MASS SPECTROMETRIC STUDY OF RING-SUBSTITUTED SECONDARY AND TERTIARY γ-AMINOPIPERIDINES

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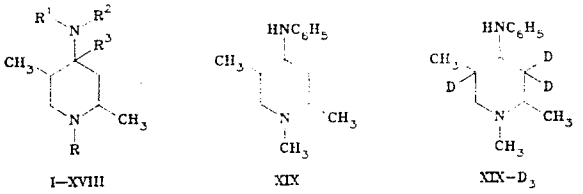
Fragmentation of secondary and tertiary γ-aminopiperidines proceeds via elimination of γ-amino radicals and the ring substituents of piperidine, and is accompanied by their cleavage. High-resolution mass spectral data, DADI spectra, and fragmentation of deutero analogs confirm this decomposition. On the basis of quantum chemical MNDO calculations the most probable alternate structures have been proposed for a number of typical ions. From the features of dissociative ionization we can determine the kind and location of substituents in the piperidine ring.

Intensive study of piperidine derivatives is due to their practical importance as physiologically active compounds [1]. In the present work, the mass spectral behavior of secondary and tertiary piperidyl amines (I)-(XVIII) has been studied in order to find a correlation between their structure and their mass spectra. It was of interest to study the effect of alkyl and aryl substituents in geminal position to the γ-amino group, and of radicals of the exocyclic nitrogen on decomposition, in order to apply the results to analysis.



I—XVIII XIX XIX-D_3

I—X, XII—XVIII R=CH_3; XI R=$CH_2C_6H_5$; I, IX, XIII R^1=$CH_2C_6H_5$; II, VII, X, XI, XIV, XV R^1=C_6H_5; III, XVI R^1=$C_6H_4OCH_3$-*o*; IV, XVII, XVIII R^1=$C_6H_4OCH_3$-*p*; V R^1=C_5H_5N-α; VI R^1=$C_{10}H_7$-α; VIII R^1=$(CH_2)OH$; XII R^1=C_6H_{11}; I—XI R^2=H; XII—XIV, XVI, XVII R^2=$CH_2C_6H_5$; XV, XVIII R^2=$CH_2C_6H_4OCH_3$-*p*; I—VI R^3=$CH_2CH{=}CH_2$; VII R^3=$CH_2C_6H_5$; VIII—XI R^3=C_6H_5; XII—XVIII R^3=H

The mass spectra of the N-aryl(alkyl)-γ-aminopiperidines (I-XVIII) contain peaks of molecular ions M^+ of medium and low intensity (Table 1). Their decomposition can be depicted by the general Scheme 1 which is confirmed by high-resolution mass spectra, DADI spectra for compounds (IX) and (X), and fragmentation of the deuteroanalogs (I), (II), (VII), and (XI).

The dissociative ionization of compounds (I)-(XVIII) proceeds via several competitive routes. The presence of the α-methyl causes the formation of the characteristic ion $[M - CH_3]^+$ [2, 3]. In the mass spectra of (I)-(XVIII) the low intensity of this peak is apparently due to partial localization of the positive charge on the exocyclic nitrogen and the subsequent intensive decomposition of $[M - CH_3]^+$ by two routes. The first route is cleavage of the ring by retro-diene decomposition (RDD) [4] and the appearance of ion F_1 with m/z 70* (R = CH_3) or 146 (R = $CH_2C_6H_5$); this cleavage brings information concerning the substituent on the cyclic nitrogen. Peak fragment F_1 has maximal intensity in the mass spectra of the

*Here and subsequently the m/z values determine the numbers that characterize the ion.

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TABLE 1. Mass Spectra of Compounds (I)-(XVIII), and (XIX-D_3)*

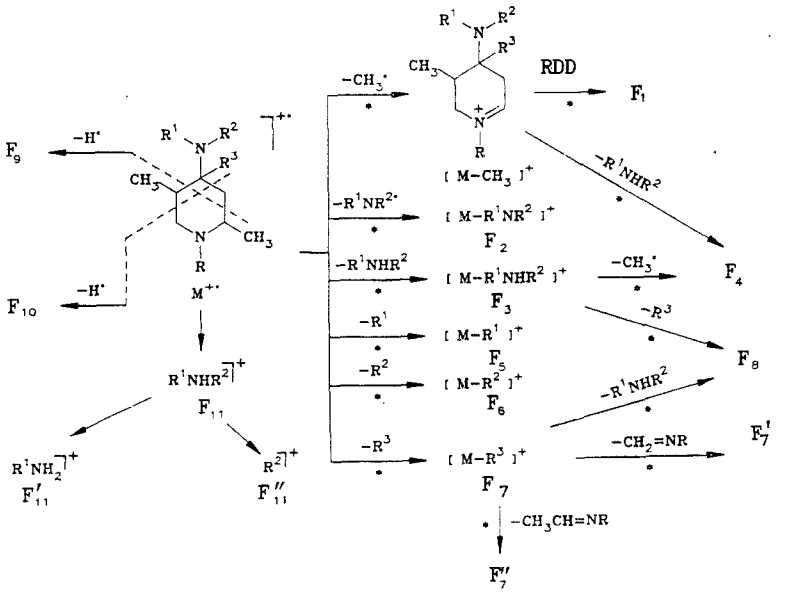
Compound	m/z (I_{rel}, %)
I	58 (8), 70 (60), 84 (20), 91 (88), 98 (20), 124 (100), 166 (9), 167 (18), 181 (7), 231 (41), 272 (M^+, 10)
I-D_1	58 (6), 70 (58), 84 (21), 91 (80), 98 (18), 124 (100), 166 (10), 167 (19), 182 (5), 232 (39), 273 ($M^+_{D_3}$, 8)
II	58 (20), 70 (100), 77 (22), 84 (19), 98 (11), 124 (62), 160 (8), 166 (8), 174 (6), 217 (33), 258 (M^+, 8)
II-D_1	70 (100), 70 (20), 84 (17), 98 (9), 124 (60), 150 (5), 161 (7), 166 (8), 175 (5), 218 (30), 259 ($M^+_{D_1}$, 7)
III	58 (16), 70 (100), 84 (11), 98 (7), 124 (51), 150 (6), 166 (10), 190 (10), 204 (7), 247 (64), 288 (M^+, 35)
IV	58 (19), 70 (100), 84 (13), 98 (9), 123 (8), 124 (62), 166 (10), 190 (16), 204 (13), 247 (77), 288 (M^+, 24)
IV**	70 (6), 124 (26), 165 (3), 166 (3), 190 (3), 204 (3), 247 (100), 273 (3), 288 (M^+, 47)
V	58 (16), 70 (18), 78 (19), 84 (13), 98 (14), 124 (100), 150 (19), 166 (15), 175 (21), 218 (34), 259 (M^+, 15)
VI	58 (27), 700 (100), 84 (17), 98 (13), 124 (89), 143 (22), 166 (30), 210 (20), 224 (15), 267 (65), 308 (M^+, 36)
VI**	70 (8), 124 (40), 143 (3), 165 (11), 166 (15), 210 (4), 224 (4), 267 (100), 293 (3), 308 (M^+, 88)
VII	58 (20), 65 (10), 70 (100), 77 (18), 84 (10), 91 (39), 124 (20), 160 (18), 174 (20), 217 (70), 308 (M^+, 22)
VII-D_1	58 ((20), 65 (9), 70 (100), 77 (15), 84 (9), 91 (27), 124 (17), 161 (10), 175 (15), 218 (68), 309 ($M^+_{D_1}$, 20)
VIII	58 (8), 70 (6), 84 (13), 98 (8), 144 (5), 158 (6), 186 (100), 187 (16), 201 (81), 202 (15), 262 (M^+, 2)
VIII**	56 (7), 70 (5), 84 (5), 98 (3), 144 (1), 158 (2), 186 (46), 187 (7), 201 (65), 202 (28), 263 (MH^+, 100)
IX	70 (7), 84 (22), 91 (57), 98 (15), 186 (100), 187 (17), 188 (17), 201 (86), 202 (17), 203 (39), 308 (M^+, 3)
IX***	84 (8), 91 (22), 98 (7), 186 (45), 187 (7), 188 (7), 201 (74), 202 (24), 203 (21), 309 (MH^+, 100)
X	70 (8), 77 (42), 84 (20), 91 (27), 98 (17), 144 (7), 158 (7), 186 (100), 201 (73), 202 (16), 294 (M^+, 9)
X**	70 (3), 84 (2), 98 (3), 186 (47), 201 (100), 202 (21), 294 (M^+, 49)
XI	65 (13), 91 (100), 118 (14), 146 (68), 160 (16), 174 (14), 200 (66), 242 (16), 243 (11), 293 (52), 334 (M^+, 8)
XI-D_1	65 (10), 91 (100), 119 (13), 146 (59), 161 (10), 175 (11), 200 (65), 242 (14), 244 (9), 294 (51), 335 ($M^+_{D_1}$, 5)
XII	84 (20), 91 (45), 98 (30), 110 (100), 125 (31), 126 (57), 127 (31), 189 (50), 223 (17), 231 (35), 314 (M^+, 10)
XIII	70 (20), 77 (45), 84 (20), 91 (47), 98 (29), 110 (100), 125 (20), 126 (40), 197 (38), 231 (50), 322 (M^+, 7)
XIII***	70 (5), 77 (17), 84 (16), 91 (29), 98 (20), 110 (40), 125 (30), 126 (25), 197 (50), 231 (80), 323 (MH^+, 100)
XIV	70 (30), 84 (18), 91 (15), 98 (15), 110 (100), 125 (13), 126 (58), 127 (19), 183 (11), 217 (15), 308 (M^+, 9)
XIV***	70 (3), 84 (10), 91 (11), 98 (9), 110 (35), 125 (30), 126 (19), 127 (31), 183 (44), 217 (19), 309 (MH^+, 100)
XV	70 (25), 84 (19), 98 (11), 108 (18), 110 (100), 121 (19), 125 (30), 126 (27), 213 (16), 217 (13), 338 (M^+, 8)
XVI	70 (60), 84 (25), 91 (55), 98 (20), 110 (100), 123 (20), 125 (56), 126 (40), 213 (24), 247 (23), 338 (M^+, 10)
XVII	70 (61), 84 (30), 91 (38), 98 (20), 110 (100), 123 (18), 125 (45), 126 (40), 213 (19), 247 (13), 338 (M^+, 8)
XVII***	84 (15), 91 (10), 108 (40), 110 (60), 123 (40), 125 (80), 126 (20), 127 (14), 213 (15), 247 (39), 339 (MH^+, 100)
XVIII	70 (60), 84 (30), 98 (21), 110 (100), 121 (30), 125 (56), 126 (40), 127 (31), 243 (15), 247 (20), 368 (M^+, 9)
XIX-D_3	58 (30), 72 (100), 86 (30), 99 (10), 112 (79), 121 (20), 127 (23), 129 (33), 134 (15), 206 (16), 221 ($M^+_{D_3}$, 69)

*M^+ peaks and the 10 most intensive fragment peaks are shown.
**Mass spectrum obtained at 12 eV.
***Mass spectrum obtained under conditions of chemical ionization (reagent gas, ammonia).

TABLE 2. Intensity of Peaks of Characteristic Ions (%, Σ_{50}) in Mass Spectra of Secondary and Tertiary γ-Aminopiperidines (I)-(XVIII)

Compound	M^+	$[M-CH_3]^+$	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_7'	F_7''	F_8	F_9	F_{10}	F_{11}
I	2,0	0,7	10,0	1,5	1,0	1,2	1,2	—	6,8	1,2	1,0	16,7	8,3	3,3	0,8
II	2,6	0,3	28,6	2,3	1,7	1,4	—	—	9,4	1,7	2,3	17,7	8,2	5,4	1,7
III	10,5	0,8	27,0	2,7	1,4	1,6	—	—	17,3	1,9	2,7	13,8	1,9	3,0	1,6
IV	6,8	0,8	25,0	2,5	1,8	1,5	—	—	19,3	3,3	4,0	15,0	2,2	3,3	2,0
V	5,1	1,1	5,1	4,3	3,4	5,5	—	—	9,7	6,0	4,0	28,6	4,0	3,7	1,7
VI	19,9	0,4	20,0	6,0	2,2	2,0	—	—	13,0	3,0	4,0	17,8	2,6	3,4	4,4
VII	7,5	0,8	25,0	—	—	—	—	—	17,5	5,0	4,5	5,0	1,8	2,0	2,0
VIII	0,6	0,4	2,0	5,0	27,0	33,4	—	—	—	2,0	1,7	—	2,7	4,3	—
IX	0,9	0,2	1,7	4,0	20,4	23,8	0,2	—	—	1,7	1,4	—	3,6	5,2	1,4
X	7,0	0,3	2,0	4,0	18,3	25,0	—	—	—	1,8	1,8	—	4,3	5,0	1,0
XI	2,3	0,5	15,8	3,7	2,6	2,3	—	—	12,1	1,6	1,9	15,3	1,6	1,9	2,1
XII	2,7	1,3	3,3	11,9	6,5	20,8	7,3	3,5	—	—	—	—	6,3	4,2	10,4
XIII	1,8	0,4	4,0	8,0	4,0	20,0	5,0	5,0	—	—	—	—	5,8	4,0	7,6
XIV	3,2	0,5	8,1	15,7	3,5	27,0	—	4,1	—	—	—	—	4,1	4,9	3,0
XV	2,3	0,6	7,2	7,7	8,6	28,6	—	3,7	—	—	—	—	3,1	5,4	4,6
XVI	2,9	0,7	13,3	8,9	12,4	22,2	—	5,1	—	—	—	—	4,4	5,6	5,3
XVII	2,5	0,5	15,3	10,0	11,2	25,0	—	3,3	—	—	—	—	5,0	7,5	4,8
XVIII	2,6	0,4	13,0	8,7	12,2	21,7	—	4,3	—	—	—	—	4,6	6,5	3,3

Scheme 1



secondary N-aryl-γ-aminopiperidines (II)-(IV), (VI), (VII), and (XI) (Table 2). In these compounds the nitrogen of the γ-amino substituent is bound directly to an aromatic ring that does not contain an electron-acceptor substituent.

The second fragmentation route of $[M - CH_3]^+$ is caused by a rearrangement in which a hydrogen migrates from the piperidine ring to the γ-amino segment that is being eliminated. This process forms ion F_4, the peak of which has maximal intensity in the mass spectra of the tertiary piperidyl amines (XII)-(XVIII) and secondary amines (VIII)-(X) which have a phenyl radical in the γ-position.

The decomposition of the molecular ions (M^+) of (I)-(XVIII) is accompanied by elimination of R^1NR^2 and R^1NHR^2 particles to form ions F_2 and F_3, respectively. The elementary composition of F_2 was determined from the high-resolution mass spectrum of compound (XI) (empirical formula $C_{17}H_{24}N$; measured: 242.1884; calculated: M 242.1903). The origin of F_4 by the scheme $M^+ \rightarrow F_3 \rightarrow F_4$ was confirmed by the respective metastable transitions in the DADI spectra of compounds (IX) and (X).

The ejection of radicals R^1 and R^2 from M^+ and the appearance of the characteristic fragments F_5 and F_6 is observed only when the substituents are bonded to exocyclic nitrogen through an aliphatic carbon. This makes it easy to distinguish the isomeric compounds (XV) and (XVI) by the appearance in their mass spectra of F_6 ions (217 and 247, respectively), and fragments 121 (F''_{11}) $[CH_2C_6H_4OCH_3\text{-}p]^+$ (XV), 123 (F'_{11}) $[o\text{-}CH_3OC_6H_4NH_2]^+$, and 91 ($F''_{11}$) $(C_7H_7)^+$ (XVI).

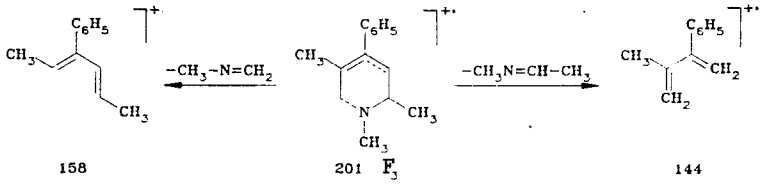
The elimination of radical R_3 and the formation of F_7 occur only when substituent R_3 is attached to the piperidine ring by an sp^3-hybridized carbon. F_7 decomposes further to eliminate R^1NHR^2, but the F_8 ion thus formed, as shown by DADI spectra, is due to the ejection of R^3 from F_3 (Scheme 1).

The $[M - R^3]$ fragment also dissociates by the unusual loss of neutral $CH_2{=}N{-}R$ and $CH_3{-}CH{=}N{-}R$ particles to form F'_7 and F''_7, respectively. In the mass spectra of the deutero analogs (I), (II), (VII), and (XI) the peaks of these fragments shift by 1 amu to higher masses; this confirms the proposed mechanism for their formation.

When the ionization voltage is reduced to 12 eV, elimination of an allyl radical becomes the energetically favored process for decomposition of (IV) and (VI); in the fragmentation of (X) ($R^3 = C_6H_5$), the cleavage of the γ-amino substituent R^1NH_2 and formation of the rearranged ion F_3 become predominant.

A feature of the dissociative ionization of the secondary piperidyl amines (VIII)-(X) ($R^3 = C_6H_5$) is RDD of $[M - R^1NH_2]^+$ (201) (Scheme 2) to form fragment 158 (compound (X), empirical formula $C_{12}H_{14}$; measured: M 158.1095; calculated: M 158.1092) and fragment 144 (empirical formula $C_{11}H_{12}$; measured: M 144.0935; calculated: M 144.0936).

Scheme 2



158 201 F_3 144

The mechanism of the formation of the F_3 ions 158 and 144 is confirmed by the following experimental data. First, the mass spectrum of the deutero analog XIX-D_3* showed that migration of hydrogen to the γ-amine radical that is splitting off proceeds from ring positions 3 or 5, because in this case the F_3 that is formed contains two deuterium atoms, but not three as in the initial M^+. Second, it was previously established [5] that RDD of the isomeric 1,2,5-trimethyl-4-phenyl-Δ^3- and 1,2,5-trimethyl-4-phenyl-Δ^4-piperidines (M^+ 201) gives ions 158 and 144, respectively. Consequently, in the F_3 fragment that is formed by decomposition of (VIII)-(X), the initial cyclic structure is retained. The F_3 ions that are isomeric in position of the terminal double bond determine the presence in the mass spectra of (VII)-(X) of the peaks of fragments 144 and 158. The spectrum of the metastable ions of fragment 201 of (X) shows only the process: $F_1 \rightarrow [F_1 - CH_3]^+$ (F_4, 186); this is evidence for the relatively high activation energy for formation of ions 144 and 158 by RDD. It is also confirmed by the absence of these peaks from the mass spectrum of γ-aminopiperidine (X) that is obtained at 12 eV ionizing energy.

A characteristic feature of the fragmentation of compounds (I), (IX), and (XII)-(XVIII), which contain a methylene that is bonded to exocyclic nitrogen, is the formation of $[M - (R^1NR^2 - H)]^+$. Its appearance is due to the migration of hydrogen from methylene to the piperidine ring; this is confirmed by the signal of this fragment in the mass spectrum of deutero analog (I) which does not shift on the m/z scale. The decomposition of 1-benzyl-2,5-dimethyl-4-allyl-4-(N-phenylamino)piperidine (XI) is accompanied by formation of the characteristic ions $[M - CH_2C_6H_5]^+$ (243, empirical formula $C_{16}H_{23}N_2$; measured M 243,1862; calculated M 243.1856), F_1 (146, empirical formula $C_{10}H_{12}N$; measured M 146.0971; calculated M 146.0967), and the peak maximum intensity of $C_7H_7^+$ (91). A distinguishing feature of the mass spectrum of tertiary piperidyl amines (XII)-(XVIII) is the increased intensity of the F_{11} peaks as compared with those in the spectra of the secondary piperidyl amines (I)-(XI).

As we have noted, the intensity of the M^+ peaks of (I)-(XVIII) is small; therefore we obtained their chemical ionization spectra (Table 1). Here the principal peaks are those of the protonated molecular ions MH^+. The fragmentation follows the same rules as in decomposition under electron impact, but there is a relative increase in peak intensity for the rearranged F_3 and F_{11} fragments.

Thus the mass spectra of γ-aminopiperidines (I)-(XVIII) contain specific information concerning the nature and relative location of substituents in the piperidine ring and in the γ-amino group, and can be used for analytical purposes. The regularities of decomposition enable us to identify structural isomers of secondary and tertiary piperidyl amines, and to distinguish these compounds by their mass spectra (Fig. 1).

The dissociative ionization of (I)-(X), (XII)-(XVIII), and other derivatives of 1,2,5-trimethylpiperidine [2, 4, 6] are characterized by the presence in their mass spectra of the peaks of characteristic fragments: 70 (F_1), 84, and 98. The 98 ion (F_9) is formed by scission of the $C_{(2)}$–$C_{(3)}$ and $C_{(4)}$–$C_{(5)}$ bonds, and the migration of a hydrogen from position 6 to the fragment being eliminated (Scheme 1). In the mass spectrum of the deutero analog (XIX-D_3), F_9 is shifted by 1 amu toward larger masses. The scission of the $C_{(3)}$–$C_{(4)}$ and $C_{(5)}$–$C_{(6)}$ bonds causes an 84 ion to appear (F_{10}). When deutero analog (XIX-D_3) decomposes, this fragment contains 2 deuteriums; consequently when it forms, a hydrogen must migrate from position 2.

*Fragmentation of N-(1,2,5-trimethylpiperidin-4-yl)-N-phenyl amine (XIX) was studied in detail in [2].

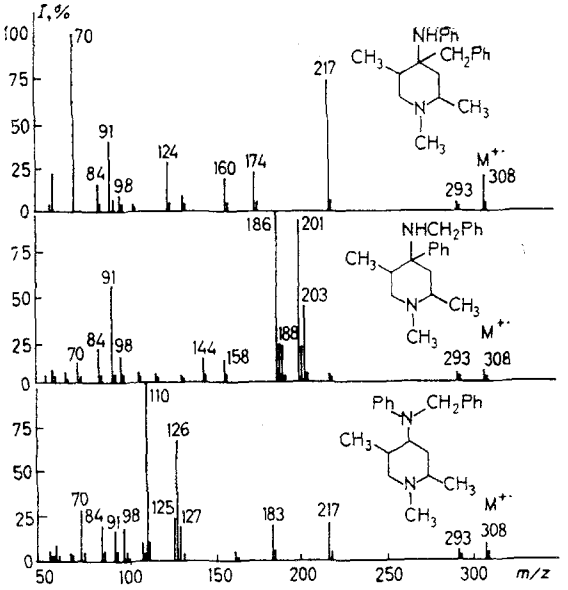
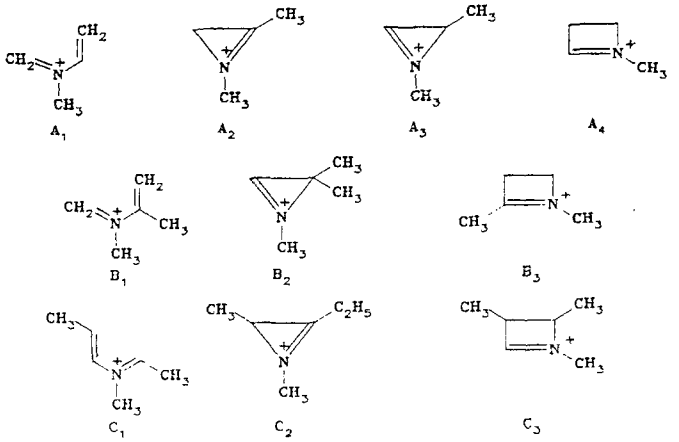


Fig. 1. Electron-impact mass spectra (70 eV) of isomeric γ-aminopiperidines (VII), (IX), and (XIV).



Although the formation of ions 70, 84, and 98 was determined from the total of the experimental methods, it was not possible to determine their structure experimentally. We calculated the total energy (E_t) and the atomization energy (E_a) of fragments 70, 84, and 98 by the quantum chemical MNDO method [7, 8]. For each of these ions several alternative structures can be proposed to agree with the empirical formula that was determined by high-resolution mass spectroscopy.

According to [2, 4, 9] the most likely structures for ions 70, 84, and 98 are acyclic A_1, B_1, and C_1, which contain a system of conjugated double bonds. Calculation of E_t and E_a of these structures with optimization of all geometric parameters showed that the cyclic four-membered ring ions A_4, B_3, and C_3 are the most stable (Table 3). The acyclic fragments A_1, B_1, and C_1 are less stable, although they differ in E_a insignificantly from the former ions, while the three-membered-ring cyclic ions are the least stable. Thus the characteristic 70, 84, and 98 fragments in the mass spectra of all the 1,2,5-trimethylpiperidine derivatives most likely have a four-membered-ring structure.

EXPERIMENTAL

Compounds (I)-(XVIII) were synthesized by the method of [10, 11]. Electron-impact and chemical-ionization (reagent gas, ammonia) mass spectra were obtained with a LKB-2091 instrument at 70 and 12 eV ionization voltages, cathode emission current 300 μA, accelerating voltage 3 kV, with programmed temperature (10°/min, from 50° to 200°C). Exact mass

TABLE 3. Experimental and Calculated Values for Characteristic Structures of Ions 70, 84, and 98*

Ion	Mass of ion		Elemental composition of ion	Path of formation	Structure of ion	E, kcal/mole	
	found	calc.				atom.	total
70	70,0656	70,0655	C_4H_8N	$[M-CH_3]^+ \rightarrow 70$	A_1	203,6	−823,62
					A_2	216,6	−823,06
					A_3	224,6	−822,71
					A_4	192,8	−824,09
84	84,0810	84,0811	$C_5H_{10}N$	$M^+ \rightarrow 84$	B_1	202,1	−979,93
					B_2	218,5	−979,22
					B_3	177,9	−980,97
98	98,0969	98,0967	$C_6H_{12}N$	$M^+ \rightarrow 98$	C_1	185,4	−1136,89
					C_2	201,2	−1136,21
					C_3	179,3	−1137,16

*Elemental composition of ions and paths of their formation were determined by high-resolution mass spectroscopy and DADI of γ-aminopiperidine (XIX).

values were determined with a Varian MAT-311A instrument at 10,000 resolution. DADI spectra were obtained with a Varian MAT 112 instrument by direct introduction of sample into the source; electron energy 70 eV, temperature of ionization chamber 180°C. Mass spectra of deutero analogs (I), (II), (VII), and (XI) were obtained with a MX-1303 instrument equipped with a system for direct sample introduction into the ion source; conditions were set for deuterium exchange of test vapors with CD_3OD vapors in ionization chamber at 70 V ionization voltage and 50-80°C temperature of sample introduction. Deutero derivative (XIX-D_3) was synthesized from 3,3,5-trideutero-1,2,5-trimethylpiperidin-4-one and $C_6H_5ND_2$ by the method of [10]. The DAC* spectrum of ion 201 for compound (X) was obtained with a Finnigan MAT H-SQ 30 instrument.

LITERATURE CITED

1. R. S. Vartanyan, Khim.-farm. Zh., No. 5, 540 (1983).
2. Q. N. Porter and J. Baldes, Mass Spectrometry of Heterocyclic Compounds, Wiley-Interscience, New York (1971), p. 364.
3. E. E. Stashenko, P. I. Zakharov, V. V. Kuznetsov, L. A. Gaivoronskaya, B. S. Subbotin, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 6, 813 (1988).
4. A. I. Ermakov, Yu. N. Sheinker, Zh. K. Torosyan, and V. A. Zamureenko, Khi. Geterotsikl. Soedin., No. 12, 1647 (1975).
5. E. E. Stashenko, P. I. Zakharov, V. V. Kuznetsov, I. V. Klyavina, L. M. Kirillova, A. V. Varlamov, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 6, 795 (1989).
6. E. E. Stashenko and V. V. Kuznetsov, Report Summaries, 9th Conf. Young Scientists, "Synthesis and Study of Biologically Active Compounds," Riga (1987), p. 107.
7. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977).
8. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4907 (1977).
9. A. I. Ermakov and Yu. N. Sheinker, Khim. Geterotsikl. Soedin., No. 1, 65 (1981).
10. V. V. Kuznetsov, L. A. Gaivoronskaya, A. A. Fomichev, R. M. Romero, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 7, 949 (1987).
11. V. V. Kuznetsov, L. A. Gaivoronskaya, R. M. Romero, E. E. Stashenko, P. I. Zakharov, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 7, 954 (1987).

*Dissociative activation by collision (argon).