Processes of dissociative electron capture by 20-hydroxyecdysone molecules

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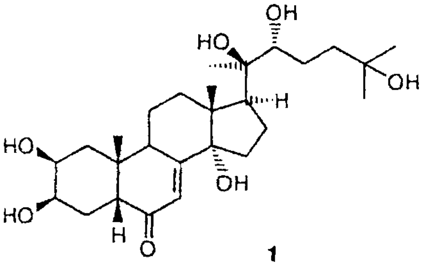
The peculiarities of dissociative electron capture by 20-hydroxyecdysone molecules with the formation of fragment negative ions were studied. In the region of high electron energies (5—10 eV), processes of skeleton bond rupture are accompanied by the elimination of H_2O and H_2 molecules. In the region of thermal energies of electrons (~0 eV), the mass spectrum is formed mainly by the $[M - n\,H_2O]^{\bullet-}$ (n = 1—3) and $[M - H_2 - n\,H_2O]^{\bullet-}$ (n = 0—3) ions that are generated exclusively by the rearrangement.

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

Electron impact mass spectrometry[1,2] with detection of positive ions is widely used for structural analytical studies of ecdysteroids, whereas mass spectrometry of negative ions (NI) with chemical ionization[2] is used to a lesser extent. In this work, we studied 20-hydroxyecdysone (**1**) by mass spectroscopy of NI in the regime of resonant capture of electrons (RCE).



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Experimental

Compound **1** was isolated from the plant *Serratulla coronata* as described previously[3] with m.p. 246 °C (AcOEt—MeOH, 9 : 1). The NI mass spectrum was obtained on an MI-1201 mass spectrometer adapted for the work in the regime of resonant electron capture[4] under the following conditions: electron current 1 μA, width of their energy distribution at the half-height $\Delta E_{1/2}$ = 0.3—0.4 eV, electron energy scan in the 0—14 eV range with calibration of the energy scale by maxima of the curves of effective yield (CEY) of SF_6^-/SF_6 (~0 eV) and NH_2^-/NH_3 (~5.65 eV) ions, temperature of the evaporator of the system of direct introduction of a sample 200 °C, and temperature of the ionization chamber ~220 °C.

Results and Discussion

Under the RCE conditions, compound **1** forms no long-lived molecular negative ions $[M^{\bullet-}]$. Only dissociative electron capture (DEC) was observed in the energy range from 0 to 10 eV, which is characterized by a low cross section due to the great number of saturated bonds in the molecule and the absence of electron-withdrawing groups. The last fact and the presence of six OH groups determine the specific features of the behavior of **1** under the DEC conditions. Rearrangement processes related to the migration of the hydrogen atom to the OH groups result in the elimination of one to three water molecules to form the $[M - n\,H_2O]^{\bullet-}$ ions with m/z 462, 444, and 426, and the peak of the $[M - H_2O]^{\bullet-}$ ions has the highest intensity in the mass spectrum (Fig. 1).

The relative intensity of other peaks in the mass spectrum does not exceed 1—3%. In addition to H_2O, the H atom and the H_2 molecule are eliminated to form

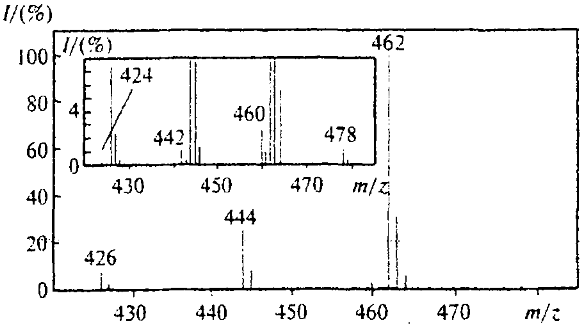

Fig. 1. Fragment of the NI mass spectrum of compound **1** in the interval m/z 420—485 recorded at thermal energies of electrons. The following peaks of ions are marked (m/z): 424 $[M - H_2 - 3\,H_2O]$, 426 $[M - 3\,H_2O]$, 442 $[M - H_2 - 2\,H_2O]$, 444 $[M - 2\,H_2O]$, 460 $[M - H_2 - H_2O]$, 462 $[M - H_2O]$, and 478 $[M - H_2]$.

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the $[M - H - n\ H_2O]^-$ ions (n = 1—3) with *m/z* 461, 443, and 425 and the $[M - H_2 - n\ H_2O]^{\cdot -}$ ions (n = 0—3) with *m/z* 478, 460, 442, and 424, respectively. The peaks of ions of the two last groups were detected only at the thermal energies of electrons. Their absence or a low yield in the region of non-thermal energies are probably related to the short lifetime of $M^{\cdot -}$ as compared to that of electron autoelimination.[5] By contrast, the ions formed by simple bond rupture (*m/z* 343, 325, 301, 255, 159, 141, and 85) followed by H shift were detected in the whole interval of electron energy or only in the high-energy region (Fig. 2).

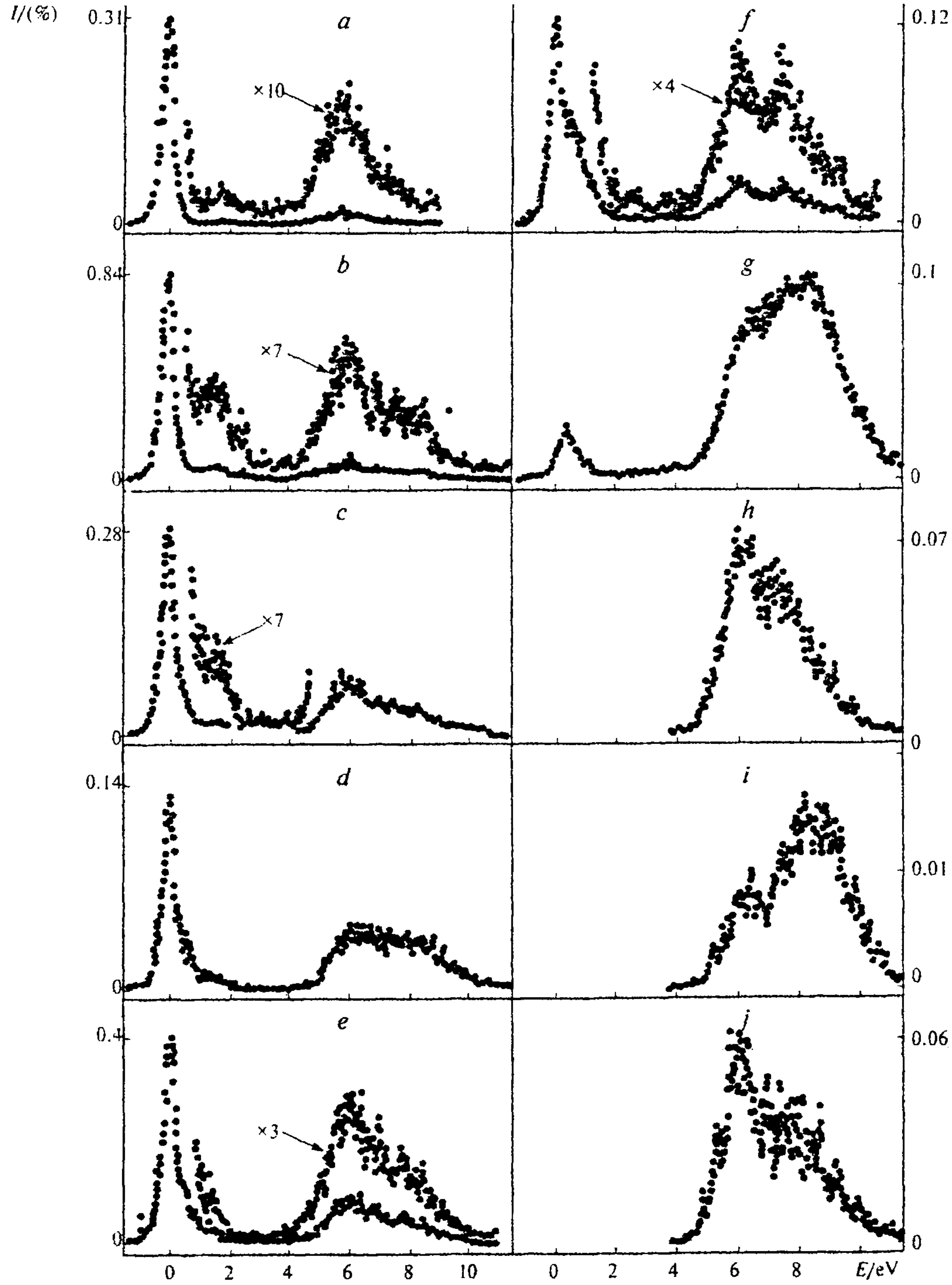
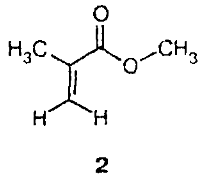


Fig. 2. Curves of effective yield of NI from compound **1** in the electron energy interval (*E*) of 0—11 eV at *m/z* 479 (*a*), 461 (*b*), 443 (*c*), 425 (*d*), 343 (*e*), 325 (*f*), 301 (*g*), 159 (*h*), 141 (*i*), and 85 (*j*). The intensity (*I*) was normed by the maximum of the curve of the yield of $[M - H_2O]^{\cdot -}$ ions (100%).

In the context of existence of the rearrangement of $[M - H_2 - n\ H_2O]^{\cdot -}$ and $[M - n\ H_2O]^{\cdot -}$ ions, the question arises about the magnitude of the electron affinity (E_{ea}) of the corresponding neutral species. It is known[6] that the simplest carbonyl-containing molecules in the ground electron state are characterized by a negative value of the electron affinity. However, when the C=O group is bound to the allyl group, the lowest unoccupied molecular orbital $\pi_{CO}{}^*$ is stabilized due to the interaction with the unoccupied $\pi_{CC}{}^*$ MO. For example, for the methyl methacrylate (**2**) molecule, the energy of the $\pi_{CO}{}^*$ MO, according to the MNDO quantum-chemical calculations,[7] has a negative value, which indicates positive electron affinity of the molecule in the ground state, although this compound forms no long-lived $M^{\cdot -}$ radical anion under RCE conditions. Similarly, for the fragmentation of **1** with the removal of H_2O or H_2, the formed π_{CC} bond is conjugated with the available π_{CC} and π_{CO} bonds and stabilizes the lowest unoccupied $\pi_{CO}{}^*$ MO to a still greater extent. Thus, one of the main conditions of the NI formation takes place for the $[M - H_2 - n\ H_2O]$ and $[M - n\ H_2O]$ fragments: E_{ea} of the corresponding radical or molecule is positive. A possible process of autoelimination of an electron (autoneutralization) cannot impede the detection of these fragment ions, because the excessive energy of the DEC process is very low or converted to the kinetic energy of the uncharged dissociation fragment and redistributed over the vibrational degrees of freedom of the ion.



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The curves of effective yield of the $[M - H - n\ H_2O]^-$ ions (n = 0—3) with m/z 479, 461, 443, and 425 (see Fig. 2) exhibit maxima in four resonance regions: ~0.5, 1—2, 5—7, and >7 eV, and the intense peaks of the $[M - H_2 - n\ H_2O]^{\cdot -}$ ions (n = 0—3) are observed in the region of thermal energies (see Fig. 1). The estimation of the energy balance of monomolecular decomposition, for example, for the $[M - H]^-$ ions with the elimination of the H atom from any position show a theoretical threshold >2 eV,[8,9] and thus, these ions cannot be formed in the energy interval of 0—2 eV. Of course, the elimination of one H_2O molecule with the formation of the C=C bond gives a small energy gain (0.4—0.5 eV),[8] which likely results in a more efficient yield of the $[M - H - H_2O]^-$ and $[M - H - 2\ H_2O]^-$ ions as compared to that of the $[M - H]^-$ ions (in the energy region of 1—2 eV). However, this additional energy is insufficient for the formation of these ions in the epithermal region (~0.5 eV). It can be assumed that the appearance of the ions discussed in this energy range is related to the effect of a "hot" band,[10] where some molecules exist in the vibration-excited states even at low temperatures, and the fragment ions can appear at an energy lower than the theoretical threshold. This is indirectly confirmed by the substantial (by two orders of magnitude) difference in the intensities of the peaks of the $[M - H_2O]^{\cdot -}$ and $[M - H_2]^{\cdot -}$ ions. This is related to the fact that the energy of elimination of the H_2 molecule to form the C=C bond is negative (−(0.2—0.3 eV)).[8]

The resonance state $M^{\cdot -}$ at $E_e \approx 6$ eV as a maximum or a shoulder on CEY of low-intensity ions is the most pronounced in the high-energy range (see Fig. 2). The existence of the $[M]^{\cdot -}$ state at $E_e \approx 7.5$ eV is indicated by the shape of the curves of yield of the ions with m/z 325 and 159, and CEY of other ions verify DEC by molecules **1** in the range $E_e \approx 7$—10 eV. The broad unstructured curves in this energy region are the result of overlapping of several nearby resonance states $[M]^{\cdot -}$, which can appear by the mechanism of electron-excited Feschbach resonance. This assumption is based on the results of our previous studies of the simplest carbonyl compounds.[11—13] For comparative analysis of the ion formation by molecules **1** in this energy region, we studied the mass spectrum of NI DEC of methyl methacrylate **2** (Fig. 3).

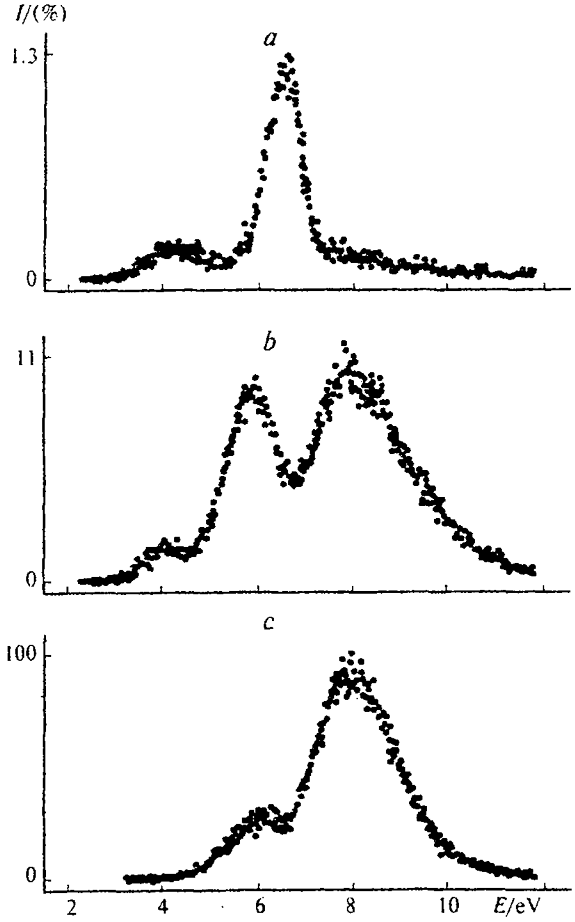

Fig. 3. Curves of effective yield of ions $[M - H]^-$ (*a*), $[H_2C{=}CCH_3]^-$ (*b*), and $[OCH_3]^-$ (*c*) from compound **2**. *I* is the intensity of the peak, and *E* is the electron energy.

According to the published data,[12,13] the resonance state $[M]^{\cdot -}$ in **2** at $E_e \approx 5.9$ eV is probably formed due to Vangier resonance, of which the lowest Rydberg states of the molecule are parent. The narrow resonance $[M - H]^-$ with a maximum at $E_e \approx 6.3$ eV indicates the dissociation of the electron-excited state $[M]^{\cdot -}$ similar to the $[M]^{\cdot -}$ state of the propylene molecule in the region of 6—7 eV.[14] Comparison of Figs. 2 and 3 reveals an analogy in the shape of CEY of the ions from compounds **1** and **2** in the region of high energies, which indicates a resemblance of the processes of electron capture by these molecules. According to the results of the study of alkenes by transmitted electron spectroscopy,[6] the resonance states that with E_e = 1.78 eV in ethylene and with E_e = 1.99 eV in propylene were attributed to the $^2[\pi^*]$ state that appeared by the mechanism of the shape resonance of the ground state of the molecules. It cannot be ruled out that the $[M]^{\cdot -}$ state in compound **1** in this energy region (1—2 eV) is formed according to a similar mechanism by capture of an electron to the unoccupied molecular orbital π_{CC}^*.

Thus, 20-hydroxyecdysone (**1**) does not form long-lived molecular negative ions under the conditions of resonance capture of electrons. Rearrangements with elimination of H_2O and H_2 are the specific feature of DEC.

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