MASS-SPECTROMETRIC STUDY OF SOME DERIVATIVES OF FURO- AND DIHYDROFUROCOUMARINS

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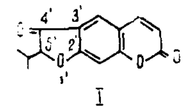
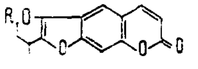
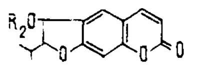
Various published papers have given the results of investigations of the mass spectra of columbianetin (IX), marmesin (X), and their acyl derivatives [7-9], which belong to the class of angular and linear dihydrofurocoumarins, and also the mass spectra of the angular and linear dihydropyranocoumarins, isomeric with these compounds: xanthogalol (XI), agasyllol (XII), and their acyl derivatives [5, 10]. In the present communication we consider the mass spectra of substances related to them in structure [oreoselone (I), oreoselone propionate (II), oreoselone butyrate (III), oreoselone valerate (IV), peucedanin (V), dihydrooreoselol (VI), [D]dihydrooreoselol (VII), and dihydrooreoselol propionate (VIII)] in order to establish the main laws of their decomposition under the action of electron impact and to determine the possibility of distinguishing these substances from previously studied compounds by mass spectrometry. Compound (V) was isolated from the plant Peucedanum morisonii Bess [1], and substances (I-IV and VI-VIII) were obtained from it synthetically. The main fragments and their relative intensities in the mass spectra of substances (I-VIII) are given in Table 1.

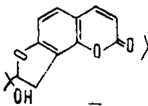


I

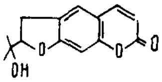




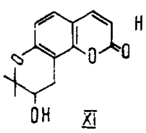
II. R_1=$-COCH_2CH_3$
III. R_1=$-CO(CH_2)_2CH_3$
IV. R_1=$-CO(CH_2)_3CH_3$
V. R_1=$-CH_3$
VI. R_2=$-H$
VII. R_2=$-D$
VIII. R_2=$-COCH_2CH_3$



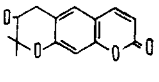
IX



X



XI



XII

The fragmentation of oreoselol (I) under the action of electron impact proceeds in several competing directions. The main one of them is the splitting off of an isopropyl radical by the M^+ ion with the transfer of one of its hydrogen atoms to the oxygen of the carbonyl group of the dihydrofuran ring, as shown in Scheme 1 (I), route A, which is typical for the decomposition of alkylated monocyclic ketones [11]. As a result, an ion with m/e 202 – the main ion in the mass spectra of oreoselone – is formed. Then the ion with m/e 202 eliminates a CO molecule giving a fragment with m/e 174, which then loses two CO groups, directly or after the elimination of a hydrogen atom, leading to the appearance of ions with m/e 146 and 118, and 145 and 117, respectively. Although no metastable peak has been detected for the ejection of a formaldehyde molecule from the ketone form of the ion with m/e 202, this decomposition pathway appears to us to be very possible and explains the appearance of a series of ions with m/e 172, 144, 116, and 88.

The second direction of the decomposition of oreoselone in terms of intensity is the elimination by its molecular ion of a C_4H_7 group, as a consequence of which an ion with m/e 189 arises. This process, illustrated in Scheme 1 [compound (I), route B], includes the cleavage of the α bond relative to the ether

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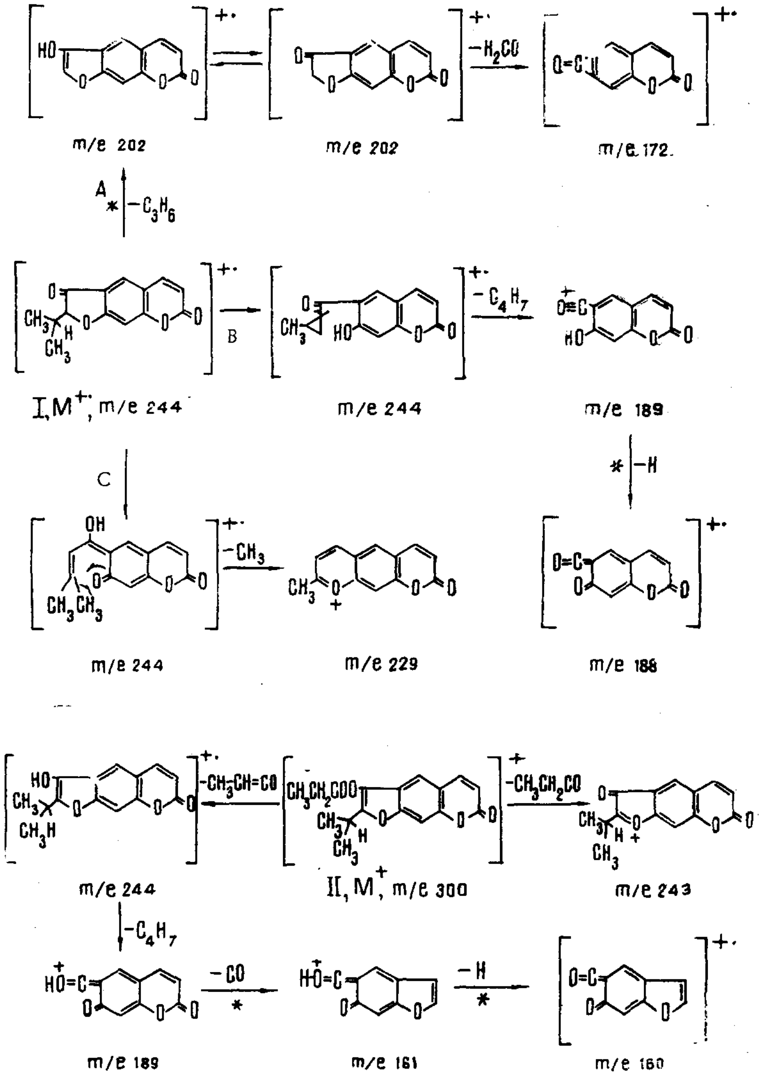
TABLE 1. Mass Numbers and Relative Intensities of the Fragments Observed in the Mass Spectra of Compounds (I-VIII)

Compound	Mass number, m/e (relative intensities, %)										
I	244 (31)	229 (27)	202 (100)	201 (4)	189 (23)	188 (28)	174 (5)	173 (4)	172 (3)	161 (4)	160 (10)
	146 (2)	145 (4)	144 (3)	133 (2)	132 (4)	117 (2)	116 (5)	105 (3)	104 (4)	89 (5) 91 (2)	88 (7)
	77 (5)	76 (8)									
II	300 (14)	244 (45)	243 (8)	229 (54)	228 (13)	215 (8)	213 (6)	201 (9)	200 (11)	189 (12)	188 (3)
	185 (2,4)	173 (2,8)	172 (5,6)	171 (8)	161 (11)	160 (11)	159 (5,6)	145 (8)	144 (6)	143 (3,8)	133 (7)
	132 (9,4)	131 (5)	129 (6)	128 (7,2)	127 (5,3)	117 (6,6)	116 (10)	115 (13)	105 (11)	104 (6)	89 (12) 91 (7)
	88 (13)	87 (9,8)	77 (11)	76 (10)	69 (9,4)	60 (9,4)	59 (10)	57 (100)			
III	314 (3.3)	244 (18)	243 (5.2)	229 (19)	228 (10)	215 (4)	213 (1,9)	201 (5,5)	200 (8)	189 (8)	188 (1,7)
	185 (1,0)	173 (3,6)	172 (3,3)	171 (6,7)	161 (6,9)	160 (6,9)	159 (3,6)	145 (5,6)	144 (4,8)	143 (2,7)	133 (4,5)
	132 (5)	131 (2,5)	129 (3,6)	128 (4,8)	127 (3,6)	117 (5,5)	116 (7,9)	115 (8,6)	105 (7,1)	104 (3,8)	91 (4)
	89 (7,9)	88 (10)	87 (6,7)	77 (8,3)	76 (7,6)	71 (61)	43 (100)				
IV	328 (7,3)	244 (42)	243 (7,8)	229 (33)	228 (15)	215 (8.1)	213 (1,9)	201 (6,8)	200 (9,4)	189 (13)	188 (1,6)
	187 (4,7)	173 (4,2)	172 (4,9)	171 (7,7)	161 (8,3)	160 (7,8)	159 (3,6)	145 (7,8)	144 (7,3)	143 (2,6)	133 (1,7)
	132 (6,3)	131 (6,8)	129 (3,5)	128 (6,5)	127 (4,6)	117 (7.3)	116 (10)	115 (13)	105 (9,4)	104 (2,1)	91 (5,9)
	89 (9,9)	88 (12)	87 (7,3)	85 (100)	77 (14)	76 (14)	69 (11)				
V	258 (26)	243 (100)	229 (2,3)	228 (5,1)	215 (1,4)	200 (4)	189 (2,3)	172 (1)	171 (2)	161 (1,1)	160 (2)
	145 (1,3)	144 (1,3)	132 (1,3)	131 (1,1)	129 (1,2)	117 (1,1)	116 (1,1)	115 (2,4)	89 (1,1)	88 (2,1)	87 (1,2)
	77 (1,1)	76 (1,1)	69 (2,3)	63 (1,4)	62 (2,1)						
VI	246 (55)	231 (4,4)	229 (4,4)	228 (6,6)	213 (100)	204 (3,2)	203 (4,4)	200 (4,4)	199 (7,7)	191 (29)	190 (44)
	189 (22)	185 (6,1)	175 (5,5)	174 (3,3)	173 (6,6)	163 (66)	162 (20)	161 (6,6)	159 (3,3)	158 (4,4)	157 (3,3)
	147 (4,4)	145 (5,5)	134 (3,3)	133 (4,5)	129 (6,6)	128 (6)	127 (4,4)	119 (4,4)	117 (4,4)	115 (4,4)	107 (4,4)
	105 (10)	103 (3,3)	102 (4,4)	101 (3,3)	91 (4,5)	89 (6,6)	77 (16)	69 (19)			
VII	247 (100)	232 (3,6)	229 (6,4)	228 (2,9)	213 (44)	205 (2,8)	204 (2,8)	192 (31)	191 (65)	190 (51)	189 (14)
	185 (1,5)	176 (3,1)	175 (3,3)	174 (4,4)	163 (29)	162 (19)	161 (5,6)	158 (2)	147 (4,3)	146 (3,6)	145 (1,4)
	135 (4)	133 (1,1)	132 (1,4)	131 (2,0)	130 (3)	129 (2,6)	128 (1,4)	121 (3)	118 (3)	115 (3)	108 (1,4)
	107 (1,4)	105 (1,4)	103 (1,4)	102 (2,6)	101 (1,4)	91 (5,7)	89 (5,7)	79 (5,7)	77 (7,1)	76 (6,6)	69 (4,7)
VIII	302 (27)	246 (12)	229 (45)	228 (44)	213 (60)	204 (4,7)	202 (5,3)	200 (4,7)	199 (3)	187 (39)	186 (16)
	185 (11)	175 (6.7)	174 (5,3)	171 (5,3)	162 (4,8)	161 (5)	159 (8)	158 (17)	147 (4)	146 (3,3)	145 (3,3)
	143 (4)	131 (12)	130 (10)	129 (13)	127 (17)	116 (4,7)	115 (13)	105 (4,7)	103 (5)	102 (13)	101 (4,7)
	91 (5,3)	89 (9,3)	77 (11)	76 (8)	75 (8)	69 (16)	57 (69)	51 (18)	29 (100)	27 (65)	

oxygen of the dihydrofuran ring with the transfer to this oxygen of a hydrogen atom from the isopropyl grouping that is typical for the decomposition of ethers of umbelliferone [12, 13] with the subsequent cleavage of the α bond relative to the keto group of this ring, which is analogous to the fragmentation process observed in the decomposition of ketones [14]. No metastable peak corresponding to this process is observed in the mass spectrum of substance (I), but in the mass spectrum of compound (VI), the analogous decomposition is confirmed by a metastable transition. The fragment with m/e 189 loses a hydrogen atom, forming an ion with m/e 188, which successively eliminates four CO molecules, giving ions with m/e 160, 132, 104, and 76. The ejection of four CO groups from the ion with m/e 189 gives rise to fragments with m/e 161, 133, 105, and 77.



Scheme 1

The third direction of decomposition of oreoselone, which is also shown in Scheme 1 [compound (I), route C] and the intensity of which is lower than that of the first two, consists in the splitting out of a CH_3 radical by its molecular ion with the formation of a fragment having m/e 229. The fragment with m/e 229 possibly undergoes in the process of its formation a rearrangement into an ion of more stable form with the expansion of the dihydrofuran ring into a pyran ring. Only in this way is it possible, in our opinion, to explain the stability of this ion, which is expressed in the low intensity of the fragments with m/e 201 and 173 apparently arising from it partially through the subsequent loss by this ion of two CO groups.

The acyl derivatives of oreoselone (II-IV) show fragmentation under the action of electron impact which can be represented, for the case of oreoselone propionate, as shown in Scheme 1 [decomposition of compound (II)]. The main direction is a splitting out of an acyl residue from their molecular ions with the formation of a fragment with m/e 243 which is common to all these compounds and fragments with m/e 57, 71, and 85 for substances (II), (III), and (IV), respectively. In this process, the positive charge is mainly localized on the ions belonging to the acyl residues. As a result, the latter have a greater intensity in the mass spectra of substances (II-IV), which enables their weights in proton units to be determined mass-spectrometrically. The ion with m/e 243 then undergoes decomposition with the ejection of a CO molecule or a CH_3 group, giving ions with m/e 215 and 228 of low intensity; they eliminate four CO groups, leading to the appearance of ions with m/e 187, 159, 131, and 103, and 200, 172, 144, and 116, respectively.

The second direction of the fragmentation of acyl derivatives of oreoselone consists in the elimination by their molecular ions of a molecule of ketene [Scheme 1, route B, decomposition of compound (II)] with the formation of a fragment with m/e 244.

A characteristic difference of the mass spectra of acyl derivatives of oreoselone from the mass spectrum of oreoselone itself is the absence from the former of an intense fragment with m/e 202, in spite of the presence in them of an ion with m/e 244 of high intensity from which this fragment arises in the mass spectrum of oreoselone. This can be explained by the assumption that in the decomposition of substances (II-IV) by direction B the ion with m/e 244 produced is present in the enolic form, while the molecular ion of oreoselone with m/e 244 has the keto form, the presence of which is confirmed by the mass spectra of deuterooreoselone, obtained by the deuteration of oreoselone by its exchange reaction with vapors of methan[D]ol directly in the ionization chamber. In these circumstances, the partial shift of the molecular peak of oreoselone expected for the enolic form is absent. This property of the acyl derivatives (II-IV) on decomposition through the ejection of a molecule of ketone of giving the ion of the enolic form is also observed in the fragmentation of 4-acyloxycoumarins in which, just as in substances (II-IV), a hydroxyl of the phenolic type is acylated [3].

As a result, on decomposition the ion with m/e 244 in the mass spectra of compounds (II-IV) forms a fragment with m/e 189 of a different structure from that formed in the fragmentation of oreoselone. This fragment does not give an intense ion with m/e 188 through the splitting off of an hydrogen atom but mainly undergoes decomposition with the ejection of a CO group, forming an ion with m/e 161 which loses three molecules of CO directly or after the elimination of a hydrogen atom. As in the decomposition of oreoselone, the ion with m/e 244 splits off a CH_3 radical, giving a fragment with m/e 229.

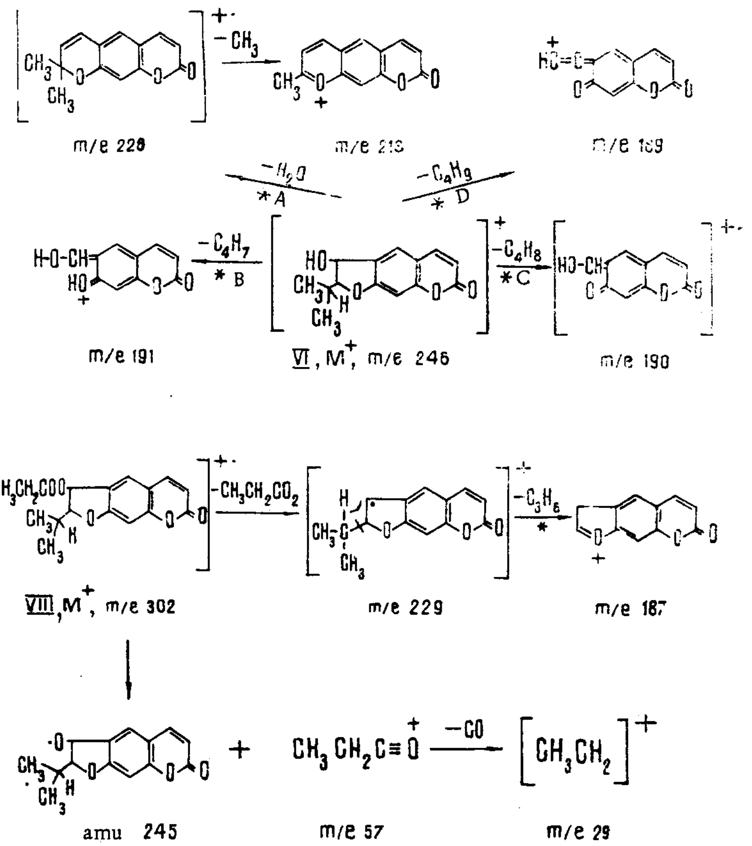
Peucedanin (V), the methyl ether of the enolic form of the ketone oreoselone, has a mass spectrum differing from the mass spectrum both of oreoselone itself and of the mass spectra of its acyl derivative. The molecular ion of peucedanin, unlike the molecular ion of substance (I), does not show the splitting off of an isopropyl group with the transfer of a hydrogen atom to the furan ring [see Scheme 1, decomposition of compound (I)] as the fragment with m/e 244 in the mass spectra of the acyl derivatives (II-IV). This fact is another confirmation of the enolic form of the fragment with m/e 244 in the mass spectra of the compounds mentioned. In contrast to the fragmentation of substances (II-IV), the cleavage of the ether bond, leading to the appearance of an ion with m/e 243, takes place less intensively in the decomposition of peucedanin, the positive charge being localized completely in this ion. This ion is the main one in the mass spectrum of compound (V), and it then undergoes a decomposition analogous to that of the fragment with m/e 243 in the mass spectra of substances (II-IV). It is not excluded, also, that part of the ions with m/e 243 in the mass spectrum of peucedanin is formed as the result of the splitting off of a methyl radical from the isopropyl grouping with the expansion of the furan ring into a pyran ring, as in the case of the appearance of the fragment with m/e 229 in the decomposition of compound (I) (see Scheme 1).

The main direction of the decomposition of dihydrooreoselol (VI) is the elimination by its molecular ion of a molecule of water with the subsequent splitting out of a CH_3 group, as shown in Scheme 2 [decomposition of compound (VI), route A]. This process probably takes place similarly to the decomposition of marmesin (X) [4], which is isomeric with compound (VI), with the expansion of the dihydrofuran ring to a six-membered pyran ring, but at a considerably greater rate.

The molecular ion of dihydrooreoselol also ejects from the dihydrofuran ring an isobutenyl grouping with and without the transfer from the latter of a hydrogen atom to the oxygen atom of this ring, and also with the transfer of one hydrogen atom from the dihydrofuran ring to the grouping mentioned, as shown in Scheme 2 by directions B, C, and D, respectively. The first two decompositions give fragments with m/e 191 and 190 and are analogous to the processes leading to the appearance of the ions with m/e 189, 188, and 176, 175, in the mass spectra of oreoselone and marmesin [4], respectively. They are typical for the fragmentation of substances containing ortho-substituted benzene rings and give stable ions of orthoquinoid structure in their mass spectra [5, 6]. The third direction characteristic for the fragmentation of compound (VI) is not observed in the mass spectra of oreoselone and marmesin. In the decomposition of [D]dihydrooreoselol (VII), the fragments with m/e 191, 190, and 189, and also the fragments with m/e 163, 162, and 161 arising from them through the ejection of a CO molecule, are shifted by one unit in the direction of higher masses, which confirms the route of their formation shown in Scheme 2.

In the dissociative ionization of dihydrooreoselol, again the elimination by its molecular ion of methyl and hydroxy groups takes place, leading to the formation of ions with m/e 231 (M^+-CH_3) and 229 (M^+-OH)

of low intensity. The first of them is shifted by one unit in the direction of higher masses in the mass spectrum of [D]dihydrooreoselol, and the second is not shifted, which proves the formation mechanism proposed for them.



Scheme 2

The fragmentation of dihydrooreoselol propionate (VIII) under the action of electron impact takes place by several competing directions. The most intensive of them [see Scheme 2, decomposition of compound (VIII), route A] is the ejection from its molecular ion of the acyl group with the localization of the positive charge on it and the formation of a fragment with m/e 57 which, losing a CO group, gives an ion with m/e 29 – which is the main ion in the mass spectrum of substance (VIII). The second direction of the decomposition of the molecular ion of this compound (route B) is the splitting off by the latter of a molecule of acid with the formation of a fragment with m/e 228 upon which the positive charge is localized. Then the ion with m/e 228 decomposes similarly to the ion with m/e 228 in the mass spectrum of dihydrooreoselol (VI). The third direction of the fragmentation of the M^+ ion of substance (VIII) (route C) is the loss from it of the acid residue, as a result of which an ion with m/e 229 is formed. The ion with m/e 229, on further decomposition, splits out a propyl radical or a propylene molecule forming fragments with m/e 187 and 186 which, losing a CO group, give ions with m/e 159 and 158. The latter, eliminating two CO molecules in succession, form ions with m/e 131, 103, and 130, 102, respectively.

The molecular ion of dihydrooreoselol propionate, likewise, splits out a molecule of ketene [see Scheme 2, route D, giving an ion with m/e 246 coinciding in structure with the molecular ion of substance (VI)].* It must be noted that the intensity of the ion with m/e 246 is less than in the mass spectra of the acyl derivatives of oreoselone (II-IV), but considerably exceeds the intensity of the ions with m/e 246 in the mass spectra of the acyl derivatives of marmesin and columbianetin [7, 8].

The mass-spectrometric method permits dihydrooreoselone (VI) and its acyl derivatives (VIII) to be distinguished reliably from their isomers marmesin (X), columbianetin (IX), xanthogalol (XI), agasyllol (XII) (see formulas on p. 575) and their acyl derivatives, belonging to the class of linear and angular dihy-

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* As in Russian original – Publisher.

drofuro- and dihydropyranocoumarins. The main ion in the mass spectrum of dihydrooreoselone is that with m/e 213, while in the mass spectra of compounds (IX) and (X) it is the ion with m/e 188 and in the mass spectra of substances (XI) and (XII) the fragments with m/e 176. The results of a comparison of the mass spectrum of an acyl derivative of dihydrooreoselol (VIII) with the acyl derivatives of compounds (IX-XII) shows that in the mass spectrum of substance (VIII) the peak of the ion with m/e 187 amounts to 68% of the peak of the main fragment with m/e 213, and in the mass spectra of the acyl derivatives of (IX-XII) the intensity of the ion with m/e 187 does not exceed 30% of that of the main ion in their mass spectra with m/e 213.

Thus, the characteristics of the decomposition of substances (I-VIII) under the action of electron impact that have been considered give valuable information on their structure, enabling the mass-spectrometric method to be used in series of this class of compounds for structural-analytical purposes.

EXPERIMENTAL

The mass spectra of substances (I-VIII) were taken on a modified MKh-1303 instrument at an ionizing voltage U = 70 V and at the following temperatures: for (I) and (III), 75°C; for (II), 70°C; for (IV) and (V), 100°C; for (VI), 90°C; for (VII), 125°C; and for (VIII), 80°C. Direct introduction of the sample in the ion source was used.

SUMMARY

The mass spectra of eight compounds belonging to the class of linear furo- and dihydrofurocoumarins have been studied. A scheme of the fragmentation of these substances under the action of electron impact has been proposed. It has been shown that the mass-spectrometric method permits acyl derivatives of oreoselone to be distinguished reliably from acyl derivatives of dihydrooreoselol and the latter series of substances from derivatives isomeric with them belonging to the class of dihydrofuro- and dihydropyranocoumarins.

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