33(47)]^+$
	daughter ions					
	$(M-33)^+$	$(M-35)^+$	$(M-47)^+$	$(M-81)^+$	$(M-67)^+$	$[M-33(47)-16]^+$
I. Isotalatisidine	0,1	0,04	0,05	0,05	—	0,1
III. Talatisamine	3,4	0,7	15	0,6	1,2	0,1
IV. Lappaconidine	0,1	0,2	0,01	0,05	—	0,2
V. Lappaconine	0,9	2,0	7,9	1,0	1,6	0,2
VI. Delcosine	3,0	0,2	0,1	0,3	—	0,1
VII. Browniine	57	0,9	2,8	0,8	1,4	0,7

Compound	Parental ion				
	$[M-33(47)]^+$				
	daughter ions				
	$[M-33(47)-18]^+$	$[M-33(47)-28]^+$	$[M-33(47)-30]^+$	$[M-33(47)-31]^+$	$[M-33(47)-32]^+$
I. Isotalatisidine	0,1	0,07	0,07	0,1	0,2
III. Talatisamime	0,2	0,08	0,3	0,2	0,3
IV. Lappaconidine	0,3	0,05	0,1	0,1	0,1
V. Lappaconine	0,6	0,1	0,3	0,3	0,4
VI. Delcosine	0,5	0,1	0,1	0,2	0,3
VII. Browniine	2,8	0,1	0,6	0,4	0,8

(compounds (I-V), (XV), (XVI), (XVIII), and (XIX)), the value of A lies between 0.2 and 0.5, with the exception of (XIX), where it amounts to 1.1%. For the compounds of the second group, splitting out $\dot{C}H_3$, mainly from C_6–OMe, this magnitude amounts to 1.8-8.2%, the greatest differences being observed once again for the position-isomers (VII) and (XVIII). An exception in this series of bases is 6-OMe-delcorine (XIII), the molecule of which contains no OH groups (A = 0.4%).

We have shown previously that the $(M-47)^+$ ions are nonhomogeneous in elementary composition, and for different alkaloids consist of the particles $(M-C_2H_7O)^+$ and $(M-CH_3O_2)^+$ in various ratios [1, 4]. The first type of fragment is formed predominantly by the elimination of $\dot{C}H_3$ + CH_3OH. It can be seen from Tables 1 and 2 that this process is realized for all compounds with the exception of N-normonticamine, which indicates the participation of the N-Et group in this process. The majority of compounds show small values of A for the $(M-15)^+ \rightarrow (M-47)^+$ transition, with the exception of talatisamine (III) and lappaconine (V), which emphasizes the role of the substituent at C-1 in the splitting out of a molecule of methanol and is in harmony with previous results obtained by the MD method [1]. We shall consider other mechanisms for the appearance of the $(M-47)^+$ ions below.

B/E Spectra of $(M-(OR_1)^+$ and of Some Other Ions. The center of attention of this section is an evaluation of the possibility of considering the $(M-OR_1)^+$ ions as objects with coincident reaction configurations (RCs) [13] when the R_1 groups are different – H, Me, and Ac [compounds (I-XIV)]. In other words, it was necessary to find how the redistribution of energy between the charged and neutral fragments with a change in the nature of R_1 affects the parameters of the B/E spectra in such complex substances, which, moreover, contain monotypical substituents. However, information of the overwhelming advantage of the process of splitting out OR_1 above others permitted the hope of only quantitative variations in the B/E spectra of the $(M-OR_1)^+$ ions in series of compounds with different R_1 radicals. Our previous experiments with MD spectra [1] did not give unambiguous results in this regime. Thus, the parameters of the transitions of the $(M-OR_1)^+$ ions of delcosine (VI) and of delcoline (X) to the $(M-OR_1-H_2O)^+$ ions differ sharply from those for compounds with $R_1 \neq H$. The B/E spectra of the $(M-OR_1)^+$ ions of all the bases investigated, in combination with the B/E spectra of some other fragments, permit not only an explanation of the reason for the above-mentioned anomalies but also give an idea of the alternative processes of the fragmentation of different parental ions and, in a number of cases, permit an estimation of their contributions.

The main feature of each of these spectra is the presence of the MP for the $(M-OR_1)^+ \rightarrow (M-OR_1-16)^+$ transition, characterized by an increased value of A for compounds with R_1 = H and its absence or extremely low intensity in the spectra of the other compounds (apart from (XIII) and (XIV)). The values of A for delcosine (VI) and delcoline are relatively large (about 3%), while for the compounds analogous to them with R_1 = Me and Ac the MP of this transition is not observed or is of low intensity ((IX), (XI), and (XII)). The differences between the values of A for compounds of the first group (I-V) are less sharp, although fairly appreciable (Table 1).

The compositions of the $(M-33)^+$ ions show that the $(M-17)^+ \rightarrow (M-33)^+$ transition takes place with the loss of a molecule of methane. Such a direction of fragmentation was first suggested by Pelletier [10] on the basis of an analysis of the mass spectra of bases of the heteratisine group, but the authors considered that the splitting out of CH_4 takes place from the $(M-OR_1)^+$ ions regardless of the nature of R_1 (H or Me). However, experiments with the B/E spectra have shown that when R_1 = Me the splitting out of methane molecules from the $(M-OR_1)^+$ ions has an extremely inappreciable magnitude. Furthermore, they have permitted a refinement of the conclusions drawn previously on the basis of an analysis of the MD spectra of the processes involved in the formation of $(M-33)^+$ ions [1]. It has now been established that the appearance of these ions in the case of the bases with C_1-OH of the first and second groups can take place by the loss both of $CH_3 + H_2O$ and of $OH + CH_4$.

Together with the qualitative differences of the B/E spectra of the $(M-OH)^+$ ions from the B/E spectra of the $(M-OMe)^+$ and $(M-OAc)^+$ ions in the series of compounds (VI), (VII), (IX), and (X-XII), it is possible to note an obvious similarity between the spectra of the two latter ions (Table 1), which indicates a similarity of the RCs of their precursors.

To explain the qualitative differences mentioned, we have made attempts to estimate the influence of alternative pathways for the formation of the $(M-OH)^+$ ions through other substituents of the lycoctonine skeleton, and, for a check, we obtained the B/E spectra of the $(M-OH)^+$ ions of compounds with R_1 = Me – talatisamine (III), lappaconine (V), and browniine (VII). The relative intensities of these ions in the synoptic spectra of compounds (III), (V), and (VII) amount to 2-3%. The values of A for the $(M-17)^+ \rightarrow (M-33)^+$ transition in the B/E spectra are 3.4% for (III), 0.9% for (V), and 57% for (VII) (Table 3). They are many times greater than the values of A of the same transitions in the B/E spectra of the analogues with R_1 = H: isotalatisidine (0.1%), lappaconidine (0.12%), and delcosine (3.0%) (Table 1). This shows that it is just the alternative methods for the formation of the $(M-OH)^+$ ions for the compounds with R_1 = H that cause the qualitative differences of the B/E spectra of the $(M-OR_1)^+$ ions. A common feature of all the molecules being compared is an OH group at C-8, and it is just the splitting out of this group, following the cleavage of the C-7–C-17 bridge bond, that may be the most probable cause of the appearance of $(M-17)^+$ ions of a different type, although it is impossible to exclude the participation of other hydroxyls, as well, in this process. If it is assumed that the mechanism of the alternative method for forming $(M-OH)^+$ ions is the same for compounds (I) and (III), (IV) and (V), and (VI) and (VII), then from the parameters of the B/E spectra of the $(M-OR_1)^+$ ions of compounds (I), (IV), and (VI) and the $(M-17)^+$ ions of compounds of (III), (V), and (VII) it is possible to evaluate the contribution of this process to the total height of the peaks of the $(M-OH)^+$ ions in the synoptic spectra of the bases (I), (IV), and (VI): for isotalitisidine, ~3%; for lappaconidine, ~15%; and for delcosine, ~5%. At the same time, the differences in the set of substituents for these compounds do not permit us to predict the cause and the source of the subsequent elimination from the $(M-17)^+$ ion of a molecule of methane in view of the absence of the necessary set of deutero analogues.

The other directions of the breakdown of the $(M-OR_1)^+$ ions do not show such considerable qualitative and quantitative differences for different R_1 radicals. Thus, on the loss of H_2O molecules the compounds of the first group ((I) and (III), and (IV) and (V)) show values of A that are close to one another but differ somewhat between the subgroups. For the compounds of the second group the compounds with R_1 = H have some advantage in the values of A, but the influence of alternative processes for the formation of the $(M-17)^+$ ions is not excluded. At the same time, the difference in the values of A for the $(M-OR_1)^+$–$(M-OR_1-H_2O)^+$ transition of the isomeric browniine (VII) and lycoctonine (X) is extremely considerable.

Approximately analogous laws are observed in the process involved in the $(M-OR_1)^+ \rightarrow (M-OR_1-CH_2O)^+$ transition (Table 1): at R_1 = H , the values of A are several times higher than in the cases with R_1 = Me or Ac, with the exception of the pair of compounds (IV) and (V).

TABLE 4. Values of A in the B/E and MD Spectra and the A_{av}/Σ_d Ratios

Compound	$M^+ \rightarrow (M-15)^+$			$M^+ \rightarrow (M-OR_1)^+$		
	A		A_{av}/Σ_d	A		A_{av}/Σ_d
	B/E	MD		B/E	MD	
I. Isotalatisidine	8,6	6,8	0,60	21	31	0,65
II. Talatisidine	13	13	0,42	7,0	7,2	0,37
III. Talatisamine	0,4	0,3	0,17	78	57	0,98
IV. Lappaconidine	8,5	6,8	0,42	21	16	0,47
V. Lappaconine	0,6	0,4	0,12	120	68	1,16
VI. Delcosine	65	47	1,93	7,5	9,3	0,70
VII. Browniine	31	16	1,30	55	32	0,93
VIII. Lycoctonine	28	15	1,54	75	39	1,21
IX. Delcosine diacetate	8,2	6,7	1,26	55	59	0,82
X. Delsoline	48	45	1,55	9,2	11	0,83
XI. Delphatine	22	15	1,42	69	37	0,97
XII. Delsoline acetate	8,0	7,4	1,26	50	48	0,81
XV. Monticamine*	7,6	8,9	0,64	4,4	2,8	0,21
XVIII. Monticoline*	14	14	0,42	0,3	0,3	0,13
XIX. Δ^2-Dihydromonticamine*	36	37	0,70	3,4	2,8	1,11
XX. Excelsine (9-hydroxymonticamine)*	5,9	7,6	0,36	5,2	3,6	0,27

*For the compounds marked with an asterisk, instead of the values of A for the $M^+ \rightarrow (M-OR_1)^+$ transition, those for the $M^+ \rightarrow (M-31)^+$ transition are given.

The values of A for the $(M-OR_1)^+ \rightarrow (M-OR_1-CH_3OH)^+$ transition for the compounds of the first group (0.03-0.07%) are an order of magnitude lower than for the compounds of the second group (0.3-0.5%). Similar differences have been found previously in a consideration of the parameters of the MD spectra [1], where it was established unambiguously by an investigation of the spectra of delphatine with a CD_3 group at C-6, that it is just this substituent that acts as the main source of the loss of a molecule of methanol from the $(M-OR_1)^+$ ions.

The B/E spectrum of the $(M-OR_1)^+$ ion of 6-OMe-delcorine (XIII) shows marked qualitative differences in comparison with delphatine (XI), which is structurally close to it. It lacks the MP of transitions to the $(M-47)^+$ and $(M-49)^+$ ions, and the value of A for the peak of the $(M-31)^+ \rightarrow (M-61)^+$ transition (loss of CH_2O at the expense of the 7,8-MDOG [4]) is the highest. Furthermore, this spectrum of compound (XIII) contains the peak of the $(M-31)^+-(M-59)^+$ transition, which confirms the conclusion based on an analysis of the MD spectra of the loss by the $(M-31)^+$ ions of CO molecules at the expense of 7,8-MDOGs [4]. A comparison of the B/E spectra of the $(M-OCH_3)^+$ and $(M-OCD_3)^+$ ions of 6-OCD_3-delcorine (XIV) showed that the value of A for the process involving the loss of a CO molecule was approximately 40 times higher in the second case than in the first (Table 1). Since the contributions of the above-mentioned parental ions in the synoptic spectrum of (XIV) are in a ratio of 8:1, this means that this process of the fragmentation of a 7,8-MDOG takes place predominatly after the elimination of the substituent from C-6.

There is one more feature of the spectra under consideration – the existence of transitions with the loss of 29 m.u., which corresponds to a formyl radical. Although the processes of successive elimination of two radicals are unlikely, here they are due to the comparatively high stabilities of ĊHO and of the odd-electron ions formed as a result.

The presence of the MPs of transitions with the loss of 31 and 32 m.u. in the B/E spectrum of the $(M-31)^+$ ions from the deutero derivative (XIV) can be partially explained by the elimination of CHDO and CD_2O molecules, and the MP of a transition with the loss of 33 m.u., which is not present in the B/E spectrum of $(M-34)^+$, by the splitting out of a CH_3OD molecule.

Now let us turn to the interpretation of the results incorporated in Table 3. Important information obtained from the B/E spectra of the $(M-17)^+$ ions of compounds (III), (V), and (VII) is given by the presence in them of an intense MP of the $(M-17)^+ \rightarrow (M-47)^+$ transition, indicating the loss of a molecule of formaldehyde and confirming the formation of ions with the alternative composition $(M-CH_3O_2)^+$ [1]. A comparison of the structures of the three compounds has shown that on the splitting out of CH_2O the greatest contribution is probably made by the OMe group at C-1.

TABLE 5. $T_{B/E}$ Values of Some Transitions

Compound	$T_{B/E}$, eV	
	$M^+ \rightarrow (M-15)^+$	$M^+ \rightarrow (M-OR_1)^+$
Delcoline (X)	0,072	0,045
Delphatine (XI)	0,058	0,028
Delcoline acetate (XII)	0,069	0,022
6-OCD_3-Delcorine (XIV)	0,055 ($-CH_3$) 0,084 ($-CD_3$)	
Δ^2-N-C_2D_5-Dihydromonticamine (XXI)	0,083 ($-CD_3$) 0,074 ($-CH_3$)	
Monticamine (XV)	0,061	0,048*
Monticoline (XVIII)	0,042	0,042*
Δ^2-Dihydromonticamine (XIX)	0,072	0,047*
Excelsine (XX)	0,049	0,037*

*Values of T for the $M^+ \rightarrow (M-31)^+$ transition.

In spite of the different positions of the OH groups participating in the elimination of a molecule of water following the ejection of ȮH from C-8 (at C-10 for (III), C-9 for (V), and C-7 and C-10 for (VII)), the values of A for the $(M-17)^+ \rightarrow (M-35)^+$ transition (Table 3) do not differ very sharply from one another. Still smaller is the observed difference between the values of A for the other transitions recorded in the B/E spectra – $(M-17)^+ \rightarrow (M-49)^+$ and $(M-17)^+ \rightarrow (M-65)^+$. The formation of the $(M-65)^+$ ions takes place in three stages, and, while the third is the elimination of ȮH, the second and third include the alternative ejection of $CH_4 + CH_3OH$ or of $CH_2O + H_2O$ in different sequences. Measurement of the accurate masses of the $(M-65)^+$ ions has shown that the composition of the ejected fragment is $C_2H_9O_2$. Consequently, the first variant is the more probable. In the same investigation the loss of the characteristic nature of the MD spectra of the daughter ions formed in 3-4 stages was noted, which was explained by the presence of a multiplicity of alternative sequences of fragmentation and the nonhomogeneity of the $(M-75)^+$, $(M-77)^+$, and $(M-79)^+$ ions with respect to elementary composition. The same features of multistage processes is well illustrated by the B/E spectra of the $(M-33)^+$ ions of isotalatisidine (I), lappaconidine (IV), and delcosine (VI) when compared with the spectra of the $(M-47)^+$ ions of their analogues with R_1 = Me – talatisamine (III), lappaconine (V), and browniine (VII). In spite of the fact that we have shown differences in the pathways for the formation of these ions above, their subsequent breakdown shows no qualitative and, in many transitions, no appreciable quantitative differences (Table III). Exceptions are the spectra of the pair delcosine–browniine, where the values of A of the transitions with the loss of identical particles differ from one another in the majority of cases by a factor of 3-7. The reason for this is the greatest qualitative difference, among the pairs of compounds studied, in the B/E spectra of the $(M-OR_1)^+$ ions of (VI) and (VII) (Table 1).

Comparison of the Parameters of the B/E and MD Spectra. Table 1 gives the values of A for the $M^+ \rightarrow (M-15)^+$, $M^+ \rightarrow (M-OR_1)^+$, and $M^+ \rightarrow (M-31)^+$ transitions for various lycoctonine bases calculated previously from the MD spectra [1, 5] and from the B/E spectra with an opened β-slit. In all cases, the values obtained by the two methods were of the same order, and half of them differed by not more than 20%. This circumstance once more enables us to be convinced of the fact that the values of A have a physical sense, namely: they are a measure of the breakdown of metastable daughter ions in definite directions [14].

For the $M^+ \rightarrow (M-15)^+$ transition the dependence of the values of A on the nature of R_1 and on the method of eliminating a methyl radical can be seen more clearly than in Tables 1 and 2. These values decrease in the series R_1 = H, Me, Ac, and for the R_1 radicals increase for compounds splitting out Me predominantly from C_6–OMe. We have established that the criterion of the common nature of the fragmentation reactions is the closeness of the values of the ratio of A to the contributions of the daughter ion in the total in the total ion current Σ_d [1, 4]. Within the framework of this empirical rule, compounds mainly splitting out Me from the N-Et group have a A_{av}/Σ_d ratio (where A_{av} is the average of the values obtained by the two methods) in the range from 0.12 to 0.70, while compounds splitting out Me from C_6–OMe have values of 1.26-1.93. At the same time, in each of the series a tendency to a decrease in this magnitude with an increase in the volume of R_1 can clearly be seen. So far as concerns the $M^+ \rightarrow (M-OR_1)^+$ transition, here the scatter of the values of A_{av} is smaller, and the ratio A_{av}/Σ_d ranges between 0.47 and 1.21. The value of A for the

above-mentioned transition in the case of talatisidine (II) (C_1–β-OH) is several times smaller than for the stereoisomer (I) (A_{av}/Σ_d = 0.37 and 0.65, respectively). However, this example is insufficient for judging the possibility of distinguishing this type of isomerism by the method under discussion.

The B/E spectra under the conditions of an open β-slit not only increase the values of A but also permit the MPs corresponding to a more far-reaching breakdown of the M^+ ions of bases taking place in several stages to be recorded. In additions to transition to $(M-33)^+$ ions, MPs of the synchronous elimination of 43, 45, 47, 49, 61, 65, 75, 77, 89, and 93 a.m.u. are observed, which agrees with the results of the MD spectra obtained for the corresponding bases. We have also compared the values of A for the direct $M^+ \rightarrow (M-33)^+$ transitions for some of the bases investigated by both methods:

	B/E	MD [1]
Talatisamine (III)	5.1	3.4
Lappaconidine (IV)	2.0	1.3
Lappaconine (V)	3.3	1.6
Delcoline (X)	2.0	2.2
Delphatine (XI)	3.7	5.1
Delcoline acetate (XII)	3.6	3.4

The value of A for the $M^+ \rightarrow (M-47)^+$ transition of talatisamine calculated by both methods is 0.9%. These examples indicate a level of agreement of the values similar to the one-stage transition given in Table 4.

* * *

It is considered that the form of the MPs obtained in a B/E spectrum is unsuitable for calculating the energies of the metastable transitions T [9]. Nevertheless, we have made an attempt at such calculations using the linear scanning of the B/E spectra and decreasing its rate to such an extent that measurements of the energy width of the MPs became reproducible.

The $T_{B/E}$ values of the following transitions were measured: $M^+ \rightarrow [M-CH_3(CD_3)]^+$ for a number of bases of the second and third groups, $M^+ \rightarrow (M-OR_1)^+$ for compounds (X-XII), and $M^+ \rightarrow (M-31)^+$ for compounds (XV), (XXI), and (XVIII-XX). From the spectrograms of the deuterated bases (XIV) and (XXI) it could clearly be seen that the splitting out of a methyl radical from a methoxy group gives MPs of close to triangular shape, while the fragmentation of the N-Et group is accompanied by peaks of Gaussian form, i.e., there is an analogy with the forms of the peaks in the MD spectra [1].

The $T_{B/E}$ values were calculated by means of the formula [9]

$$T = \left(\frac{\Delta E}{E}\right)^2 \cdot \frac{m_1^2}{16 m_2 m_3} \cdot eV,$$

where ΔE is the width of the metastable peak, eV;

E is the energy of the energy analyzer corresponding to the maximum of the metastable peak;

m_1 is the mass of the parental ion;

m_2 is the mass of the daughter ion;

m_3 is the mass of the fragment split out; and

V is the accelerating voltage in the regime of the focusing of the daughter ion (5000 V).

The values of $T_{B/E}$ are given in Table 5. As can be seen, they are two orders of magnitude lower than those obtained for the same transitions from the MD spectra [4, 5] by means of Beynon's formula [15, 16]. This is due to the greater energy width of MPs in MD spectra (of the order of 70-100 eV). Some authors [13] have proposed the use in this case of reduced widths calculated from the formula

$$\Delta W_{red} = \sqrt{\Delta W_{mp}^2 - \Delta W_{dp}^2},$$

where ΔW_{dp} is the width of the peak of the daughter ions; and

ΔW_{mp} is width of the metastable peak.

The values of T_{red} obtained in this way are smaller by an order of magnitude, on average, but at the same time, they still do not approach the values of $T_{B/E}$. Consequently, it is necessary to use another, independent method, of calculating the values of T; for example, from thermochemical results. However, it must be borne in mind that with all the imperfection of the methods of calculating the energies of metastable transitions by measuring the parameters of the MPs, any of them prove to be applicable from the practical point of view for characterizing monotypical fragmentation reactions. This follows most clearly from the results for the deutero analogues (XIV) and (XXI). Simple cleavage in the N-Et group gives values of $T_{B/E}$ of 0.053 eV (XIV) and 0.033 eV (XXI); more complex processes in the splitting out of a methyl radical from C_6–OMe (XIV), C_{14}–OMe, or C_{16}–OMe (XXI) lead to values of 0.084 eV (XIV) and 0.074 eV (XXI) (Table 5). For the unlabeled bases, $T_{B/E}$ for the $M^+ \rightarrow (M-15)^+$ transition has intermediate values.

The tendency to a decrease in the energy $T_{B/E}$ for the $M^+ \rightarrow (M-OR_1)^+$ in the series delcoline–delphatine–delcoline acetate is the same as for the values of T calculated from the MD spectra [5]. A similar parallelism in the changes of energy is observed in the fragmentation process $M^+ \rightarrow (M-15)^+$ on passing from the 3,4-epoxy bases (XV), (XVIII), and (XX) to the isomeric compound (XIX).

For the conditions of the mass-spectrometric experiment, see [14].

LITERATURE CITED

1. Ya. V. Rashkes and M. S. Yunusov, Khim. Prir. Soedin., 481 (1984).
2. M. S. Yunusov, Ya. V. Rashkes, B. T. Salimov, É. F. Ametova, and G. V. Fridlyanskii, Khim. Prir. Soedin., 525 (1985).
3. M. S. Yunusov, V. E. Nezhevenko, and S. Yu. Yunusov, Khim. Prir. Soedin., 770 (1975).
4. E. G. Sirotenko and Ya. V. Rashkes, Khim. Prir. Soedin., 397 (1987).
5. E. G. Sirotenko, Ya. V. Rashkes, V. A. Tel'nov, and M. S. Yunusov, Khim. Prir. Soedin., 95 (1989).
6. J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Y. Ridley, Anal. Chem., 45, 1023A (1973).
7. W. F. Haddon, Anal. Chem., 51, 983 (1979).
8. F. W. McLafferty and F. M. Bocknoff, Anal. Chem., 50, 69 (1978).
9. J. R. Chapman, Practical Organic Mass Spectrometry, Wiley, Chichester (1985).
10. S. W. Pelletier and R. Aneja, Tetrahedron Lett., 557 (1967).
11. E. G. Sirotenko, Ya. V. Rashkes, A. S. Narzullaev, M. S. Yunusov, V. M. Matveev, and S. S. Sabirov, Khim. Prir. Soedin., 389 (1987).
12. M. S. Yunusov, Ya. V. Rashkes, and S. Yu. Yunusov, Khim. Prir. Soedin., 85 (1972).
13. J. L. Holmes and J. K. Terlouw, Org. Mass Spectrom., 15, 383 (1980).
14. Yu. M. Mil'grom, Ya. V. Rashkes, G. V. Fridlyanskii, and B. M. Voronin, Khim. Prir. Soedin., 488 (1990).
15. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, Metastable Ions, Elsevier, Amsterdam (1973).
16. M. D. Migahed and F. H. Abd El-Kader, Int. J. Mass Spectrom. Ion Phys., 28, 225 (1978).