A MASS-SPECTROMETRIC STUDY OF LINEAR MONOHYDROXY- AND MONOACYLOXYDIHYDROFUROCOUMARINS

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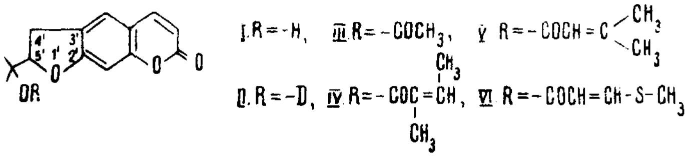
The mass spectra of angular monohydroxy- and monoacyloxydihydrofurocoumarins have been studied previously [1]. It was of interest to compare the fragmentation of these substances with the fragmentation of the linear compounds isomeric with them and to determine the possibilities of the mass-spectrometric method for solving structural problems in this series of compounds. For this purpose, we have studied the mass spectra of marmezin (I), [D]marmezin (II), O-acetylmarmezin (III), deltoin (IV), pranchimgin (V), and seseliflorin (VI) [2-5].



The main fragments and their relative intensities in the mass spectra of compounds (I-VI) are given in Table 1.

The mass spectrum and fragmentation of marmezin have been described previously [6]. In the published mass spectrum of marmezin, in contrast to its angular isomer columbianetin [1], there are no M^+-CH_3, M^+-CH_3-H, and M^+-OH ions (m/e 231, 230, 229). However, in other respects their spectra are very similar. We decided to check whether this difference between them does exist and to study the mass spectrum of marmezin again. For a more far-reaching investigation of its fragmentation, we also studied the mass spectrum of [D] marmezin.

In the mass spectrum of marmezin we found the ions M^+-CH_3, M^+-CH_3-H, and M^+-OH. The mass spectrum of this substance differed from the mass spectrum of its isomer columbianetin only in the region of high masses, where we detected the ion M^+-H_2O-H (m/e 227), which Abdel-Hay et al. [6] also stated to be absent.* The appearance in the mass spectrum of marmezin of ions in the region of high mass numbers with m/e 231-227 may be shown by Scheme 1, which is similar to this process in the mass spectrum of [D]marmezin. In spite of the low intensity of these ions (see Table 1), they are important since they show the presence in marmezin of a hydroxyisopropyl grouping (appearance of the ions Φ_1, Φ_3, Φ_4) and also the capacity of the dihydrofuran ring of ions Φ_1 and Φ_4 for eliminating a hydrogen atom (formation of ions Φ_2 and Φ_5). The angular and linear dihydropyranocoumarins isomeric with marmezin (xanthogallol and agasylol) do not show the ions Φ_2, Φ_3, and Φ_5 [7].

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*The absence of these ions from the published mass spectrum can probably be explained by the recording conditions, which differed from ours, although they are given incompletely by Abdel-Hay et al. [6]: the energy of the ionizing electrons and the temperature at which the mass spectrum of marmezin was recorded are not given.

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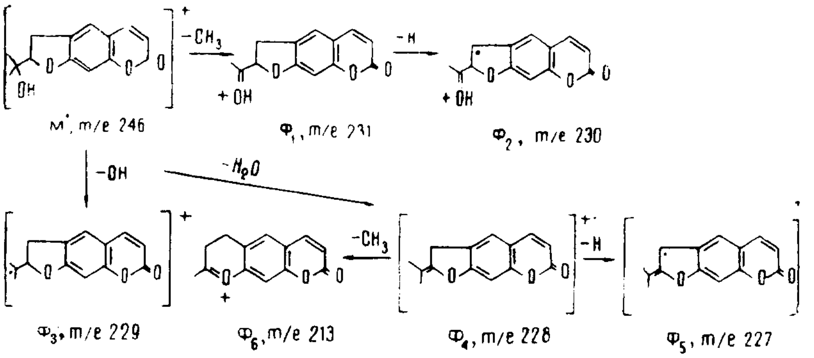
TABLE 1. Main Fragments and Their Relative Intensities in the Mass Spectra of the Linear Monohydroxy- and Monoacyloxydihydrofurocoumarins

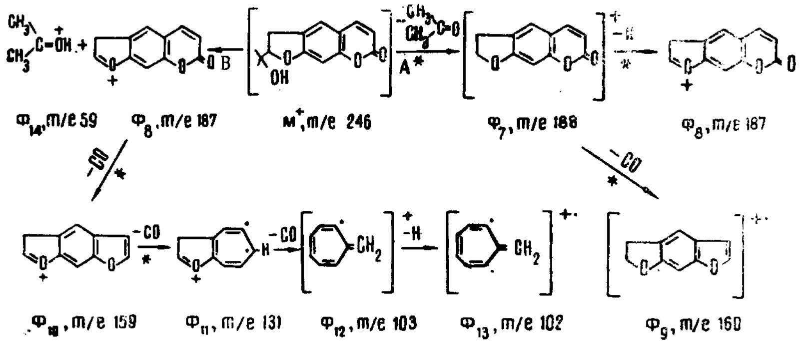
Substance	Mass numbers, m/e (relative intensities, %)								
I	246 (65) 202 (1,2) 175 (17) 103 (9,5)	231 (2,6) 201 (1,4) 161 (3,0) 102 (11)	230 (1,3) 200 (1,4) 160 (42) 77 (20)	229 (2,1) 199 (1,8) 159 (17) 73 (14)	228 (3,6) 189 (13) 158 (9,5) 71 (17)	227 (1,0) 188 (92) 147 (7,2) 60 (8,3)	214 (4,7) 187 (100) 131 (31) 59 (92)	213 (24) 186 (8,4) 128 (4,8) 57 (25)	203 (1,2) 176 (7,2) 115 (3,0) —
II	247 (27) 203 (0,7) 186 (15) 148 (3,7) 77 (28)	232 (2,5) 202 (0,8) 177 (8,1) 147 (5,6) 73 (14)	231 (1,3) 201 (0,7) 176 (13) 132 (12) 71 (9,4)	230 (0,7) 200 (0,7) 175 (11) 131 (79) 60 (76)	228 (1,3) 199 (0,8) 162 (6,3) 129 (6,7) 59 (69)	227 (0,4) 190 (12) 161 (24) 115 (12) 57 (25)	214 (6,3) 189 (64) 160 (20) 104 (8,1) —	213 (19) 188 (100) 159 (20) 103 (11) —	204 (0,6) 187 (70) 158 (16) 102 (16) —
III	288 (5,5) 199 (2,5) 158 (3,2) 69 (24)	247 (0,8) 188 (13) 147 (4,5) 59 (41)	246 (0,9) 187 (31) 131 (24) 57 (82)	231 (7,7) 185 (11) 128 (6,4) 56 (37)	299 (6,8) 176 (15) 115 (8,2) —	228 (31) 175 (17) 103 (10) —	214 (6,2) 171 (2,7) 102 (23) —	213 (100) 160 (6,4) 77 (30) —	200 (2,7) 159 (14) 71 (15) —
IV	328 (10) 185 (7,9) 115 (5,7)	246 (1,4) 175 (1,4) 103 (3,6)	229 (11) 176 (2,1) 102 (4,3)	228 (56) 171 (2,9) 83 (70)	214 (22) 159 (8,6) 77 (10)	213 (100) 158 (4,3) 57 (43)	200 (2,8) 147 (1,4) 55 (75)	199 (2,7) 131 (11) —	187 (13) 128 (5) —
V	328 (5,0) 176 (1,0) 83 (100)	246 (1,0) 175 (1,5) 77 (11)	228 (36) 171 (2,0) 55 (62)	214 (14) 147 (1,0) —	213 (90) 131 (12) —	200 (2,0) 128 (4,0) —	199 (1,9) 115 (5,0) —	187 (8,0) 103 (4,0) —	185 (6,0) 102 (5,5) —
VI	346 (4,4) 171 (3,3) 102 (7,7)	246 (1,1) 159 (6,0) 101 (66)	229 (8,8) 158 (4,4) 77 (8,2)	228 (44) 147 (1,1) 73 (16)	214 (15) 131 (15) 57 (27)	213 (100) 128 (5,5) 55 (56)	187 (11) 118 (4,9) —	185 (9) 115 (5,2) —	175 (3,8) 103 (10) —

It follows from the mass spectrum of [D]marmezin that the ions Φ_1 and Φ_3 are only partially shifted into the region of higher masses, just like the Φ_{14} fragment with m/e 59 (Scheme 2), which represents the ion of the hydroxyisopropyl radical. These facts show an exchange between the hydrogen of the hydroxy group and the hydrogen atom on the 5'-carbon atom in the molecular ion of marmezin. On the basis of the isotopic effect, which changes the probability of the formation of the ions mentioned in the mass spectrum of [D]marmezin, it is possible to evaluate the magnitude of this exchange from the ratio of the peaks of the ions with m/e 59 and 60 only partially. If it is borne in mind that the cleavage of a C−C bond takes place with a greater probability when deuterium is present on one of the carbon atoms, the exchange mentioned apparently proceeds to the extent of not less than 25%.



Scheme 1

In the decomposition of the molecular ion of [D]marmezin, the elimination of a CH_3 group and of a molecule of water takes place more intensively than in the fragmentation of marmezin, and so does the formation of ions in the region of medium mass numbers. As a result, the resistance to decomposition of the molecular ion of [D]marmezin is 2.7 times lower than that of marmezin itself.

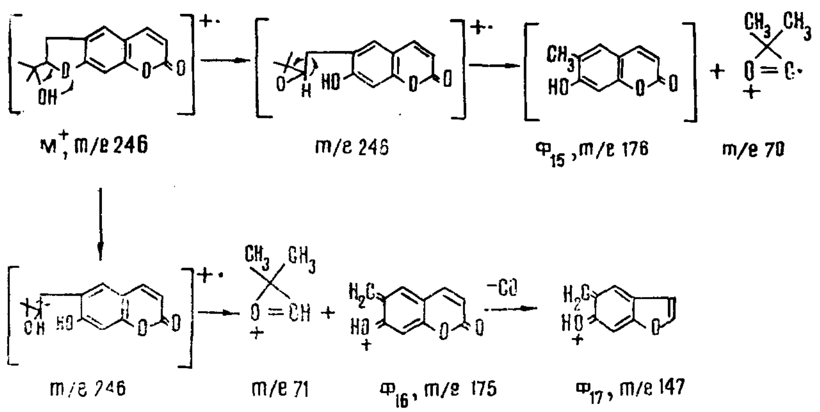


Scheme 2

The main direction of fragmentation giving the most intense ions in the mass spectrum of marmezin is connected with the splitting out of the hydroxyisopropyl group of its molecular ion with and without the transfer of the hydrogen atom of the hydroxy group to the coumarin part of the molecule. The appearance of the main ions by this route, which is shown in Scheme 2, is confirmed by the mass spectrum of [D]marmezin.

In the mass spectrum of marmezin [6], the directions of decomposition shown in Scheme 2 by asterisks are confirmed by metastable peaks. Abdel-Hay et al. [6] put forward a hypothesis of the partial formation of the Φ_8 ion from the M^+ ion by route B (see Scheme 2) because of the presence in the mass spectrum of marmezin of the Φ_{17} ion (m/e 59). However, they observed no metastable peak for this transition. We have not observed this peak for this direction of decomposition either, but the shift of the Φ_{14} ion by 1 amu in the mass spectrum of [D]marmezin shows that the latter has the structure given in Scheme 2 and is formed together with the Φ_7 ion by route B.

In the mass spectrum of [D]marmezin, the intensity of the Φ_{10} ion (m/e 159) has risen twofold as compared with the intensity of the Φ_9 ion (m/e 161), while the relative intensities of the Φ_8 and Φ_7 ions (m/e 187 and 189), from which they were formed have remained as before. This permits the conclusion that the Φ_{10} ion arises partially from the Φ_9 ion as a result of the loss by the latter of a hydrogen atom, in the same way as the Φ_8 ion is formed from the Φ_7 ion.

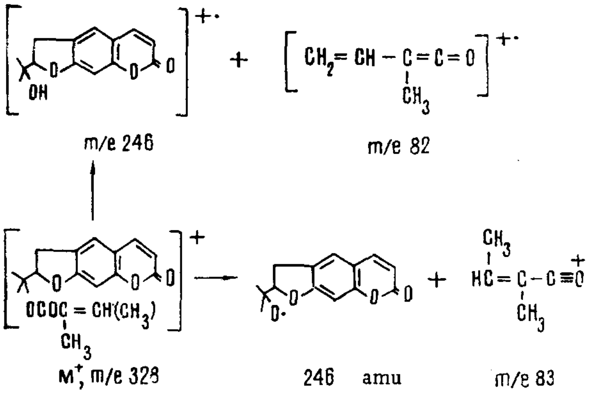


Scheme 3

The direction of fragmentation of marmezin that is second with respect to intensity is its decomposition in the manner shown in Scheme 3. In the mass spectrum of [D]marmezin the Φ_{15} and Φ_{16} ions are partially shifted by 1 amu in the direction of higher masses. The absence of a complete shift is readily explained by the hypothesis put forward above of the existence of exchange between the hydrogen of the hydroxy group and the hydrogen on the C_5 carbon atom in the molecular ion of marmezin. For the same reason, Φ_{17} undergoes only a partial shift. This direction of fragmentation was not considered in previous investigations [1, 6], although, as will be shown below, it has analytical importance.

The mass spectra of compounds (III-VI) (see Table 1), which belong to the class of linear monoacyloxydihydrofurocoumarins, are very similar to the mass spectra of the angular compounds isomeric with them [1].

In the fragmentation of substances (III-VI) ions are formed in the regions of high and medium mass numbers at the same m/e values as in the fragmentation of marmezin, but with different relative intensities of the lines.



Scheme 4

The difference consists only in the fact that the peak of the molecular ion of marmezin is fairly large (7.6% of the total ion current), while the molecular ions of its acyl derivatives are less stable, and their intensities vary between 0.7 and 1.7% of the total ion current. Additional to the fragmentation of these substances are the acyl and ketene decompositions of their molecular ions (Scheme 4) due to the fact that the molecules (III-VI) each have an acyloxy group. The acyl decomposition is the most intensive in the mass spectra of compounds (III-VI) and takes place with the localization of positive charge almost wholly on the acyl residue. From the presence of this ion and also of the ion M^+-ROH (m/e 228) in the mass spectra of the monoacyloxydihydrofurocoumarins, it is possible to determine the molecular weight of the acid residue present in a given compound of this type.

On comparing the mass spectra of deltoin (IV) and pranchimgin (V) it can be seen that in the series of substances studied the mass-spectrometric method permits the acyl radical of angelic acid to be distinguished from the acyl residue of senecionic acid. As for the monoacyloxydihydropyranocoumarins [7], in the acyl radical of angelic acid (see Table 1, IV) the intensities of the ions with m/e 83 and 55 are approximately the same: $I_{83} = 0.9\ I_{55}$; while for the acyl radical of senecionic acid (see Table 1, V) the ion with m/e 83 is considerably more intense than that with m/e 55 ($I_{83} = 1.7\ I_{55}$). This can be explained by the assumption that in the acyl radical of senecionic acid the CH_3 group apparently participates to a greater extent in the stabilization of this ion by the hyperconjugation mechanism than in the angeloyl radical.

As already mentioned, the mass spectra of the linear monohydroxy- and monoacyloxydihydrofurocoumarins are very similar to the mass spectra of their angular isomers. However, small differences enable the two classes of compounds to be distinguished by the mass-spectrometric method. The mass spectra of the angular substances lack the Φ_{17} ion (m/e 147; see Scheme 3), since the angular position of the dihydrofuran ring apparently affects the stabilization of the ions to a somewhat greater extent, and their decomposition takes place with a greater comsumption of internal energy than that of the corresponding ions in the linear compounds, which decreases the probability of the fragmentation of the former in the subsequent stages of decomposition.

The mass-spectrometric method easily permits the linear and angular monohydroxy- and monoacyloxydihydrofurocoumarins to be distinguished from the monohydroxy- and monoacyloxydihydropyranocoumarins isomeric with them [7].

The main difference in the mass spectra of these compounds is that for substances of the first class the Φ_8 ion (m/e 187, see Scheme 2) is more pronounced that the Φ_{16} ion (m/e 175, see Scheme 3) and for the second class the situation is the opposite. This relationship is expressed particularly clearly for the monohydroxy derivatives, but it is also preserved reliably for the monoacyloxy derivatives.

Thus, the characteristic features of the mass spectra of the linear monohydroxy- and monoacyloxydihydrofurocoumarins that have been studied show that the mass-spectrometric method can be used successfully for structural-analytical purposes in this series of compounds.

EXPERIMENTAL

The mass spectra of compounds (I-VI) were taken on a modified MKh-1303 instrument at an ionizing voltage U of 65 V and at the following temperatures: for (I) and (II) 130°C, for (III) 105°C, for (IV) and (V) 86°C, and for (VI) 120°C; using the direct introduction of the sample into the ion source.

SUMMARY

The mass spectra of the following six linear monohydroxy- and monoacyloxydihydrofurocoumarins have been studied: marmezin (I), [D]marmezin (II), O-acetylmarmezin (III), deltoin (IV), pranchimgin (V), and seseliflorin (VI). It has been shown that it is possible by the mass-spectrometric method of analysis to determine the molecular weights of the acids the acyl radicals of which are present in these substances, to distinguish the acyl radical of angelic acid from that of senecionic acid, and also to distinguish this class of compounds from the angular dihydrofurocoumarins and from the angular and linear dihydropyranocoumarins isomeric with them.

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