A MASS SPECTROMETRIC STUDY OF SOME DIHYDROPYRANOCOUMARINS

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We have studied the mass spectra of some angular and linear dihydropyranocoumarins: dihydroseselin (I), xanthogalol (II), xanthogalol-d (III), agasyllol (IV), agasyllol-d (V), acetylxanthogalol (VI), acetylagasyllol (VII), xanthogalin (VIII), buchtormin (IX), and agasyllin (X).

The mass spectra of compounds (I–V) contain molecular peaks of medium intensity and those of compounds VI–X peaks of low intensity.

A characteristic feature of the compounds studied is the presence of a structural element common to them (dimethylchroman ring). The mass spectra of the compounds studied have some peculiarities depending on the nature of the substituent in position 3 of this ring and on the position of attachment of the ring to the coumarin nucleus. The main fragments of these compounds and their relative intensities are given in Table 1.

The presence of a substituent in position 3 of the dimethylchroman ring leads to a marked decrease in the intensity of the M^+-CH_3 fragment for the hydroxydihydropyranocoumarins (II–V) or its complete absence in the case of the acyloxydihydropyranocoumarins (VI–X), while in the mass spectrum of dihydroseselin (I) with an unsubstituted dimethylchroman ring this fragment is of medium intensity, as in other compounds with this ring [1].

TABLE 1. Main Fragments and Their Relative Intensities in the Mass Spectra of the 3-Hydroxy- and 3-Acyloxydihydropyranocoumarins

Compound	Mass numbers, m/e (relative intensity, %)							
I	230 (70)	215 (23)	213 (6)	187 (20)	175 (100)	174 (25)	146 (20)	131 (6)
II	246 (34)	231 (5)	228 (9)	213 (27)	176 (100)	175 (82)	147 (24)	131 (11)
III	247 (20)	232 (1)	228 (2)	213 (7)	177 (100)	176 (60)	148 (7)	132 (5)
IV	246 (54)	231 (1)	228 (3)	213 (11)	176 (97)	175 (100)	147 (27)	131 (8)
V	247 (20)	232 (1)	228 (2)	213 (6)	177 (90)	176 (100)	148 (13)	132 (3)
VI	288 (8)	228 (16)	213 (100)	176 (30)	175 (25)	147 (8)	131 (13)	71 (70)
VII	288 (9)	228 (22)	213 (100)	176 (18)	175 (24)	147 (13)	131 (9)	71 (4)
VIII	328 (6)	228 (32)	213 (91)	176 (3)	175 (5)	147 (2)	83 (91)	55 (100)
IX	328 (4)	228 (27)	213 (100)	176 (5)	175 (8)	147 (1)	83 (96)	55 (50)
X	328 (3)	228 (28)	213 (100)	176 (1)	175 (4)	147 (3)	83 (62)	55 (74)

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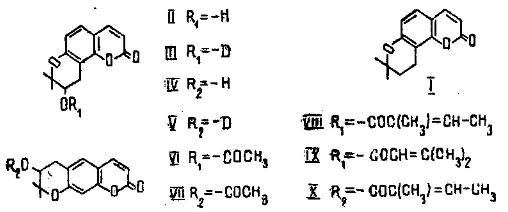
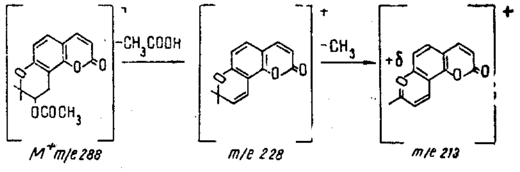
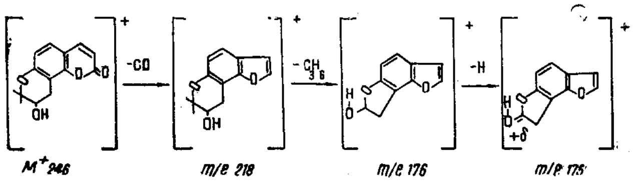


The mass spectra of the compounds with acyloxy groups as substituents differ from the mass spectra of compounds containing hydroxy groups by the increased intensity of the fragments with m/e 228 and 213 formed as the result of the decomposition of their molecular ions by scheme 1 (shown for the case of compound VI).



Scheme 1

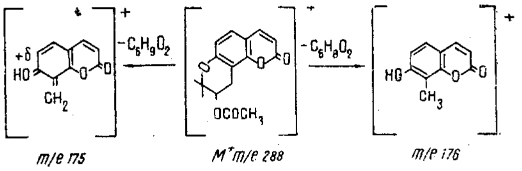
Conversely, the fragments with m/e 176 and 175 have an increased intensity in the mass spectra of the hydroxydihydropyranocoumarins, where the peaks of maximum intensity correspond to them. In the deuterium-substituted xanthogalol-d (III) and agasyllol-d (VI), these fragments undergo a shift of one mass unit in the direction of higher masses, and their formation can be represented by scheme 2, in which xanthogalol (II) is used as an example.



Scheme 2

The presence in the deuterium-substituted compounds (III) and (V) of a fragment with m/e 175 shows that the fragment with m/e 176 in the scheme shown loses a hydrogen atom in compound 2 to the extent of about 70% from position 2 of the dihydropyran ring and about 30% from its hydroxy group. For compound (IV), these losses are 60% and 40%, respectively.

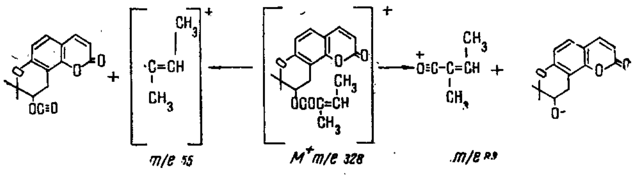
The formation of fragments with m/e 176 and 175 for the acyloxydihydropyranocoumarins is shown in scheme 3 using compound (VI) as an example.



Scheme 3

It can be seen from Table 1 that in compounds (VI-X) the intensity of these fragments is the smaller the larger the number of atoms present in the acyloxy group in position 3 of the dihydropyran ring.

The mass spectra of compounds (VIII) and (IX) permit the presence of a senecionic acid residue in the molecule of an angular dihydrocoumarin to be distinguished from that of an angelic acid residue from the relative intensities of the fragments with m/e 83 and 55. These fragments arise by scheme 4, shown for the case of compound (VIII).



Scheme 4

In the case of the angeloyl group, the fragment with m/e 55 has twice the intensity of the fragment with m/e 83 in the senecionoyl fragment.

The mass spectra of compounds differing by the position of attachment of the dimethylchromane ring to the coumarin ring differ in the intensities of a number of fragments. In compounds containing a hydroxy group as substituent, the molecular peaks of greatest intensity are possessed by the linear dihydropyranocoumarins. Angular hydroxy- and acetoxydihydropyranocoumarins are distinguished from their linear isomers also by the fact that in the mass spectra of these compounds the intensities of the fragments with m/e 176 are higher than that of the fragments with m/e 175. For the angular compounds (VIII) and (IX) with angeloyl and senecionoyl residues the fragment with m/e 83 has approximately the same intensity as the fragment with m/e 213, and for the linear compound (X) with an angeloyl group the fragment with m/e 83 possesses a lower intensity than the fragment with m/e 213.

Thus, the features studied in the mass spectra of the 3'-hydroxy- and 3'-acyloxydihydropyranocoumarins will reflect both the similarities and the differences in their structure and can therefore be used for structural-analytical purposes in this group of compounds.

EXPERIMENTAL

The mass spectra of the compounds were obtained on a MKh-1303 instrument with an ionizing voltage of 50 V using a system for the introduction of the sample into the ion source. Compounds (I, VIII-X) were studied at 60° C, (II-V) at 100° C, and (VI and VII) at 80° C. The temperature stability of the inlet system was maintained to an accuracy of ±1° C.

SUMMARY

The mass spectra of ten angular and linear dihydropyranocoumarins without substituents and with hydroxy and acyloxy substituents in position 3 of the dimethylchroman ring have been studied. Depending on the presence and nature of these substituents the mass spectra of the compounds considered have different relative intensities of the fragments with m/e 228, 213, 176, 175, 83, and 85, which permits mass spectrometry to be used in this group of compounds for structural-analytical purposes.

LITERATURE CITED

1. C. S. Barnes and J. L. Occolowitz, Austral. J. Chem., 17, 975 (1964).