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

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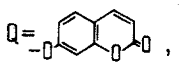
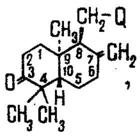
UDC 543.51 +547.985

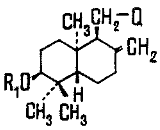
We have previously reported the mass-spectral behavior of terpenoid coumarins of the kamalone (a), kamalol (b), and mogoltin (c) group [1, 2]. In the present paper we consider the dissociative ionization of mogoltadone (I), gummosin (II), and farnesiferol A (III) and their deuterium analogs (IV-VI).

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).

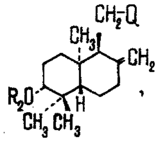




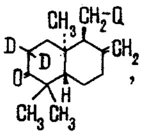
I



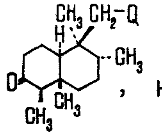
II. R_1=-H, V. R_1=-D



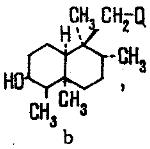
III. R_2 = -H, VI. R_2 = -D



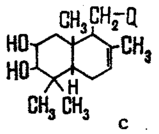
IV



a



b



c

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_{Φ_1}/I_{Φ_2} for substances (I) and (a) are 2.2 and 3.4, respectively, i.e., in the mass spectra of these compounds the inequality $I_{\Phi_1} > I_{\Phi_2}$ is retained. For Kamalol (b), gummosin (II), and farnesiferol A (III), these

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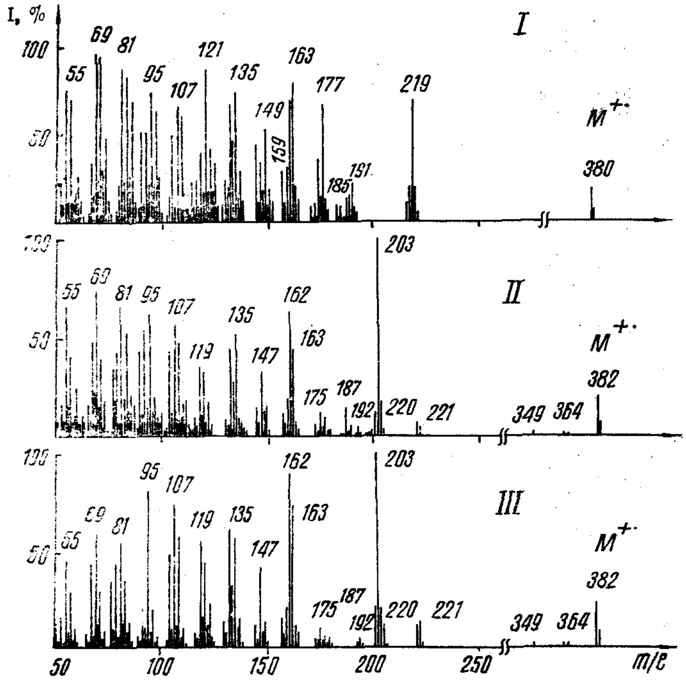
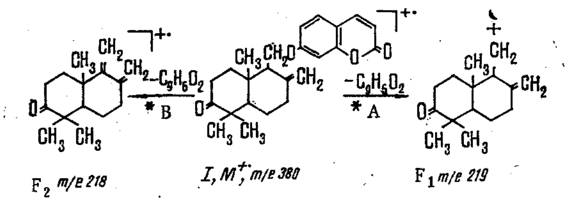


Fig. 1. Mass spectra of mogoltadone (I), gummosin (II), and farnesiferol A (III).



Scheme 1

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 Φ_1 and Φ_2 in the mass spectra of (a, I, b, 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 mogoltin [2], i.e., a tendency to an increase in the intensity of the rearrangement ion Φ_2 as compared with the fragmentary ion Φ_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 Φ_1 and $(\Phi_1 - H_2O)$. In the mass spectra of kamalone (a) and of kamalol (b) the ratios $I_{(\Phi_1 - H_2O)}/I_{\Phi_1}$ 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 $\Phi_1 \rightarrow (\Phi_1 - H_2O)$ (m/e 219 → 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 $I_{(\Phi_1 - H_2O)}/I_{\Phi_1}$ for the decompositions of the stereoisometric compounds (II) and (III) permits the equatorial position of a hydroxy group at $C_{3'}$ 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 Φ_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 Φ_1 (m/e 221)

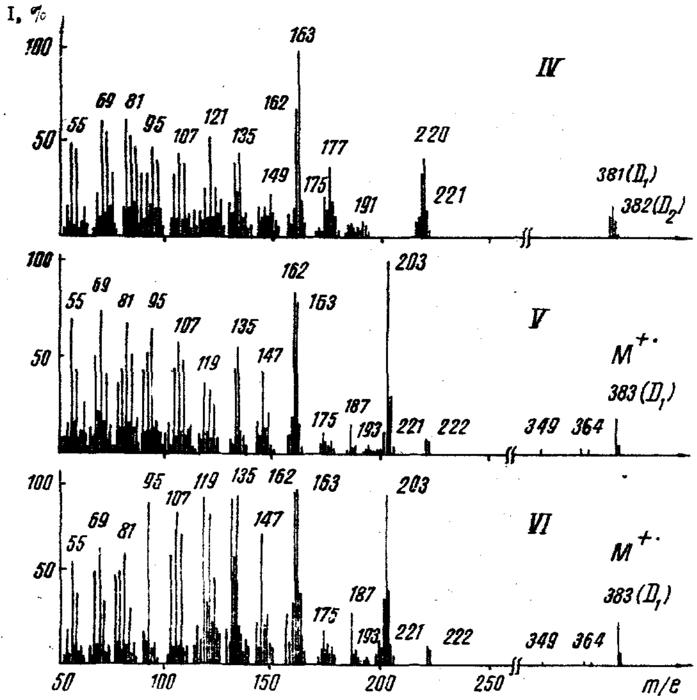
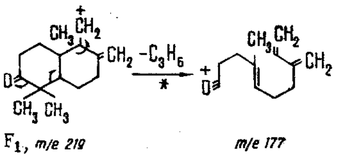


Fig. 2. Mass spectra of mogoltadone-d_2 (IV), gummosin-d (V), and farnesiferol A-d (VI).

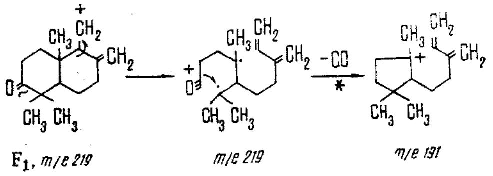
in the mass spectra of gummosin (II) and of farnesiferol A (III) and leads to the formation of an ion with m/e 179, which is displaced by one mass unit in the mass spectra of deuterium analogs of these substances, (V) and (VI). In view of the fact that the ejection of the neutral particle C_3H_6 is not observed in the mass spectra of kamalone (a) and kamalol (b), its elimination by the terpene ion Φ_1 in the dissociative ionization of compounds (I-III) can be explained by the presence in the terpene moieties of their molecules of a gem-dimethyl grouping in the α position to the keto or hydroxy group. This process probably takes place by Scheme 2. In the case of the decomposition of mogoltin (c), the ejection of the neutral particle C_3H_6 as a result of the same structural factor is observed in the third stage of the decomposition of the ion Φ_1 after the elimination of two H_2O molecules by it [2].



Scheme 2

The ease of cleavage of the carbon–carbon bond between the $C_{3'}$ atom to which a ketal or hydroxy group is attached, and the quaternary $C_{4'}$ atom to which a gem-dimethyl grouping is attached is apparently responsible for the appearance in the mass spectra of (I and II) and (III) of the ions $(\Phi_1 - CO)^+$ and $(\Phi_1 - HCO)^+$, respectively, which are not found in the decomposition of compounds (a) and (b). These ions with m/e 191 (I) and 192 (II, III) are partly shifted by two and one units in the region of high masses in the mass spectra of the deuterium-substituted substances (IV-VI). In connection with this process of their formation, we can give Scheme 3 as illustrated for compound (I). Thus, the facts mentioned are due to the vicinal position of the carbonyl or hydroxy group in relation to the gem-dimethyl grouping in the bicyclic terpenoid systems of compounds (I-III) (see Scheme on following page.)

In contrast to the dissociative ionization of kamalone (a) and kamalol (b), the loss of methyl radicals by the terpene ions Φ_1 and Φ_2 in the mass spectra of (I-II) takes place not in the first but in the second stage of their decomposition, after the ejection of an H_2O molecule, and is limited to the splitting out of only one CH_3 group, which is probably due to the different positions of the methyl groups in the terpene residues of these



Scheme 3

substances. This process takes place most intensively in the decomposition of the rearranged terpene ions Φ_2 with m/e 218 (I) and 220 (II, III), as the result of which fragments are formed with m/e 185 (I) and 187 (II, III), the appearance of which is confirmed by the metastable peaks $m^* = 171.2$ (I) and $m^* = 173$ (II, III).

Thus, a comparison of the dissociative ionizations of the terpenoid coumarins (a, b, c, and I-III) confirms the possibilities of the mass-spectrometric method for determining a number of structural features of the terpenoid residues of their molecules.

EXPERIMENTAL

The mass spectra of substances (I-VI) were taken on a standard MKh-1303 instrument fitted with means for the direct introduction of the sample into the ion source, at an ionizing voltage U = 70 V and at temperatures of 150°C (I, IV) and 160°C (II, III, V, VI). Compounds (IV-VI) were obtained by published methods [7, 8]. The high-resolution mass spectrum of (I) was measured on a IMS-01-CG-2 instrument.

SUMMARY

The mass spectra of the terpenoid coumarins mogoltadone (I), gummosin (II), and farnesiferol A (III) and their deuterium analogs (IV-VI) have been studied. It has been shown that the main and auxiliary directions of the decomposition of the molecular ions of the substances are similar to the dissociative ionization of the terpenoid coumarins studied previously. The fragmentation of the ions corresponding to the terpene residues of these compounds permits the determination of the presence of keto and hydroxy groups in the bicyclic terpene system and provides the possibility of distinguishing the stereoisomers (II) and (III) with different orientations of the hydroxy groups and also of determining the presence in the terpene residue of a gem-dimethyl grouping in the vicinal position to the keto or hydroxy group.

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