

MASS SPECTRA OF THE NEGATIVE IONS OF
SOME STEROIDS

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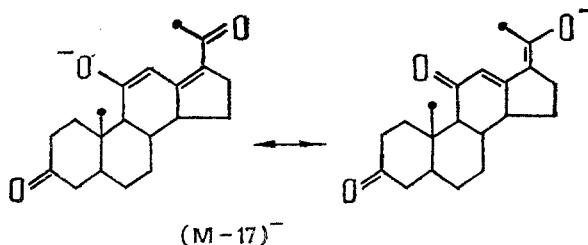
It has been shown that the main directions of the fragmentation of the molecular negative ions are connected with the formation of systems of conjugated bonds and the delocalization of the negative charge over a π -system of electrons. The mass spectrometry of the negative ions formed by the dissociative capture of electrons (DCE) is promising for the study of the molecules of steroid compounds.

Previously, in a study of the mass spectra of the negative ions of a number of derivatives of carbohydrates and the acetates of epimeric diterpene glycols a high stereospecificity of the fragmentation of the molecular negative ions on the capture of slow electrons was established [1-5].

In continuing these investigations, and also in order to elucidate the possibilities of the mass spectrometry of negative ions (NIs) for investigating other classes of natural compounds, we have studied the mass spectra of the negative ions of a number of steroids — progesterone (I), 11α -hydroxyprogesterone (II), 5β -pregnane-3,11,20-trione (III), 5α -pregnane-3,11,20-trione (IV), $3\alpha,20\beta$ -dihydroxy- 5β -pregnan-11-one (V), and 3-methoxyestradiol-1,3,5,8,14-ene-17-one (VI) which are shown in Table 1.

The dissociative capture of electrons by the molecules of compounds (I-V) takes place mainly in the range of electron energies of 8-9 eV. The fragmentation of the molecular negative ions (MNIs) of the steroids mentioned takes place with the formation of $(M - H)^-$ ions having the maximum intensity in the mass spectra.

The majority of the peaks in the region of high mass lines is formed by the detachment of substituents, the stabilization of the negative ions taking place through the formation of a system of conjugated bonds with a delocalized negative charge over the π -system of electrons, as in the case of the formation of negative ions in cyclic derivatives of hydrocarbons and diterpenoids [1-5]. Thus, for the $(M - 17)^-$ ions formed as the result of the elimination of a CH_3 group and two hydrogen atoms it is possible to suggest the following structures of compounds (III) and (IV):



The formation of the ions $(M - 19)^-$ (m/z 311 and 315) in the case of compounds (II) and (V) having similar structures,* may serve as an indirect confirmation of this hypothesis. The ions $(M - 59)^-$ (m/z 255, 271) formed as the result of the ejection of CH_3CO .

*The formation of negative ions as a consequence of the ejection of OH and H_3O groups is less probable since in a "model" compound — the cyclohexanone molecule — the peaks of the $(M - 17)^-$ and $(M - 19)^-$ ions are absent [1].

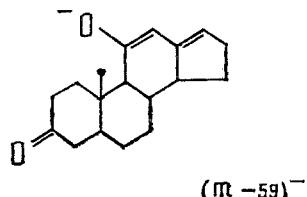
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TABLE 1. Mass Numbers and Relative Intensities of the Negative Ions in the Mass Spectra of Steroids (I)–(VI).

<i>m/z</i>	1, %	<i>m/z</i>	1, %	I		II mol. wt. 330		III mol. wt. 330		IV mol. wt. 330		V mol. wt. 334		VI mol. wt. 280	
				<i>m/z</i>	<i>I, %</i>	<i>m/z</i>	<i>I, %</i>	<i>m/z</i>	<i>I, %</i>	<i>m/z</i>	<i>I, %</i>	<i>m/z</i>	<i>I, %</i>	<i>m/z</i>	<i>I, %</i>
313	100	329	100	329	100	329	100	329	100	333	100	333	100	279	76
297	4,5	313	5,0	313	5,0	313	6,2	313	4,0	315	6,0	315	6,0	265	36*
285	1,5	295	25,0	295	25,0	297	1,5	297	2,0	299	1,5	299	1,5	264	100
281	0,8	285	2,5	285	32	287	2,5	287	4,0	289	19,0	289	19,0	250	15
269	1,1	271	4,0	271	4,0	271	26,3	271	20,5	273	2,5	273	2,5	235,8*	83
255	1,0	259	4,0	259	4,0	259	7,0	259	4,0	271	1,5	271	1,5	43	2,0
241	1,5	247	2,0	247	2,0	245	2,5	245	2,5	261	1,0	261	1,0	41	2,5
123	7,0	241	10,0	241	10,0	205	11,2	205	2,0	207	5,0	207	5,0	31	10
57	1,5	189	12,5	191	12,5	191	2,5	191	1,0	193	1,5	193	1,5	17	2,0
43	2,5	123	12,0	163	9,0	163	9,0	163	11,5	181	2,0	181	2,0	57	1,5
41	0,5	67	13,0	123	9,0	123	9,0	123	11,0	43	4,0	43	4,0	41	7,5
		43	60,0	57	5,0	57	5,0	57	5,0	43	4,0	43	4,0	41	2,5
		41	6,0	43	3,0	43	3,0	43	4,0	41	1,5	41	1,5	41	2,5
		17	27,0	41	1,0	41	1,0	41	1,0	41	1,5	41	1,5	41	2,5

*The formation of ions with *m/z* 279 is observed on the capture of electrons with an energy of 1.65 eV.

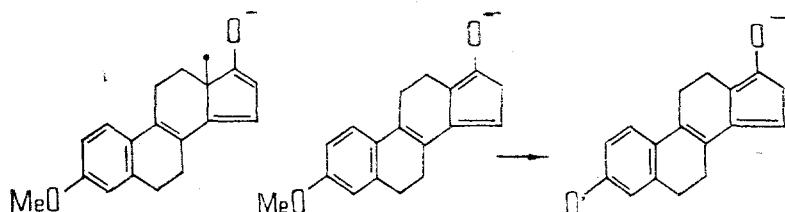
and CH_3^+ groups and a hydrogen atom probably have a similar structure, but without the side chain:



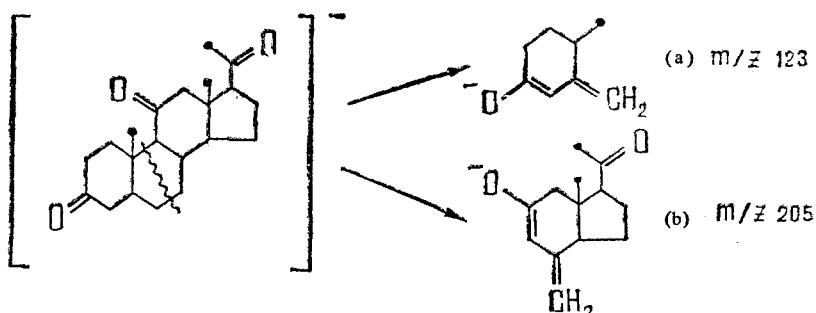
The mass spectrum of $3\alpha, 20\beta$ -dihydroxy- 5β -pregnan-11-one (V) contains the peaks of the $(M - 61)^-$ ion (m/z 273), i.e., the displacement of these peaks by two mass units takes place.

The mass spectrum of compound (VI) may serve as confirmation of the hypothesis of the stabilization of the negative ions by the formation of a system of conjugated bonds.

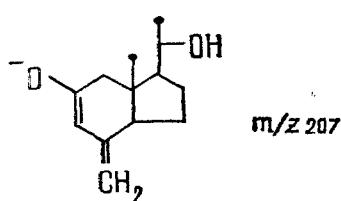
The molecule of this compound already has the "structural pre-arrangement" that is favorable for the formation of a completely conjugated system of electrons through the ejection of a hydrogen atom or a methyl group. As a result, structurally similar ions with m/z 279 and 265 are formed which subsequently eliminate a methyl group (a metastable peak with m/z 235.8 corresponding to the process $265 \xrightarrow{15} 250^-$ is observed).



The formation of ions with m/z 123 and 205 on the capture of electrons by the molecules of the pregnane-3,11,20-triones (III, IV) apparently takes place as the result of the following process of the dissociation of the molecular negative ion:



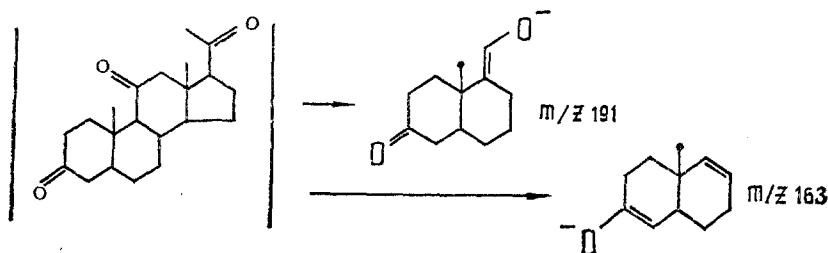
As a confirmation of such a mechanism of the fragmentation of the molecular negative ion we can take the displacement by two mass units of the negative ion of type b in the mass spectrum of the pregnanediol (V) (m/z 207):



It must be mentioned that the probability of the formation of ions of types α and β depends on the structure of the steroid molecule.

Thus, in the mass spectra of compounds (I) and (II), the molecules of which contain the pre-arrangement for the formation of ions of type α (m/z 123), no ions of type β [m/z 189 and 205, respectively, for (I) and (II)] are observed, and in the spectrum of the pregnane-diol (V) there are no peaks of ions of type α , i.e., there is probably a competition of these two channels of the fragmentation of the molecular negative ion.

The following scheme may be suggested for the formation of the ions with m/z 191 and 163 in the spectra of the pregnanetriols (III) and (IV):



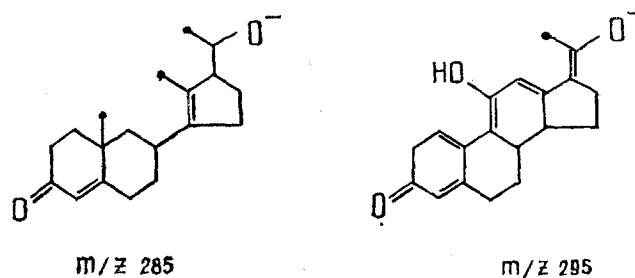
In favor of such a scheme of fragmentation of the molecular negative ion, as in the case given above (formation of ions with m/z 123 and 205) is the displacement by two mass units of the lines of the ions in the mass spectra of the hydroxysteroids (II) and (V) (m/z 189 and 193, respectively).

Thus, starting from what has been said above it may be concluded that the direction of the fragmentation of the molecular negative ions of the compounds studied is due mainly to the formation of a system of conjugated bonds, and it is predominantly rings B and C of the molecule that undergo dissociation. It is therefore not surprising that a small change in the molecule leads to a substantial change in the form of the mass spectrum of the negative ion.

Thus, in the case of the stereoisomeric pregnane-3,11,30-triones (III) and (IV), which have different configurations of the symmetric center at C_5 , the mass spectra of the negative ions differ appreciably in the relative intensities of the lines of the ions with m/z 271, 205, 191, and 123, the greatest differences being observed for the lines of the ions with m/z 205, the intensity of which is almost 5.5 times greater in the mass spectrum of the 5β isomer (III). This is probably connected with the fact that in the process of forming this ion a migration of the hydrogen atom attached to the asymmetric C_5 carbon atom takes place.

Even greater differences are observed in the mass spectra of the negative ions for compounds (II) and (III).

The presence of a hydroxy group in the molecule leads to a considerable increase in the probability of the formation of the $(M - 45)^-$ (m/z 285) and $(M - 35)^-$ (m/z 295) ions, the structures of which are also due to the formation of a system of conjugated bonds with the delocalization of the negative charge over the π -system [as examples, the structures of the ions are given for compounds (II)]:



EXPERIMENTAL

The mass spectra of the negative ions were obtained on a MKh-1303 mass spectrometer adapted for the recording of negative ions [6], and the energy electron scale was calibrated from the yield of SF_6^- ions from SF_6 .

SUMMARY

1. It has been shown that the main directions of the fragmentation of the molecular negative ions are connected with the formation of a system of conjugated bonds and the delocalization of the negative charge over a π -system of electrons.

2. It has also been shown that the mass spectrometry of DCE negative ions is promising for the study of the molecules of steroid compounds.

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