MASS SPECTRA OF THE ALKALOIDS OF *Dipthychocarpus strictus*

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The mass spectra of diptocarpaine, diptocarpamine, diptocarpiline, and diptocarpidine, isolated from *Dipthychocarpus strictus*, have been studied. These compounds have proved to be derivatives of alkylureas, the substituents in them being mainly methylthio-n-hexyl and methylsulfinyl-n-hexyl radicals and the products of their chemical transformation. It has been established that mass-spectrometric fragmentation of these compounds takes place with the formation of heterocyclic ions.

Compounds isolated from *Dipthychocarpus strictus* and the products of their chemical transformation have been described in previous papers [1-4]; they have proved to be derivatives of N-alkylureas substituents, in which are mainly n-hexyl, methylthio-n-hexyl, and methylsulfinyl-n-hexyl radicals. These compounds can be divided into the following three groups:

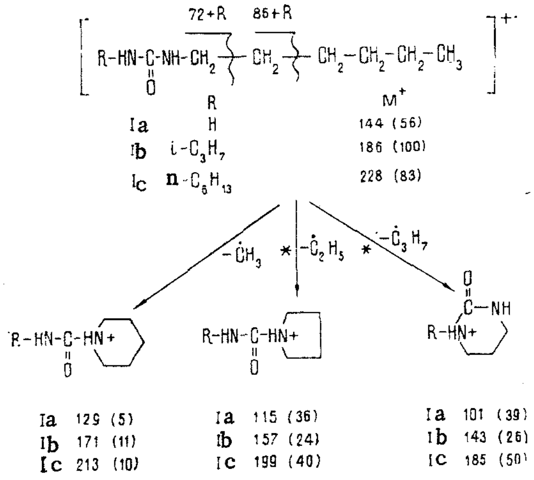
I. a) N-n-Hexylurea; b) N-n-hexyl-N-isopropylurea; and c) N,N'-di-n-hexylurea.

II. a) Deoxodiptocarpaine; b) deoxodiptocarpamine; and c) deoxodiptocarpiline.

III. a) Diptocarpaine; b) diptocarpamine; c) diptocarpiline; and d) diptocarpidine.

The common fragmentation pathway of the M^+ ions of compounds (Ia-c) is characterized by the ejection of alkyl radicals. On comparing the spectra of (Ia-c) an increase in the intensities of the peaks of these ions is observed in the sequence $(M - 15)^+$, $(M - 29)^+$, and $(M - 43)^+$ (Fig. 1), and then a fall in the intensities of the peaks of the ions corresponding to the elimination of 57 and 71 amu (Scheme 1). In the spectrum of compound (Ia) the peak of the ion with m/e 73 ($NH_2—CO—\overset{+}{N}H=CH_2$) has the greatest intensity.

The appearance of a considerable number of $(M - C_3H_7)^+$ ions is due to the formation of a stable cyclic ion via a six-membered state and the elimination of the more stable fragment in the form of a propyl radical. The ions $(M - 15)^+$ and $(M - 29)^+$ are also apparently stabilized in cyclic forms (Scheme 1).



Scheme 1

As the result of a rearrangement process, ions appear with m/e 74 (Ia), 116 (Ib), and 158 (Ic), and 88 (Ia), 130 (Ib), and 172 (Ic), which are derivatives of ions of methylurea

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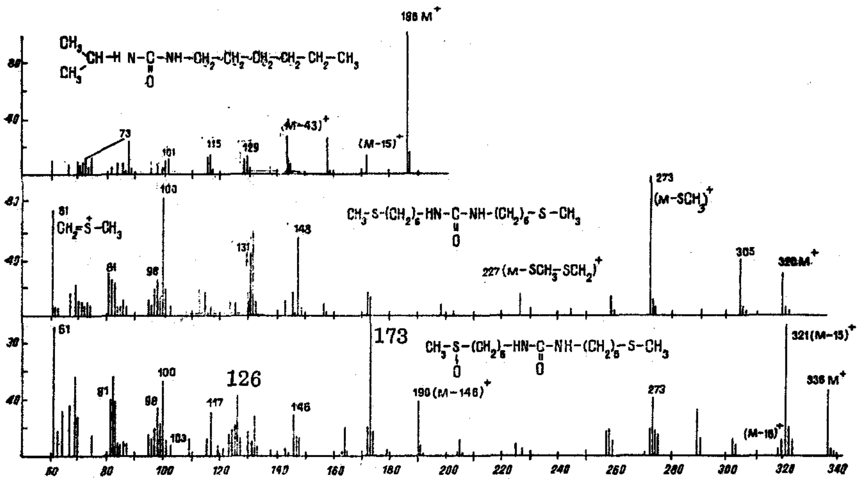
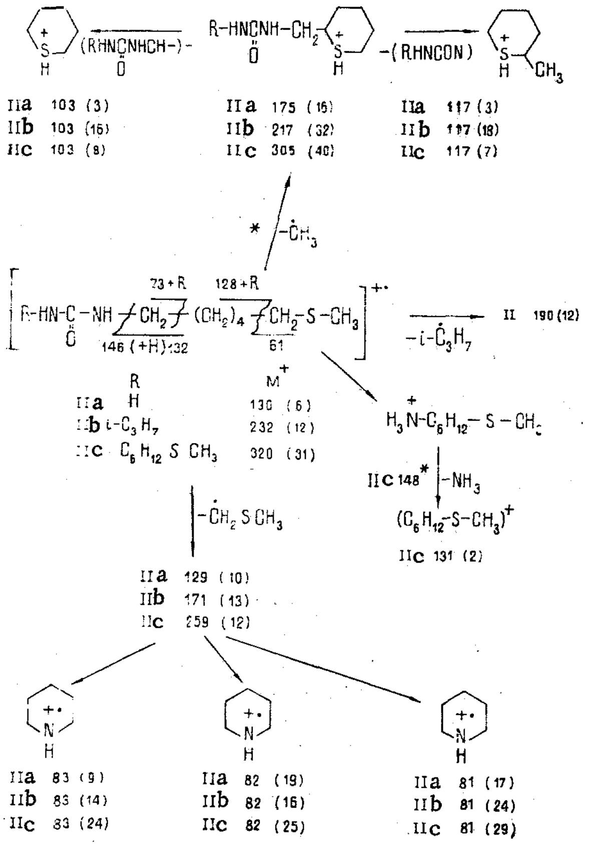


Fig. 1. Mass spectra of N-n-hexylurea, deoxodiptocarpiline, and diptocarpidine.

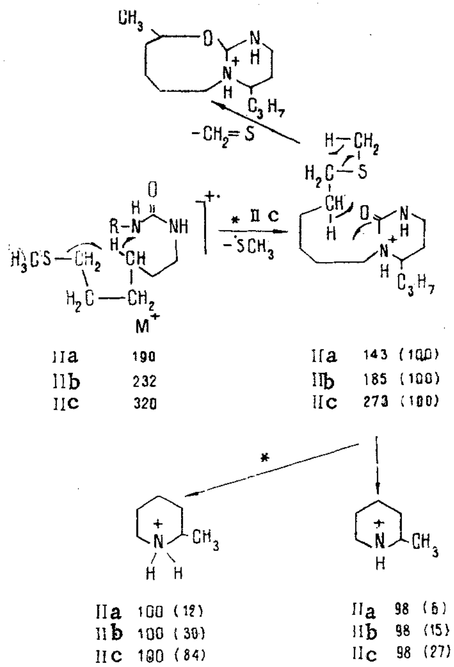
and ethylurea, respectively. Then a propylene molecule is eliminated from each of the ions 116 (Ib) and 158 (Ic) and the ions 130 (Ib) and 172 (Ic). Thus, the decomposition of the N,N'-dialkylurea molecule takes place with the localization of the positive charge on the heteroatoms nitrogen and oxygen.



Scheme 2

The spectra for compounds (IIa-c) with methyl sulfide groups are characterized by far stronger peaks of the ions $(M-15)^+$, the formation of which is accompanied by a metastable transition which permits them to be ascribed a cyclic sulfonium structure (Scheme 2). The further decomposition of the $(M-15)^+$ ions leads to the formation of ions with m/e 103 and 117. Cleavage of the bonds of the hexamethylene chain is also observed in the fragmentation of (IIa-c), meanwhile the peaks of the ions $(M-SCH_3)^+$, the structure of which is analogous to the structure of the ions $(M - 15)^+$ of the compounds of group (Ia-c) have the highest intensity.

In the spectrum of (IIc), the ion $(M - SCH_3)^+$, then eliminating a molecule of thioformaldehyde ($CH_2{=}S$), is converted into an ion with m/e 227. However, in this process a passage of fragmentation from one end of the molecule to the other is observed. Such a phenomenon is evidence in favor of a cyclic form of the ions $(M - SCH_3)^+$ through the combination of six- and five-membered states. The localization of the positive charge on the nitrogen atom activates the further decomposition of this ion. With a combination of eight- and four-membered states, the ion $(M - SCH_3 - SCH_2)^+$ is obtained. Other directions of the decomposition of the $(M - SCH_3)^+$ ion lead to nitrogen-containing ions with m/e 100 and 98 (Scheme 3).



Scheme 3

The appearance of ions with m/e 81, 82, and 83 also takes place from the N-alkyl part of the molecule via $(M - CH_2SCH_3)^+$ ions. We may note the appearance in the spectrum of (IIc) of the peak of an ion with m/e 148, because of the presence of two methylthiohexamethylene groups. Then this ion, losing an NH_3 molecule, is converted into an ion with m/e 131, as is confirmed by the detection of a M^+ peak at 116 m/e (Scheme 2).

Let us consider the behavior under electron impact of compounds with a terminal methyl sulfoxide group. The spectra of (IIIa-b) show similar fragmentation pathways. Ions $(M - OH)^+$ appear which are characteristic for the spectra of dialkyl sulfoxides [5]. The cleavage of ordinary bonds gives rise to the ions $(M - CH_3)^+$ and $(M - SOCH_3)^+$ with m/e 64 $(HSOCH_3)^+$, 119 ($C_5H_{11}OS$), 148 ($C_7H_{16}OS$), and 162 ($C_7H_{16}ONS$) (Scheme 4).

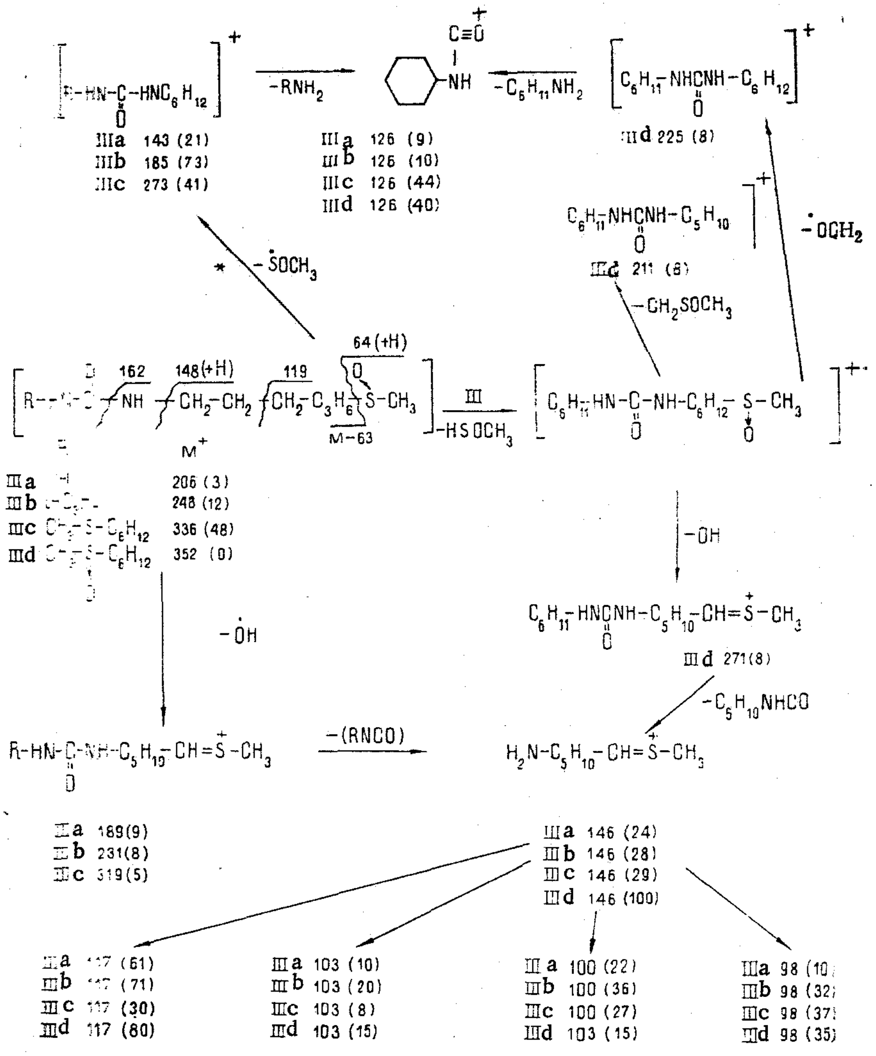
In the spectrum of compound (IIIc) with methylthio and methylsulfinyl groups, the peaks of ions characteristic for the spectra of the compounds of groups (II) and (III) are observed. So far as concerns substance (IIId) (a disulfoxide), its mass spectrum lacks the M^+ peak and shows the peaks of the ions $(M - \dot{C}H_3)^+$ and $(M - HSOCH_3)^+$ with m/e 288. The fragments $\dot{C}H_3$, $\dot{O}H$, $SOCH_3$, and $\dot{C}H_2SOCH_3$ are eliminated from the latter.

It is interesting to note the presence in the spectra of compounds (IIIa-d) of a number of peaks of ions, the appearance of which cannot be explained within the framework of the simple cleavage of ordinary bonds. Since the molecule of (IIId) has two identical alkyl sulfoxide groups, the intensities of the peaks of the ions with m/e 146, 126, 117, 103, 100, and 98 that have been mentioned, are far higher. Below we give the results of the measurement of the accurate masses of these ions for the case of the spectrum of compound (IIIa) as an example (see Table 1).

The ion with m/3 146 ($C_7H_{16}N$) has a composition analogous to that of the ion formed in the spectra of compound (IIa-c). However, in this case it can appear only as the result of the ejection of an OH radical from M^+ with the subsequent cleaveage of a $-C\equiv N$ bond. The fur-

TABLE 1

m/e	Accurate mass	Composition
206 M^+	206.1080	$C_8H_{18}O_2NS$
189	189,1040	$C_8H_{17}ON_2S$
148	148,0802	$C_7H_{16}OS$
146	146.1012	$C_7H_{16}NS$
143	143.1178	$C_7H_{15}ON_2$
126	126,0934	$C_7H_{12}NO$
119	119,0515	$C_5H_{11}OS$
117	117,0730	$C_6H_{13}S$
103	103,0579	$C_5H_{11}S$
100	100,1119	$C_6H_{14}N$
98	98,0974	$C_6H_{12}N$



Scheme 4

ther decomposition of the ion with m/e 146 leads to sulfur- and nitrogen-containing ions (Scheme 4).

The source of the ion with m/e 126 is formed in all probability by the $(M - SOCH_3)^+$ ions.

An analysis of the spectra of compound (Ia-c), (IIa-c), and (IIIa-c) and of literature information on the spectrum of diisopropylurea [6] shows that N-alkyl derivatives of urea undergo the fragmentation characteristic for substituted amides, i.e., α-cleavage and O=C—N-cleavage, as a result of which strong peaks of $H_2\overset{+}{N}{=}CHR$ ions appear [7, 8].

EXPERIMENTAL

The mass spectra were obtained on a MKh-1303 instrument using a system for the direct introduction of the sample, at a temperature of 110-120°C and ionizing voltage 40 V.

The elementary compositions of the ions were measured on a MKh-1310 high-resolution mass spectrometer.

SUMMARY

The mass spectra of natural urea derivatives with alkyl, alkylthio, and alkylsulfinyl substituents have been studied. It has been established that the fragmentation of these compounds takes place with the formation of heterocyclic ions.

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TRANSFORMATIONS OF SOLASODINE

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Solasodine (I) has been subjected to a number of transformations. The following compounds have been obtained from it by described procedures: 3β-acetoxypregna-5,16-dien-20-one (II), 3β-acetoxypregn-5-en-20α-ol (III), and 3β-acetoxypregn-5-en-20β-ol (IV). The oxidation of (III) and (IV), the formation of an oxime, and the reduction of the oxime with sodium in ethanol, followed by Hess methylation, has led to 20α-dimethylaminopregn-5-en-3β-ol (IX) and to 20β-dimethylaminopregn-5-en-3β-ol (X). From compounds (IX) and (X), by analogy with (III) and (IV) by their oxidation and the preparation of oximes, which were then reduced and methylated, the following were obtained: 3β,20α-bisdimethylaminopregnane (XVII) and 3β,20β-bisdimethylaminopregnane (XVIII), and also quaternary salts of the latter.

It has been shown previously that solasodine is a convenient starting material for the synthesis of progesterone, cortisone, and other compounds [1-7]. By a method described previously [3], from solasodine (I) we have obtained 3β-acetoxypregna-5,16-diene-20-one (II) the IR spectrum of which contains characteristic absorption bands at 1730 cm^{-1} (O—Ac) and 1665 and 1590 cm^{-1} (CO—C=CH).

When (II) was hydrogenated in ethanol with Raney nickel, two isomeric substances were obtained: 3β-acetoxypregn-5-en-20α-ol (III) and 3β-acetoxypregn-5-en-20β-ol (IV). It must be mentioned that under these conditions the double bond at C_{16}-C_{17} was also hydrogenated. The IR spectra of both substances showed characteristic absorption bands for a hydroxy group at 3560-3390 cm^{-1}.

The oxidation of (III) and (IV) with chromium trioxide in acetic acid gave 3β-acetoxypregn-5-en-20-one (V) [3]. The IR spectrum of (V) showed the characteristic absorption

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