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USE OF THE METHOD OF METASTABLE DEFOCUSING FOR THE ANALYSIS OF THE PROCESSES INVOLVED IN THE FRAGMENTATION OF LYCOCTONINE BASES

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The metastable transitions in the mass spectra of 21 lycoctonine bases have been studied by the method of metastable defocusing (MD). It has been established that as a criterion of the monotypicity of single-stage fragmentation reactions it is possible to use a linear dependence of the relative intensities of the metastable peaks (MPs) on the stability of the daughter ion. In the MD spectra of the ions formed in several stages, to characterize the generality of the breakdown reactions, in addition to the intensities of the MPs, the accurate positions of their maxima and the general shape of the curve are important.

The mass spectra of diterpene bases with the lycoctonine skeleton give important information on the structures of these compounds, thanks to the characteristic redistribution of the intensities of the peaks of the ions M^+, $(M - CH_3)^+$, and $(M - OR)^+$ in the spectra of the alkaloids of various subgroups. In the majority of cases, the nature of the fragment OR split off is known, while the processes involved in the formation of the ions $(M - CH_3)^+$ are ambiguous. On studying the spectra of delcosine (VII) and its derivatives, Waller et al. [1] suggested that a CH_3 group was split off from the CH_3O at C-6. Previously Pelletier and Aneja [2] had come to the conclusion that the $(M - 15)^+$ ions arose on the fragmentation of the N-ethyl group. These authors [2] considered the spectra of compounds containing no methoxyl at C-6.

On comparing the spectrum of neoline (III) and its N-nor analogue we detected a sharp decrease in the height of the peak of $(M - CH_3)^+$ ion. Two conclusions followed from this: 1) M^+ of the neoline ion breaks down with the elimination of CH_3 predominantly from N—Et; and 2) in the absence of an OH group at C-7 a methoxyl at C-6 does not take an appreciable part in the formation of the $(M - CH_3)^+$ ions.

Having these facts available, in the present paper we shall consider these processes from the point of view of the parameters of the metastable ions obtained by the method of metastable defocusing (MD). How sensitive these parameters are to the various methods of splitting out identical fragments and what are the criteria for the monotypicity of the

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fragmentation reactions of the lycocotonine bases were the main points that were to be determined. In addition to the results obtained for single-stage fragmentation processes, our attention was attracted by the MD spectra of the ions of diterpene bases formed under electron impact in 2-4 stages.

The literature relating to modern aspects of the investigation of metastable transitions is fairly voluminous, but we have isolated that part of it which relates directly to the solution of the problem posed in the present paper.

The two main parameters of metastable peaks (MPs) are form and intensity. The forms of the MPs depend mainly on the structure of the parent and daughter ions, and the intensities on the rate constant of the reaction, which, in its turn, depends on the structures of the reactants and of the fragmentation products [3]. Ions with the same reserve of internal energy and the same structure can be identified if as the result of their subsequent decomposition MPs appear with the same parameters [4]. A multiplicity of competing reactions in the fragmentation of a given parent ion takes its origin from isomeric reacting configurations (RCs). The term RC was introduced by Holmes and Terlouw [5] to denote ionic structures which, without rearrangement, lead to concrete transition states.

For such relatively complex objects as the ions of diterpene bases, the idea of RCs can be used only in individual cases and, in particular, in the recording the MPs arising on the fragmentation of ions of the same structure having different precursors. For example, in the fragmentation of the particles $(M - OR_1)^+$, which were derived from molecular ions differing only by the nature of R_1.

In order to broaden the possibilities of using the parameters of the MPs by including the maximum number of objects, we started from the following assumptions. Since it is known that in the main processes of fragmentation of the lycoctonine bases definite substituents take part, in subgroups of the substances with different peripheral but identical "reacting" substituents (lycoctonine — browniine — delphatine; isotalatisidine — condelphine; delcosine — delsoline, etc.), for metastable transitions taking place with the loss of identical particles from identical positions one may expect the appearance of MPs with close parameters in spite of the different m/z values of the parental ions.

For confirmation we measured the ratio of the intensities [4] of the MPs (h_{MP}) recorded by the MD method and the intensities of the peaks of the parental ions (h_P) in the metastable transitions $M^+ \rightarrow (M - 15)^+$ and $M^+ \rightarrow (M - OR_1)^+$ in the spectra of 21 compounds. The ratios (A) expressed in percentages are given in Table 1, where the bases are arranged in groups according to the nature of the substituent at C-1, C-6, and C-7. The 3,4-epoxy bases form a separate subgroup.

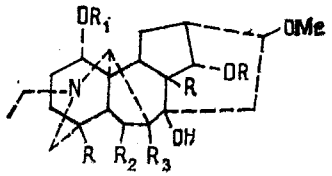
The value of A for the process of splitting out of OR_1 always [with the exception of the epoxy compounds (XIX-XXI)] has the same order and closer values within the limits of each structural group of compounds. Thus, the 1-methoxy bases (IX-XI) have the mean value A = 61.6%, and the 1,8-dihydroxy-6-methoxy bases (XIII-XV) a mean value of 36%. The corresponding 1-hydroxy compound (I-VI) and (VII and VIII) give mean values of A two or three times more than the values for the 1-methoxy derivatives (25.7% and 10.0%).

So far as concerns the form of the MPs in the process under consideration, as a rule, they have slightly flat vertices and rapidly falling wings (Fig. 1), which distinguishes them from the peaks of Gaussian form given in the literature [5]. We have not given a detailed discussion of the shape of the MPs, limiting ourselves to the intensities of the peaks.

Yeo and Williams [6] have proposed as a criterion of the similarity of ionic structures differences between the ratios of the intensities of the MPs not exceeding a factor of 5. As can be seen from Table 1, these differences do not exceed a factor of 2 for the 1-hydroxy bases, and in the other groups of compounds they are considerably smaller. Thus, our suggestion of a possible closeness of the relative heights of the MPs in monotypical reactions of the breakdown of the parental ions with different m/z values has been confirmed. The larger differences in the values of A between groups of compounds with different R_1's can be explained by differences in the distribution of energy in the preceding molecular ions [6, 7].

The values of A for the transition $M^+ \rightarrow (M - OR_1)^+$ in the epoxy bases (XIX-XXI) are several tens of times lower than for the other 1-hydroxy bases (I-VI). This may be a con-

TABLE 1. Values of $A = \frac{h_{MP}}{h_P}$ 100 for Various Metastable Transitions



Type and name of the base	Single-stage processes				Multistage processes															
	daughter ions																			
	$(M-15)^+$		$(M-OR_1)^+$		$(M-33)^+$			$(M-35)^+$	$(M-47)^+$			$(M-49)^+$		$(M-61)^+$	$(M-63)^+$			$(M-65)^+$		
	metastable transitions																			
	$M^+ \rightarrow (M-15)^+$	$\Sigma(M-15)^+$, %	$M^+ \rightarrow (M-OR_1)^+$	$\Sigma(M-OR_1)^+$, %	$M^+ \rightarrow (M-33)^+$	$(M-15)^+ \rightarrow (M-33)^+$	$(M-17)^+ \rightarrow (M-33)^+$	$M^+ \rightarrow (M-35)^+$	$(M-17)^+ \rightarrow (M-35)^+$	$M^+ \rightarrow (M-47)^+$	$(M-15)^+ \rightarrow (M-47)^+$	$(M-17)^+ \rightarrow (M-47)^+$	$(M-17)^+ \rightarrow (M-49)^+$	$(M-31)^+ \rightarrow (M-49)^+$	$(M-31)^+ \rightarrow (M-61)^+$	$(M-15)^+ \rightarrow (M-63)^+$	$(M-17)^+ \rightarrow (M-63)^+$	$(M-31)^+ \rightarrow (M-63)^+$	$(M-33)^+ \rightarrow (M-65)^+$
$R_1=R_2=R_3=H$																				
I. Condelphine	9,5	11,2	32,2	41,2	1,7—1,8			0,081	0,10	0,34		0,22	0,88	3,0	2,4		0,32	1,4	0,44
II. Isotalatisidine	6,8	12,8	31,0	40,3	1,4—1,8			0,040	0,11	0,24		0,24	1,0	2,9	1,2		0,32	1,6	0,67
III. Neoline (R_2= OMe)	6,7	10,3	27,2	43,8	1,4—1,6			0,062	0,08	0,20	0,72		0,83	1,9	1,6		0,27	2,5	2,4
IV. Dihydromonticamine	6,7	11,3	20,3	35,5	1,1—2,1			0,10	0,62	0,075		0,11	0,17	4,9	2,6	0,62		3,0	3,0
V. Lappaconidine	6,8	11,5	16,0	38,6	1,3—2,0			0,070	0,46	—		0,24	0,24	5,6	1,6	0,60		1,4	1,0
$R_1=R_2=H$; R_3=OH																				
VI. Dihydromonticoline	16,7	22,7	27,3	34,7	1,2	—	—	0,082	1,0	0,068		0,11	0,50	4,2	1,7	0,50		2,2	1,3
R_1 = H; R_2 = OMe; R_3=OH																				
VII. Delcosine	47,2	28,8	9,3	12,3	1,6	12,8	—	0,56	1,5		0,48		1,8	1,2	0,60		0,50	0,32	0,90
VIII. Delsoline	45,5	29,6	10,6	12,3	2,2	11,3	—	0,60	1,6		0,40		1,9	1,1	0,31		0,25	0,42	0,87
$R_1=CH_3$; $R_2=R_3=H$																				
IX. Talatisamine	0,3	2,0	56,5	69,0	3,4	1,2	—	—	—	0,90	7,4		6,7	0,24	0,12		1,8	0,30	1,5

X. Aconoridine	0.5	2,2	60,0	78,5	3.7	1 7	—	—	—		6,5		18,0	0,30				0 22	
XI. Lappaconine $R_1=CH_3$; $R_2=H$; $R_3=OH$	0,4	4,1	68 2	80,8	1,6	1,0	—	—	—		2.6		9,2	0,38	0,040			0,065	9.0
XII. Demethylene desoxydelcorine $R_1=CH_3$; $R_2=OMe$; $R_3=OH$	0,3	2,8	60,0	72,0	3.4	4,3	—	—	—	1,5	3,6		10.0	0,33	0,075		3,6	0.41	3.9
XIII. Lycoctonine	15,5	14,4	39,0	47,0	6 6	15 2	—	—	—		1.2		8,3	0,54	0,39			1,2	2,8
XIV. Browniine	15,8	17,6	31,5	46,7	5,8	12,5	—	—	—		0,60		9,0	0,38	0,24		2,4	0,92	2 2
XV. Delphatine	15,0	13,3	37,0	50,0	5,1	13 3	—	—	—		1,2		9.8	0,48	0.27		3,5	0,95	5,8
XVI. [D_3]delphatine* ($R_2=OCD_3$) $R_1=COCH_3$; $R_2=OMe$; $R_3=OH$	15,3	13,5	2,5		4 1	13 9	—	—	—		0,95		9,5	0.70	0.48			1,2	3,0
	0.5		50,0		3,7	1,5	—	—	—		4.7		9,8	0,44	1,1			0,28	3,0
XVII. 1,14-Diacetoxydelcosine	6,7	5,9	50,0	63,6	2,8	25,6	—	—	—		0.87		6,4	0,89	0,25		2,4	0,75	0,64
XVIII. 1-Acetoxydelsoline $R_1=R_2=R_3=H$; 3,4-epoxy	7,4	6,1	48,2	61,2	3,4	26,3	—	—	—		0,90		10,0	1,0	0,10		1,0	0,39	0,32
XIX. Excelsine	6 0	21,3	0,88	4,7	0,45	1 2	—	0,16	5,2	0,20	0,35		2,0	2,7	0,29	0,16		0,39	2,9
XX. Monticamine	4,4	20,8	0,8	5,0	0,22	0,74	—	0,084	2.3	0,064	0,27		2,2	2,2	0,20	0,25		0,22	4,0
XXI. Monticoline ($R_3=OH$)	15,4	54.0	0,75	2.6	0,23	1.2	—	0,025	2,9	0.12	0,07		3,6	6,4	4,2	0,16		4,7	3.8

*The first line of figures relates to processes involving the loss of labeled fragments and the second to that of unlabeled fragments.

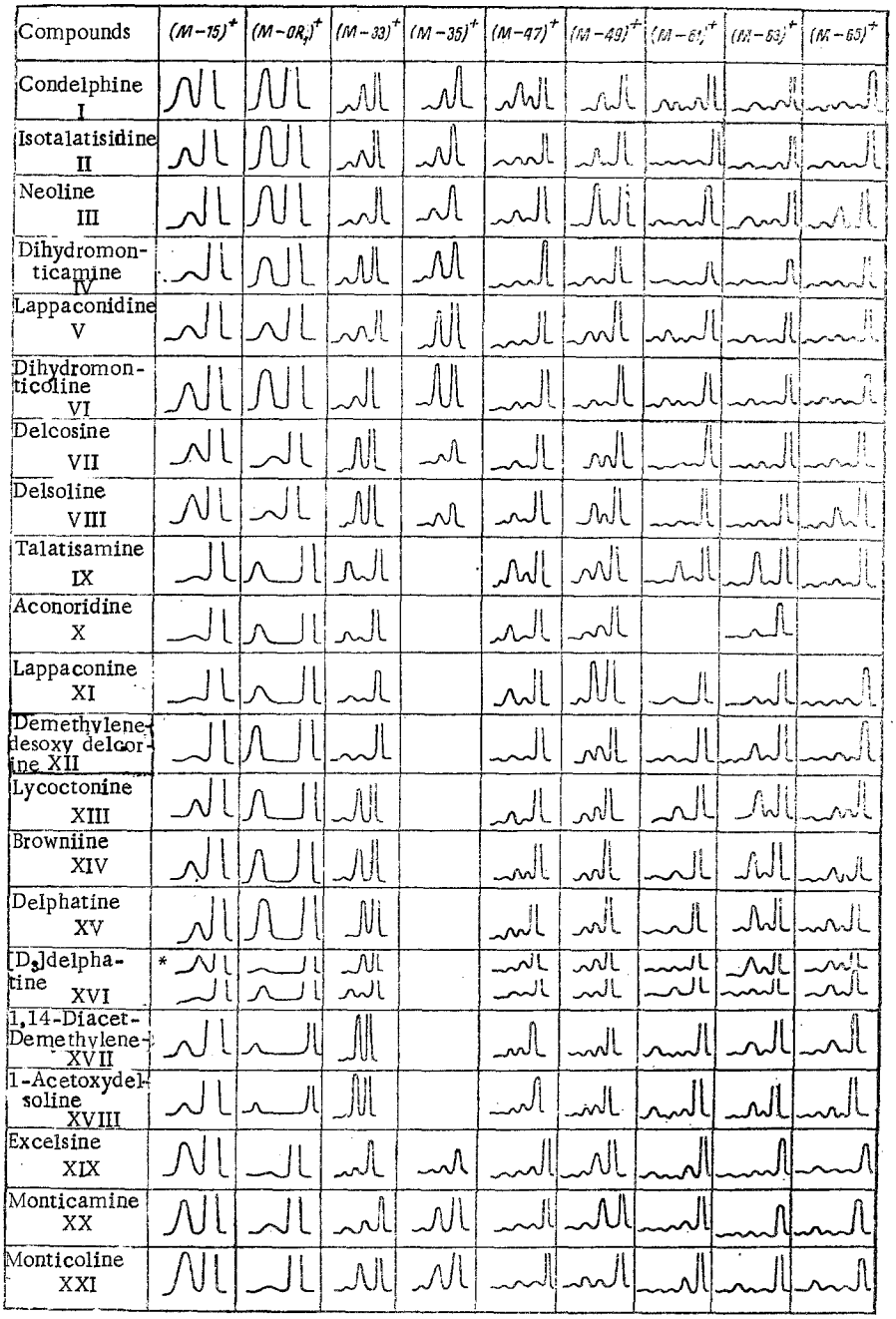


Fig. 1. MD spectra of the ions $(M - 15)^+$-$(M - 65)^+$ of the lycoctonine bases (I-XXI).

sequence of a different mechanism of the splitting out of a ÔH radical from M^+. However, on comparing the figures for all the compounds we directed our attention to the symbatic dependence of the value of A on the contributions of the $(M - OR_1)^+$ ions to the total ion current $[\Sigma(M - OR_1)^+]$ (Table 1). This relationship is satisfactorily characterized by a straight line (Fig. 2a), upon which the points corresponding to the epoxy bases also fall. Only lappaconidine (V) has a value of A appreciably smaller than follows from this relationship.

Since there is every reason for considering that the mechanism of the formation of the $(M - OR_1)^+$ ions is the same for all the compounds appearing in Table 1, as a criterion of the common nature of the mechanism of fragmentation to a first approximation we may take the linear nature of the relationship $A = f(\Sigma d)$ where d is a daughter ion. On the basis of this assumption, let us analyze the values of A for the ions $(M - 15)^+$. Here the differences between the groups are more considerable, but within the individual groups the same order of magnitude is retained (Table 1). Thus, the 1-hydroxy bases (I-V), splitting out a methyl

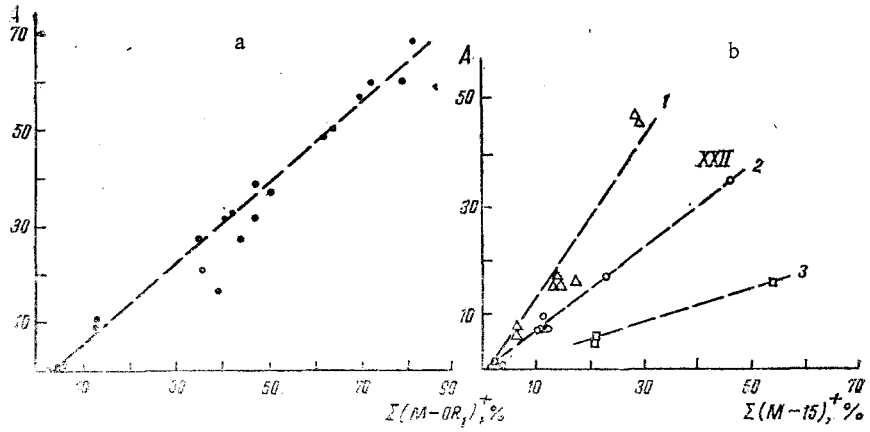


Fig. 2. Graph of the relation A = f(Σd) for the transitions $M^+ \rightarrow (M - OR_1)^+$ (a) and $M^+ \rightarrow (M - 15)^+$ (b).

predominantly from the N-ethyl group [1] give a mean value for A of 7.3%, while delcosine (VII) and delsoline (VIII), forming the $(M - 15)^+$ ions mainly through the splitting out of $\dot{C}H_3$ from C_6—OCH_3 [1] have a mean value for A of 46.4%. Even larger are the differences between the 1-methoxy compounds of the corresponding subgroups: 0.3% for talatisamine and 15.5% for lycoctonine. Compounds differing only by the nature of R_1 (isotalatisidine—talatisamine; delsoline—delphatine—1-acetoxydelsoline; etc.) also show a large difference in the magnitudes under consideration.

A graph of the relation A = f(Σ$(M - 15)^+$) for compounds (I-XXI) gives a family of three straight lines (Fig. 2b). Straight line 1 passes through the points corresponding to all the 7,8-dihydroxy-6-methoxy bases regardless of the nature of R_1. The points of the compounds forming the $(M - 15)^+$ ions by the fragmentation of the N-ethyl group fall on line 2. We may note that the points corresponding to 1-deoxycondelphine (XXII) [8] and dihydromonticoline (VI) fall on the same line. This fact confirms the intensification of the role of the splitting out of CH_3 from the N—Et group when an OR group is absent from C-1 (XXII) or when a 7,8-diol group is present (VI) [3].

Straight line 3 passes through the points corresponding to the epoxy compounds (XIX-XXI). The mechanism of the fragmentation of these bases, leading to a marked redistribution of the contributions of the processes of splitting out $\dot{C}H_3$ or OR_1 are being investigated at the present time. There is no doubt that the presence of the epoxy group has decisive importance, since the spectra of the corresponding dihydro derivatives (IV)-(VI) reveal the usual features characterizing other 1-hydroxy bases.

Under the conditions that we use for recording MPs, all the MPs of the ions arising in the process of splitting out a methyl radical from the methoxyl at C-6, without exception, have a shape close to triangular (Fig. 1).

Summing the facts given, we come to the conclusion that the results of measurements of the parameters of the metastable ions by the MD method in association with the results of ordinary mass spectroscopy can serve as a criterion for the monotypicity of fragmentation reactions in ions of complex structure with different mass numbers. Instead of the RC concept, with the aid of which the similarity or difference of the structures of relatively small decomposing particles was evaluated [5], here it is possible to introduce the ideas of a "reacting element of the structure" (RES) having in view that part of the ion which, as the result of the fragmentation process under consideration, is subjected to the greatest change. Thus, for example, in the formation of the $(M - 15)^+$ ions of delcosine (VII) the RES is the methoxy at C-6, and for alkaloids of the talatisamine (IX) type it is the N-ethyl group.

Calculation of the values of A in the spectrum of [D_3]delphatine (XVI) serves as proof of the applicability of the relationship found. Thus, for the transitions $M^+ \rightarrow (M - CD_3)^+$ and $M^+ \rightarrow (M - CH_3)^+$ they are, respectively, 15.3% and 0.5%. The former is very close to the values characteristic for the alkaloids (XIII-XV), in which the methoxy at C-6 is present as the RES, and the latter is characteristic for compounds of the talatisamine type (IX-XI).

This shows that some of the $(M - CH_3)^+$ ions of delphatine (XV) arise through the breakdown of the N-ethyl group.

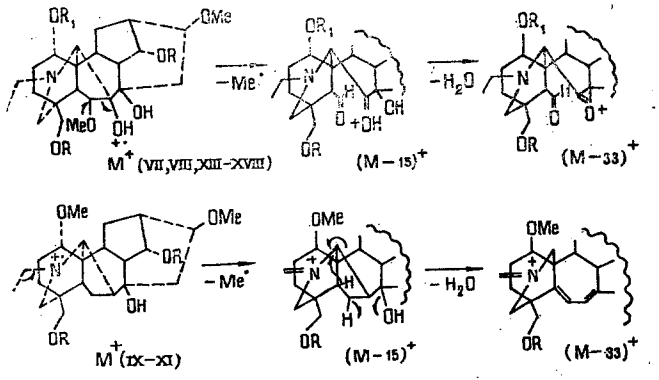
The heights of the peaks of the $(M - OCH_3)^+$ and $(M - OCD_3)^+$ in the review spectrum of $[D_3]$delphatine are in a ratio of 41:9. The first of them appears mainly on the detachment of the radical from the C-1, in view of which the value of A for the $M^+ \rightarrow (M - OCH_3)^+$ transition is 50% and is close to the corresponding values for talatisamine (Table 1). The $M^+ \rightarrow (M - OCD_3)^+$ transition, i.e., the loss of the substituent from C-6, is characterized by a low value of A (2.5%). Thus, the superposition of the two processes mentioned is the reason for the fall in the value of A for the $M^+ \rightarrow (M - OCH_3)^+$ transition in the spectra of (XIII-XV) as compared with compounds related to talatisamine.

We have considered the single-stage fragmentation processes giving in the general spectra of the diterpene bases the peaks with the greatest intensity. The subsequent stages of fragmentation have been discussed in the literature to only a slight extent in view of their small contribution and the abscence of specificity. What we have in view are the peaks of ions differing from M^+ by 33, 47, 49, 59, 61, 63, 65, 75, 77, and 79 mass units observed in all the spectra.

For a number of reasons, the application of the MD method in relation to these ions can give a large volume of information. In the first place, because we pass from the characterization of a single MP in single-stage fragmentation reactions to a MD spectrum containing information on several successive and competing reactions. In the second place, in view of the obvious relationship between the intensities of the MPs and of the parental ions, the distribution of the heights of the peaks in the MD spectrum will change according to the subgroup of substances. Finally, the specificity of the MP spectra may be the result of the participation in the multistage processes of the breakdown of the peripheral substituents or, in other words, the appearance of RESs, the set of which is an individual one for each compound.

Let us consider from this point of view the MD spectra of the daughter ions formed from M^+ of the lycoctonine bases in 2-4 stages, which include up to 5 MPs. In addition to comparing the spectrograms (Fig. 1) we also measured the values of A for those transitions where it is possible unambiguously to establish the m/z values of the daughter ions. Under the conditions of recording the MD spectra, daughter ions differing by 1-2 mass units can give irresolvable MPs.

The $(M - 33)^+$ ions in the majority of bases included in Table 1 are formed by the elimination of CH_3 and H_2O. Compounds with an OH group at C-1 can decompose by the successive loss of OH and CH_4 [2]. The MD spectra of the $(M - 33)^+$ ions always contain two peaks each (Fig. 1), the first of which corresponds to the synchronous elimination of 33 m.u. from M^+. All the spectra are divided into three types. To the first type belong the 1-hydroxy bases (I-VI). The second MP in these spectra is slightly broadened through the superposition of two transitions: $(M - 15)^+ \rightarrow (M - 33)^+$ and $(M - 17)^+ \rightarrow (M - 33)^+$, but the position of the maximum of the MP always (with the exception of dihydromonticoline (VI), corresponds to the second process. All the compounds of this group are characterized by close values of A (Table 1) for both transitions. The heights of the two MPs here are in a ratio of 1:2-1:3.



In the spectra of compounds (VII-XXI), the position of the second maximum corresponds strictly to the $(M - 15)^+ \rightarrow (M - 33)^+$ transition. The spectra of the epoxy bases and the spectra of all the 7,8-dihydroxy-6-methoxy bases, regardless of the nature of the substituent at C-1, are monotypical. They differ only by the ratio of the heights of the MPs. The fluctuations in the value of A in the spectra of the substances of the last group do not exceed a factor of 4 for a synchronous transition and a factor of 2 for a $(M - 15)^+ \rightarrow (M - 33)^+$ transition. Within the subgroups with identical substituents at C-1 the difference is even less considerable. These facts indicate that the process of forming the ions $(M - 33)^+$ for the 7,8-dihydroxy-6-methoxy bases is localized in the C_6–C_8 chain (scheme). It may also be assumed that the triangular form of the MP for the first stage of this process is due a migration of the positive charge to this section of the lycoctonine skeleton.

The third type of MD spectra of the $(M - 33)^+$ ions is given by the 1-methoxy bases (IX-XI). This distinguishing feature is the fact that the height of the first MP is several times greater than that of the second, while both transitions have values of A of the same order. Demethylenedesoxydelcorine (VI) is distinguished from them by an increased height of the second peak and a corresponding rise in A which is possibly due to a mechanism of the elimination of a water molecule different from that in (IX-XI).

Analysis of the transitions in the spectrum of [D_3]delphatine (VI) shows that some of $(M - 33)^+$ ions are formed by a different mechanism. This can also be seen from the fact that the peaks of the ions $(M - CH_3 - H_2O)^+$ and $(M - CD_3 - H_2O)^+$ in the spectrum have a ratio of ~1:2. The MD spectrum of the first ion is similar both in external form and with respect to the value of A to the corresponding spectra of alkaloids of the talatisamine type. It follows from this that some of the $(M - 33)^+$ ions of delphatine may be formed by the splitting out of a methyl radical from N–Et with the subsequent loss of a molecule of water. Since the only common hydroxyl in the bases (IX) and (XV) is the OH at C-8, this stage takes place with the participation of just this group (scheme). The MD spectrum of the ion $(M - CD_3 - H_2O)^+$ is, as was to be expected similar in all characteristics to the spectrum of the $(M - 33)^+$ ions of delphatine (Fig. 1 and Table 1).

The $(M - 35)^+$ ions are obtained as the result of the successive elimination of $\dot{O}H$ and H_2O. They are observed in the spectra of the 1-hydroxy bases in the form of extremely weak peaks and have no analytical value. Below, these ions will be considered from the point of view of possible analogies between the MD spectra of fragments with a common formula $(M - OR_1 - H_2O)^+$.

The MD spectra of the $(M - 35)^+$ ions are monotypical and each contain two peaks with a ratio of the heights of 1:4-1:10. The peaks of the synchronous elimination of 35 m.u. has a low intensity. The value of A for this transition has the same order in all the compounds apart from the 6-methoxy bases – delcosine and delsoline. The second peak corresponds to the loss of a molecule of water by the $(M - 17)^+$ ions. Its height amounts to 30-70% of the height of the peak of the daughter ion $(M - 35)^+$. The value of A for the transition under consideration in the case of compounds with an OH group at C-4 (IV-VI) is several times higher than for the bases with a methoxymethylene substituent at this atom (I-III) (Table 1). This can be explained by the participation of this hydroxyl in fragmentation in this direction. At the same time the value A for dihydromonticoline (VI) approximates to that for other the 7,8-dihydroxy bases (VII) and (VIII), which shows the participation of the diol grouping in fragmentation by this route.

Using the $(M - 35)^+$ ions as examples, it is easy to see that a single external similarity of the MD spectra cannot serve as a proof of the common nature of the process by which a fragmentary ion is formed.

The $(M - 47)^+$ ions are inhomogeneous in their elementary compostions and arise by the loss of either C_2H_7O or CH_3O_2 fragments. The relative proportions of the ions of the two varieties for some of the alkaloids investigated are as follows: condelphine (2:3), neoline (2:1), lappaconidine (3:2), lycoctonine (1:1). The first type of $(M - 47)^+$ ions is formed by the successive elimination of $\dot{C}H_3$ and CH_3OH, but the possibility of the elimination of $CH_3\dot{O} + CH_4$ is not excluded [2]. The two-oxygen fragment can be split out in the form of $\dot{O}H + CH_2O$ or $CH\dot{O} + H_2O$. Because of the superposition of different processes the MD spectra of the $(M - 47)^+$ ions are less specific than the spectra of $(M - 33)^+$ ions. The difference in the corresponding intensities of the individual MPs for representatives of different subgroups of compounds is not so obvious. Thus, the MD spectra of delcosine diacetate (XVII)

and of monticamine (XX) are superficially similar. At the same time, the spectra of condelphine (I) and of isotalatisidine (II), which are close in structure, differ although they have A values of the same order of magnitude. An example of monotypical bases giving similar MD spectra and A values is formed by the 1-hydroxy bases with OH at C-4 (IV-VI).

The peak of the synchronous elimination of two particles has a variable but for the most part low intensity. The position of the second maximum depends on the particular group to which the substance belongs. In the case of the 1-hydroxy bases (I, II, IV-VI) it corresponds to the transition $(M - 17)^+ \rightarrow (M - 47)^+$, which confirms the sequence of elimination of $\dot{O}H$ and CH_2O. The value of A in this transition in the compounds mentioned are also close. The position of this maximum in the spectrum of neoline (III), as in the spectra of the other compounds, corresponds to the transition $(M - 15)^+ \rightarrow (M - 47)^+$. It is possible that this feature of neoline is caused by the presence of a methoxyl at C-6, which is responsible for the elimination of a methanol molecule from the $(M - 15)^+$ ions.

As can be seen from Table 1, the order of magnitude of A for the transition under consideration depends substantially on the type of base. For all compounds with a 7,8-dihydroxy-6-methoxy group (VII, VIII, XIII-XVIII), the parental ion $(M - 15)^+$ was formed by a single mechanism through the splitting out of a methyl radical from the methoxyl at C-6. Since this decomposition with the liberation of a molecule of methanol gives similar values of A in all cases (averaging 0.8%), this can be taken as a proof of the common nature of the mechanism of this stage. For the 1-methoxy bases (IX-XI), the elimination of $\dot{C}H_3$ from the N—Et group is obviously accompanied by the splitting out of a molecule of methanol from C-1. The mean value of A for the latter transition is 5%.

The MD spectra of the ions $(M - 47)^+$ and $(M - 50)^+$ $[(M - CD_3 - CH_3OH)^+]$ of deuterodelphatine (XVI) serve as an illustration of the competing methods for the formation of the $(M - 47)^+$ ions. In the first spectrum the value of A for $(M - 15)^+ \rightarrow (M - 47)^+$ amounts to 0.95%, and on the second the $(M - 18)^+ \rightarrow (M - 50)^+$ transition gives A = 4.7%.

These two magnitudes are close, respectively, to the mean values given above that are characteristic for substances of the type of lycotonine and talatisamine.

The position of the third maximum in the MD spectra of the $(M - 47)^+$ ions does not permit it to be assigned to a definite transition.

The $(M - 49)^+$ ions, together with the $(M - 33)^+$ ions, give the most characteristic MD spectra. The two main processes for their formation are the successive splitting out of $\dot{O}H + CH_3\dot{O}H$ or of $CH_3\dot{O} + H_2O$. Fragmentation by the first route is more characteristic for the 1-hydroxy derivatives, and in all cases, apart from the epoxy compounds (XIX-XXI), the peak of the $(M - 17)^+ \rightarrow (M - 49)^+$ transition is the most intense. The $(M - 31)^+ \rightarrow (M - 49)^+$ transition is represented by a weak peak in the case of compounds (I-III). Its intensity rises for delcosine and delsoline and for the bases with an OH group at C-4 the peaks of the two transitions are of comparable height.

The external characteristics of the MD spectra of the epoxy bases differ substantially: the spectrum of monticoline (XXI) is close to that of its dihydro derivative (VI), and the spectra of monticamine and of excelsine are distinguished by the height of the peak of the $(M - 31)^+ \rightarrow (M - 49)^+$ transition.

In the spectra of all the 1-hydroxy bases apart from delcosine a peak of the synchronous elimination of 49 amu can be seen. This feature is not characteristic for the 1-methoxy bases (IX-XV). They form monotypical spectra where the peak of the $(M - 31)^+ \rightarrow (M - 49)^+$ transition is 2-3 times higher than the peak of the $(M - 17)^+ \rightarrow 49)^+$ transition. This feature is also characteristic for the acetates (XVII) and (XVIII). An exception is the spectrum of lappaconine (XI), the ratio of the heights of the peaks for which amounts to 1:10.

The order of magnitude of A for both transitions in the case of 1-hydroxy bases varies according to changes in the external form of the MD spectra, but within the individual subgroups close mean values of this magnitude are retained. For the 1-methoxy and 1-acetoxy derivatives the similarity of the MD spectra is also reflected in the similar order of magnitude of A for the first of the transitions. To elucidate the reason for the closeness of these magnitudes in the case of compounds with different substituents at C-1, let us consider the MD spectra of the $(M - 49)^+$ and the $(M - 52)^+$ $M - OH - CD_3OH)^+$ ions of compound (XVI). In their external characteristics, the two spectra are similar to the spectrum of the $(M - 49)^+$ ion of delphatine (XV). The ratio of the intensities of the first and second peaks in

the latter occupies an intermediate position between the analogous ratios in the two spectra of [D_3]delphatine (XVI) that have been mentioned. The heights of the peaks of $(M - 49)^+$ and $(M - 52)^+$ ions in the review spectrum of this compound have a ratio of approximately 2:1. The values of A in the spectra of the $(M - 49)^+$ ions of (XV) and (XVI) coincide, and in the spectrum of $(M - 52)^+$ ion the peak of the $(M-17)^+ \overline{-CD_3OH} (M-52)^+$ transition is characterized by the same magnitude as the $(M - 17)^+ \overline{-CH_3OH} (M-49)^+$ in the MD spectrum of the $(M - 49)^+$ ions of the same compound. Thus, the similarity of the MD spectra of the 1-methoxy and 1-acetoxy bases is determined by the fortuitous coincidence of the values A in the processes of losing CH_3OH from two different positions of this skeleton.

So far as concerns the second peaks of the MD spectra, measurements for the $(M - OCD_3)^+ \rightarrow (M - OCD_3 - H_2O)^+$ transition gave a value of 0.7%, close to the values for the $(M - 31)^+ \rightarrow (M - 49)^+$ transition of the 1-acetoxy bases (XVII) and (XVIII).

The $(M - 61)^+$ Ions. Their composition always corresponds to the elimination from M^+ of a $C_2H_5O_2$ fragment in two stages, but the nature of the separate stages varies according to the type of compounds. For the 1-methoxy bases the main sequence of processes is $M - \dot{C}H_3O - CH_2O$, and in the MD spectra the height of the MP of $(M - 31)^+ \rightarrow (M - 62)^+$ transition stands out. Although all the spectra of this group of substances are monotypical, the values of A for this transition differ substantially in the cases of talatisamine and lycoctonine (0.12 and 0.39%), which is due to the participation of different methoxyls in the process of eliminating a formaldehyde molecule. This has been confirmed in the following way. In the spectrum of [D_3]delphatine (XVI), in addition to the peak of the $(M - 61)^+$ ion there is the peak of a $(M - 64)^+$ ion half the height of the first one. The position of the main maximum in the MD spectrum of the ion $(M - 64)^+$ corresponds to the $(M - 34)^+ \rightarrow (M - 64)^+$ transition. This means that a formaldehyde molecule can be eliminated from this compound as the result of the splitting out of $CD_3\dot{O}$ from C-6. The values of A for the $(M - 31)^+ \rightarrow (M - 61)^+$ transition in the case of the other 7,8-dihydroxy-6-methoxy bases with an OH or an AcO group at C-1 (VII, VIII, XVII, XVIII) are of the same order as for compounds with a CH_3O group in this position. It is likely that the contribution of the initial splitting out of COH_3 from C-6 is also fairly great here. To prove this it is possible to compare the A values of the $M^+ \rightarrow (M - OCH_3)^+$ transition with the contributions to the total ion current of the $(M - OCH_3)^+$ ions for bases of this type with different R_1's:

		$A(M-31)^+$	$\Sigma(M-31)^+$
Delsoline	$R_1 = H$	3.7	17.8
[D_3]Delphatine	$R_1 = CH_3$	2.5 (ion $(M-34)^+$)	8.6
1-Acetoxydelsoline	$R_1 = COCH_3$	2.0	7.5

The symbatic dependence of A on $\Sigma(M - OCH_3)^+$ confirms that the mechanism of the ejection of $\dot{O}CH_3$ from the bulk of the M^+ ions of (VIII) and (XVIII) is the same as the mechanism of the elimination of $\dot{O}CD_3$ in the case of (XVI).

The MD spectra of the $(M - 61)^+$ ions of the 1-hydroxy bases are more diverse in external form, reflecting certain individual and group structural features of these compounds. For delcosine and delsoline the peak of the $(M - 31)^+ \rightarrow (M - 61)^+$ transition remains the most intense, although it is relatively weaker.

In the spectrum of compounds with an OH group at C-4 (IV-VI), the peak of the $(M - 17)^+ \rightarrow (M - 61)^+$ transition taking place with the loss of an acetaldehyde molecule, stands out. In the spectra of the epoxy bases (XIX-XXI) an alternative process $(M - CH_3CO)^+ \rightarrow (M - 61)^+$, in which a water molecule is eliminated, is observed more rarely.

The spectra of the acetates (XVII) and (XVIII) have a characteristic feature. Here the strongest MP is a broadened one obviously arising by the overlapping of two processes—the synchronous elimination of 61 amu from M^+ and the loss of a CH_3COOH molecule by the $(M - 1)^+$ ions. A similar feature is characteristic for the MD spectrum of the $(M - 61)^+$ ion of condelphine (I), the molecule of which contains an acetoxy group at C-14. The set of compounds studied is insufficient to draw the conclusion that this feature is characteristic for all acetates of lycoctonine bases. However, the marked differences between the MD spectra of the $(M - 61)^+$ ions of condelphine and its de-acyl analogue isotalatisidine (II) show that the MD method is sensitive to individual "nonreacting" substituents. It is sufficient to state that the greatest difference between the review spectra of (I) and (II) is shown only in the relative intensities of the peaks of the ions $(M - 59)^+$ (4 and 1.5%) and $(M - 61)^+$ (2 and 0.7%).

The $(M - 63)^+$ ions have the composition $M - C_2H_7O_2$. In the case of the 1-methoxy derivatives they are formed predominantly by the successive elimination of $CH_3\dot{O}$ and CH_3OH, in connection with which in the MD spectra the $(M - 31)^+ \rightarrow (M - 63)^+$ transition appears with the greatest clarity. The corresponding values of A within the individual subgroups of compounds are close to one another, which indicates the participation of definite substituents in the process of splitting out a methanol molecule. In the case of the alkaloids (XIII-XVI), it has been possible to establish that it is mainly the substituent at C-6 that participates in this stage of fragmentation. In the spectrum of (XVI), the peak of $(M - 66)^+$ ion is twice as intense as the peak of the $(M - 63)^+$ ion. The MD spectrum of the $(M - 66)^+$ ion coincides with that of the $(M - 63)^+$ ion of delphatine (XV), and the position of the maximum of the main MP in the first spectrum corresponds to the $(M - 31)^+ \xrightarrow{-CD_3\dot{O}H} (M-66)^+$ transition. The values of A of the corresponding transitions are also close.

In addition to this, the $(M - 63)^+$ ions arise as the result of the following alternative sequences: $M - \dot{O}H - C_2H_6O$ and $M - C_2H_5\dot{O} - H_2O$. The composition of the fragments eliminated permits the assumption that in this process the methoxymethylene substituent at C-4 is split out. In actual fact, in the MD spectra of compounds lacking this substituent, (X, XI, XIII), the $(M - 17)^+ \rightarrow (M - 63)^+$ transition is very ill-defined. In the other 1-methoxy bases the value of A for this transition is of the same order of magnitude (1.8-3.6%). Consequently, identical RESs participate in this process. A common feature of these four alkaloids (IX, XII, XIV, and XV) is an OH group at C-8 the elimination of which from M^+ leads to the monotypical $(M - 17)^+$ ions. Then a molecule of dimethyl ether is split out from C-4.

The MD spectra of the $(M - 63)^+$ ions of delcosine and delsoline are distinguished by the approximate equality of the heights of the three peaks. So far as concerns the other 1-hydroxy bases, the superficial similarity of their spectra is apparent. While in the case of (I-III), one of the main MPs in height corresponds to the $(M - 17)^+ \rightarrow (M - 63)^+$ transition, in the spectra of (IV-VI) (with an OH group at C-4) it corresponds to the process $(M - 15)^+ \rightarrow (M - 63)^+$ in which, apparently, the particles H_2O and CH_2O are eliminated synchronously. These subgroups of bases of characterized by similar values of A.

The position of the maximum of the second peak in the spectra of the epoxy bases is the same as in the dihydro derivatives (IV-VI) corresponding to them.

The $(M - 65)^+$ ions are formed in three stages. The overall composition of the fragments split out is $C_2H_9O_2$. In all the MD spectra the clearest transition is $(M - 33)^+ \rightarrow (M - 65)^+$, although the peaks of the synchronous elimination of two and even three particles are also observed. The position of the second maximum in the spectra is not constant: in (I-III) it favors the $(M - 15)^+ \rightarrow (M - 65)^+$ transition. The position of the MP closest to the peak of the daughter ion is indefinite.

The general form of the MD spectra of the $(M - 65)^+$ ions is uncharacteristic. Although all the 1-methoxy bases apart from lappaconine (XI) form complex spectra, the same distribution of intensities is also observed for many 1-hydroxy bases. As in the case of other ions, the characteristics of the changes in the values of A for the $(M - 33)^+ \rightarrow (M - 65)^+$ transition are unclear. Only some structurally close compounds such as (VII) and (VIII), and (XIX-XXI) give similar values of A.

The $(M - 65)^+$ and $(M - 68)^+$ ions of [D_3]delphatine show identical MD spectra in relation to the distribution of the heights of the MPs. The position of the main maximum in the spectrum of the $(M - 68)^+$ ion corresponds to the splitting out of CH_3OH from the $(M - 36)^+$ ion formed as the result of the ejection of CD_3 and H_2O. The values of A for the $(M - 33)^+ \rightarrow (M - 65)^+$ and the $(M - 36)^+ \rightarrow (M - 68)^+$ transitions are of the same order as in the analogous transitions of talatisamine and delphatine.

Condelphine and neoline have widely differing values of A (0.44 and 2.4%), although their spectra are monotypical. Since the process of forming the maternal ions $(M - 33)^+$ for bases with an OH group at C-1 (I-V) was characterized by similar MD spectra and values of A, an explanation of the differences observed in the subsequent splitting out of CH_3OH may be the participation of different substituents of the lycoctonine skeleton in this stage.

The $(M - 75)^+$, $(M - 77)^+$, and $(M - 79)^+$ ions arise as the result of three- or four-stage fragmentation processes. In view of the superposition of a multiplicity of alterna-

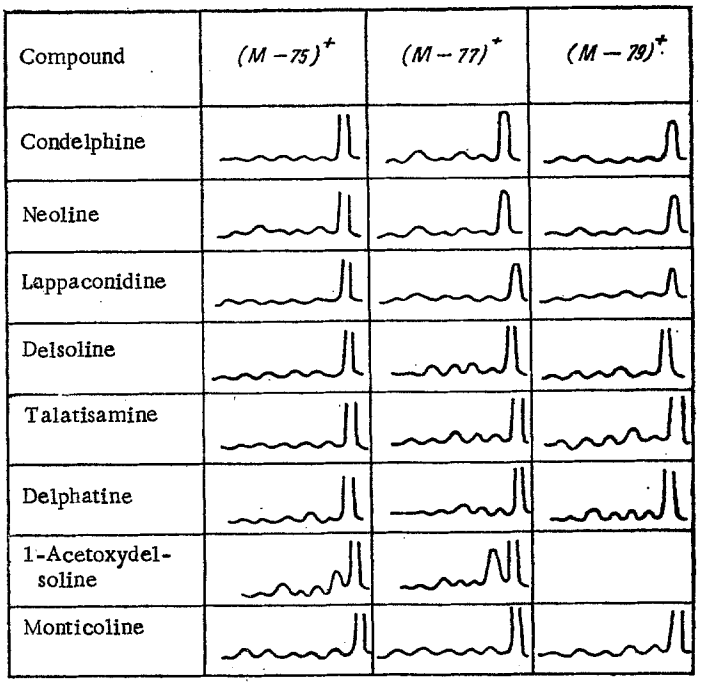


Fig. 3. MD spectra of the $(M - 75)^+$, $(M - 77)^+$, and $(M - 79)^+$ ions of a number of bases.

TABLE 2. Comparison of the Values of A with the Contributions of the Daughter Ions (Σd) Arising in the Breakdown of the Fragments $(M - OR_1)^+$

Compound	Daughter ions											
	$(M-OR_1-H_2O)^+$				$(M-OR_1-CH_3OH)^+$				$(M-OR_1-CH_2O)^+$			
	m/z	A	Σd	A/Σd	m/z	A	Σd	A/Σd	m/z	A	Σd	A/Σd
Isotalatisidine (II)	372	0,11	0,3	0,37	358	1,0	4,4	0,22	360	0,24	1,5	0,16
Talatisamine (IX)		0,24	0,9	0,27		0,30	1,7	0,18		0,12	1,3	0,09
Lappaconidine (V)	374	0,46	0,5	0,92	360	0,24	1,5	0,16	362	0,24	0,9	0,27
Lappaconine (XI)		0,38	0,5	0,76		0,065	0,4	0,16		0,04	0,3	0,13
Delcosine (VII)	418	1,5	1,5	1,0	404	1,8	2,0	0,90	406	—		
Browniine (XIV)		0,38	1,9	0,20		0,92	2,4	0,38		0,24	1,7	0,14
1,14-Diacetoxydelcosine (XVII)*	460	0,22	1,0	0,22	446	1,0	1,8	0,56	448	0,10	0,6	0,16
Delsoline (VIII)		1,6	1,0	1,6		1,9	3,2	0,59		—		
Delphatine (XV)	432	0,48	1,6	0,30	418	0,95	2,0	0,48	420	0,27	2,0	0,14
Acetoxydelsoline (XVIII)		0,18	0,7	0,26		0,98	1,6	0,61		0,05	0,5	0,10

*Additional acetyl group at C-14.

tive sequences of breakdown in their MD spectra, as a rule, it is difficult to single out the peaks of competing transitions. Furthermore, it must be borne in mind that these ions are inhomogeneous in elementary composition. Thus, the $(M - 77)^+$ ions from lycoctonine consist to the extent of 3/4 of the fragments $(M - C_2H_5O_3)^+$ and to the extent of 1/4 of the ions $(M - C_3H_9O_2)^+$. The $(M - 79)^+$ ions of the same spectrum contain the $(M - C_2H_7O_3)^+$ and $(M - C_3H_{11}O_2)^+$ in a ratio of 4:1. Consequently, the calculation of values of A for transitions in these fragments is not justified.

Typical MD spectra of the $(M - 75)^+$, $(M - 77)^+$, and $(M - 79)^+$ ions are given in Fig. 3. Each of the spectra contains five peaks, including a peak of the synchronous elimination of 75, 77, and 79 amu from M^+. There are no MPs sharply distinguished by their height. Exceptions are the spectra of the $(M - 75)^+$ and $(M - 77)^+$ ions of acetoxydelsoline (XVIII). In the first the peaks of transitions corresponding to the alternative successive elimination of $\dot{C}H_3$ and AcOH are well seen. In the second spectrum the highest peak corresponds to the $(M - 59)^+ \rightarrow (M - 77)^+$ transition.

There is a marked similarity between the spectra of the ions from condelphine, neoline, and lappaconidine. At the same time, they differ from the corresponding spectra of the

1-methoxy bases talatisamine and delphatine. However, the differences are insufficient for the recognition of the types of compounds. The noncoincidence between the spectra of the last two alkaloids can be explained by the participation of different peripheral substituents in multistage fragmentation processes, but these facts alone are few for the elucidation of the mechanism of far-reaching breakdown. At the same time this does not mean that the use of the MD method in relation to multistage processes is ineffective. In later publications examples will be given of the use of MD spectra in association with the results of high-resolution mass spectrometry to investigate the fragmentation pathways of the skeleton of the lycoctonine bases.

Ions with Conjecturally Identical RCs. We have already mentioned the possibility of considering the $(M - OR_1)^+$ ions as objects with the same RCs if the M^+ ions preceding them differ only by the nature of R_1. Pairs and triplets of substances in the spectra of which there are $(M - OR_1)^+$ ions satisfying this condition, with the same m/z values, are collected in Table 2. A criterion of the coincidence of the RCs is a similarity of the parameters of the MPs arising in the breakdown of the ions of the given type [5]. The DADI method [9], which provides the possibility of comparing the whole set of daughter ions, would be preferable for this purpose. However, we have limited ourselves only to that information that can be obtained by using the MD method. The values of A have been compared for transtions in which the $(M - OR_1)^+$ ions lose their most characteristic elements — H_2O, CH_2O, and CH_3OH molecules.

As can be seen from Table 2, the pairwise-compared values of A are of the same order in the majority of cases, the mean differences between them being close to a factor of 3, and the maximum differences to a factor of 6. If, by analogy with single-stage processes, we compare the values of A with the contributions of the corresponding daughter ions, a proportionality of these magnitudes clearly appears, which is evidence in favor of the common nature of the structures of the pairs of ions under consideration. An exception is formed by the $(M - 17)^+ \rightarrow (M - 35)^+$ transitions of delcosine and delsoline, which are characterized by anomalously large values of the ratio $A/\Sigma d$, in comparison with browniine and delphatine.

Thus, a comparison of Tables 1 and 2 shows that the application of the idea of RCs to ions with the same m/z values with the aim of estimating the common nature of the fragmentation mechanism of the diterpene alkaloids is on approximately the same level of proof as the use of the idea of RESs for ions with different mass numbers.

Experimental Conditions. MKh 1310 mass spectrometer with double focusing, SVP5 system for the direct introduction of the sample, temperature 70-80°C, ionizing voltage 50 V, collector current 40 μA. Defocusing: E, H = const, automatic scanning of the accelerating voltage from 2.5 to 4.5 kV at the rate of 0.1 kV/sec, chart speeds 5 and 10 mm/sec.

SUMMARY

1. The splitting out of monotypical substituents from various positions of the lycoctonine skeleton is accompanied by the appearance of MPs of different shapes and intensities. Compounds with identical "reacting" substituents, even with different peripheral substituents, give MPs with close values of these parameters. A direct interrelationship has been found between the ratio of the heights of the peaks of the metastable and daughter ions and the contribution of the daughter ion to the total ion current for the processes of detachment of the $\dot{O}R_1$ and $\dot{C}H_3$ radicals from M^+. This interrelationship may serve as a criterion of the common nature of fragmentation mechanisms.

2. The MD spectra of the ions formed in two or three stages have been studied. Group characteristics of the spectra have been found, the mass numbers of the precursor ions have been determined, and the parameters of the MPs for strictly definite transitions have been measured. Only an agreement of the results with respect to all three of the characteristics mentioned can show a similarity of the "reacting elements of the structure" (RESs). A dissimilarity of the MD spectra indicates a difference in the mechanism of the formation of a given ion, and a difference in the parameters of the MP may be a consequence of the superposition of alternative fragmentation processes.

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INTEGRAL INTENSITIES OF THE IR BANDS OF THE SKELETAL VIBRATIONS OF THE AROMATIC RING IN THE 1480-1630 cm^{-1} REGION AND THE UV SPECTRA OF THE APORPHINE ALKALOIDS

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The integral intensities of the skeletal vibrations of the aromatic rings of 12 aporphine alkaloids have been measured. It has been established that with an increase in the twisting of the C_1—C_{11} bond (cos Q) caused by the different natures of the spatial interaction of the 1,11-substituents ΣA decreases.

We have previously shown that the total integral intensities (ΣA 10^4 liter·mole·cm^{-2}) of the skeletal vibrations of the aromatic rings of aporphine alkaloids depend on the nature of the intramolecular hydrogen bonds of the 1,11-substituents [1]. However, no estimate was made of the spatial influence of a methylenedioxy group on the resonance interaction of the two phenyl rings of the biphenyl system of the aporphine alkaloids. In view of the fact that the series of aporphine alkaloids investigated has been supplemented by new compounds containing this substituent in the 1,2 or the 9,10 positions, the possibility has arisen of continuing the study of the total integral intensities of the absorption bands in the 1480-1630 cm^{-1} region and making a comparison with the characteristics of the UV spectra.

As can be seen from Table 1, the integral intensities in remerine (ΣA = 1.40), nantenine (ΣA = 3.20), and domesticine (ΣA = 3.00) are smaller than in glaucine (ΣA = 4.10). This gives grounds for considering that in aporphines with unsubstituted positions 11 [2, 6], because of its noncoplanarity with the nucleus A, a methylenedioxy group (—O—CH_2—O—) leads to a decrease in the values of ΣA.

Among the aporphines with a substituted position 11 the lowest value of ΣA is found for bulbocapnine (ΣA = 1.70), which distinguishes it from isothebaine, isocorydine, and corydine. Apparently, a methylenedioxy group noncoplanar with rings A and D increases the degree of twisting of the phenyl rings A and D of the biphenyl system of the bulbocapnine molecule.

The results of a study of the UV spectra of ortho-bridged biphenyls has revealed a link between the intensity of the absorption band at about 270 nm and the interplanar angle of the two phenyl rings [2-6], which is expressed by the relation

$$\cos^2 Q = \frac{E}{E_0},$$

where E is the extinction coefficient at the maximum of the absorption of the sample under

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