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MASS-SPECTROMETRIC INVESTIGATION OF SOME NEW DERIVATIVES OF THE ALKALOID LUPININE

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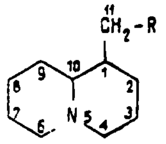
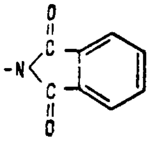
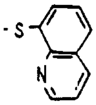
The mass spectra of some new derivatives of lupinine have been studied with the use of the spectra of metastable ions. On the basis of the results of an investigation of DADI spectra it has been shown that in the formation of low-mass quinolizidine ions the ions with m/z 152-150 are of considerable importance.

In the present work we consider the mass spectra of derivatives of 1-methylquinolizidine synthesized with the aim of finding new physiologically active compounds.



where R -NH-CO-CH$_2$Cl (I), -NH-CO-CF$_3$ (II),


(III).


(IV).


(V)

Features of the fragmentation of bases of the quinolizidine series have been described fairly fully in the literature [1-6], but at the same time some characteristics of such fragmentation remained unconsidered. We have examined these characteristics for the case of lupinine derivatives, using the spectra of metastable ions. The peaks of the molecular ions of amides (I) and (II) in the corresponding ordinary spectra are fairly strong and the pathways of their fragmentation are reproduced along the line of the ejection of the hydrocarbon units of the quinolizidine ring and of the formation of key nitrogen-containing fragments. The process of fragmentation in the spectrum of monochloroacetylaminolupinane (I) is accompanied by the appearance of the far more intense fragment $(M-HCl)^+$ with m/z 206 and of ions

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TABLE 1. Metastable Transitions of Key Ions in the DADI Spectra

Parental ions		Daughter ions
M+ 264	(II)	249, 236, 222, 167, 152, 138, 136, 124, 111, 97, 83
(M—H)+ 263		248, 221, 179, 167, 152, 138, 136, 124, 110, 97, 96, 83
(M—F)+ 245		217, 161, 147
222		125, 110, 96, 83
195		152.
167		150, 138, 98, 84
152		137, 125, 124, 110, 109, 98, 97, 83, 69
138		110, 108, 98, 84, 55
136		109, 108, 96, 83, 81
M+ 298	(III)	283, 269, 256, 242, 160, 150, 138, 136, 124, 110, 97,
(M—H)297		269, 265, 160, 150, 136, 123, 110, 98, 97
160		136,
152		137, 124, 123, 111, 110, 98, 97, 83, 69
150		135, 124, 123, 111, 110, 98, 97, 83, 69, 55,
M+ 312	(IV)	279, 265, 228, 183, 152
(M—H)311		278, 151,
(M—2H)310		150, 136,
(M—SH)279		194, 96
152		137, 124, 123, 109, 98, 96, 83, 69
M+ 317	(V)	169, 152, 124

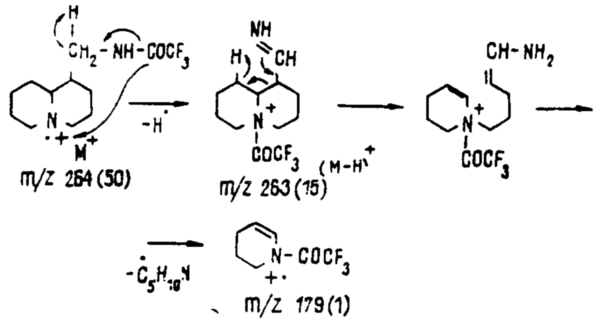
corresponding to the elimination of a number of fragments from the latter: $[(M-HCl)-15]^+$ and $[(M-HCl)-29]^+$.

According to the literature, the formation of quinolizidine ions takes place only from the molecular ion. In order to confirm this mechanism of the formation of quinolizidine fragments and to reveal the participation of other ions in this process, we studied the spectra of metastable ions. With the aim of excluding the isotope effect and of obtaining a clearer pattern, for the investigation we took only trifluoroacetylaminolupinane (II). The DADI* spectrum of the M^+ ion of (II) obtained showed that all the main quinolizidine fragments down to particles with m/z 83 (Table 1) were formed directly from the M^+ ion.

It was of interest to compare the DADI spectra of M^+ and $(M-H)^+$, since the latter is usually ascribed a more stable ammonium structure formed through the elimination of the angular hydrogen atom from C_{10}.

It was found that the further breakdown of the $(M-H)^+$ ions led to the formation of quinolizine fragments, and the mass values of the majority of the ions recorded coincided with those of the ions obtained on the breakdown of M^+ (Table 1). However, a quantitative redistribution of relative intensities of the (daughter) metastable ions was observed, for example, in case of the ion with m/z 152. The ratio of the intensities of the metastable peak of the ion with m/z 152 to the parental ion is three times greater in the DADI spectrum of the $(M-H)^+$ ion than that of M^+. A certain analogy was observed also in the case of the metastable ions with m/z 166 from $(M-H)^+$ and 167 from M^+. This phenomenon can be explained by the assumption that the process of formation of the ions with m/z 152 and 166 and of the $(M-H)^+$ ions is a rearrangement process, which is slower, and, apparently, under these conditions the bulk of the energy of the parental ions is consumed in the formation of the metastable ions [7, 8].

The DADI spectrum of $(M-H)^+$ of compound (II) contained the peak of a metastable ion with a fairly high intensity, corresponding to the transition $(M-H)^+ \rightarrow 179$ m/z, while in the case of M^+ no similar transition was observed. In the ordinary spectrum of compound (I) the mass of this fragment corresponded to the ion $[(M-HCl)-29]^+$, but in the spectrum of (II) the relative intensity of the peak of the ion with m/z 179 amounted to only ~1%. We may note that in individual cases the investigation of such ions in the spectra of the metastable ions assists in the explanation of some characteristic directions of fragmentation. In view of this, we measured the accurate mass of the ion with m/z 179. The calculated composition, $C_7H_8ONF_3$, confirmed the complex mechanism of the formation of this ion. The most probable pathway for the formation of this fragment may be assumed to be from the other form of $(M-H)^+$ shown in the scheme, with the transposition of the trifluoroacetyl radical to the nitrogen atom of the quinolizidine nucleus. Such migration of a whole group to the charged nitrogen atom has been described in the analysis of the mass spectra of pyrrolizidine bases [9].



It was of interest to follow the fate of some other ions given in Table 1. As can be seen from the Table, each daughter ion, in its turn, gave a series of fragmentary ions, while from the ion with m/z 152 the series of ions with low values of m/z characteristic for quinolizidine bases was formed.

In the ordinary spectrum of (III) the maximum ion was the quinolizidine ion with m/z 150, while the peak of the ion with m/z 152 had a low intensity. The process of the formation of the ion with m/z 150 from the ions M^+ and $(M-H)^+$ appeared of interest since the

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*DADI) Direct Analysis of Daughter Ions (metastable ions).

transition $M^+ \rightarrow 150^+$ m/z was accompanied by the migration of two hydrogen atoms to the neutral fragment, while the $(M-H)^+ \rightarrow 150^+$ m/z transition was accompanied by the migration of one hydrogen atom.

The peaks of these transitions appeared in the DADI spectrum of the ions M^+ and $(M-H)^+$, while in a comparison of the ratio of the intensities of the metastable parental ions in the case of the transition $(M-H)^+ \rightarrow 150$ m/z a far lower value was obtained. This phenomenon is in harmony with the version described above in the case of the formation of the ion with m/z 152 in the DADI spectrum of compound (II) from the M^+ and $(M-H)^+$ ions. The subsequent breakdown of the ions with m/z 152 and 150 led to low-mass quinolizidine fragments down to an ion with m/z 55 (Table 1).

From the aromatic moiety of the molecule of (III) in the DADI spectra of M^+ and $(M-H)^+$ only an ion with m/z 160 was recorded, and this then, losing HCN, passed into an ion with m/z 133.

In the ordinary spectrum of (IV) there were the peaks $(M-HS)^+$ and $(M-H_2S)^+$ that are characteristic for sulfur-containing compounds. Although in this spectrum the quinolizidine ions possessed fairly high intensity in the DADI spectrum of the M^+ ion, in contrast to the substances considered above, only a very intense daughter ion with m/z 152 was formed from the quinolizidine fragments, and practically no others were detected. Consequently, it was mainly the ions with m/z 152, 151, and 150 that were responsible for the appearance of the low-mass ions. In addition to this, this spectrum contained the metastable ions given in Table 1.

It is interesting to note that although the quinoline ions with m/z 174 and 161 were, according to the method of their formation, rearrangement ions, nevertheless in the DADI spectra of M^+, $(M-H)^+$, $(M-2H)^+$, and $(M-SH)^+$ the corresponding transitions did not appear for them, and with an intensified introduction of the sample hardly appreciable signals were obtained from M^+. A certain analogy was also observed in the DADI spectrum of M^+ for compound (V): Ions of aromatic nature were absent. To confirm the authenticity of the $M^+ \rightarrow$ m/z 169^+ transition (see Table 1), we recorded the metastable defocusing (MD) spectrum of the m/z 169 ion and obtained an unambiguous result in the form of an intense peak of the metastable ion.

Mass numbers and relative intensities of the ions in the spectra of compounds (I-V) (m/z, %):

(I). 246(10), 245(8), 244(35), 243(12), 231(0.4), 230(0.5), 229(1), 217(1), 215(3), 210(2), 209(8), 208(25), 207(2), 204(3), 203(3), 202(6), 201(2), 196(3), 195(20), 180(2), 179(8), 169(2), 168(6), 167(12), 166(8), 165(8), 153(25), 152(87), 151(35), 150(85), 140(4), 139(45), 138(100), 137(35), 135(90), 134(10), 126(3), 125(24), 124(48), 123(10), 122(25), 112(20), 111(84), 110(85), 109(20), 108(17), 98(70), 97(86), 96(86), 95(40), 84(70), 83(90), 82(50), 81(18), 80(20), 79(10), 78(9), 77(17), 70(13), 69(26), 68(20), 67(25), 56(30), 55(65), 54(23).

(II). 265(7.5), M^+ 264(50), 263(15), 249(1.5), 245(2.5), 236(0.5), 235(1), 231(1), 223(1.5), 222(3), 221(1), 216(1), 208(0.5), 196(2.5), 195(14), 193(1), 179(1), 169(1.5), 167(4), 165(1), 153(6), 152(50), 151(11), 150(12), 139(11), 138(85), 136(18), 126(6), 125(10), 124(18), 122(8), 112(7), 111(72), 110(43), 108(5), 98(20), 97(43), 96(25), 95(14), 84(23), 83(100), 82(20), 70(5), 69(49), 68(8), 67(9), 56(10), 55(25), 54(10), 51(15), 50(8).

(III). 299(12), M^+ 298(45), 297(17), 296(7), 283(3), 269(4), 257(4), 256(15), 242(1), 241(1), 186(2), 169(1), 161(5), 160(25), 152(12), 151(32), 150(100), 149(12), 148(22), 147(12), 139(12), 138(70), 137(10), 136(52), 134(10), 133(6), 130(7), 128(9), 124(22), 123(10), 122(10), 111(37), 110(42), 105(7), 104(10), 99(25), 98(37), 97(32), 96(10), 84(17), 83(57), 82(37), 77(6), 76(10), 70(5), 69(15), 68(7), 67(10), 56(12), 55(37).

(IV). 314(9), 313(27), M^+ 312(77), 311(3), 310(3), 279(10), 265(1), 255(1), 228(1), 200(2), 197(1), 184(3), 183(4), 175(3), 174(9), 173(7), 168(3), 167(4), 162(9), 161(45), 160(11), M^{++} 156(18), 153(68), 152(100), 151(95), 150(79), 149(16), 148(16), 137(14), 136(75), 134(11), 130(11), 129(20), 124(9), 123(20), 122(45), 117(18), 116(9), 110(18), 109(25), 108(9), 98(50), 97(16), 96(29), 95(16), 94(11), 84(38), 83(11), 82(11), 81(9), 80(7), 70(9), 69(20), 68(70), 67(17), 56(20), 55(27), 54(7).

(V). M^+ 317(4), 316(0.6), 273(1), 170(7), 169(54), 168(47), 167(3), 153(11), 152(100), 149(11), 148(54), 139(20), 138(65), 136(11), 134(3), 127(9), 125(9), 124(24), 122(20), 111(34), 110(40), 105(27), 104(9), 98(34), 97(61), 96(40), 84(38), 83(85), 82(32), 78(20), 77(20), 76(95), 75(20), 74(30), 70(8), 69(11), 68(9), 67(9), 65(8), 57(8), 56(13), 55(47), 54(13), 53(9), 52(8), 51(8), 50(67).

EXPERIMENTAL

The ordinary mass spectra were taken on a Varian MAT-311 instrument using a direct-introduction system with a temperature of the ionization chamber of 100-120°C, an ionizing voltage of 70 V, and an ionizing current of 300 μA. The temperature of the evaporator was 30-50°C.

Daughter ions were recorded in the DADI regime with scanning of the voltage of the energy analyzer from 488 to 80 V.

MD spectra were obtained by scanning the accelerating voltage from 1000 to 3000 V. The mass units of the signals in the spectra of the metastable ions were calculated by the standard procedure, apart from the fact that for such a calculation in the DADI spectra a formula has been proposed which greatly shortens the time of the experiment to determine the position of the signals of the metastable ion:

$$m_d = M_p \left[\left(\frac{U_e}{U_0} - 1 \right) \frac{l_d}{l_e} + 1 \right],$$

where m_d is the calculated mass of the daughter ion; M_p is the mass of the parental ion; U_0 is the initial voltage of the energy analyzer; U_e is the voltage of the energy analyzer at the end of the recording of the DADI spectrum; ℓ_d is the distance between the parental and daughter ions; and ℓ_e is the distance between the parental ion and the point at which the scanning of the spectrum is stopped.

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