MASS SPACTRA OF DITERPENE ALKALOIDS WITH THE LYCOCTONINE SKELETON

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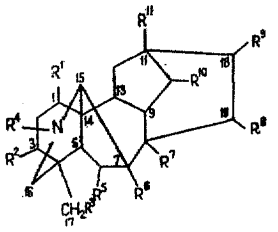
Pelletier and Aneja's paper [1] is still the only one in which the mass spectra of diterpene alkaloids are discussed. It describes a number of one- and two-stage processes of the fragmentation of the molecular ions of four substances containing a lactone ring. In the opinion of these authors, the maximum peak is formed through the detachment of the substituent from position 1.

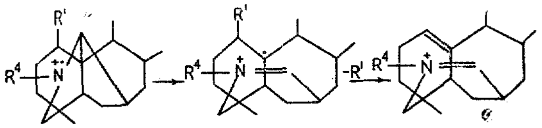
We have studied the mass-spectrometric behavior of alkaloids with the lycoctonine skeleton (I):



isotalatisidine, talatisamine, condelphine, lycoctonine, and aconine, and some of their derivatives (table). The mass spectra were recorded on a MKh-1303 instrument fitted with a glass system for the direct introduction of the substance into the ion source. The temperature of the experiments was 80–120° C and the ionizing voltage 40 V.

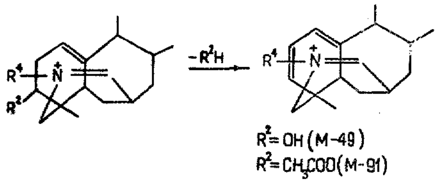
Under the action of electron impact, an electron of the nitrogen atom is knocked out. The decomposition of the molecular ion consists in the detachment of several substituents located close to the nitrogen atom. The stable systems so arising do not undergo further destruction. The role of other ionization centers is evidently insignificant.

With the exception of special cases, the maximum peaks of the mass spectra of the compounds studied appear with the elimination of the substituent from position 1. The sequence of acts leading to the formation of these ions is, in our opinion, the opposite of the sequence given by Pelletier [1].



The mass spectra of aconine (X) and its triacetate (XI), the molecules of which contain a substituent in position 3, possess an interesting feature. In both cases the M − 31 peaks are the maximum peaks. In the spectrum of aconine, the second most intense (21%) is the M − 31 − H_2O peak arising through the elimination of the elements of water from $C_{(3)}$ and $C_{(2)}$. In aconine triacetate there is a strong peak (89%) of the M − 91 ion, the formation of which may take place by two independent routes:

1) after the elimination of R' by the mechanism described above, the elements of acetic acid one split out from $C_{(3)}$ and $C_{(2)}$:

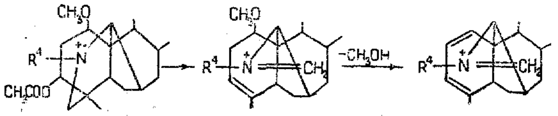


2) an ammonium ion arises as a consequence of the cleavage of the $C_{(4)}$—$C_{(16)}$ bond. This act is accompanied by the elimination of the acetoxy radical from $C_{(3)}$ with the subsequent expulsion of methanol.

Main Fragments in the Mass Spectra of Alkaloids with the Lycoctonine Skeleton

Compound	R (unspecified R = H)	*M*	Relative intensity, %						Other important peaks
			M^+	$M-15$	$M-17$	$M-18$	$M-31$	$M-33$	
Isotalatisidine (I)	R^1, R^7, R^{10}=OH; R^3, R^9=OCH_3; R^4=C_2H_5	407	34	30	100	10	5	16	—
Talatisamine (II)	R^7, R^{10}=OH; R^1, R^3, R^9=OCH_3; R^4=C_2H_5	421	3	1.5	0.5	0.5	100	2.5	M—49 (15)
19-Desmethoxy-8-anhydrotalatisamine (III)	R^{10}=OH; R^1, R^3=OCH_3; R^4=C_2H_5; $\Delta^{8,18}$	373	4	4	1	—	100	5	—
Dimethyltalatisamine (IV)	R^1, R^3, R^7, R^9, R^{10}=OCH_3; R^4=C_2H_5	449	1.5	1	—	—	24	—	M—63 (100)
Talatisamine diacetate (V)	R^1, R^3, R^9=OCH_3; R^7, R^{10},=$OCOCH_3$; R^4=C_2H_5	505	0.3	0.3	—	—	2	—	M−60 (21) M−91 (100)
16-Oxotalatisamine (VI)	R^7, R^{10}=OH; R^1, R^3, R^9=OCH_3; R^4=C_2H_5; C_{16}=O	435	18.5	100	6	0.4	50	4	M—47 (41)
Condelphine (VII)	R^1, R^7=OH; R^3, R^9=OCH_3; R^{10}=$OCOCH_3$; R^4=C_2H_5	449	29	28.5	100	25	4	24	—
Condelphine acetate (VIII)	R^7=OH ; R^3, R^9=OCH_3; R^1, R^{10}=$OCOCH_3$; R^4=C_2H_5	491	0.5	0.4	0.2	0.5	0.5	0.2	M−59 (100) M−77 (84)
Deoxycondelphine (IX)	R^7=OH; R^3, R^9=OCH_3; R^{10}=$OCOCH_3$; R^4=C_2H_5	433	58	100	8	4	6	2.5	—
Aconine (X)	R^2, R^7, R^8, R^{10}, R^{11}=OH; R^1, R^3, R^5, R^9=OCH_3; R^4=C_2H_5	499	1.2	3,2	2	2	100	11	M—49 (21)
Aconine triacetate (XI)	R^7, R^{11}=OH; R^1, R^3, R^5 R^9=OCH_3; R^2, R^8, R^{10}=$OCOCH_3$; R^4=C_2H_5	625	3.5	6	5	0.5	100	1.5	M—59 (48) M—91 (89)
Lycoctonine (XII)	R^3, R^6, R^7=OH; R^1, R^5, R^9, R^{10}=OCH_3; R^4=C_2H_5	467	4.5	26	3	5	100	1.5	M—49 (6)
Lycoctonine acetate (120° C) (XIII)	R^6, R^7=OH; R^1, R^5, R^9, R^{10}=OCH_3; R^3=$OCOCH_3$; R^4=C_2H_5	509	5	21	37	90	100	64	M- 49 (53) M—137 (68)
N-Methyl-des-N-ethyllycoctonine (XIV)	R^3, R^6, R^7=OH; R^1, R^5, R^9, R^{10}=OCH_3; R^4=CH_3	453	5	25	4	5	100	26	M—49 (3.5)
Des-N-ethyllycoctonine (XV)	R^3, R^6, R^7=OH; R^1, R^5, R^9, R^{10}=OCH_3	439	9.5	48	2	9	100	26.5	M—49 (15.5)
16-Oxolycoctonine (XVI)	R^3, R^6, R^7=OH; R^1, R^5, R^9, R^{10}=OCH_3; R^4=C_2H_5, C_{16}=O	481	6	100	9	19	6	23,5	M—47 (19)
N-Methyl-des-N-ethyloxolycoctonine (XVII)	R^3, R^6, R^7=OH; R^5, R^9, R^{10}=OCH_3; R^4=CH_3; C_{16}=O	467	(7)	100	8.5	2.5	5	19	M—47 (19)

The metastable transitions: 1) 480* = $594^+ \rightarrow 534^+$ and 2) 504* = $566^+ \rightarrow 534^+$ confirm these directions of decomposition.



The majority of the mass spectra contain the peaks of the M – 18 ions. In addition to this, the expulsion of water accompanies all the main processes of decomposition. The main contribution to the appearance of these peaks is made by the hydroxyl at $C_{(8)}$ that is present in all the initial alkaloids considered, as is confirmed by the absence of M – 18 and M – 49 peaks in the spectrum of 19-desmethoxy-8-anhydrotalatisamine (III), the molecule of which contains a $C_{(8)}$—$C_{(19)}$ double bond. The mobility of the substituent at $C_{(8)}$ becomes still more considerable in the spectra of the products of the methylation and acetylation of talatisamine. In the spectra of IV and V the peaks of the ions M – 31 – CH_3OH and M – CH_3OH – 31, respectively, become the maximum peaks.

The intensities of the peaks connected with the elimination of water vary considerably according to the nature of the surrounding substituents. Thus, in the spectrum of condelphine (VII) and its acetate (VIII), which has an acetoxy group in position 10, the intensity of the M – 18 (condelphine) and M – HCO – 18 (condelphine acetate) peaks are higher than in the spectra of the talatisamine derivatives. An increase in the intensity of the dehydration peaks is also observed in the mass spectra of lycoctonine derivatives (XII). This is possibly connected with the presence of a neighboring OH group at $C_{(7)}$, the elimination of water taking place by another route. The probability of the processes taking place with the elimination of water depends strongly on the temperature of the experiment. Thus, in the case of lycoctonine acetate (XIII), raising the temperature of the inlet system from 100 to 120° C leads to a marked increase in the intensities of the peaks of the M – 18, M – 33, and M – 49 ions.

Apparently, under the action of electron impact, the splitting out of the substituent on the quaternary $C_{(4)}$ atom should take place. However, this process proves to be unimportant and appears appreciably only in the mass spectrum of lycoctonine acetate. The cleavage is accompanied by the expulsion of methanol (probably through the OCH_3 group at $C_{(6)}$) and then methyl acetate is eliminated from position 4. The relative intensity of the peak of the M – 137 ion obtained in this way amounts to 68% of the maximum peak at 120° C.

Pelletier's assumption [1] that the M – 15 peaks are due to the splitting out of CH_3 from N—C_2H_5 with the formation of a stable ammonium ion appeared to us to be completely correct. The further process may take place in parallel with the process of the origin of the M – 31 ions, but they cannot take place successively. In actual fact, the peaks of the M – 46 ions have low intensities. The peaks of the M – 33 ions, corresponding either to M – 15 – H_2O or to M – H_2O – 15 have a considerable intensity in all the mass spectra. In a number of cases, both sequences are confirmed by metastable peaks. In the mass spectrum of deoxycondelphine (IX, R' = H), the M – 15 peak is the maximum one. For a definitive confirmation of Pelletier's hypothesis, we recorded the mass spectra of two derivatives of lycoctonine, in the molecules of which the N—C_2H_5 group is replaced by N—CH_3 (XIV) and by N—H (XV). In the spectra obtained, the intensity of the peaks of the M – 15 ions with respect to the total ion current was the same as in lycoctonine. This fact confirms Pelletier's hypothesis. Having then taken the mass spectra of the 16-oxo derivatives of talatisamine (VI) and lycoctonine (XVI), we found that the peaks of the M – 15 ion are the maximum peaks in them. It could be assumed, however, that in the oxidized products the detachment of CH_3 from N—C_2H_5 still took place, since this reaction would lead to the formation of a conjugated system of bonds. However, after having obtained the mass spectrum of des-N-ethyl-N-methyloxolycoctonine (XVII) we found that the peak of the M – 15 ion retained the maximum intensity. Consequently, the splitting out of a methyl radical from N—C_2H_5 is excluded.

A comparison of the spectra shows, moreover, that the appearance of the M – 15 peaks is not connected with the splitting out of methyl from a methoxy group at $C_{(1)}$, $C_{(17)}$, or $C_{(19)}$. Here, rather, there is a rearrangement process with participation of the methylene group in position 12. Furter experimental confirmation is necessary to elucidate this fact.

CONCLUSIONS

The main routes of fragmentation of diterpene alkaloids with the lycoctonine skeleton under the action of electron impact are discussed.

REFERENCES

1. S. W. Pelletier and R. Aneja. Tetrah. Let., 557, 1967.

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