FEATURES OF MASS-SPECTROMETRIC FRAGMENTATION OF RACEMIC DIPTOCARPIDINE AND DIPTOCARPILINE

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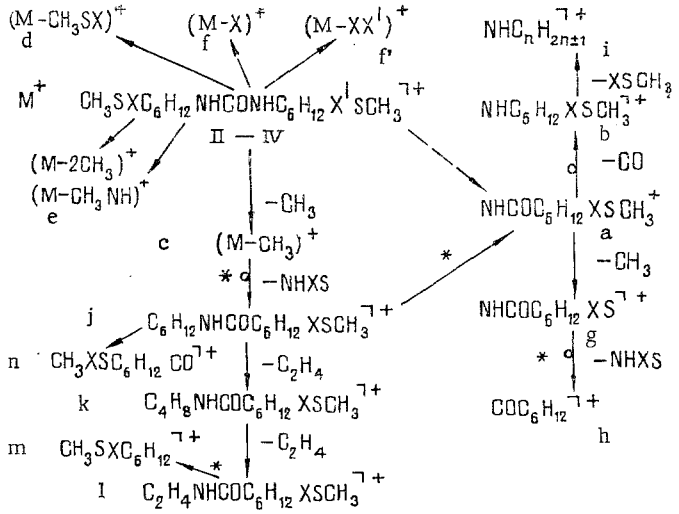
The mass-spectrometric fragmentation of the positive and negative molecular ions of diptocarpidine and diptocarpiline and of two model compounds have been studied, and it has been shown that the formation of the fragmentary ions takes place both by direct bond cleavage and with the involvement of complex skeletal rearrangements. The composition of the rearranged ions formed from M^+ has been confirmed with the aid of high-resolution mass spectrometry. An intramolecular interaction of the this (sulfoxy) and urea groups as a consequence of the existance of the molecules under investigation in a folded conformation has been established.

The results of a mass-spectrometric investigation of the fragmentation of substituted ureas have been given in [1-4]. In view of the fact that contradictory results were obtained in the interpretation of certain mass spectra [1, 2] as was shown, in particular, in different estimates of the influence of rearrangement processes in the breakdown of the molecular ions (MIs), prediction of the fragmentation of the MIs of urea derivatives is difficult. It may be expected that the introduction of several heteroatoms into the molecules of alkyl-substituted ureas will complicate the nature of the breakdown of the MIs still further. Consequently, to investigate the influence of a sulfo group on the fragmentation processes of the MIs of racemic diptocarpidine $CH_3SOC_6H_{12}NHCONHC_6H_{12}SOCH_3$ (III) and diptocarpiline $CH_3SOC_6H_{12}NHCONHC_6H_{12}SCH_3$ (IV) a mass-spectrometric investigation of the model compounds $C_{10}H_{21}NHCONHC_{10}H_{21}$ (I) and $CH_3SC_6H_{12}NHCONHC_6H_{12}SCH_3$ (II) appeared to be desirable. With this aim we have obtained the positive- and negative- ion mass spectra of compounds (I)-(IV) that we have synthesized [5], the spectra being given in the Experimental part.



Main pathways for the breakdown of M^+ of compounds (II)-(IV). In (II), X and X^1 are absent, in (III) X = X^1 = O, and in (IV) X = O, and X^1 is absent. The dashed line represents the presumable route of the formation of fragments of type a according to [1].

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Positive Ions. According to results given in the literature [1-3] where the general processes of fragmentation of urea derivatives are described, the breakdown of the MIs of compounds (I-IV) takes place with the formation of characteristic ions of types a — $RNHCO^{7+}$ and b — RNH^{7+}, with R = R' = $C_{10}H_{21}$ (I), R = R' = $CH_3SC_6H_{12}$ (II), R = R' = $CH_3SOC_6H_{12}$ (III), R = $CH_3SC_6H_{12}$ and R' = $CH_3SOC_6H_{12}$ (IV). In addition, fragments c, d, e, f, g, h, and i, formed by cleavages in the MIs and in the ions a and b of bonds more remote from the nitrogen atom are observed.

We have analyzed the peaks of the ions in the spectra of compounds (I-IV) by measuring the accurate values of the mass numbers and have come to the conclusion that only the decomposition of (I) takes place in the directions described in the literature. A feature of the decomposition of M^+ for compounds (II-IV) is that the formation of fragments of the a^+ type takes place in several steps and is accompanied by skeletal rearrangements such as have not been observed in the breakdown of alkylureas. The main pathways in the breakdown of M^+ for (II-IV) are shown in the scheme.

For compounds (II-IV) we have established one more fragmentation channel which is due to a skeletal rearrangement in the $(M - CH_3)^+$ ions and is accompanied by the splitting out of an NH group in the case of (II) and (III) and of NHSO in the case of (III) and (IV).

The peaks of the ions j recorded in the spectrum of (II) have the composition $CH_3SC_6H_{12}\cdot OCNHC_6H_{12}^{7+}$ (measured: 258.1862; calculated: 258.1891), the $305^+ \rightarrow 258^+$ transition being confirmed by the peak of a metastable ion (218.6) (97%) and by the ion $(M - C_2H_6S)^+$ (3%; 258.1798). The peaks of the ions j and j' in the spectra of (III) and (IV) have the composition $CH_3SOC_6H_{12}OCNHC_6H_{12}^{7+}$ (measured: 274.1748) and $CH_3SC_6H_{12}OCNHC_6H_{12}^{7+}$ (measured: 258.1862). Fragments j are parental for a whole series of fragments: n — $CH_3XSC_6H_{12}CO^{7+}$, k — $C_4H_8NHCOC_6H_{12}\cdot XSCH_3^{7+}$, l — $C_2H_4NHCOC_6H_{12}XSCH_3{}^{7+}$, and a — $CONHC_6H_{12}XSCH_3^{7+}$ (the j → a transitions are confirmed by the corresponding peaks of metastable ions).

No isocyanate ions of the type $(a - H)^+$ were recorded in the spectra of (I-IV). We consider that since in an actual isocyanate the stability of M^+ is high only for the first members of the series [3], such ions should be observed only in the spectra of the lower alkylureas.

The formation of ions h is accompanied by skeletal rearrangement in the ions g and by the ejection of an NHXS group.

A large number of intense peaks of the ions $C_n H_{2n\pm1}^{7+}$ n = 3-6, $C_n H_{2n\pm1} NH^{7+}$ n = 2-5, $C_n H_{2n} SH^{7+}$ n = 3-5 is present in the low-molecular-weight parts of the mass spectra but the nature of their formation is uncertain our main attention was therefore devoted to those groups of ions the appearance of which seemed unlikely according to known ideas about the breakdown of urea.

Negative Ions. Since the processes of fragmentation in the electron-impact mass spectra of compounds (I)—(IV) have a fairly complex nature, we obtained their resonance electron-capture (REC) mass spectra.

It was established that in N, N'-didecylurea (I), the OCN- and $(M - H)^-$ ions are formed with high probability, and the intensities of the peaks of the other ions are low. All the ions contain the atoms of the urea group in their structure: m/z 26 (CN^-), 42 (OCN^-), 58 ($HNCONH^-$), 59 (H_2NCONH^-), 155 ($C_{10}H_{21}N^-$), 156 ($C_{10}H_{21}NH^-$), 182 ($C_{10}H_{20}NCO^-$), 184 ($C_{10}H_{21}NHCO^-$), 199 ($C_{10}H_{21}NHCONH^-$), $(M-H)^-$ and are probably formed with the aid of direct bond-cleavage processes. The capture of an electron by the molecules of (I) takes place in four resonance states (0.5-0.8), 2.3, 4.95, and (7.4-8.0) eV, while in the region of electron energies of 2.3 eV only the $(M - H)^-$ ions are formed, and at 4.95 eV only $C_{10}H_{21}NH^-$. In the REC mass spectrum of n-decylamine that we obtained, the formation of an intense peak of the $(M - H)^-$ ions of the same structure with a resonance maximum also at 4.95 eV was recorded, i.e., no appreciable influence on the position of the resonance maximum in compound (I) as compared with n-decylamine was observed.

Koch and Frenking [6] have shown that the capture of an additional electron by the OCN group causes a shortening of the C—N bond and an elongation of the C—O bond, leading to the formation of a multiple C—N bond and an ordinary C—O bond with the most probable localization of the negative charge on the acceptor vacant orbital of the carbonyl group. Another of their results [6], and also of [7], is the prediction that the most stable isomers of all the possible combinations of OCN and OCNH are the isomers of the sequence just of OCN and OCNH,

both for neutral groups and for their anions. Because of the fact that on REC in compound (I) OCH^- ions are formed with the highest probability and because the structures of all the fragmentary ions include the atoms of the urea group, there is every ground for assuming that the processes of the formation and dissociation of the molecular negative ions in dialkylureas are determined just by the presence of the urea grouping in them, which is in good agreement with the results of the papers cited [6, 7].

On the basis of what has been said above, it may be assumed that the capture of an electron by molecules of (I) takes place in the following way: the addition of an electron to the molecule leads to the formation of a multiple C—N bond in one half of the molecule and to a lengthening of the C—O and C—N bonds in its other half. The $(M - H)^-$ ions are formed by the elimination of an H atom from the nitrogen atom bearing the multiple bond. The same nitrogen atom participates in the subsequent formation of OCN^- ions, while $C_{10}H_{21}NH^-$ ions are formed from the other half of (I). Furthermore, in the region of electron energies of 8.0 eV the peaks of the ions $C_{10}H_{20}NCO^-$ and $C_{10}H_{21}NHCONH^-$ are recorded.

It follows from a comparison of the REC mass spectra of compounds (I) and (II) that on the introduction of sulfur atoms into the alkyl chain, both the directions of fragmentation of compound (I) and also the appearance of new directions due to the presence of sulfide groups in compound (II) are observed. By analogy with the REC spectrum of (I), ions are recorded with m/z 26 (CN^-), 42 (OCN^-), 59(H_2NCONH^-), 146 ($CH_3SC_6H_{12}NH^-$), 174 ($CH_3SC_6H_{12}NHCO^-$), 189 ($CH_3SC_6H_{12}NHCONH^-$), and $(M-H)^-$, which are probably formed by direct bond cleavage. In addition, negative ions due to the presence of sulfide groups in the molecule are formed: m/z 32 (S^-), 33 (HS^-), 47 (CH_3S^-), 206 ($CH_3SC_6H_{12}NHCOS^-$), 259 $(M-NSCH_3)^-$, 273, and 305 $(M-CH_3)^-$. The molecules of (II) form negative ions at (0.7-1.2), 2.3, (3.4-4.15), 4.5, 4.95, and (5.9-6.5) eV, i.e., in a larger number of resonance states than compound (I). In view of the fact that the molecules of dialkyl sulfides from negative ions in three resonance states, ~1.5, ~5, and ~8 eV [8], it may be assumed that in the molecules of (II) there is an interaction of the sulfide and urea groups. The following circumstances are evidence in favor of this hypothesis: fragmentary "sulfide" and "urea" ions are formed from identical resonance states of the molecular and negative ions; the fact that the maximum yield in the mass spectrum of (II) is of CH_3S^-, and not of OCN^- ions; the presence in the mass spectrum of the peaks of ions with m/z 206, 259, and 273; and the fact that negative ions with m/z 146 are formed from (I) in two resonance states in contrast with the ions having m/z 156 of compound (I).

It has been shown previously that the interaction in molecules of functional groups separated by more than four methylene groups is negligibly small [9, 10] and therefore the interaction of the sulfide and urea groups in the molecules of (II) can be explained only by the spatial propinquity of these groups in a folded conformation of the molecules. As the most probable it appears to us that interaction in the molecules of (II) takes place between the sulfide and carbonyl groups; since it has been shown previously that it is just ketosulfides that are the most successful example of the intramolecular orbital overlap (depending on the steric conditions) of the highly localized orbitals of the CO and S groups [10]. The presence in the mass spectrum of (II) of the peaks of ions with m/z 206 agrees well with this hypothesis, since in these ions the CO and S groups are present in neighboring positions. In an interpretation of the processes of formation of the ions with m/z 259 and 273 it is also difficult to manage without the assumption of a folded conformation of the molecules of (II) since otherwise it is hard to explain the existence of these ions at all.

The REC mass spectrum of compound (III) differs substantially from those of (I) and (II). Thus, in the mass spectrum of (III) more peaks of ions in general and of rearranged ions, in particular, were recorded. Apparently only the following ions are formed by direct bond cleavage: m/z 26, 32, 42, 47 (CH_3S^-), 48 (SO^-), 59, 63 (CH_3SO^-), 146, 321 $(M-OCH_3)^-$, 336 $(M-O)^-$, and $(M-H)^-$. A large number of rearrangement ions simultaneously containing NH and SO groups is observed — m/z 64 $(SONH_2)^-$, 78 (CH_3SONH^-), 79 (CH_3SONH^-) 107 ($H_2NCONHOS^-$), — which may serve as a basis for the possibility of the existence of an intramolecular interaction of the NH and SO groups through a hydrogen bond in the sulfinylureas. The weightiest factor in favor of the existence of such an interaction is the presence of the peaks of ions with m/z 178 ($CH_3SOC_6H_{12}NHO^-$), 210 ($CH_3SOC_6H_{12}NHOS^-$), and 225, where, as the result of rearrangement processes the NH and SO groups are apparently in neighboring positions.

The formation of ions with m/z 290 $(M-NSO)^-$, 288 $(M-NHSOH)^-$, and 275 has also been reported. Ions with m/z 259 may be formed from $(M - H)^-$ ions and be daughter ions for the ions with m/z 336. A more complex problem is the determination of the structures of the negative ions with m/z 258, 256, 242, and 240 because of the large number of possible combinations. However, because of the even mass numbers of the peaks it is possible to assume that they are all connected with the elimination of various fragments containing one nitrogen atom.

Molecules of diptocarpidine (III) form ngeative ions at 0.55, (1.05-1.1), 1.6, 3.3, (4.2-4.4), 6.3, (7.2-7.3), and 8.5 eV, while in the region of electron energies of 4 eV both purely "sulfoxide" ions, such as SO^-, and also "urea" ions with m/z 26 and 42 are formed. In addition to this, in the same region a large number of rearrangement ions are also formed and this is likewise evidence in favor of the existence of an intramolecular interaction between the NH and SO groups in the molecules of (III).

The molecule of diptocarpiline (IV) contains elements of molecules (II) and (III). It was therefore of interest whether REC mass spectrum of (IV) was an additive scheme of the REC mass spectra of compounds (II) and (III). On considering the spectrum it could be seen that there was no additivity, and this is one more piece of evidence in favor of the existence in the molecules of (II—IV) of an intramolecular interaction of the functional groups. It was observed that the REC mass spectrum of (IV) resembled the mass spectrum of (III) far more, i.e., the main directions of fragmentation are determined by the presence of the sulfoxide, and not the sulfide, grouping in (IV), leading to the formation of the maximum ion peak with m/z 275 $(M - NSCH_3)^-$. The fact that in compound (IV) the main directions of fragmentation are determined by the sulfoxide group may also serve as an indication of the more effective interaction of the NH and SO groups in comparison with the S and CO groups. On the whole, the REC mass spectrum of (IV) contains basically the same ion peaks as the mass spectrum of (III): m/z 26, 32, 33, 42, 47, 48, 49, 59, 63, 64, 78, 79, 107, 210, 240, 242, 256, 258 etc. A substantial difference is the presence in the spectrum of (IV) of the peaks of ions with m/z 91 $(SOHNCO^-)$ and 222 $(CH_3SOC_6H_{12}NHOCS^-)$, the latter being an analog of the peak of ions with m/z 206 in the REC mass spectrum of (II).

We may also note that in spite of the similarity of the process involved in the fragmentation of the negative molecular ions of compounds (III) and (IV), the regions of resonance electron capture are shifted relative to one another with respect to energy. The molecules of (IV) form negative ions at 0.35, (0.65—0.7), 1.1, 1.4, (3.2—3.7), (4.25—4.7), 5.1, 6.1 and (7.0—7.1) eV.

Thus, it has been established that on the resonance capture of electrons by the molecules of racemic diptocarpidine and diptocarpiline negative ions are formed not only by processes of direct bond cleavage but also as the result of complex rearrangement processes. The structures of the fragmentary rearranged ions of compounds (II)—(IV) and the main laws of the fragmentation of the molecular ion (I)—(IV) permit the conclusion that there is an intramolecular interaction of NH and SO groups separated by a saturated chain of six carbon atoms in diptocarpidine and diptocarpiline because of the existence of these molecules in a folded conformation.

EXPERIMENTAL

The positive-ion mass spectra were obtained on an MKh-1320 mass spectrometer using a system for the direct introduction of the sample. Ionizing voltages 70, 22, 20, and 18 V; temperature of the ionization chamber 70-80°C. Accurate values of the mass numbers were measured on a Varian MAT CH-5 high-resolution instrument under the same conditions. The negative-ion mass spectra were obtained on an MI-1201 mass spectrometer reequipped for recording negative ions [11]. The electron-energy scale was calibrated from the effective field curves ...*

N,N'-Didecylurea (I). Positive-ion Mass Spectrum, m/z (%): 340 (M^+, 33.3), 339 (2.1), 325 (1.9), 311 (6.7), 297 (7.3), 283 (7.3), 269 (7.3), 256 (4.5), 255 (13.3), 242 (4.6), 241 (13.3), 228 (3.5), 227(3.6), 214 (9.3), 213 (3.5), 201 (4.5), 199 (2.4), 185 (2.7), 184 (5.9) 171 (2.9), 167 (2.7), 158 (12.0), 157 (6.1), 156 (8.0), 143 (4.8), 130 (2.1), 129 (3.3), 119 (4.0), 115 (4.2), 112 (3.0), 102 (2.5), 101 (4.9), 100 (3.5), 99 (6.0), 98 (3.5), 97 (3.3),

*Some words are apparently missing in the Russian original — Translator.

91(4.3), 87(4.9), 86(4.5), 85(5.1), 84(2.5), 83(4.7), 81(3.7), 77(10.0), 74(3.9), 73(4.3) 71(5,7), 67(3.9), 65(3.1), 57(16.7), 56(8.0), 55(16.7), 44(21.3) 43(26.7), 41(16.7),30(100.0).

REC mass spectrum*: 339—0.1(0.5), 5.2(2.3), 19.8(7.4); 199—0.3(0.8), 1.3(8.0); 184—0.3 (0.7); 182—0.2(0.7), 0.1(7.7); 156—0.5(4.95); 155—1.4(0.6); 59—1.7(0.7); 58—1.6(0.5); 42—100(0.8); 26—2.0(0.8).

N,N'-(7-Thiaoctyl) urea (II). Mass spectrum, m/z (%): 320(M^+, 0.4),305 (c, 14.2), 290 (e, 10.4), 273 (d, 2.1), 258 (j, 100), 246(3.8), 244(4.6), 230 (k, 1.3), 216(2.5), 212(5.4), 210(3.8), 202(1, 10.9), 174(a, 10.8), 159(g, 12.5), 148(4.8), 146(b, 7.1), 143(12.5), 142(6.3), 141(2.5), 133(3.1), 132(22.5), 131 (m, 26.7), 130(4.2), 129(3.3), 128(8.3), 115(12.1), 111 (h, 15.4), 103(2.5), 101(5.2), 100(i, 29.2), 98 (i, 12.5), 87(10.4), 86(10.8), 83(25.4), 82(15.0), 81(25.1), 75(11.3), 73(13.9), 72(13.3), 69(15.0), 67(14.2), 61(62.5).

REC mass spectrum: 319—2.0(1.2), 0.5(4.0), 0.9(5.9); 305—1.2(0.95), 0.5(4.0), 1.1(5.95); 273—1.8(3.4), 0.4(5.9); 259—0.2(3.4), 0.3(6.3); 206—0.3(6.4); 189—5.1(6.3); 174—3.0(6.4); 146—0.4(4.15), 0.7(6.4); 59—1.0(0.9), 1.2(3.75), 2.0(6.25); 47—2.6(0.7), 37.1(3.75), 100 (6.25); 46—0.9(2.3), 0.8(4.5), 1.1(6.5); 42—68.1(1.2), 21.6(6.35); 33—2.9(0.85), 1.3(3.9), 1.9(6.2); 32—23.0(3.75), 5.9(4.95), 7.0(6.0); 28—6.0(4.95); 26—6.2(0.8), 1.9(3.75), 6.4(6.0).

N,N'-(6-Methylsulfinylhexyl)urea — (±)-Diptocarpidine (III). Mass spectrum, m/z (%): 352(M^+, 0.3), 337(c, 10.5), 336(f, 1.4), 322(e, 14.5), 320(f', 5.2), 308(3.1), 294(4.2), 292 (2.8), 289(d, 21.0), 288(7.4), 275(7.6), 274(16.2), 273(7.8), 260(5.3), 258(3.1), 247(2.5), 246(k, 3.3), 232(2.9), 226(3.7), 225(15.7), 219(4.6), 218(1, 4.3), 212(3.7), 211(6.2), 210 (8.1), 197(10.2), 196(3.1), 190(a, 100), 182(5.8), 176(5.5), 175(n, g, 31.4), 174(9.0), 172 (15.2), 164(45.2), 162(b, 24.8), 149(7.1), 148(16.9), 147(m, 2.2), 146(3.3), 144(3.6), 142 (4.3), 137(6.0), 131(8.1), 128(6.7), 126(28.6), 119(4.8), 117(57.4), 111(h, 6.5), 103(15.5), 101(8.6), 100(i, 69.0), 98(i, 40.0), 87(6.2), 86(10.6), 63(20.5), 61(24.3).

REC mass spectrum: 351—0.1(0.55); 336—0.1(0.55), 0.3(4.4); 321—0.3(0.55); 290—0.2 (0.55), 0.3(4.4); 288—0.1(0.55), 0.3(4.4); 275—1.9(0.55); 259—0.7(0.55); 258—0.4(4.4); 256—0.3(4.4); 242—0.4(4.3); 240—0.3(4.4); 225—0.5(0.55); 210—1.9(4.2); 208—0.1(4.3); 178—1.5(4.2); 146—0.4(0.55); 0.1(4.4); 107—1.2(0.55); 2.1(4.3); 79—12.1(0.55), 9.7(4.2), 2.1(7.2); 78—2.1(3.3), 3.2(6.3); 64—4.1(3.3), 3.9(6.3); 63—34.4(1.1), 7.7(4.4), 8.6(7.25); 59—8.7(0.55); 49—1.5(4.4); 48—100(4.2); 47—10.4(4.4), 11.5(7.2); 42—62.8(1.6), 6.0(4.4), 9.8(7.3); 33—0.7(1.05), 0.2(3.3), 0.2(4.4), 0.2(7.2); 32—2.7(0.55), 8.2(3.3), 15.5(4.4), 5.1(6.3), 4.2(8.5); 26—12.6(1.05), 1.8(4.4), 2.2(7.2).

N-6-(Methylsulfonylhexyl)-N'-(7-thiaoctyl)urea — (±)-Diptocarpiline (IV). Mass spectrum: m/z (%): 336(M^+, 2.5), 322(36.0), 321(c, 5.0), 320(f, 12.0), 306(e, 19.0), 290(10.5), 276(7.1), 275(19.0), 274(j, 63.1), 273(5.5), 260(15.1), 258 (j', 22.1), 256 (13.0), 246(k, 1.3). 232(9.1), 218(1, 14.0), 212(11.2), 210(46.0), 205(6.0), 202(1', 3.0), 196(0.0), 190(a, 13.5), 188(13.5), 175(n, 95.8), 175(g, 4.2), 174(a', 1.4), 164(56.0), 162(b, 14.0), 159(g, 5.0), 154(9.5), 148(17.0), 147(m, 37.0), 146(b', 13.0), 142(20.0), 131(m', 17.0), 128(13.5), 126(10.0), 117(19.0), 111(h, 24.0), 103(15.0), 101(8.0), 100(i, 75.0), 98(i, 32.5), 87(11.0), 86(10.0), 84(19.0), 83(95.0), 82(11.0), 81(33.0), 63(15.0), 61(25.0).

REC Mass spectrum: 335—0.2(0.35); 305—6.7(0.35); 291—0.9(0.35); 289—0.2(0.35); 275—100(0.35), 1.5(7.1); 258—1.0(0.35), 0.7(4.5); 256—0.9(0.35), 0.5(4.5); 242—1.2(0.35), 1.1 (4.4); 240—2.3(0.35), 1.7(4.5); 222—36.6(0.35), 2.7(4.7); 210—0.2(0.7); 107—1.1(3.7), 1.5(4.7), 1.5(7.1); 91—2.7(1.1), 8.3(4.5),1.2(7.1); 79—14.9(0.35), 0.9(3.2), 0.9(5.1), 1.4(7.1), 0.6 (8.9); 78—5.3(0.35), 0.4(3.7), 0.3(7.1); 64—0.9(0.35),2.5(3.4). 6.1(6.1); 63—8.9(1.1), 6.9 (4.5), 24.7(7.05); 59—3.0(0.35); 49—1.1(4.5); 48—62.0(4.25); 47—11.3(0.35), 8.2(3.7), 12.0 (4.65), 18.9(7.1); 46—2.7(0.35), 0.7(5.1); 42—91.3(0.65), 4.5(7.1); 33—3.3(0.35), 3.4(1.4), 0.7(4.5), 0.3(7.0); 32—0.9(0.65), 36.3(3.3), 79.6(4.5), 62.1(5.1), 5.8(7.05); 26—5.7(1.4), 1.2(4.7), 1.1(7.0).

SUMMARY

The fragmentation of the positive and negative molecular ions of racemic diptocarpidine and diptocarpiline is accompanied by complex rearrangement processes, as is shown in the simultaneous elimination of nitrogen and sulfur atoms from the molecular ions. An intra-

*Here and below in the REC mass spectra: mass number, intensity of the peak of the ion as a percentage of the maximum peak, and in parentheses, the energy of the resonance maximum of the yield of ions in electron-volts.

molecular interaction of thio (sulfoxy) and urea groups separated by a saturated chain of six carbon atoms as a consequence of the existence of the molecules under investigation in a folded conformation has been established.

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STRUCTURE OF TERDELINE

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A new alkaloid which has been called terdeline has been isolated from the epigeal part of Delphinium ternatum. Its structure has been demonstrated on the basis of spectral characteristics and the preparation of a demethylene derivative, and also by direct passage from eldelidine to terdeline.

We have previously reported the isolation from Delphinium ternatum of a base $C_{27}H_{43}NO_7$ (I) with mp 116-118°C (ether—hexane), which proved to be new and eas called terdeline [1].

The PMR spectrum of the alkaloid has the signals of C-methyl and N-ethyl groups and of five methoxy groups and a methylenedioxy group. When terdeline was heated in 10% sulfuric acid, product (II) was obtained the PMR spectrum of which lacked the signal of a methylenedioxy group and contained the signals of five methoxy groups. The IR spectrum and the deuteration of the base showed the absence of hydroxy groups form (I). The following developed formula may be given for terdeline:

$$C_{17}H_{18}(C—CH_3)\ (N—C_2H_5)\ (CH_2O_2)\ (OCH_3)_5$$

The mass spectrum of (I) was characteristic for the spectra of diterpene bases with the lycoctonine skeleton, and the maximum peak, corresponding to $M^+ - 31$ ion, showed the presence of a methoxy group at C-1 [2]. The ^{13}C NMR spectrum of terdeline with complete decoupling from protons consists of 26 isolated signals, and only one of them, at 50.3 ppm, corresponds to two carbon atoms (C-9 and $-CH_2-CH_3$) the values of the chemical shifts of

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