POSITIVE- AND NEGATIVE-ION MASS SPECTRA OF RACEMIC DIPTOCARPAMINE AND ITS SULFIDE PRECURSOR

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Features of the fragmentation on electron impact and resonance electron capture of racemic diptocarpamine (I), its sulfide precursor (II), and N-decyl-N'-isopropylurea have been determined which consist in a predominance of simple bond cleavages over the rearrangement processes involving the elimination of S(O)NH-containing neutral fragments that are typical for diptocarpidine. The elementary compositions of the characteristic lines in the EI mass spectra were established by measuring accurate values of the mass numbers of the ions. An estimate of the efficacy of the spatial interaction of the heteroatomic groupings separated by carbon chains in the $M^{+\cdot}$ and M^{-} ions of compounds (I) and (II) has been made. On the basis of the REC mass spectra it has been concluded that the molecules of compounds (I) and (II) exist in twisted or folded conformations.

In order to elucidate features of the structure of diptocarpamine (I) and its sulfide precursor (II) we have studied the resonance electron capture (REC) mass spectra, and the positive-ion mass spectra of compounds (I) and (II) and also of N-decyl-N'-isopropylurea (III):

$CH_3S(O)C_6H_{12}NHCONH\text{-i-}C_3H_7$ (I) $CH_3SC_6H_{12}NHCONH\text{-i-}C_3H_7$ (II)

$C_{10}H_{21}NHCONH\text{-i-}C_3H_7$ (III)

In the literature, features of the fragmentation of the molecular ions of lower N,N'-dialkyl-, alkylaryl-, and diarylureas have been considered [1, 2]. It has been reported that of great value for their identification is the formation of carboimine (a), imine (b), amino (bH), and isocyanate (a – H) fragments through processes involving the cleavage of bonds at the carbonyl carbon atoms. The laws of the fragmentation of ureas containing additional heteroatomic groupings in the alkyl chains are of more complex nature [3, 4]. We have previously described the positive- and negative-ion mass spectra of the racemic alkaloids diptocarpidine and diptocarpiline and their sulfide analog [4], and on the basis of their REC spectra it was concluded that these molecules exist in twisted or folded conformations.

Positive Ions. Since the compounds considered in the present communication are similar in structure to those studied previously [4], it was desirable to perform a comparative analysis of the features of the breakdown on electron impact (EI) of both groups of compounds and to determine to what extent the laws of the fragmentation of the dithia derivatives [4] are applicable to monothia derivatives (compounds (I) and (II)].

In the first place, as the simplest model case let us consider features of the fragmentation of N-decyl-N'-isopropylurea (III) on EI in comparison with the results obtained for N,N'-didecylurea [4]. The fragmentation of the compounds being compared takes place by common channels and, on the whole, agrees with the features of the fragmentation of the lower N,N'-dialkylureas [1]. In contrast to N,N'-didecylurea, in the mass spectrum of

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compound (III) the maximum peak is that of an ion with m/z 44 ($CH_3-\overset{+}{C}H=\overset{+}{N}H_2$), the formation of which is typical for amines with isopropyl radicals [5]. In addition, in the spectrum of (III), because of the presence of the short isopropyl chain, we recorded the peaks of the isocyanate ion a—$H^{+\cdot}$ m/z 85 (i-$C_3H_7-\overset{+}{N}=C=O$), the amine fragment $bH^{+\cdot}$ $(M-85)^+$, and a considerable peak of a metastable ion (m*) corresponding to the transition

$$M^{+\cdot}\ (III) \xrightarrow[*101,9]{-i\text{-}C_3H_7-N=C=O} \left(C_{10}H_{21}\overset{+\cdot}{N}N_2\right) + i\text{-}C_3H_7-N=C=O$$
$$m/z\ 242 \qquad\qquad m/z\ 157$$

The presence of sulfur atoms in the alkyl chains of N,N'-dialkylureas led to additional fragmentation channels because of the competitive localization of the positive charge on the S atom. It is more readily capable than N and O atoms of forming "onium" ions, which must lead to skeletal rearrangements [6]. In particular, in the spectrum of diptocarpidine and the like [4], a loss of the NH and NHSX groupings from the $(M - CH_3)^+$ ions was observed.

In the EI mass spectra of compounds (I) and (II) the peaks of the ions M^+ (14.0 and 19.7% of the maximum peak) were recorded which, according to measurements of accurate mass numbers, corresponded to the presumed empirical formulas $C_{11}H_{24}N_2O_2S$ (measured: 248.1585, calculated: 248.1559) and $C_{11}H_{24}N_2OS$ (measured: 232.1633, calculated: 232.1609).

On the breakdown of M^+ (I and II), the peaks both of the $(M - NHC_3H_7)^+$ and $(M - CONHC_3H_7)^+$ ions that are characteristic for ureas [1] and also $(M - SXCH_2)^+$ and $(M - SXCH_3)^+$ ions that are characteristic for sulfur-containing compounds [6] were recorded; however, the recording of these fragmentary ions indicated not that the charge was present in different parts of the molecular ions but that the charge migrated within the M^+ ion, for which the interaction of the S and N atoms was necessary, this being determined, in its turn, by the spatial propinquity of the heteroatoms and not by a migration of the charge along a system of σ-bonds. The efficacy of the interaction between SX and N can be evaluated from the magnitude of the intensity ratio $I(M - NHC_3H_7)^+/I(M - SXCH_3)^+$. In the spectrum of (II), the ratio I(m/z 174)/I(m/z 185) = 0.02 indicated that the positive charge was stabilized on the S atom more effectively, i.e., there was little spatial interaction. In the spectrum of diptocarpanine (I), the value I(m/z 190)/I(m/z 185) = 0.98 showed a considerable degree of migration of the positive charge from the sulfoxy group to the carbamide group, other evidence for which was the quantitative predominance of the carbamide-, carboimine-, imine-, and amine-containing ions (ℓ_i, a, b, and i, respectively) over the peaks of the sulfur-containing ions. The efficacy of the interaction between S(O) and N was apparently due to the presence of the radical ion pair ($S^+-O^\cdot$) [6] in the M^+ ion (I). As can be seen from the occurrence of the corresponding metastable transitions, the splitting out of the isopropylamine radical took place in stages:

$$M^{+\cdot} \xrightarrow[*219.0]{-CH_3} (M-CH_3)^+ \xrightarrow[*154,9]{-NHC_3H_7} (M-NHC_3H_7)^+$$
Measured: c, 233.1339 a, 190.0915
Calculated: 233.1324 190.0902

Thanks to the localization of the charge on the sulfoxy group in M^+ (I), breakdowns typical for alphatic sulfoxides [8] were also realized, and in the mass spectrum of (I) the fragments f $(M - OH)^+$, m/z 231.1508 ($C_{11}H_{23}N_2OS$, calculated: 231.1531), $(M - OCH_3)^+$, and d $(M - OSCH_3)^+$ were observed.

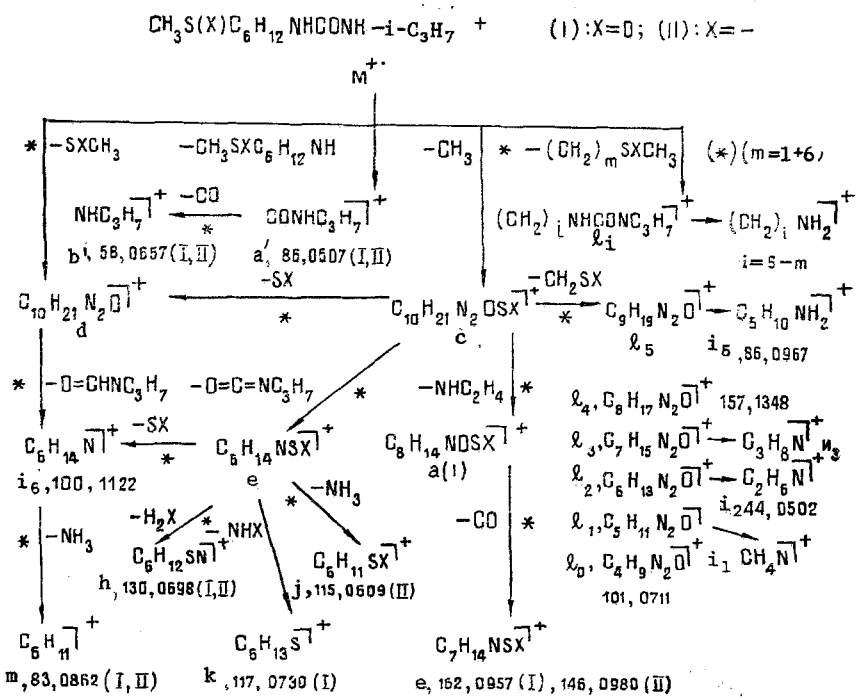
A comparison of the behavior on EI of compounds (I) and (II) with that of the dithia derivative studied previously [4], showed a substantial decrease in the proportion of processes connected with the combined ejection of the NH and S(O) groups on the fragmentation of the compounds under investigation. They were recorded as minor components $(M - CH_3SNH)^+$ m/z 186.1523 ($C_{10}H_{20}NO_2$, calculated: 186.1494) in the spectrum of compound (I); and $(M - HNS)^+$ m/z 185.1785 ($C_{10}H_{21}NO$, calculated: 185.1780) and $(M - CH_2SNH)^+$ m/z 171.1693 ($C_{10}H_{21}NO$, calculated: 171.1623) in the spectrum of (II) from the peaks of the respective ions dH $(M - OSCH_2)^+$ m/z 186.1735 ($C_{10}H_{22}N_2O$, calculated: 186.1732), d m/z 185.1657 ($C_{10}H_{21}N_2O$, calculated 185.1654) and ℓ_5 $(M - CH_2SOCH)_3^+$ m/z 171.1506 ($C_9H_{19}N_2O$, calculated 171.1497).

Thus, the main fragmentation pathways in the EI of compound of (I) and (II) are due, as in the case of the lower N,N'-dialkylureas [1] to simple bond cleavages and are grouped around the following primary fragmentation processes:

$$(M-CH_3SX)^+ \xleftarrow{-CH_3SX} M^{+\cdot} \xrightarrow{-CH_3} (M-CH_3)^+ \xrightarrow{-CONC_3H_7} (SXC_6H_{12}NH_2)^+$$

d	*138.2 (I)	*219.0 (I)	c *94.2 (I)	e 148.0856 (I)
	*147.8 (II)	*203.2 (II)	*80.5 (II)	132.0862 (II)

The most characteristic ion peaks and the values of the measured accurate mass numbers (the latter with the exception of those already discussed in the text) in the mass spectra of compound (I) and (II) are given in the scheme



Negative Ions. The processes of REC by the molecules (I)-(III) largely resemble the processes of REC by the molecules of diptocarpidine, diptocarpiline, their sulfur precursor, and didecylurea [4]. In the mass spectrum of all the above-mentioned compounds the peaks of ions due to the presence in them of the carbamide group were recorded: m/z 59 $(H_2NCONH)^-$, 42 $(OCN)^-$, 26 $(NC)^-$.

The REC mass spectrum of (I) contained a series of the same ion peaks as the spectra of racemic diptocarpidine and diptocarpiline; $(M - H)^-$, m/z 107 $(H_2NCONHSO)^-$ and/or $(i\text{-}C_3H_7NHSOH)^-$, 64 $(H_2NSO)^-$, 63 $(CH_3SO)^-$, 48 $(SO)^-$, 47 $(CH_3S)^-$, 32 $(S)^-$. The peaks of ions formed by the elimination of SO and NH groups from M^-, m/z 171 $(M - CH_2SONH)^-$ and also two peaks of rearranged ions with m/z 177 and 134 and the presumable composition $(M - i\text{-}C_3H_7\text{-}CO)^-$ and $(i\text{-}C_3H_7NHCOSO)^-$ were also observed. In the REC mass spectrum of (II) the ion peaks were observed that were recorded in the spectrum of the sulfide precursor of diptocarpidine and diptocarpiline: $(M - H)^-$, m/z 147 $(CH_3S)^-$, 46 $(CH_2S)^-$, 33 $(HS)^-$, 32 $(S)^-$, and also the peak of the rearrangement ion m/z 171 $(M - CH_2SNH)^-$, analogous to m/z 259 $(M - CH_2SNH)^-$ in [4].

The REC mass spectrum of (III) contained a set of the same ion peaks as the spectrum of didecylurea $(M - H)^-$, m/z 199 $(C_{10}H_{21}NHCONH)^-$, 184 $(C_{10}H_{21}NHCO)^-$, 182 $(C_{10}H_{19}NHCO)^-$, 156 $(C_{10}H_{21}NH)^-$. In addition, all the REC mass spectra of (I-III) contained the peaks of ions due to the presence of an isopropyl fragment in their molecules: $(M - i\text{-}C_3H_7)^-$, m/z 101 $(i\text{-}C_3H_7NHCONH)^-$, 86 $(i\text{-}C_3H_7NHCO)^-$, 58 $(i\text{-}C_3H_7NH)^-$. In contrast to the REC mass spectra of didecylurea, in the spectrum of (III) the peaks of the ions m/z 239 $(M - 3H)^-$, 226 $(M - 16)^-$, 211 $(M - 31)^-$ were observed. The composition of the ion peak $(M - 16)^-$ in the resonance state with an energy of the captured electrons of 1 eV can be only $(M - CH_4)^-$, which is possible if a hydrogen atom migrates from a nitrogen atom to one of the methyl groups of the isopropyl radical. The dissociation of M^- connected with the elimination of H and CH_3 is impossible in this resonance from any consideration, just like the ejection of NH_2 or of an oxygen atom.

The presence of an isopropyl fragment in each of the molecules (I)-(III) led to a shift in the resonance states into the region of higher energies in comparison with the compounds of [4]. In the urea molecule, the lowest unoccupied molecular orbital (LUMO) is the MO π_{CO}^* [9], which means a destabilization of this vacant orbital, although on the basis of the known σ-donor capacity of the isopropyl radical one should have expected the stabilization of the LUMO. The destabilization of the LUMO π_{CO}^* can be explained by the π-acceptor capacity of the isopropyl radical in (I-III), which is expressed in a switching of electron density from the π-orbital of the urea group to the pseudo-π-orbital of the isopropyl fragment.

The presence in the REC mass spectra of compounds (I) and (II) of the peaks of the rearrangement ions $(M - CH_2S(O)NH)^-$ due to the elimination of the fragments NH and SO from M^-, and also the peaks of ions including NH and SO groups, with m/z 134, 107, and 64 (I), permitted the conclusion that the molecules (I) and (II) existed in a folded conformation. We may also note that the negative ions NC^- are formed with the highest probability in the molecules (I) and (II), and $(M - CH_4)^-$ in (III).

Thus, in the presence in the diptocarpamine molecules of an isopropyl substituent leads to the appearance of new directions of fragmentation and to a change in the relative intensities of the ion peaks as compared with the dithia alkaloids.

EXPERIMENTAL

Positive-ion mass spectra were obtained on a MKh-1320 instrument at a temperature of the ionization chamber of 70-100°C with energies of the ionizing electrons of 70, 18, and 16 eV using a SVO-5 direct-inlet system. Accurate values of the mass numbers were measured on a Varian MAT CH-5 instrument at an energy of the ionizing electrons of 70 eV and a temperature of the ionization chamber of 150-200°C.

REC mass spectra were obtained on a MI-1201 mass spectrometer reequipped for recording negative ions [10], using a system of direct introduction of the sample. The temperature of direct introduction was 70-110°C. The electron energy scale was calibrated from the curves of the effective yields of SF_6^- from SF_6 and of NH_2^- from ammonia.

At a temperature of direct introduction of 70-110°C, in compounds (I) and (II) the peaks of the ions m/z 248 and 232 formally corresponding to the M^- peak were recorded. However, when the temperature of the ionization chamber was raised to 150-200°C the peaks of these ions disappeared and also the peaks of ions with m/z 166, 123, 91, and 33 in (I) and m/z 152 and 143 in (II), and these were therefore not included in the true REC mass spectra of these compounds. It is characteristic that the regions of resonance electron capture of the peaks of the ions with m/z 248, 166, 123, 91, and 33 in (I) coincided and amounted to 0.3, 1.9, and 3.4 eV. A similar pattern was observed for the peaks of the ions with m/z 232, 152, and 143 (II) – 0.3 and 2.6 eV. We may note that at the given values of electron energy the existence of other ions in the true REC mass spectra were not recorded.

In the EI mass spectra of compounds (I) and (II) intense peaks of the $(M + 1)^+$ ions were recorded (the expected contributions of the peaks of the ions from heavy isotopes had far smaller values). The spectra of the compounds investigated were obtained after they had been kept in H_2O and D_2O vapors. A rise in the intensities of the $(M + 1)^+$ and $(M + 2)^+$ peaks was observed. With a rise in the temperature of direct introduction to 150-200°C the intensities of the peaks of the $(M + 1)^+$ and $(M + 2)^+$ ions became close to the values of the natural distributions of the isotopes.

N-Isopropyl-N'-(6-methylsulfinylhexyl)urea (I). EI mass spectrum, m/z (%): 248 (M^+, 14.0), 233 (c, 32.7), 231 (f, 8.0), 218 (0.8), 217 (g, 1.1), 192 (7.3), 190 (a, 56.7), 186 (dH^+; 18.3), 185 (d, 58.0), 174 (4.7), 171 (ℓ_5, 19.3), 162 (b, 18.0), 148 (e, 10.0), 146 ($b\text{-}O^{1+}$, 19.3), 144 (5.3), 143 (ℓ_3, 8.3), 130 (h, 7.3), 129 (ℓ_2, 8.0), 126 (6.0), 119 (10.0), 117 (k, 53.3), 115 (ℓ_1, 10.0), 103 (15.3), 100 (i_6, 30.0), 98 (13.3), 87 (5.3), 86 (i_5, a', 7.3), 83 (m, 20.0), 81 (10.3), 73 (5.0), 70 (17.3), 69 (12.3), 65 (5.7), 64 (15.3), 63 (6.7), 61 (13.3), 60 (19.3), 58 (b', i_3, 66.7), 56 (24.0), 55 (58.0), 45 (5.3), 44 (i_2, 100), 43 (44.7), 42 (17.3), 41 (43.3), 39 (7.0), 30 (i_1, 83.3).

REC mass spectrum* of (I): 247 - 11 (0.5), 21 (2.1), 10 (3.1), 233-18 (1.0), 205-9 (0.5), 3 (8.0), 177-40 (1.0), 6 (4.2), 171-12 (0.5), 26 (1.6), 134-5 (0.5), 5 (4.2), 107-50 (0.5), 101-3 (0.3), 3 (4.9), 11 (8.4), 86-4 (1.0), 3 (4.5), 3 (8.4), 64-12 (0.3), 7 (2.3), 5 (4.0), 4 (6.2), 63-10 (1.6), 4 (4.9), 17 (7.9), 7 (9.2), 59-18 (1.0), 5 (2.8), 5 (7.7), 58-15 (4.9), 48-13 (4.5), 3 (7.2), 47-62 (0.2), 9 (5.4), 19 (8.0), 42-24 (1.0), 59 (2.2), 32-5 (1.2), 4 (3.9), 11 (5.1), 26-100 (1.6), 5 (4.9), 9 (6.4).

N-Isopropyl-N'-(7-thiaoctyl)urea (II). Mass spectrum: m/z (%): 232 (M^+, 19.7), 217 (c, 33.3), 186 ($dH^{\dagger}$, 17.6), 185 (d, 100), 174 (1.2), 171 (ℓ_5, 12.4) 157 (ℓ_4, 6.2), 148 (3.0), 146 (b, 8.8), 143 (ℓ_3, 12.4), 132 (d, 30.0), 130 (6.1), 129 (ℓ_2, 6.1), 116 (9.1), 115 (j, ℓ_1, 23.3), 103 (13.6), 101 (ℓ_0, 7.9), 100 (i_6, 23.6), 98 (9.7), 87 (12.4), 86 (i_5, 8.2), 83 (m, 5.2), 82 (11.2), 81 (16.1), 73 (6.4), 70 (7.6), 69 (6.4), 67 (5.8), 61 (30.0), 60 (27.3), 58 (b', i_3, 46.7), 56 (12.7), 55 (19.1), 44 (i_2, 96.7), 43 (28.3), 42 (11.2), 41 (23.3), 39 (5.2), 30 (i_1, 76.7).

REC mass spectrum of (II): 231-23 (0.4), 16 (2.4), 189-5 (1.9), 21 (8.5), 171-11 (0.5), 24 (1.8), 3 (4.4), 5 (8.4), 101-5 (5.1), 23 (8.2), 86-6 (4.9), 4 (8.4), 59-7 (0.8), 3 (2.4), 2 (8.4), 58-4 (0.9), 5 (5.5), 3 (7.8), 47-3 (0.8), 5 (5.5), 38 (7.8), 46-69 (0.2), 4 (1.8), 4 (3.2), 42-32 (1.2), 11 (2.4), 33-8 (0.7), 4 (2.3), 32-1 (1.2), 1 (4.0), 7 (5.2), 2 (7.7), 26-100 (0.9), 68 (1.8).

N-Decyl-N'-isopropylurea (III). Mass spectrum, m/z (%): 242 (M^+, 25.0), 241 (1.6), 227 (c, 1.9), 213 (3.2), 200 (1.6), 199 (4.8), 185 (ℓ_6, 5.2), 184 (α, 1.9), 172 (1.9), 172 (1.9), 171 (ℓ_5, 4.3), 158 (3.2), 157 ($bH^{\dagger}$, ℓ_4, 9.1), 156 (b, 2.7), 144 (3.2), 143 (ℓ_3, 8.8), 130 (3.7), 129 (ℓ_2, 5.6), 126 (2.4), 116 (11.2), 115 (ℓ_1, 7.8), 113 (3.7), 112 (5.6), 111 (2.9), 103 (4.4), 102 (2.9), 101 (ℓ_0, 4.5), 100 (2.7), 99 (13.4), 98 (5.3), 97 (7.2), 96 (2.9), 95 (2.9), 87 (6.4), 86 (α', i_5, 4.5), 85 ($\alpha' - H^{\dagger}$, 7.0), 84 (4.8), 83 (m, 11.0), 82 (4.3), 81 (3.7), 73 (2.9), 71 (5.3), 70 (15.8), 69 (14.4), 68 (5.3), 67 (4.8), 60 (7.5), 59 ($b'H^{\dagger}$, 2.7), 58 (b', i_3, 25.1), 57 (14.7), 56 (15.2), 55 (25.7), 45 (6.7), 44 (i_2, 100), 43 (41.2), 41 (29.4), 39 (8.3), 30 (i_1, 94.1).

REC mass spectrum of (III): 241-13 (1.0), 37 (2.6), 53 (7.6), 9 (9.4), 239-9 (1.0), 20 (2.7), 19 (3.8), 8 (8.2), 226-100 (1.0), 12 (2.6), 13 (7.8), 7 (9.4), 211-6 (2.6), 31 (8.7), 27 (10.2), 199-5 (1.5), 30 (8.6), 185-14 (1.5), 5 (5.0), 184-4 (1.1), 3 (2.5), 182-5 (2.7), 156-24 (1.0), 7 (2.6), 6 (5.0), 101-5 (5.0), 16 (8.5), 86-7 (1.5), 10 (4.8), 5 (7.9), 5 (9.5), 59-9 (0.9), 7 (2.0), 58-8 (1.0), 6 (5.6), 6 (8.4), 42-41 (1.5), 25 (2.6), 13 (5.2), 15 (9.2), 26-80 (1.5), 54 (2.2), 13 (3.2).

SUMMARY

1. The EI fragmentation of the compounds investigated takes place predominantly by processes of simple bond cleavage.

2. The presence in the REC mass spectra of the peaks of rearrangement ions containing S(O) and NH groups indicates the existence of the molecules of diptocarpamine and of its sulfide precursor in twisted or folded conformations.

3. The efficacy of the intramolecular interaction of the functional groups of diptocarpamine and its sulfide precursor is lower than in the dithia alkaloids, as is witnessed by the decrease in the relative proportion of the rearrangement atoms in the EI and REC mass spectra.

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*Here and below, in the REC mass spectra: mass number, intensity of the peak of the ions in % of the maximum, and in parentheses the energy of the resonance maximum of the yield of ions, eV.

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MOLECULAR STRUCTURE OF THE ALKALOID SOLASODINE

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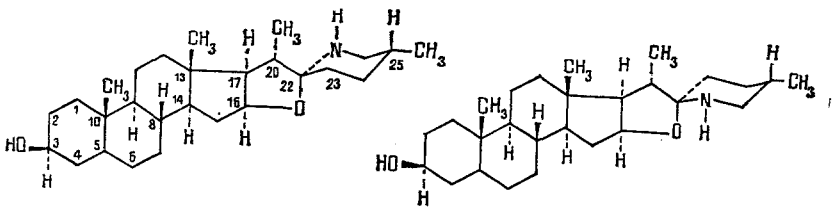
UDC 548.373

An x-ray structural study of the monohydrate of the alkaloid solasodine has been made. Rings A, C, and F have the chair conformation, ring B half-chair, and rings D and E envelope conformations. The linkages of rings B/C and C/D are trans and that of rings D/E cis. It has been shown that solasodine is a diastereomer of the alkaloid tomatidenol.

The determination of the structures of the alkaloids solasodine (I) and soladulcidine (II) and of their stereoisomers tomatidenol (III) and tomatidine (IV) have been reported previously (1) and an X-ray structural investigation has been carried out for the last-mentioned of them.



I Δ^5: solasodine
II 5αH: soladulcidine
III Δ^5: tomatidenol
IV 5αH: tomatidine

To determine the structure of solasodine independently and objectively, we have made an x-ray structural study of it in the form of the monohydrate $C_{27}H_{25}NO_2 \cdot H_2O$ (V) and have confirmed the structure proposed for it previously. The linkages of rings B/C and C/D are trans and that of rings D/E cis. Rings A, C, and F have the chair conformation (the torsion angles are shown in Fig. 1), and ring B the half-chair conformation; the C10, C5, C6, and C7 atoms are in one plane with an accuracy of ±0.001 Å, and the C8 and C9 atoms depart from it on either side by 0.25 and 0.45 Å, respectively. Rings D and E have the envelope conformation: the C14 atom departs from the plane of the C13, C17, C16, and C15 atoms (±0.06 Å) in the β-direction by 0.68 Å, and the O16 atom departs from the plane of the C17, C16, C20, and C22 atoms (±0.05 Å) in the β direction by 0.55 Å.

The methyl group at the C25 atom and the OH group at the C3 atom have the equatorial orientations. The longitudinal twisting of the "steroid" skeleton (the C19C10C13C18 pseudotorsion angle) amounts to 10.1°. The lengths of the bonds and the valence angles in rings C, D, E, and F are close to the corresponding values in tomatidine hydroiodide [1] and hydrobromide [11] and in rings A and B they are close to the corresponding values in Δ^5-steroids (see, for example, [3]). The molecules of (I) in water are linked in the crystal by the

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