COMPARATIVE MASS-SPECTROMETRIC INVESTIGATION OF QUINOLIZIDINE ALKALOIDS AND CYTISINE, SPARTEINE, AND MATRIDINE DERIVATIVES

N. S. Vul'fson, Z. S. Ziyavidinova, and V. G. Zaikin

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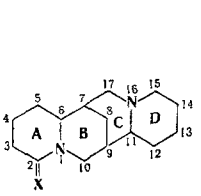
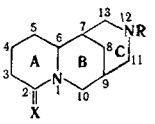
The low- and high-resolution mass spectra of pachycarpine, tetrahydrodesoxocytisine, matridine, α-isolupanine, tetrahydrocytisine, matrine, d-thermopsine, cytisine, and isosophoramine, as well as some of their stereoisomers and deutero analogs, make it possible with a high degree of probability to relate the investigated compounds to one or another group of quinolizidine alkaloids.

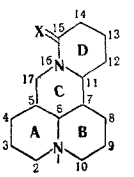
The mass spectra of the thoroughly studied cytisine and sparteine derivatives [1-3] and the considerably less well studied matridine derivatives [4-6] have many features in common. On the basis of an analysis of the literature and our own experimental investigations carried out in the case of pachycarpine (Ia), matridine (IIIa), allomatridine (IIIb), isosophoridan (IIIc), sophoridan (IIId), α-isolupanine (IVa), lupanine (IVb), matrine (VIa), allomatrine (VIb), isosophoridine (VIc), sophoridine (VId), d-thermopsine (VIIa), cytisine (VIIIa), isosophoramine (IXa), sophoramine (IXb), and a number of their deutero analogs, we attempted to make a comparative mass-spectrometric investigation of alkaloids of these three types with the aim of possibly identifying them. Since differences in the mass spectra of stereoisomers are manifested in most cases in a change in only the relative intensities of the individual peaks, we will discuss the peculiarities of the mass spectra in the cases of structural isomers – alkaloids Ia (Fig. 1a), IIa, IIIa (Fig. 1c), IVa (Fig. 2a), Va, VIa (Fig. 2c), and VIIa, VIIIa, IXa (Fig. 3a-c). The spectra of alkaloids IIa and Va are presented in [1, 3].



I a,b, IV a, b

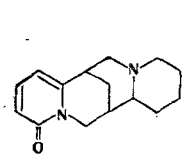


II a,b, V a, b

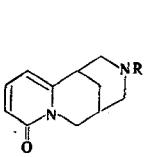


III a-d, VI a-d

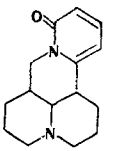
X = H_2, Ia pachycarpine; Ib sparteine; X = O, IVa α-isolupanine; IVb lupanine; X = H_2, IIa desoxotetrahydrocytisine (R = H); IIb N-methyldesoxotetrahydrocytisine (R = CH_3); X = O, Va tetrahydrocytisine (R = H); Vb N-methyltetrahydrocytisine (R = CH_3); X = H_2, IIIa matridine; IIIb allomatridine; IIIc isosophoridan; IIId sophoridan; X = O, VIa matrine; VIb allomatrine; VIc isosophoridine; VId sophoridine.



VII a, b



VIII a, b



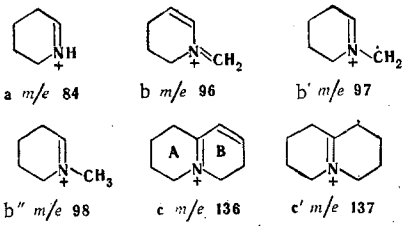
IX a, b

M. M. Shemyakin Institute of the Chemistry of Natural Compounds, Academy of Sciences of the USSR. A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 251-260, February, 1974. Original article submitted July 4, 1973.

VIIa d-thermopsine; VIIb anagyrine; VIIIa cytisine (R = H); VIIIb N-methylcytisine (R = CH_3); IXa isosophoramine; IXb sophoramine.

Only in individual cases, primarily in the examination of alkaloids of the III and VI type, will we deal with problems associated with the stereochemical peculiarities of the molecules.

According to the data in [1-4], ion peaks with m/e 84 (a), 96 (b), 97 (b'), 98 (b"), 136 (c), 137 (c'), and 150 (d), which apparently characterize the quinolizidine system [7], are typical for almost all of the quinolizidine alkaloids. The origin of the ions, the peaks of which are situated in the high-molecular-weight region of the spectra, has not been adequately discussed.



One should first note that the affiliation of the alkaloids with the group of cytisine alkaloids (II, V, VIII) can usually be established from the molecular weight because of the absence of a D ring in them. The task is somewhat complicated if the substituent attached to the nitrogen atom of the C ring is larger than a methyl group or if the alkaloid is dimeric (as, for example, argentine, octahydroargentine [8], or dimethamine [9]). But here also, as a result of α cleavage and elimination of a large portion of the substituent from the nitrogen atom or disintegration of the molecular ion of the dimeric alkaloid, the low-molecular-weight regions of the spectra are practically identical to the spectra of the corresponding cytisine derivatives.

In the case of alkaloids of the I type with a formally symmetrical structure, it might be expected that the a, b–b", c, and c' ions are formed equally probably as a result of cleavage of the bonds in the B and C

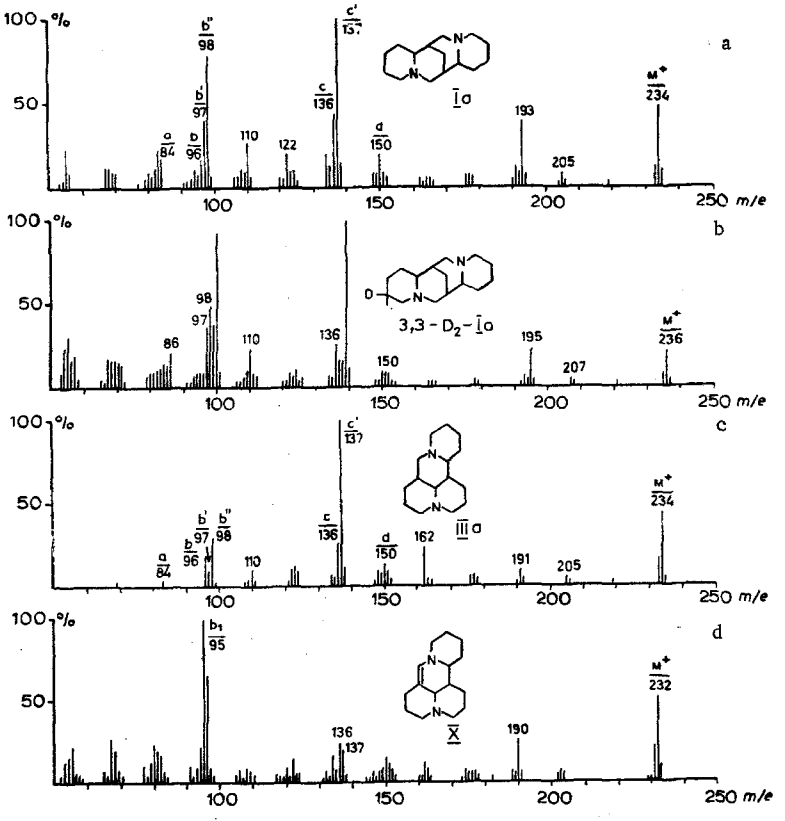


Fig. 1. Mass spectra: a) pachycarpine; b) 3,3-D_2-pachycarpine; c) matridine; d) 5,17-dehydroallomatridine.

rings and contain A and D or AB and CD rings, respectively. However, in the case of sparteine [1], these ions contain chiefly an A ring (or AB ring, respectively); Neuner-Jehle and co-workers [1] explain this by the effect of the stereochemistry of the fusion of the A/B and C/D rings. A similar situation is also retained in pacycarpine Ia, which is the d-isomer of sparteine (Ib) and has the same stereochemistry of fusion of the A/B and C/D rings. In fact, the peaks of the a, b–b", c and c' ions in the mass spectrum of 3,3-D_2-Ia (Fig. 1b) are shifted basically by 2 amu. The formation of these ions for alkaloids II is also primarily associated with cleavage of the bonds in the B or C ring and with localization of the charge on the fragment containing the A or AB ring, respectively.

On the basis of an analysis of the mass spectrum of the 15,15-D_2- analog of matridine (IIIa), Yunusov and co-workers [4] arrived at the conclusion that the a and b–b" ions for IIIa contain A or B rings and arise as a result of three C–C bonds in the A (or B) and C rings with migration of two hydrogen atoms. However, this required subsequent refinement, since the formation of ions with localization of the charge on the D ring should proceed via a simpler mechanism with cleavage of only two C–C bonds in the C ring, just as in the case of alkaloids I. We therefore studied the mass spectra of 14,14-D_2 analogs of alkaloids IIIa-c.* It has been shown [10] that, depending on the stereochemical peculiarities of the investigated alkaloids, the a and b–b" ions may contain both an A (or B) ring and a D ring. Thus, for example, in the case of IIIb, the b" ion primarily includes a D ring, while an A or B ring is included in the case of IIIa and IIIc.

In this connection, it is interesting to note that the peaks of the a, b', and b" ions in the mass spectrum of 6,17-dehydroallomatridine (X) (Fig. 1d), which contains a double bond in the C ring, are practically

* The three-dimensional structures of their carbonyl-containing derivatives (VIa-c) are presented in Table 1.

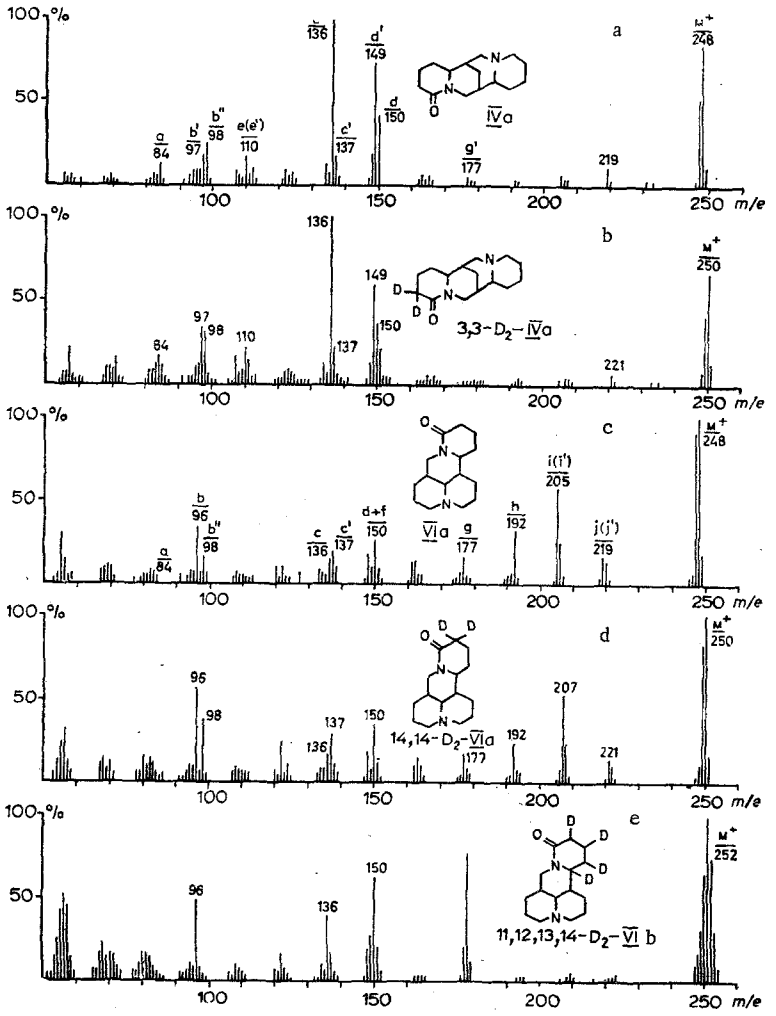
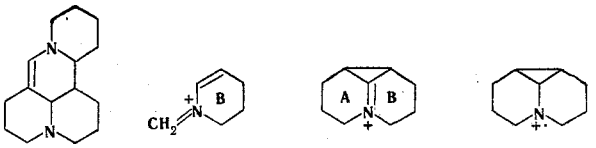


Fig. 2. Mass spectra: a) α-isolupanine; b) 3,3-D_2-α-isolupanine; c) matrine; d) 14,14-D_2-matrine; e) 11,12,13,14-D_4-allomatrine.

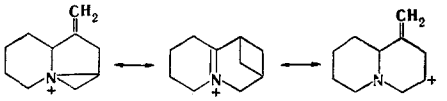


X b, *m/e* 95 c_1 *m/e* 136 c_1' *m/e* 137

absent, while the ion peak with m/e 95, to which structure b_1 can be assigned, is a maximum.

Insofar as ions with m/e 136 and 137 are concerned, for alkaloids III they form exclusively as a result of cleavage of the bonds in the C ring with localization of the charge on the fragment containing the A and B rings. In contrast to the analogous fragments of alkaloids I and II, these ions apparently have c_1 and c_1' structures, respectively. The intensity of the peaks of these ions is naturally considerably reduced in the spectrum of X (Fig. 1d).

According to the data in [1], the formation of a d ion with m/e 150 in the case of alkaloids I does not depend on the stereochemistry of fusion of the A/B and C/D rings, and ion d is due approximately to an equal degree to localization of the charge on both nitrogen atoms. This conclusion is also in agreement with our observation that the intensities of the peaks with m/e 150 and 152 in the mass spectrum of the 3,3-D_2 analog of Ia are approximately equal (Fig. 1b).



d *m/e* 150

In the case of the stereoisomers of alkaloids III, ions d are formed exclusively through cleavage of the bond in the C ring and as a consequence of localization of the charge on the nitrogen atom of the A and B rings. This is indicated by the absence of a shift in their peaks in the mass spectra of the 14,14-D_2 analogs [10].

The mass spectra of IIIa and IIIc contain rather intense ion peaks with m/e 162, the intensity of which in the spectra of Ia,b is considerably lower (Fig. 1a,c). However, this ion can scarcely have substantial diagnostic value, since the intensity of its peak in the spectrum of derivative IIIb is also somewhat lowered [10]. It is difficult to form a judgment regarding the nature of the ion with m/e 162, and one can only note that it does not include the C-14 [10] and C-15 [4] atoms, but, according to the data from the high-resolution mass spectrum of IIIc, has the composition $C_{11}H_{16}N$.

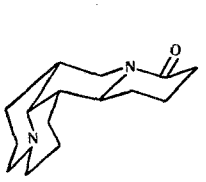
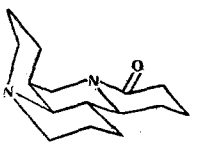
The mass spectra of alkaloids I and III contain low intensity N-43 and M-29 ion peaks with m/e 191 and 205, respectively. Since the first of these peaks in the spectra of the 14,14-D_2 analogs of III [10] are only partially shifted to m/e 192 and 193, it can be supposed that they are formed due to ejection of a propyl radical or an ethyleneimine molecule. The formation of ions with m/e 205 is associated with ejection of an ethyl radical from the A or B rings. The peaks of these ions in the spectra of the deutero analogs of III are completely shifted to m/e 207.

The most substantial (from a diagnostic point of view) difference between the mass spectra of alkaloids of the I and III type is the presence in the spectra of I of rather intense M-41 ion peaks with m/e 193, which are practically absent in the spectra of III (Fig. 1, spectra a and c). In the case of alkaloids of the I type, this ion is apparently formed as a result of elimination from the molecular ion of a cyclopropyl radical during cleavage of the bonds in the B and C rings. This is confirmed by the shift in its peak by 2 amu (to m/e 195) in the mass spectrum of the 3,3-D_2 analog of Ia (Fig. 1b), and also by the shifts of 16 amu to m/e 209 in the mass spectra of 13-hydroxy-Ib [1] and 14-hydroxy-Ib [2]. Ejection of a cyclopropyl radical from the molecular ion is less likely in the case of alkaloids III.

The presence of a lactam carbonyl group in alkaloids IV-VI has a substantial effect on the character of the disintegration of their molecular ions under electron impact; this considerably facilitates differentiation of their mass spectra (Fig. 2, spectra a and c).

The most characteristic peculiarities of the mass spectra of alkaloids VI are the extremely intense M^+ and M-1 ion peaks; the dominant ion peak in the case of VIa is M^+, while M-1 ions dominate in the case of VIc-d (Table 1). The intensities of these peaks are considerably lower in the spectra of alkaloids IV and V.

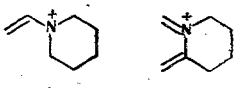
TABLE 1. Data from the Mass Spectra of Alkaloids VI (the intensities are given in percent of the maximum)

m/e	Matrine, (VI) 	Allomatrine (VIb) 	Isosophoridine (VIc) 	Sophoridine* (VIb) —
249	19	10	13	9
248	100	59	86	53
247	92	100	100	100
220	14	1	7	1
219	16	3	7	3
206	25	3	12	4
205	58	6	26	7
192	33	3	8	2
178	5	9	5	3
177	16	49	20	10
164	5	1	3	1
163	6	2	4	—
162	14	4	10	3
161	12	3	7	—
151	10	7	14	5
150	27	39	36	24
149	10	19	12	10
148	17	14	15	8
138	11	7	8	17
137	20	10	12	6
136	14	21	17	16
135	5	4	4	2
134	7	7	5	3
122	9	8	8	8
120	10	3	5	3
110	6	5	4	8
98	17	7	12	7
96	33	10	25	30
86	—	5	1	—
85	1	7	1	—
84	7	5	4	7
83	7	6	5	8
82	9	7	4	7

* The stereochemistry has not been definitively established.

The intensities of the peaks of ions a and b–b" in the spectra of alkaloids IV and VI are generally lower than in the spectra of I-III. In the case of alkaloids IV, these ions contain exclusively a D ring, as attested to by the absence of a shift in their peaks in the spectrum of the 3,3-D_2 analog of IVa (Fig. 2b). However, in the case of alkaloids VI, these ions are formed due to the A or B rings; this is confirmed by the absence of a shift in their peaks in the spectrum of the 14,14-D_2 analog of VIa (Fig. 2d).

In addition, the spectrum of derivatives IVa (Fig. 2a) is characterized by a peak of medium intensity with m/e 110, which is absent in the spectrum of Va and is of insignificant intensity in the spectrum of VIa. According to the data from the high-resolution mass spectrum of alkaloids IVa, this ion has the $C_7H_{12}N$ composition and, according to the assumption in [3], may have the e or e' structure. The ions with m/e 110 in the case of alkaloids I-III probably also have a similar structure.



e m/e 110 e' m/e 110

According to the data in [3], a characteristic peculiarity of the mass spectrum of alkaloid VA is the presence of a rather intense ion peak with m/e 82 and a maximum peak with m/e 95, while the peaks of the a and b–b" ions are of low intensity. The ions with m/e 82 and 95 contain a C ring, since their peaks are shifted by 14 amu (to m/e 96 and 109) in the mass spectrum of N-methyltetrahydrocytisine (Vb) [3].

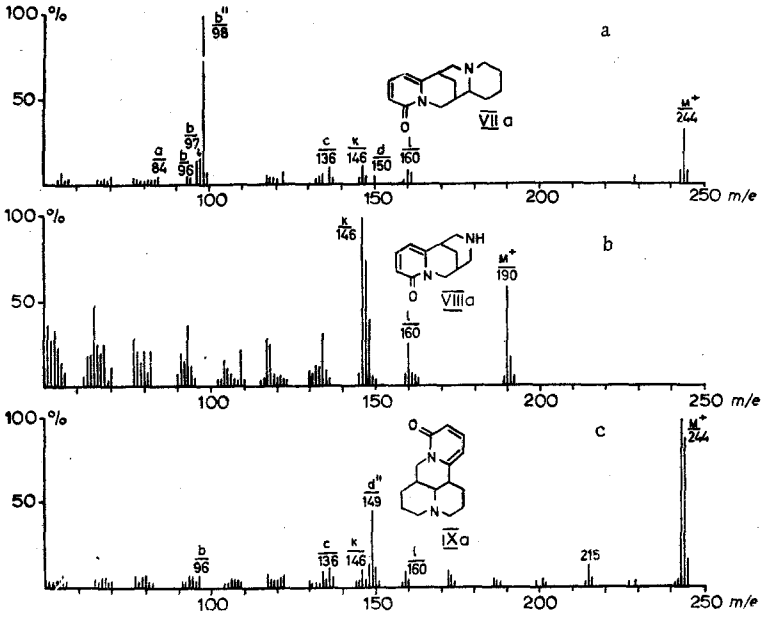
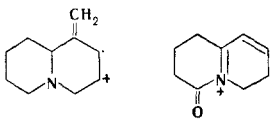


Fig. 3. Mass spectra: a) d-thermopsine; b) cytisine; c) isosophoramine.

The mass spectra of alkaloids IV-VI differ substantially with respect to the intensities of the peaks of the c and c' ions. In the spectrum of IVa, the peak of ion c is a maximum, while the peak of ion c' is insignificant. The peaks of these ions in the spectra of Va,b are practically absent [3], while they are of medium intensity in the spectrum of VIa (the c' peak is greater than the c peak). The presence in the spectra of IVa and VIa of peaks of metastable ions with m* = 74 (calculated 73.7) and 75 (calculated 74.9), respectively, is evidence that in the first case ion c is formed directly from the molecular ion, while in the second case ion c' arises from the M-1 ion.

The ion peak with m/e 150 in the spectrum of IVa is of medium intensity and, judging from its insignificant shift in the spectrum of the 3,3-D_2 analog, IVa contains primarily C and D rings and has a structure of the b type. A distinctive characteristic of the spectrum of IVa is the presence of a considerably more intense ion peak with m/e 149, to which the d' structure is assigned [3].



The peak with m/e 150 in the mass spectra of alkaloids V is of low intensity and, from its nature, differs sharply from ion b, since it contains A and B rings, as attested to by the absence of its shift in the spectrum of Vb [3]. It apparently has the f structure.

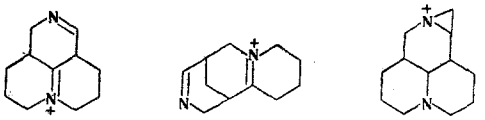
In the case of alkaloid VIa, the ion with m/e 150 forms directly from the M-1 ion; this is confirmed by the presence of a peak with m* = 91.3 (calculated 91.1). According to the data of the high-resolution mass spectra of VIa and VIc, the peak with m/e 150 is a composite and is caused by isobaric $C_{10}H_{16}N$ and $C_9H_{12}NO$ ions in a ratio of 65 : 35. The dominant ion apparently has a structure of the b type, while the second has a structure of the f type. However, it should be noted that these data do not agree with the results obtained from the mass spectra of the 14,14-D_2 and 11,12,13,14-D_4 analogs of VIa (Fig. 2, spectra d and e), in which such a large shift in the peak with m/e 150 is not observed. This places in doubt the data on the quantitative ratio of the isobaric ions with m/e 150.

The high-molecular-weight region of the mass spectra of alkaloids IV (from m/e 150 up to M^+) contains only low intensity peaks, in contrast to the spectra of alkaloids VI (Fig. 2, spectra a and c; Table 1).

According to the data of the high-resolution mass spectrum of VIa, the peak with m/e 161 is due to the $C_{10}H_{11}NO$ ion, while the peak with m/e 162 is a composite and corresponds to $C_{10}H_{12}NO$ and $C_{11}H_{16}N$ ions in a ratio of 55 : 45. According to the same data, the peak with m/e 177 is due to an ion with the composition $C_{11}H_{16}N_2$. The complete shift of this peak by 1 amu to m/e 178 in the spectrum of 11,12,13,14-D_4 analog

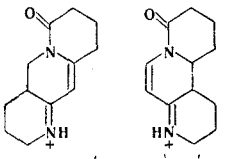
of VIb (Fig. 2e) indicates that it contains A=C rings and apparently has the g structure. According to the data of the high-resolution mass spectrum of IVa, the low-intensity peak with m/e 177 is also due to the ion with composition $C_{11}H_{17}N_2$, which possibly has the g' structure.

Ejection of a portion of the D ring from the molecular ion as C_3H_4O leads, in the case of alkaloid VIa, to a relatively stable $C_{12}H_2ON_2$ ion radical, which probably has the h structure.



g *m/e* 177 g' *m/e* 177 h *m/e* 192

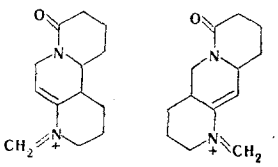
One of the most intense peaks in the spectrum of VIa with m/e 205 (Fig. 2c) is completely shifted by 2 amu to m/e 207 in the spectrum of the 14,14-D_2 analog (Fig. 2d). According to the data of the high-resolution mass spectrum, the ion corresponding to this peak has the composition $C_{12}H_{17}N_2O$. Consequently, it is formed as a result of ejection of a C_3H_6 particle (most likely from the A or B ring) and migration of two hydrogen atoms from the C ring and has the i or i' structure.



i *m/e* 205 i'

In contrast to this, the peak with m/e 206 is a composite (of isomeric ions of the composition $C_{12}H_{18}N_2O$ and $C_{14}H_{21}N$); this is confirmed by the partial shift in this peak in the spectrum of the 14,14-D_2 analog of VIa (Fig. 2d).

The peaks with m/e 219 and 220 in the spectrum of VIa are completely shifted to m/e 221 and 222 in the spectrum of its 14,14-D_2 analog. The second of these peaks is due to the $C_{14}H_{24}N_2$ ion, which is formed as a result of elimination of a CO group from the molecular ion, while the first is a composite and is due to $M-C_2H_5$ ($C_{13}H_{19}N_2O$) and M−CO−H ($C_{14}H_{23}N_2$) ions. In the formation of the first of these, an ethyl radical is apparently eliminated from the A or B rings, and it has the j or j' structure.



j *m/e* 219 j'

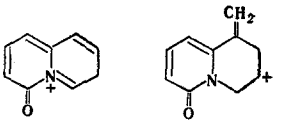
The introduction of two double bonds into the lactam ring of alkaloids IV-VI leads to the appearance of substantial differences in the mass spectra of the corresponding alkaloids (VII-IX) (Fig. 3, spectra a-c). As in the case of alkaloids VI, the dominant peaks in the spectra of alkaloids IX are those of the M^+ and M-1 ions, while peaks of b" ions with m/e 98, which are formed with retention of the D ring, predominate in the spectrum of VII. The peaks of b" ions in the spectra of IX are of insignificant intensity, while they are completely absence in the spectra of alkaloids VIII (Fig. 3, spectra a-c).

The peak of the b ion with m/e 96 is relatively intense in the spectrum of IXa, while the remaining peaks of the low-molecular-weight region are of low intensity (Fig. 3, spectrum c).

Low intensity of the peaks of the c ion (m/e 136), which contain C and D rings, and of ions with m/e 146 and 160, which have the k and *l* structures, is characteristic for alkaloids of the VII type. These ions contain A and B rings, since they are not shifted in the spectrum of 13-hydroxy-VIIa (argentamine) [11], while the peak of ion c is shifted by 16 amu to m/e 152.

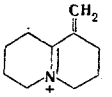
The peak of ion k in the spectrum of VIIIa is a maximum, while the intensity of the peaks of ions *l* is low (Fig. 3, spectrum b).

It should be noted that the spectra of the homologs of VIIIa and VIIIb differ substantially. The maximum peak with m/e 58 in the spectrum of VIIIa is due to the $Me_2\overset{+}{N}=CH_2$ ion, the intensity of the molecular ion increases sharply, and the remaining peaks are of insignificant magnitude.



k *m/e* 146 l *m/e* 160

The peaks of ions c, k, and *l* are small in the spectrum of IXa. A distinctive peculiarity of the spectrum of this compound is the rather significant intensity of the ion peak with m/e 149, which probably has the d" structure, and the presence of a peak with m/e 215, which, according to the data of the high-resolution mass spectrum, is a composite caused by isobaric $C_{13}H_{15}N_2O$ and $C_{14}H_{19}N_2$ ions, the first of which is formed as a result of elimination of an ethyl radical from the molecular ion (apparently from the A or B rings, as in the formation of ion j or j'), while the second is formed by elimination of a CO group and a hydrogen atom. The ion with m/e 201 is similar to the i or i' ions, differing from them only with respect to the presence of two double bonds in the D ring.



d" *m/e* 149

Thus the data are evidence that it is possible, with a high degree of reliability, to relate an investigated compound to one or another group of quinolizidine alkaloids, as was used to establish the structure of argentamine [11].

EXPERIMENTAL*

The low-resolution mass spectra were recorded with an MKh-1309 spectrometer with direct introduction of the sample into the ion source at an ionization energy of 70 eV and sample-volatilization temperatures of 30° (Ia, IIIa-d) and 50-70° (IVa,b, VIa-d, VIIa, VIIIa, and IXa,b). The high-resolution mass spectra of IIIc, IVa, and IXa were recorded with an MS-3301 spectrometer, while the high-resolution mass spectra of VIa,c were recorded with a JMS-01-S spectrometer.

3,3-D_2-d-Lupanine. A 3-mg sample of Na and 20 mg of d-lupanine (IVb) were dissolved in a mixture of 3 ml of absolute tetrahydrofuran (THF), 1 ml of D_2O, and 1 ml of C_2H_5OD, and the solution was refluxed for 6 h, after which it was cooled and evaporated. The residue was extracted with chloroform, and the extract was dried over Na_2SO_4 and filtered. The filtrate was evaporated to dryness, and the crystals of 3,3-D_2-IVb, with mp 50° were used without further purification for the recording of the mass spectrum. The isotopic purity of the product was 97% D_2, 2% D_1, and 1% D_0 analogs. A similar method was used to obtain 3,3-D_2-α-isolupanine (3,3-D_2-IVa), with mp 49° (ether), and 3,3-D_2-matrine (3,3-D_2-VIa), with mp 79° (petroleum ether), the mass spectra of which are presented in Fig. 2 (spectra b and d).

11,12,13,14-D_4-Allomatrine (11,12,13,14-D_4-VIb). A solution of 20 mg of isosophoramine IXa in 3 ml of ethanol was hydrogenated with gaseous deuterium over Raney Ni, after which the catalyst was removed by filtration, and the filtrate was evaporated (with the addition of acetone) to give 15 mg of a product with mp 105-106°, which was used to record the mass spectrum (Fig. 2, spectrum e). According to the mass spectrum, the product contains 4.3% D_0, 5.4% D_1, 7.5% D_2, 40.8% D_3, 20.5% D_4, and 21.5% D_5 analogs. The presence of the D_5 product is evidence for partial deuterium exchange of one of the hydrogen atoms of the A–C rings in the hydrogenation over Raney Ni. This effect has been previously observed [12].

3,3-D_2-Pachycarpine (3,3-D_2-Ia). A solution of 14 mg of 3,3-D_2-d-lupanine in 1 ml of THF was added dropwise to a suspension of $LiAlH_4$ in absolute THF, and the mixture was refluxed for 3 h. It was then cooled, and the $LiAlH_4$ was decomposed with ethyl acetate. The mixture was filtered, and the filtrate was evaporated to give 3,3-D_2-pachycarpine, the mass spectrum of which is presented in Fig. 1 (spectrum b).

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