FEATURES OF THE SPLITTING OUT OF SUBSTITUENTS FROM RING A OF LYCOCTONINE ALKALOIDS ON ELECTRON IMPACT

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We have previously reported some features of the mass spectra of diterpene alkaloids with the lycoctonine skeleton. The maximum peak in the spectra of these compounds, with a few exceptions, is due to the fragment formed by the ejection of the substituent at C-1 from the molecular ion [1, 2].

It was of interest to study the dependence of this process on the orientation of the substituent at C-1. The figures in Table 1 show that the ease of detachment of the substituent from C-1 is connected to a considerable degree with its configuration, while compounds having hydroxy and methoxy groups in this position must be considered separately. The ease of detachment of a substituent increases with an increase in its size (isotalatisidine → talatisamine → condelphine acetate). It is convenient to compare the intensities of the peaks $M-OR_1$ and $M-15$, since they arise as the result of parallel processes and cannot take place successively [1], and also $M-OR_1$ and M^+. The size of the $M-H_2O$ peak depends on several factors [1] and is therefore not appropriate for this purpose.

On comparing the spectra of isotalatisidine, condelphine, and neoline with the spectrum of talatisidine it can be seen that the change in the configuration of the hydroxy group at C-1 from α to β stabilizes the molecular ion, considerably decreases the peak of the $M-17$ ion, and increases that of the $M-15$ ion. A similar change of configuration in the case of a methoxy substituent (talatisamine, and aconine, and lycocto-

TABLE 1

Compound (configuration of OR_1)	R (when not otherwise indicated, R = H)	Relative intensities of the peaks, %				
		M^+	$M-15$	$M-OR_1$	$\frac{M-OR_1}{M^+}$	$\frac{M-OR_1}{M-15}$
Neoline (α)	$R_3=CH_3$; $R_4=OCH_3$	25	25	100	4,0	4,0
Condelphine (α)	$R_3=CH_3$; $R_7=COCH_3$	29	28	100	3,4	3,6
Isotalatisidine (α)	$R_3=CH_3$	34	30	100	2,9	3,3
Talatisidine (β)	$R_3=CH_3$	100	93	57	0,57	0,61
Talatisamine (α) [3]	$R_1=R_3=CH_3$	3	1,5	100	33	67
Aconine (α) [4]	$R_1=CH_3$; $R_2=R_6=R_8=OH$; $R_4=OCH_3$	1,2	3,2	100	83	31
Lycoctonine (β)	$R_1=R_7=CH_3$; $R_5=OH$; $R_4=OCH_3$	4,5	26	100	22	3,8
Delphatine (β)	$R_1=R_3=R_7=CH_3$; $R_5=OH$; $R_4=OCH_3$	3	20	100	33	5,0
Browniine (β)	$R_1=R_3=CH_3$; $R_5=OH$; $R_4=OCH_3$	7	28	100	14	3,6
Condelphine acetate (α)	$R_3=CH_3$; $R_1=R_7=COCH_3$	1,3	0,65	100	77	154
Talatisidine diacetate (β)	$R_3=CH_3$; $R_1=R_7=COCH_3$	19,5	6	100	5,1	16,6

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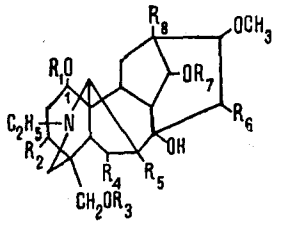
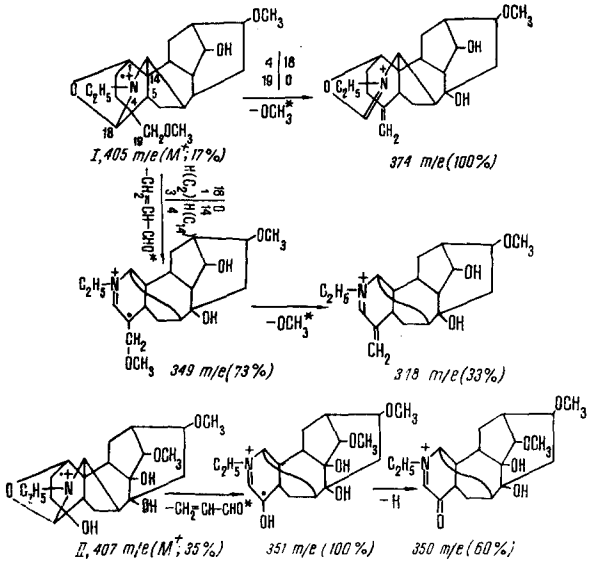
nine, delphatine, and browniine), while it does not lead to an appreciable stabilization of the molecular ion, nevertheless leads to a sharp increase in the intensity of the M−15 peak. The last two columns of the table give the ratios of the intensities of the M−OR_1 and the M^+ and M−15 peaks.



For each type of substituent OR_1 a change in its configuration leads to a change in the ratio by practically an order of magnitude, with the exception of the ratio I_{M-OR_1}/I_{M^+} for the 1-methoxy derivatives, where this distinction is not so pronounced. With a change in the temperature of the experiments from 80 to 110°C, the ratio of the intensities of the peaks changed only slightly, and the figures given in the table remained practically constant.



We have shown [1] that a methoxymethylene residue at C-4 does not as a rule take part in the fragmentation of the group of alkaloids considered. In the determination of the structure of the compounds mentioned, the determination of the presence of this grouping presents great difficulty. It has proved very useful in answering this question to study the mass spectra of the carbinolamine ethers which are readily formed by the oxidation of alkaloids with an α-hydroxy group at C-1 by Marion's method [5]. Attention must be paid to the influence of the orientation of a methoxy group at C-6 in the formation of the carbinolamine ethers [5]. A characteristic feature of the mass spectra of such compounds is the presence of an intense M−56 peak due to the ejection of a molecule of acrolein from the molecular ion. The ion-radical arising ejects a methoxy radical from C-19. This practically completes the decomposition of the molecule. Another direction of the fragmentation of the carbinolamine ethers is the ejection of the methoxy radical at C-19 from the molecular ion. When a methoxy group is present at C-19 [carbinolamine ether of isotalatisidine (I)] this process is responsible for the maximum peak in the spectrum. When there is no methoxymethylene grouping [carbinolamine ether of lapaconidine (II)] the maximum peak is M−56, and the peak corresponding to the ejection of 31 amu is small (3%). All the transitions mentioned are confirmed by metastable peaks.

We have observed a similar decomposition previously in the case of songoramine [6]. However, there the stabilization of the ion-radical formed after the ejection of an acrolein molecule took place through a series of skeletal cleavages and the appearance of an ion with m/e 122. In the carbinolamine ether of lapaconidine (II) the stabilization of the corresponding ion-radical is effected by the ejection of hydrogen from the hydroxy group at C-4 and the formation of the stable system of an α,β-unsaturated ketone.

The mass spectrum of the carbinolamine ether of N-norisotalatisidine possesses an interesting feature. In it the M−31 peak is the maximum peak while the M−56 peak amounts to only 8%, the M−56−31

peak to 4%, and the peak of the molecular ion to 11%. Apparently, this is connected with the influence of the N-ethyl group on the fragmentation of compounds of this type.

The mass spectra were recorded on an MKh-1303 instrument fitted with a system for the direct introduction of the substance into the ion source. The temperature of the experiment was 90-110°C and the ionizing voltage 40 V.

SUMMARY

A mass spectrometric method for determining the configuration of the substituent at C-1 in the lycoctonine alkaloids has been proposed. The mass spectra of the carbinolamine ethers of three diterpene alkaloids have been studied. The possibility of using these spectra for determining the nature of the substituent at C-4 has been shown.

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