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Specific features of resonance electron capture mass spectra of ecdysteroid molecules

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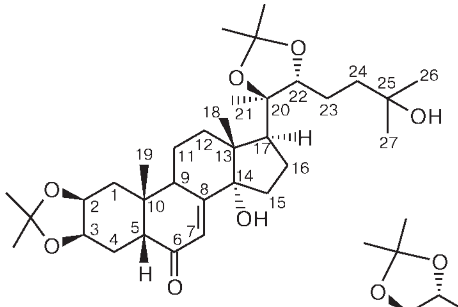
Specificity of the dissociative attachment of low-energy electrons to ecdysteroid molecules (*viz.*, 20-hydroxyecdysone 2,3:20,22-diacetonide, 20-hydroxyecdysone 20,22-acetonide, and poststerone 2-acetate) was found, which is manifested as the formation of long-lived pseudomolecular negative ions that appeared due to the elimination of the H_2 and H_2O molecules. These rearrangements are resulted from the formation of the system of conjugated double bonds in the ecdysteroid skeleton, stabilizing the lowest vacant molecular orbital.

Key words: ecdysteroids, resonance electron capture mass spectrometry, negative ions, rearrangement processes.

In continuation of our studies of resonance electron capture (REC) by ecdysteroid molecules,[1] in this work we studied the 20-hydroxyecdysone derivatives by resonance electron capture mass spectrometry: 20-hydroxyecdysone 2,3:20,22-diacetonide (**1**) (m.p. 234 °C), 20-hydroxyecdysone 20,22-acetonide (**2**) (m.p. 222 °C), and poststerone 2-acetate (**3**) (m.p. 224 °C).



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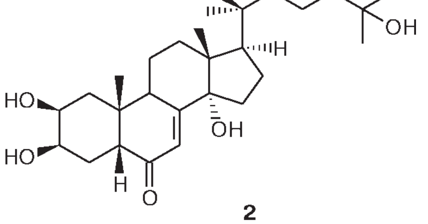

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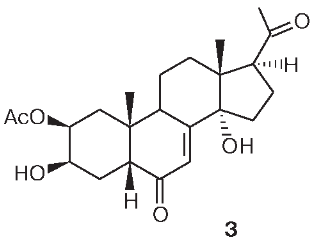

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Experimental

The compounds under study were synthesized from 20-hydroxyecdysone using known procedures.[2] REC mass spectra were obtained on an MI-1201 static mass spectrometer adapted for detection of negative ions[3] (NI) with a home-made trochoidal electron monochromator added in the ion source (accelerating voltage 2.5 kV, electron current 100—200 nA, and the width of the energy distribution at the half-maximum $\Delta E_{1/2} = 0.16—0.2$ eV). The temperature of the evaporator in the system of direct sample injection was 100—170 °C, and the temperature of the ionization chamber was by 10—20 °C higher than this temperature and lower than the melting point of samples, which prevented their thermal destruction during mass spectral experiments.

Results and Discussion

Resonance electron capture by compounds **1—3** occurs in an energy interval of 0—11 eV (Table 1, Fig. 1). In the low-energy region, the REC mass spectra (MS) of ecdysteroids **1—3** contain peaks of ions only with even mass numbers corresponding to the successive elimination of the H_2, H_2O, Me_2CO, and AcOH molecules. The $[M - H]^-$ ions and the products of their further decom-

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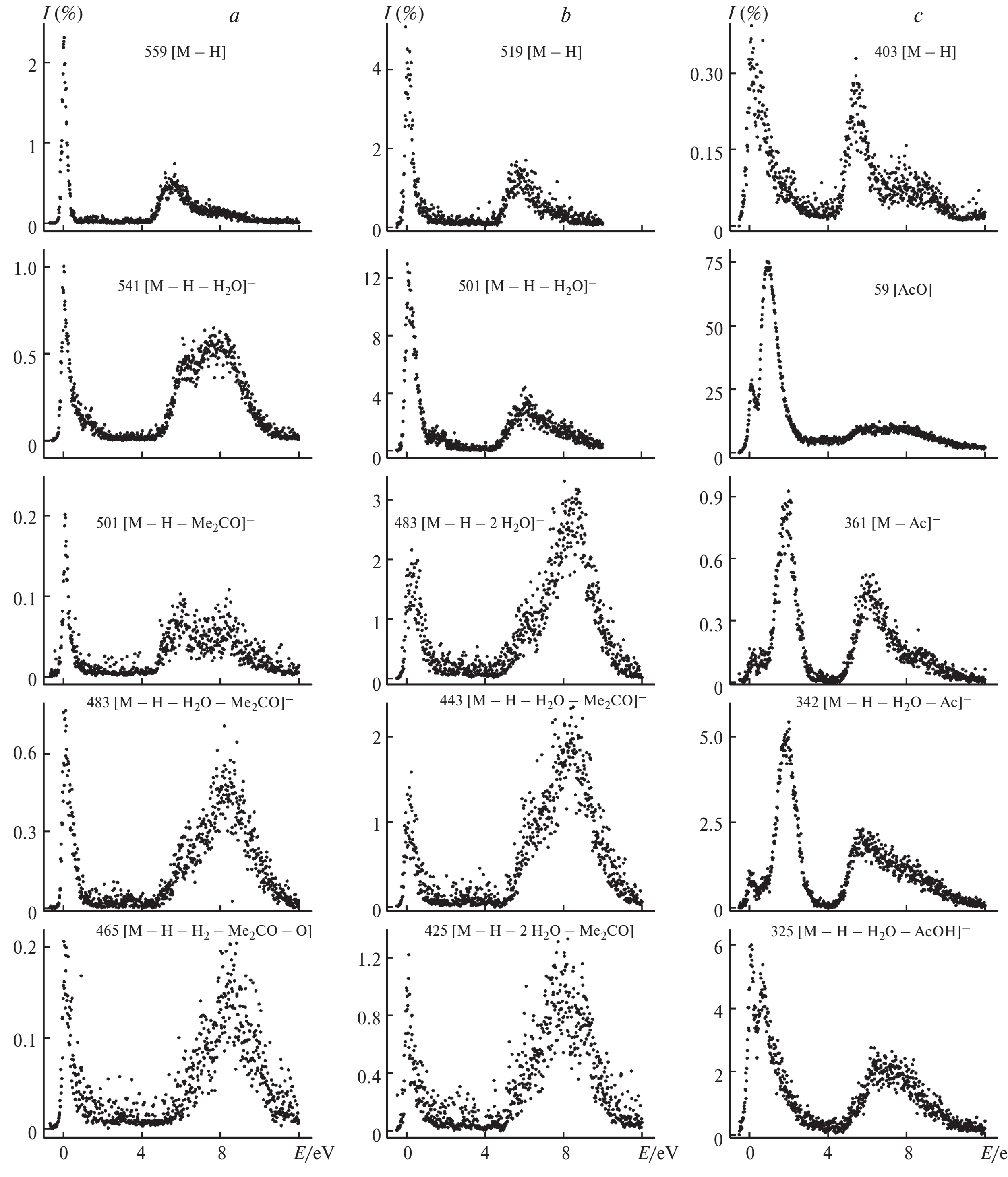


Fig. 1. Effective yield curves of NI from compounds **1** (*a*), **2** (*b*), and **3** (*c*) in a range of electron energies (*E*) of 0—12 eV. The values (m/z) of the corresponding ions are indicated for each curve; the peaks in the region of thermal electron energies are due to the isotopic contribution from ions with a lower mass (except NI with m/z 59 in compound **3**). The intensity (*I*) was normalized by the maximum of the curve of escape of ions $[M - H_2O]^{\bullet -}$ (100%).

position form in the high-energy region (see Fig. 1 and Ref. 1).

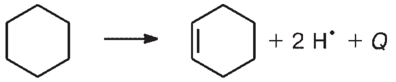
Based on the known or estimated enthalpies of formation (ΔH_f°)[4] of some simple molecules (*viz.*, cyclohexane, cyclohexanol, cyclopentane, cyclopentanol) containing the C=C and C=O double bonds, we analyzed the energies of their monomolecular decomposition with the elimination of the fragments 2 $H^\bullet$ and $H^\bullet + OH^\bullet$. The results

Table 1. Mass spectrum of NI in the REC mode for compounds **1—3** at thermal energies of electrons

Ion	m/z (I_{rel} (%))	
	1	**2**
$[M - H_2]^{\bullet -}$	558 (7.1)	518 (14.9)
$[M - 2\,H_2]^{\bullet -}$	556 (0.5)	516 (27.0)
$[M - 3\,H_2]^{\bullet -}$	—	514 (15)
$[M - 4\,H_2]^{\bullet -}$	—	512 (5)
$[M - H_2O]^{\bullet -}$	542 (100)	502 (100)
$[M - H_2 - H_2O]^{\bullet -}$	540 (2.6)	500 (32)
$[M - 2\,H_2 - H_2O]^{\bullet -}$	—	498 (37)
$[M - 3\,H_2 - H_2O]^{\bullet -}$	—	496 (6)
$[M - 2\,H_2O]^{\bullet -}$	524 (3.8)	484 (43)
$[M - H_2 - 2\,H_2O]^{\bullet -}$	—	482 (4)
$[M - H_2O - Me_2CO]^{\bullet -}$	484 (20)	444 (20)
$[M - H_2 - H_2O - Me_2CO]^{\bullet -}$	—	442 (4)
$[M - 2\,H_2O - Me_2CO]^{\bullet -}$	466 (1.9)	426 (5)

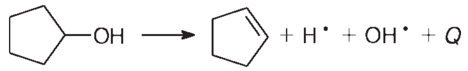
Ion	m/z (I_{rel} (%)) **3**
$[M - H_2]^{\bullet -}$	402 (2.0)
$[M - H_2O]^{\bullet -}$	386 (100)
$[M - H_2 - H_2O]^{\bullet -}$	384 (3.3)
$[M - H_2O - Me]^{-}$	371 (13)
$[M - 2\,H_2O]^{\bullet -}$	368 (5)
$[M - H_2 - H_2O - AcH]^{\bullet -}$	340 (5)
$[M - H_2O - AcOH]^{\bullet -}$	326 (75)
$[M - H_2 - H_2O - AcOH]^{\bullet -}$	324 (24)
$[M - H_2O - AcOH - Me]^{-}$	311 (12)
AcO^{-}	59 (30)
Metastable ions	
m^*_1 (m/z 386→371)	356.6
m^*_2 (m/z 386→326)	275.3
m^*_3 (m/z 326 → 311)	296.7

of thermochemical estimations show that these transformations are endothermic, and they require an energy of >4 eV to occur. For example, for the reaction



$\Delta H_f°$ /kJ mol^{-1} −123.1 −4.3 2•218.0

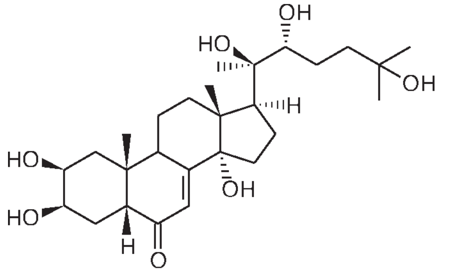
the heat (Q) is −563.4 kJ mol^{-1}. At the same time, for the elimination of the H_2 molecule the energy consumption decreases by the energy of H—H bond dissociation (436 kJ mol^{-1}). For the reaction



$\Delta H_f°$ /kJ mol^{-1} −242.6 36.0 218.0 39.3

Q = −535.9 kJ mol^{-1}, and in the case of H_2O elimination, it decreases by the energy of H—OH bond dissociation equal to 499.1 kJ mol^{-1}. This explains a high relative intensity of the peaks of NI $[M - H_2O]^{\bullet -}$ in the mass spectra of compounds **1—3**. Therefore, immediate (without rearrangements) cleavage of the C—H and C—O bonds in processes of dissociative capture of electrons with *thermal* and *superthermal* energies is barely possible because it needs very high energies of electron affinity (about 4—5 eV), which are not characteristic of organic molecules.

When analyzing the formation of the $[M - H_2O]^{\bullet -}$ ions from 20-hydroxyecdysone[1] in the low-energy region, we revealed that the OH group in position 14 participates in this process. However, this conclusion was based on the assumption about formation of the system of conjugated double bonds in these NI. This assumption is based on the data of electron transmission spectroscopy[5] for the stabilization of the lowest vacant MO in linear and cyclic unsaturated molecules by the conjugation of several double bonds. However, in 20-hydroxyecdysone the NI $[M - H_2O]^{\bullet -}$ could also be formed due to the elimination of the water molecule from any other position, for example, 2 and 3. In this case, the MS of compound **3** should contain the NI $[M - AcOH]^{\bullet -}$ peaks along with those of the indicated ions. However, they were not found, which confirms, to some extent, the validity of our assumptions.

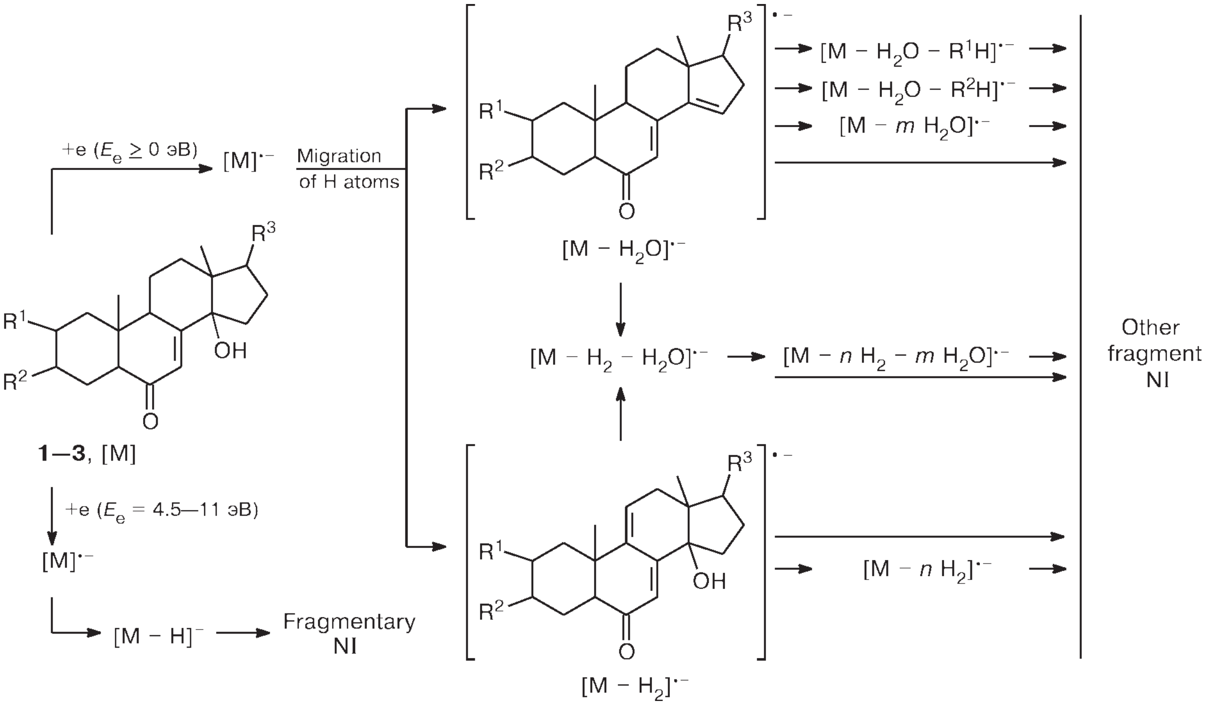


20-hydroxyecdysone

Scheme 1 shows the most general pathways of fragmentation of compounds **1—3** and 20-hydroxyecdysone[1] in the REC processes.

The elimination of the methane molecule involving methyl groups from positions 18 and 19 could also result in the formation of the system of conjugated bonds in the NI of ecdysteroids. However, as the MS of compounds **1** and **2** show, such processes do not occur in the compounds studied. Nevertheless, the MS of ecdysteroid **3** exhibits a series of peaks of the ions $[M - H_2O - Me]^{-}$, $[M - H_2O - AcOH - Me]^{-}$, $[M - H - H_2O -$

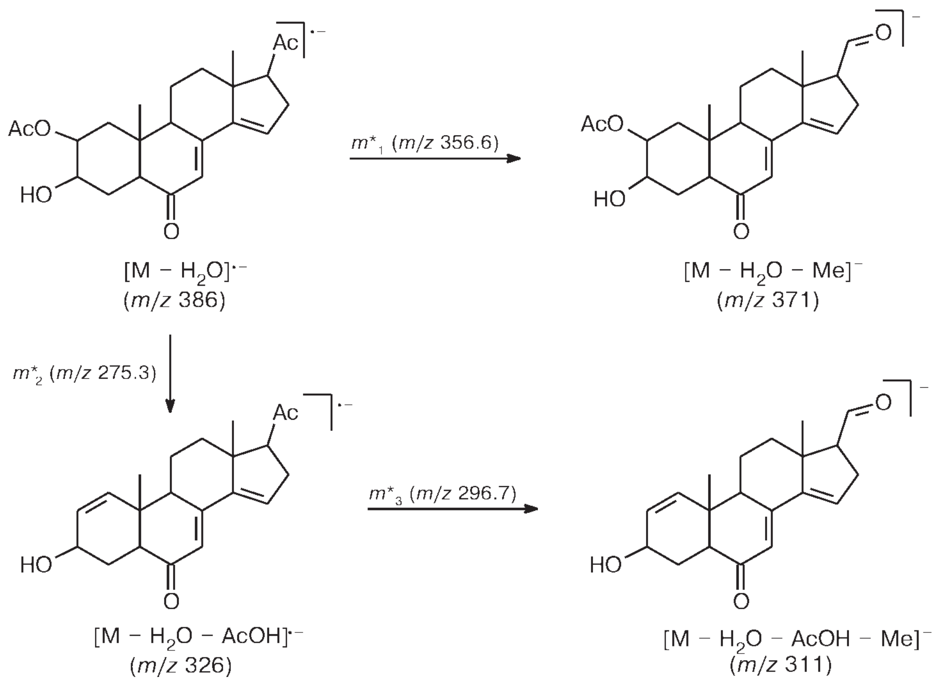
Scheme 1



– AcOH – Me]$^-$, and [M – H$_2$ – H$_2$O – AcOH – Me]$^-$ (see Fig. 1, *c* and Table 1). Their formation is due to the Ac and AcO groups only, and the peaks of the metastable ions m*$_2$ and m*$_3$ (see Table 1, Scheme 1) indicate that elimination of the Me group in the listed series of NI occurs from the acetyl group in position 17.

Thus, the processes of NI formation due to the migration of H atoms during REC by molecules are the com-

Scheme 2



mon feature of compounds of the ecdysteroid series. The fragmentation of their molecular NI during capture of low-energy electrons proceeds through the stage of elimination of the water or H_2 molecules.

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