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ANALYSIS OF METASTABLE DEFOCUSING SPECTRA OF LYCOCTONINE BASES HAVING 7,8-METHYLENEDIOXY GROUPS

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The parameters of the MD spectra of the fragmentary ions of 21 lycoctonine alkaloids with 7,8-MDOGs have been investigated. On this basis, the monotypicity of the main fragmentation processes characteristic for the individual groups of compounds have been confirmed. A decrease in the number of common group characteristics of the MD spectra of the ions arising as the result of multistage breakdown processes is caused by alternative methods for their formation. This is not shown only by the doublet nature of the fragmentary ions. The results of a comparison of the MD spectra with the structures of the molecules have confirmed the hypothesis expressed previously concerning the 7,8-MDOG as the center of localization of the charge, competing with the nitrogen atom and facilitating the elimination of various substituents from the diterpene skeleton. A comparison has been made of two methods of evaluating the common nature of the fragmentation reaction: from the energies of the metastable transitions and from the relative intensities of the metastable peaks. The two methods give mutually supplementary information concerning the nature of the fragmentaion processes.

In the preceding paper [1], we gave a general characterization of the mass spectra of lycoctonine bases with 7,8-MDOGs, analyzing and comparing the contributions of the known ions of 21 compounds of this type. The role of the methylenedioxy group in the occurrence of specific directions of breakdown was revealed. The nonagreement of the spectra with respect to the contributions of secondary processes was ascribed to the participation in the fragmentation of a larger number of substituents than for the lycoctonines studied previously.

Our work on the MD spectra of the lycoctonine bases [2] showed that these spectra are far more sensitive to a change in the set of "reacting structural elements" (RSEs) than the overall spectra. We have therefore undertaken an investigation of the MD spectra of the fragmentary ions of alkaloids with 7,8-MDOGs of the same series as in [1]. The main parameter studied, as in the preceding case, was the ratio of the intensities of the peaks of the metastable and parental ions in percentages (magnitude A). A criterion of the common nature of the mechanisms of the multistage processes was the agreement of three factors: the ratio of the heights of the peaks in the MD spectra, the positions of the maxima of all the peaks, and the closeness of the values of A.

The advantage of this approach consists of the fact that the evaluation of the monotypicity of fragmentation reactions does not depend on the contribution of the daughter ions to the total ion current. Fragments similar in the composition of the eliminated group and close in intensity in the overall spectrum frequently arise as the sum of different processes, as follows from the MD spectra. On the other hand, ions the peaks of which have the same height in the spectra of different compounds may be formed by a single mechanism. Thus, the method gives valuable information on the competing processes of breakdown under EI.

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TABLE 1. Contributions of the Components of the Doublets (%)

Compound	$(M-47)^+$		$(M-75)^+$		$(M-77)^+$		$(M-89)^+$		$(M-91)^+$	
	Elementary compositions of the fragments eliminated									
	C_2H_7O	CH_3O_2	$C_3H_7O_2$	$C_2H_3O_3$	$C_3H_9O_2$	$C_2H_5O_3$	$C_4H_9O_2$	$C_3H_5O_3$	$C_4H_{11}O_2$	$C_3H_7O_3$
III	80	20	100	—	85	15	50	50	50	50
IV			100	—	100	—	—	100	—	100
VI	100	—	100	—			—	100	—	100
VII	100		100	—	100	—	65	35	50	50
VIII	50	50	100	—	30	70	—	100	—	100
IX	75	25	70	30	15	85	—	100	—	100
XI	50	50	60	40	60	40	35	65	30	70
XII	50	50	65	35			—	100		
XV	100	—	100	—	100	—	—	100	—	100
XVI	100	—	100	—	100	—	65	35	50	50
XVIII	85	15	100	—	80	20	35	65	—	100
XIX	80	20					—	100		

In necessary cases, the correctness of the interpretation of the MD spectra was confirmed by measuring the elementary compositions of the daughter ions (Table 1).

The MD spectra of the fragments in the formulas of compounds (II-XXII) are given in Figs. 1 and 2 (the numbering of the compounds and their division into subgroups is the same as in [1]). Above the maxima corresponding to the structure of a definite transition are given the values of A, and under the peaks of the daughter ions are shown (in percentages) the contributions to the total ion current (Σ_d).

IONS FORMED AS THE RESULT OF ONE-STAGE PROCESSES

The $(M - 15)^+$ Ions. The heights of the metastable peaks in the $M^+ \rightarrow (M - 15)^+$ transition are, as a rule, small, and we do not give the corresponding spectra in Figs. 1 and 2. The mean value of A of this transition for the 6-O-methylated bases [(II-IV), 1.81%] is almost an order of magnitude lower than for the 1,6-dimethoxy-7,8-dihydroxy gases of the delphatine type [2]. However, the values of Σ_d are also diminished (by an average of 2.17%), which gives no grounds for assuming substantial differences in the mechanisms of the formation of the $(M - 15)^+$ ions in compounds with 7,8-MDOGs and 7,8-diols. In the case of compounds with an acetoxy group at C-6 (VI-IX), the mean value of A for the same transition is close to 0.1% (the mean value of Σ_d = 0.73), while for compounds (XI-XVI) it is about 0.2% (the mean value of Σ_d = 1.1%). The order of these magnitudes is the same as for 1-methoxy alkaloids of the talatisamine type [2], which confirms the formation of the $(M - 15)^+$ ions at the expense of the N-Et group.

$6\text{-}OCD_3$-10,12-Anhydroeldelidine (XXII) has A = 2.75% for the $M^+ \rightarrow (M - CH_3)^+$ transition (the average value of Σ_d = 4.85%), and A = 1.82% for the $M^+ \rightarrow (M - CD_3)^+$ transition (the mean value of Σ_d = 2.42%). The marked rise in the first magnitude as compared with that of compounds without a $\Delta^{10(12)}$-bond may indicate a contribution of the ejection of CH_3 from the methoxy groups at C-14 and C-16 activated by the double bond.

The $(M - 30)^+$ Ions. The MD spectra of these ions have been obtained only for the anhydro bases (XVII-XXII), where the presence of an isotopic peak of the $(M - 31)^+$ ion is unimportant [apart from 6-O-methyl-10,12-anhydroeldelidine (XVIII)]. The form of the metastable peak (MP) of this transition is close to triangular and the value of A exhibits a distinct symbatic dependence on Σ_d $(M - 30)^+$, which shows the common nature of the origin of these ions.

The $(M - 31)^+$ Ions. The MP of the $M^+ \rightarrow (M - 31)^+$ transition has a Gaussian form in all cases. The values of A of the compounds of the first group, where the peak of the $(M - 31)^+$ ion has the maximum height, are 46-99%. Of the same order are the values of Σ_d for compounds (II-XVI). For the MD spectra of the $(M - 31)^+$ ions of the substances of the second group (XVII-XXII), both magnitudes, on an average, are an order of magnitude smaller, which does not contradict the common nature of the mechanism of the processes of eliminating an OCH_3 group.

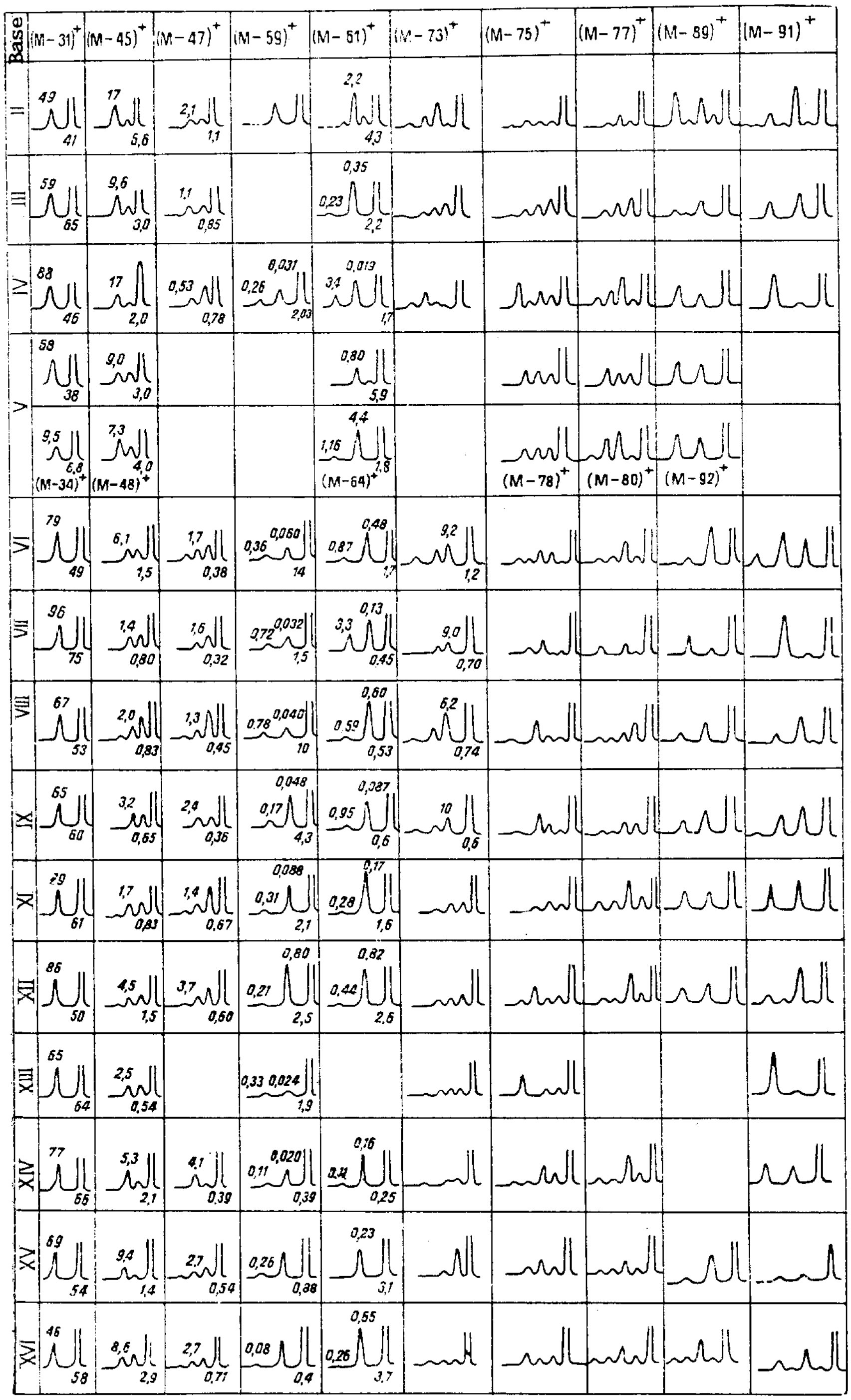


Fig. 1. MD spectra of the $(M-31)^+$-$(M-91)^+$ ions of the bases (I)-(XVI).

TWO-STAGE AND MULTISTAGE PROCESSES

The $(M-45)^+$ Ions. Although the formation of these fragments always take place through an alternative sequential or synchronous elimination of CH_3 and CH_2O, the mechanisms of the process are fairly diverse, as is shown by the dissimilarity of the nature and the parameters of the MD spectra of the $(M-45)^+$ ions even within certain subgroups. The most monotypical are the spectra of the 6-O-methyl derivatives (II-V) (see Fig. 1). The range of values of A for the $(M-15)^+ \rightarrow (M-45)^+$ transition does not exceed a factor of 2, and their mean value is ~12%. In the case of the 6-O-acetyl derivatives, the ratio of the intensities of the MPs of the individual transitions is different from that for (II-V), and although they are close to one another, the value of A of the same transition for (VI) is more than four times greater than that for O-acetyledelidine (VII).

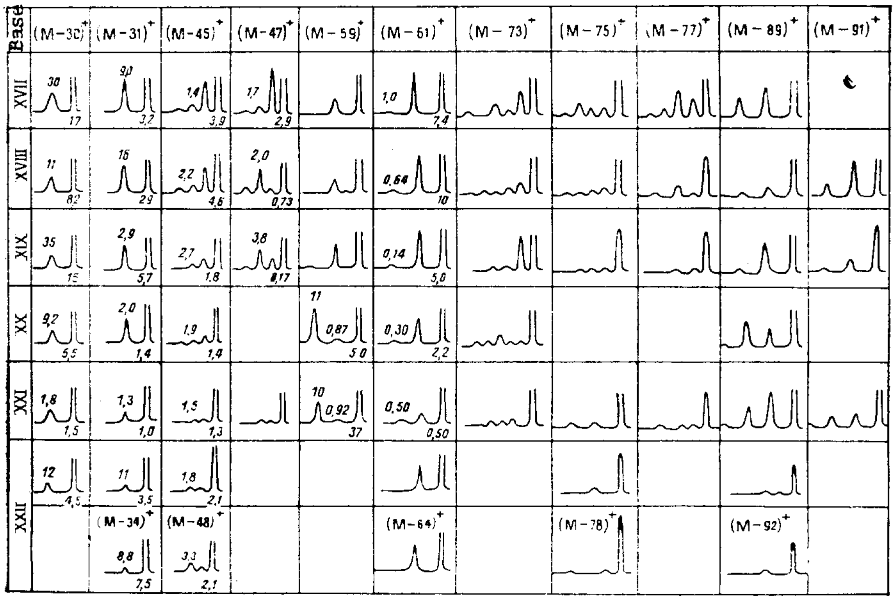


Fig. 2. MD spectra of the $(M - 30)^+$-$(M - 91)^+$ ions of the bases (XVII)-(XXII).

The MD spectra of the $(M - 45)^+$ ions have different characteristics for compounds (XI-XVI) (see Fig. 1) and for the substances of the second group (XVII-XXII) (see Fig. 2). Here differences in the nature of substituents not only at C-6 but also at C-4 and C-10 are shown [1]. We may note how sharply the MD spectra of the $(M - 45)^+$ ions of 6-O-methyleldelidine (III) and if its $\Delta^{10(12)}$ analog (XVIII) differ. Also very impressive here is the difference between the values of A for the $(M - 15)^+ \rightarrow (M - 45)^+$ transition. Both facts are a consequence of the participation of different methyl groups in the formation of the $(M - 15)^+$ ions and of different mechanisms for the elimination of the MDO group.

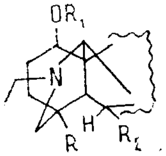
The $(M - 47)^+$ Ions may be formed by the splitting out of C_2H_7O ($\dot{C}H_3 + CH_3OH$) or CH_3O_2 ($OH + CH_2O$) fragments. The contributions of the ions of each form are given in TAble 1 for the case of twelve compounds from different subgroups. Analysis of Table 1 shows that the $(M - C_2H_7O)^+$ ions predominate in hydroxyl-free compounds while, as a rule, the spectra of OH-containing compounds have the second component of the $(M - 47)^+$ ion.

From the positions of the maxima, the two constant peaks of the MD spectra of the $(M - 47)^+$ ions correspond to the $(M - 15)^+ \rightarrow (M - 47)^+$ and $(M - 30)^+ \rightarrow (M - 47)^+$ transitions. This confirms that the elimination of OH or CH_3OH in the first stage is uncharacteristic for the compounds under consideration. Peaks of the synchronous elimination of 47 a.m.u. are observed in the spectra of compounds (VI, VIII, XI, XII, and XV-XIX).

So far as concerns the general form of the MD spectra, not one of the subgroups gives a completely repeating pattern. This distinguishes the compounds under consideration from the bases of the talatisamine or the delphatine (I) subgroup [2] and emphasizes the difference in the natures of the processes leading to the formation of the $(M - 47)^+$ ion. Thus, the MD spectra of the structurally close dictyocarpine (VIII) and eldelidine (IX) differ substantially.

On the other hand, the MD spectra of the $(M - 47)^+$ ions of delcorine (XII), dehydrodelcorine (XV) and deoxydelcorine (XVI) are fairly similar both in external form and with respect to the value A of the $(M - 15)^+ \rightarrow (M - 47)^+$ transition. The other compounds of this subgroup (XI and XIV) differ with respect to their overall parameters. Here the influence of the CH_2OCH_3 groups in the C-4 positions in the molecules of (XII, XV, and XVI) is present. We may also note a similarity of the MD spectra of deoxydelcorine and of demethylenedeoxydelcorine [2]. The values of the $(M - 15)^+ \rightarrow (M - 47)^+$ transition in the latter (3.6%) is also close to the corresponding values of the above-mentioned triplet of compounds. The spectra of dehydroeldelidine (XIV) and its $\Delta^{10(12)}$-analog (XIX), in their form and the value of A of the same transition, are analogous to those of talatisamine, in which the formation of the $(M - 47)^+$ ions take place by the elimination of $\dot{C}H_3$ from N—Et and the subsequent ejection of methanol at the expense of the C_1—OCH_3 group [2]. The values of A of the $(M - 15)^+ \rightarrow (M - 47)^+$ transition of the substances of the subgroup of the 6-O-methyl derivatives (II-IV), and

TABLE 2. Values of T and A of the Metastable Transitions $M^{+} \rightarrow (M - CH_3)^{+}$ and $M^{+} \rightarrow (M - OR_1)^{+}$ in the MD Spectra of Different Subgroups of Lycoctonine Bases



Compound	R_1	R_2	$(M-CH_3)^+$				$(M-OR_1)^+$			
			ΔW	T, eV	A	A/Σd	ΔW	T, eV	A	A/Σd
1-Deoxycondelphine	—	H	71,6 (	3,313	33,6	0,65	—	—	—	—
Condelphine	H	H	73,1	3,504	9,5	0,85	70,9	2,941	32,2	0,78
Neoline		α-OCH₃	67,2	2,955	6,7	0,65	58,9	1,989	27,2	0,62
Lappaconidine		H	70,5	3,018	6,8	0,59	73,2	2,833	16,0	0,42
Dihydromonticoline		H	69,3	2,912	16,7	0,59	71,1	2,681	27,3	0,79
Delcosine		β-OCH₃	90,4	5,531	47,2	1,64	58,0	1,987	9,30	0,76
Delcoline		β-OCH₃	89,5	5,668	45,5	1,54	57,3	2,007	10,6	0,86
Talatisamine	CH₃	H	67,3	2,867	0,3	0,15	64,4	2,306	56,5	0,82
Browniine		β-OCH₃	89,5	5,624	15,8	0,90	68,9	1,480	31,5	0,67
Delphatine		β-OCH₃	88,1	5,614	15,0	1,13	75,2	1,780	37,0	0,74
[D₃]Delphatine		β-OCD₃	88,6 (—CD₃)	4,712	15,3	1,13	66,5 (—OCD₃)	1,347	2,50	0,25
							72,9 (—OCH₃)	1,698	50,0	1,25
1,14-Diacetoxydelcosine	Ac	β-OCH₃	82,2	5,512	6,7	1,14	86,2	1,185	50,0	0,79
1-Acetoxydelcoline		β-OCH₃	78,8	4,830	7,4	1,21	88,9	1,164	48,2	0,79
6-O-Methyldelcorine (II)	CH₃	β-OCH₃	85,5	5,474	2,9	1,10	72,0	1,695	49,0	1,19
6-OCD₃-Delcorine (VI)		β-OCD₃	81,1 (—CD₃)	4,023	5,3	1,07	85,5 (—OCD₃)	2,186	9,50	1,40
			64,5 (—CH₃)	2,691	0,8	0,62	82,9 (—OCH₃)	2,265	68,2	1,78
10-O-Acetyl-6-O-methyleldelidine (IV)		β-OCH₃	87,1	5,907	1,5	0,91	67,2	1,570	95,0	1,30
O-Acetyleldeline (VII)		β-OAc	—	—	—	—	74,4	2,047	96,2	1,29
Dictyocarpine (VIII)		β-OAc	—	—	—	—	71,6	1,672	66,9	1,25
Delcorine (XII)		β-OH	65,1	3,064	0,38	0,38	69,2	1,514	85,5	1,44
Deoxydelcorine (XVI)		H	67,9	3,230	0,36	0,27	79,0	1,892	46,4	0,80

also 6-O-methyl-10,12-anhydroeldelidine (XVIII) are several times lower (averaging 1.17%) and are close to those of compounds of the delphatine group (averaging 1.00%) [2] which confirms the initial splitting out of methyl from C_6–OCH_3.

The $(M - 59)^+$ Ions. As a rule, MD spectra contain the peaks of two transitions $M^+ \rightarrow (M - 59)^+$ and $(M - 31)^+ \rightarrow (M - 59)^+$. The height of the peak of the second transition in those cases where the contributions of the $(M - 61)^+$ ions exceed the contributions of the $(M - 59)^+$ ions (II, III, XV-XIX) is distorted in the direction of an increase, since the transition between the secondary isotopic peaks of the $(M - 31)^+ \rightarrow (M - 61)^+$ process is superposed upon it.

The fact that the splitting out of an acetoxy radical from M^+ is not the only way in which the $(M - 59)^+$ ions arise is most obvious from the MD spectra of the 6-O-acetyl derivatives (VI-IX) (see Fig. 1), in which the contributions of the $(M - 59)^+$ ions exceed the contributions of the $(M - 61)^+$ ions. The values of A for the $(M - 31)^+ \rightarrow (M - 59)^+$ here are of the same order (averaging 0.045%). The corresponding values of A for compounds (IV, XIII, and XIV) are close to them. Since the $(M - 59)^+$ ions have only one composition $(M - C_2H_3O_2)$, the transition under consideration takes place with the loss of a CO molecule. The mechanism of this process is probably monotypical in the compounds mentioned and is due to a complex rearrangement of the 7,8-MDOG. We may note that in the nonacetylated 7,8-dihydroxy bases the $(M - 59)^+$ ion is absent [2]. Here it is most appropriate to emphasize the sensitivity of the MD method, which permits the reliable detection of secondary pathways for the formation of ions in compounds where the contribution of the main process of the origin of the fragments of the same mass is an order of magnitude higher.

In spite of the small contribution of the process of stepwise formation of the $(M - 59)^+$ ions and in view of the presence of peaks of the synchronous elimination of $CH_3\dot{O}$ and CO, there is no clear correlation between the values of A for the $M^+ \rightarrow (M - 59)^+$ and $\Sigma_d(M - 59)^+$ transitions even in the 6-acetoxy compounds (VI-IX).

The $(M - 61)^+$ Ions. Although the MD spectra of the fragmentary ions are monotypical for the compounds of the first group – as a rule, they contain the peaks of two transitions: $M^+ \rightarrow (M - 61)^+$ and $(M - 31)^+ \rightarrow (M - 61)^+$ – the same order of the values of the two transitions is not retained in all different groups. This is particularly characteristic of the 6-methoxy derivatives (II-IV) for which this parameter differs by one to two orders of magnitude (see Fig. 1), which, of course, is due to the superposition of processes involving the ejection of methoxy radicals from different positions of the skeleton. For the other compounds of the first group, the values of A for the $(M - 31)^+ \rightarrow (M - 61)^+$ transition are of the same order, although they may differ by a factor of 4-5.

In the MD spectra of the $(M - 61)^+$ ions of the compound of the second group, upon the peak of the last transition is superposed the peak of the alternative transition $(M - 30)^+ \rightarrow (M - 61)^+$ so that calculation of the value of A has no sense.

The $(M - 73)^+$ Ions form singlets with the composition $(M - C_3H_5O_2)^+$ in all the spectra, which corresponds to the elimination of CH_2O, CO, and CH_3 particles. The sequence of their ejection may differ [1], and therefore we mention not only the different natures of the MD spectra of this daughter ion but also differences in the positions and sets of maxima. In the MD spectra of compounds (XVII) and (XIX) the peak of the $(M - 58)^+ \rightarrow (M - 73)^+$ transition stands out because of its height (see Fig. 2). We may note that in the MD spectra of the 6-keto derivatives of the first group (XIII-XV) it is easy to record the same transition.

Closest to one another are the spectra of the $(M - 73)^+$ ions of the 6-acetoxy compounds (VI-IX) in which the peak of the $(M - 43)^+ \rightarrow (M - 73)^+$ transition appears. The corresponding values of A, just like the contributions of the daughter ions are of the same order of magnitude here. Furthermore in the $M^+ \rightarrow (M - 43)^+$ transition the values of A depend symbatically on the contribution of the daughter ion:

Compound	$A_{M^+ \rightarrow (M-43)^+}$	$\sum\limits_{(M-130)^+}^{M^+} (M-43)^+$
VI	0,45	0,62
VII	0,20	0,80
VIII	0,30	0,52
IX	0,34	0,50

This enables us to consider that in this group of compounds a specific method of formation of the $(M - 73)^+$ ions appears by the successive ejection of an acetyl radical from the

6-$OCOCH_3$ group and of formaldehyde at the expense of the 7,8-MDOG. In fact, the structure of these ions coincides with the structure of the $(M - 45)^+$ ions of the 6-methoxy compounds (II-V).

The $(M - 75)^+$ Ions for the majority of compounds included in Table 1 represent singlets with the composition $(M - C_3H_7O_2)^+$ and for the other substances they represent main components of the same composition. This corresponds to the elimination of $\dot{C}H_3$ and of two formaldehyde molecules.

The MD spectra of the $(M - 75)^+$ ions of compounds (II-XXI) are more diverse than for the lycoctonine bases described previously [2]. In addition to this, for each of the subgroups of compounds of the first group a series of common features that confirm the elimination of the above-mentioned particles is characteristic. However, there are also completely explicable exceptions. Thus, in the MD spectra of the 10-acetoxy bases (IV) and (XIII) the peak of the $(M - 15)^+ \rightarrow (M - 75)^+$ transition stands out, which, obviously, corresponds to the loss of a AcOH molecule in this stage. The composition of the daughter ion is the same as on the ejection of two CH_2O fragments and $\dot{C}H_3$.

A second component of the $(M - 75)^+$ ion with the composition $(M - C_2H_3O_3)^+$ was observed for compounds the molecules of which had OH groups. It corresponds to the elimination of three particles: $\dot{O}H$, CO, and CH_2O. The presence of this component has little effect on the nature of the MD spectra of the $(M - 75)^+$ ions [compare (XI) and (XII), and (XV) and (XVI)].

The $(M - 77)^+$ Cations correspond to the composition $(M - C_2H_5O_3)^+$ or $(M - C_3H_9O_2)^+$, and on passing from substance to substance the ratio between the components of the doublets changes within wide limits. Compounds where the major contribution is that of the first component (VIII and IX) contain OH at C-10 and form the $(M - 77)^+$ ions by the loss of H_2O from the $(M - AcO)^+$ fragments. In the corresponding MD spectra the $(M - 59)^+ \rightarrow (M - 77)$ transition can be clearly seen. In the case of compound (XVIII), the presence of the $(M - C_2H_5O_3)^+$ components is due to the breakdown of the $(M - CH_3O_2)^+$ ion with the loss of CH_2O. Other cases of the presence of this component [(III) (monool) – 15%; (XI) (diol) – 40% of the total height of the $(M - 77)^+$ ion] are due to breakdown through the loss of OH + $2CH_2O$.

Compounds not possessing the above-mentioned structural characteristics (IV, VII, XV, and XVI) give singlet $(M - C_3H_9O_2)^+$ ions as the result of the elimination of $\dot{C}H_3$, CH_2O, and CH_3OH. In the MD spectra of the $(M - 77)^+$ ions the following rule is observed: for all 6-methoxy bases the peak of the $(M-47)^+ \xrightarrow[-CH_2O]{} (M-77)^+$, transitions stands out, while in almost all the other compounds it is the peak of the $(M-45)^+ \xrightarrow[-CH\dot{O}H]{} (M-77)^*$ transition.

The $(M - 89)^+$ Ions. Their origin has been discussed in [1] as a process of the loss of $Ac\dot{O}$ and CH_2O (VII, XX, XXI) or of the elimination of CH_2O, CO, and $CH_3\dot{O}$ (XVII, XIX). Other 6-acetoxy bases (IV, VI, VIII, and IX) may breakdown by the first route. In both cases, the composition of these fragments corresponds to $(M - C_3H_5O_3)^+$.

The MD spectra of the $(M - 89)^+$ ions are predominantly monotypical and contain two main peaks differing by the ratio of their heights. In the first, the $(M - 30)^+$, $(M - 31)^+ \rightarrow (M - 89)^+$, and in the second the $(M - 59)^+$, $(M - 61)^+ \rightarrow (M - 89)^+$. Five of the twelve compounds analyzed showed the presence of a second component – $(M - C_4H_9O_2)^+$ and in two cases its height was greater than of the first (see Table 1). However, substances containing ions of this type do not possess a common feature of their structural components. The $(M - C_4H_9O_2)^+$ fragments may therefore be considered as the result of secondary alternative processes [apart from the case of compound (VII)] the contribution of which to the total height of the peak increases with remoteness from M^+ and a fall in the intensity of the peaks of the main processes. For example, the fragments under discussion may be formed by the elimination of $CH_3\dot{O}$, CH_2O, and C_2H_4 (at the expense of N–Et), and in this case the positions of the maxima in the MD spectra may not change (III, XI, XVIII). Conversely, the appearance of additional peaks in the MD spectrum of the $(M - 89)^+$ ion of deoxydelcorine (XVI) may indicate the following set of fragments eliminated: CH_2O, ethylene oxide, and $\dot{C}H_3$ (see Fig. 1).

The $(M - 91)^+$ Ions, apart from the possibility that has been mentioned of their formation by the splitting out of $CH_3\dot{O}$ + AcOH ($Ac\dot{O}$ + CH_3OH) [1], arise thorugh the successive ejection of 2 CH_2O from the $(M - CH_3O)^+$ ions. In both cases, this gives $(M - C_3H_7O_3)^+$ fragments, which, according to Table 1, are more widely distributed. In agreement with the processes mentioned, their MD spectra contain predominantly the maxima of the $(M - 31)^+ \rightarrow (M - 91)^+$ and $(M - 59, 60, 61)^+ \rightarrow (M - 91)^+$ transitions. The following characteristic feature can be clearly seen: in all the 10-acetoxy compounds (IV, VII, XIII) the first peak is several times stronger than the second, and in the other compounds the two peaks are either approximately equal or the second is 1.5-3 times higher than the first (see Figs. 1 and 2).

So far as concerns the second component of the $(M - 91)^+$ ion with the composition $(M - C_4H_{11}O_2)^+$, its formation is difficult to imagine other than as a process of the dehydrogenation of $(M - C_4H_9O_2)^+$ ions. As can be seen from Table 1, as a rule, the appearance of the former accompanies the appearance of the latter.

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Almost simultaneously with our first publication devoted to the analysis of the parameters of the metastable peaks of complex compounds [2], a series of publications by Zaretskii et al. appeared [3-5], where, in particular, the energies of the metastable transitions (T) due to the loss of angular (18- and 19-) CH_3 groups from the M^+ and $(M - H_2O)^+$ ions in saturated and unsaturated steroids were compared.

In the last paper [5], the conclusion was drawn that the approximately twofold superiority of the values of T for the reaction forming the $(M - 18\text{-}CH_3)^+$ ions over the values for the reaction forming the $(M - 19\text{-}CH_3)^+$ ions was due to the fact that the first process takes place as a rearrangement and the second as a process of simple cleavage. One of the main problems of our investigation was similar: to determine how sensitive the parameters of the metastable peaks (the relative intensity A) is to different ways of eliminating the CH_3 from the M^+ ions of the lycoctonine bases. In this connection, we decided to compare the results obtained by the two methods. We calculated the values of T in the transitions $M^+ \rightarrow (M - 15)^+$ and $M^+ \rightarrow (M - OR_1)^+$ of lycoctonine bases of different subgroups and compared them with the corresponding values of A (Table 2). The transition energy T (eV) was obtained from an equation proposed by Beynon's group [6, 7]:

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

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

$W = V_S$ is the accelerating voltage corresponding to the maximum of the metastable peak

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 focusing the daughter ion (2500 V).

As can be seen from Table 2, the widths of the ΔW peaks in the $M^+ \rightarrow (M - 15)^+$ transitions are, as a rule, somewhat greater if the ejection of CH_3 takes place predominantly at the expense of the $C_6\text{-}OCH_3$ group than when this radical is split out from N—Et. In the first place, it is in the range of 4.023-5.907 eV (averaging 5.290 eV), and in the second it is between 2.691 and 3.504 eV (averaging 3.062 eV). The ratio between the two mean values of T shows that, as compared with the clearly simple and rapid cleavage in the N—Et group, the ejection of CH_3 from $C_6\text{—}OCH_3$ can be treated as a slower process taking place with the cleavage of two bonds [1]. The value of A for the $M^+ \rightarrow (M - 15)^+$ transition changes over wide limits while remaining characteristic for the subgroup of compounds with the same ways of ejecting CH_3 and the same substituents at C-1. This also permits the prediction of the method by which the $(M - \dot{C}H_3)^+$ ion is formed. Since for each group of compounds a linear dependence of A in the contribution of the daughter ion Σ_d is characteristic [2], the ratio A/Σ_d can have different values for two pathways for the ejection of $\dot{C}H_3$. As can be seen from Table 2, for compounds ejecting a methyl radical form N—Et it is between 0.15 and 0.65, while for substances splitting out $\dot{C}H_3$ from the methoxyl at C-6 it is between 0.90 and 1.64.

So far as concerns the $M^+ \rightarrow (M - OR_1)^+$ transition, as is clear from the results obtained for $[D_3]$delphatine (labeled at the C_6—OMe) and $6\text{-}OCD_3$-decorine (V) (see Table 2), the processes of splitting out a methoxyl form C-1 and C-6 do not give appreciable differences in the value of T. At the same time, the orders of magnitude of A for these purposes are different, although when the ratios A/Σ_d are compared the values approach one another greatly, particularly in the case of $6\text{-}OCD_3$-delcorine.

The values of T for all the 1-methoxy derivatives ($R_1 = CH_3$) are between 1.480 and 2.306 eV, regardless of the nature of the substituents at C-6—C-8. At the same time, they decrease substantially with an increase in the volume of R_1 (compare delsoline, delphatine, and 1-

acetoxdelcoline — 2.007, 1.780, and 1.164 eV, respectively). This fact can be considered from the point of view of an increase in the probability of the simple cleavage of the C_1—O bond with an increase in the stability of the OR_1 radical.

The ratio A/Σ_d for the $M^{+} \rightarrow (M - OR_1)^{+}$ process for compounds without a 7,8-MDOG ranges within fairly narrow limits (averaging 0.72). The height of this magnitude is considerably greater (averaging 1.30) for compounds the molecules of which contain a methylenedioxy group and an oxygen substituent at C-6. Conversely, 6-deoxydelcorine gives $A/\Sigma_d = 0.80$, close to that for the compounds of the first group.

The conditions of the mass-spectrometric experiments were the same as in [2]. Yu. M. Mil'grom participated in the acquisition of the experimental results.

SUMMARY

The parameters of the MD spectra of the fragmentary ions of 21 lycotonine alkaloids with 7,8-MDOGs have been investigated. This has shown a monotypical nature of the main fragmentation processes characteristic for individual groups of compounds. A decrease in the number of common group characteristics of the MD spectra of the ions arising as the result of multistage breakdown processes is due to alternative methods for their formation. This is shown not only by the doublet nature of the fragmentary ions. The results of a comparison of the MD spectra with these structures of the molecules confirm the hypothesis put forward previously of the 7,8-MDOG as a center of charge localization competing with the nitrogen atom and promoting the elimination of different substituents of the diterpene skeleton.

A comparison has been made of two methods of evaluating the common nature of the fragmentation reactions: from the energies of the metastable transitions and from the relative intensities of the metastable peaks. The two methods give mutually supplementing information on the nature of the breakdown processes.

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