A MASS-SPECTROSCOPIC STUDY OF THE TERPENOID COUMARINS MOGOLTADONE, GUMMOSIN, AND FARNESIFEROL A


We have previously reported the mass-spectral behavior of terpenoid coumarins of the kamalone (a), kamalol (b), and mogoltin (c) group [1, 2]. In the present paper we consider the dissociative ionization of mogoltadone (I), gummosin (II), and farnesiferol A (III) and their deuterium analogs (IV–VI).

These compounds differ from substances a, b, and c in the positions of the methyl substituents in the bicyclic terpene systems or in the position of the double bond in it, and in the numbers of hydroxy groups. Furthermore, compounds (I) and (a) differ from substances (II), (III), and (b) by the presence of a keto or hydroxy group in the terpene residues and the isomeric substances (II) and (III) have different orientations of the hydroxy group in position 3 of this residue. In view of this, it appeared of interest to determine the influence of the structural differences mentioned above between compounds (I–III) and (a, b, and c) on the nature of the fragmentation of their terpene ions $F_1$ and $F_2$ formed by Scheme 1 (directions A and B).

Substances (I–III) were isolated from various species of Ferula. Their structures have been established [3–6, 9]. The deuterium analogs of these substances were obtained synthetically. The mass spectra of (I–VI) are shown in Figs. 1 and 2. It follows from an analysis of these mass spectra that the main and subsidiary directions of the fragmentation of their molecular ions (see Scheme 1) are similar to the dissociation ionization of the terpenoid coumarins (a), (b), and (c) studied previously (see Scheme on following page).

The ratio $I_{F_1}/I_{F_2}$ for substances (I) and (a) are 2.2 and 3.4, respectively, i.e., in the mass spectra of these compounds the inequality $I_{F_1} > I_{F_2}$ is retained. For Kamalol (b), gummosin (II), and farnesiferol A (III), these
fragments have approximately the same intensities: $I_{\Phi_1} \approx I_{\Phi_2}$. From a comparison of the structures of the two groups of substances it follows that the mutual intensities of the ions $\Phi_1$ and $\Phi_2$ in the mass spectra of (a, I, II, and III) are determined only by the presence of a keto or hydroxy group in position 3' of the terpene residue and do not depend on the position of the methoxy group and the presence or absence of a double exocyclic bond in the bicyclic terpene system. The inequality $I_{\Phi_1} < I_{\Phi_2}$ exists in the mass spectrum of mogoltadone [2], i.e., a tendency to an increase in the intensity of the rearrangement ion $\Phi_2$ as compared with the fragmentary ion $\Phi_1$ is observed with an increase in the number of hydroxy groups in the terpene moiety of the molecule.

Information on the presence of a keto or hydroxy group in the terpene residue of terpenoid coumarins can also be obtained by considering the mutual intensities of the ions $\Phi_1$ and ($\Phi_1 - H_2O$). In the mass spectra of kamalone (a) and of kamalol (b) the ratios $I_{(\Phi_1 - H_2O)/\Phi_1}$ are 0.63 and 5.6, respectively [1], and in the case of the decomposition of mogoltadone (I), gummosin (II), and farnesiferol (III) they are 0, 16.3, and 8.6. The presence in the mass spectrum of mogoltadone (I) of the metastable peak $m^* - 184.3$ corresponding to the transition $\Phi_1 - (\Phi_1 - H_2O)$ (m/e 219 $\rightarrow$ m/e 201) showed the existence of this process in the decomposition (I) and indicates an extremely low intensity of the ion ($\Phi_1 - H_2O$) in the mass spectrum of (I) that does not exceed the background level. The different ratios $I_{(\Phi_1 - H_2O)/\Phi_1}$ for the decompositions of the stereoisometric compounds (II) and (III) permits the equatorial position of a hydroxy group at C atom of the terpene residue to be distinguished from the axial position.

The increased intensity of the fragment with m/e 177 in the mass spectrum of mogoltadone (I) is due to a loss by the terpene fragment $\Phi_1$ (m/e 219) of a $C_3H_6$ group. This is confirmed by the partial shift of the m/e 177 ion by two mass units in the mass spectrum of mogoltadone-$d_2$ (IV) and by its elementary composition, $C_{12}H_{17}O$ (accurate mass 177.1292). This process also takes place in the decomposition of the ion $\Phi_1$ (m/e 221)