LOW-VOLTAGE MASS SPECTRA OF MONOHYDROXY- AND MONOACYLOXYDIHYDROPYRANOCOUMARINS AND -DIHYDROFUROCOUMARINS

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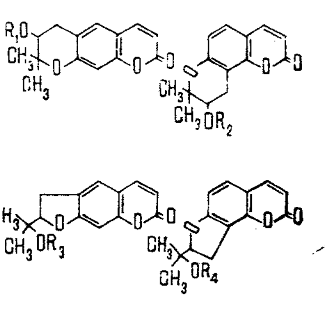
The dissociative ionization of the monohydroxy- and monoacyloxydihydropyranocoumarins and -dihydrofurocoumarins (I-VI) at energies of the ionizing electrons of 50-70 eV has been studied previously [1-3]. The characteristic features of the decomposition that were found enabled a mass-spectrometric distinction of the hydroxy derivatives from acyloxy derivatives and of dihydropyranocoumarins from dihydrofurocoumarins in this series of substance to be established. However, as a result of the investigation performed no fragmentation characteristics common for dihydropyranocoumarins and dihydrofurocoumarins permitting the pairs of linear and angular isomers of this class of compound to be distinguished by the mass-spectrometric method were found.



Scheme 1

I. $R_1 = -H$, II. $R_2 = -H$, III. $R_1 = -COCH_3$, IV. $R_2 = -COCH_3$, V. $R_1 = -CO\underset{\substack{|\\ CH_3}}{C}=CHCH_3$, VI. $R_2 = -CO\underset{\substack{|\\ CH}}{C}=CHCH_3$, VII. $R_3 = -H$, VIII. $R_4 = -H$, IX. $R_3 = -COCH_3$, X. $R_4 = -COCH_3$, XI. $R_3 = -CO\underset{\substack{|\\ CH_3}}{C}=CHCH_3$, XII. $R_4 = -CO\underset{\substack{|\\ CH_3}}{C}=CHCH_3$, XIII. $R_1 = -D$, XIV. $R_2 = -D$, XV. $R_3 = -D$, XVI. $R_4 = -D$.

At the same time, the linkage of the dihydropyran ring with the coumarin ring for the two pairs of isomeric dihydropyranocoumarins (I-IV) (at an ionization energy of 50 eV) is reflected in the relative intensities of the ions with m/e 176 and 175 [2].

Since these ions are rearrangement ions and in the mass spectra of dihydropyranocoumarin and dihydrofurocoumarin derivatives (Scheme 2) they are formed in the cleavage of the saturated heterocyclic ring, it might be expected that the difference in the intensities of the ions with m/e 176 and 175 for the angularly and linearly linked isomers will be shown to a greater degree with a reduction of the energy of the ionizing electrons [4] (see Scheme 2 on following page.)

Measurements of the low-voltage mass spectra of compounds (I-XVI) (Table I) confirmed this assumption. In addition to the specific differences characteristic for each pair of linear and angular isomers, the low-voltage mass spectra of (I-XVI) showed a general difference that is characteristic of derivatives of both the dihydropyran and the dihydrofuran series due to the type of linkage of their dihydropyran and dihydrofuran rings with the coumarin ring. It can be seen from Table 1 that the ratio I_{176}/I_{175} is always smaller for the linear isomers, and this feature is a general one and acquires analytical value at 15 eV. The reason for this fact may be, according to Hammond's postulate [7], and increased rate of formation of the ion of m/e 175 in the mass spectra

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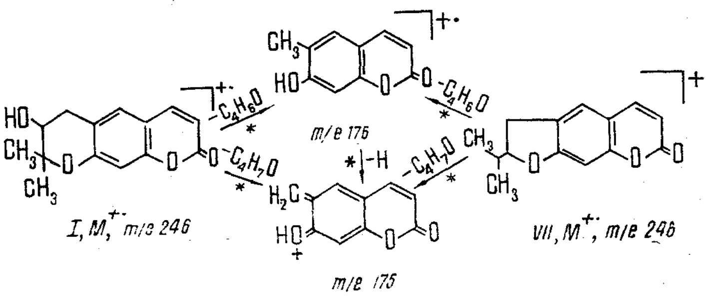
TABLE 1. Values of the Ratios I_{176}/I_{175} in the Mass Spectra of Monohydroxy- and Monoacyloxydihydropyranocoumarins and -dihydrofurocoumarins at Energies of the Ionization Electrons of 15 and 50 eV

Compound	Dihydropyranocoumarins		Dyhydrofurocoumarins	
	15 eV	50 eV	15 eV	50 eV
Hydroxy derivatives				
Linear isomer	1, 8±0,13	1,1±0,09	1,3±0,15	0,7±0,08
Angular isomer	2, 8±0,33	1,6±0,18	1,7±0,19	0,8±0,09
Acetoxy derivative				
Linear isomer	1, 2±0,14	0,8±0,09	1,5±0,17	0,9±0,1
Angular isomer	2,10±0,24	1,1±0,1	2,4±0,25	1,6±0,18
Angeloyloxy derivatives				
Linear isomer	1,33±0,15	0,45±0,05	0,33±0.03	0,3±0,03
Angular isomer	3,10±0,35	0,55±0,06	1,5±0,17	0,6±0,06



Scheme 2

of the linear isomers because of its higher stability. An estimate of the latter magnitude with the aid of a calculation analogous to the calculation of W_M [5] shows that the ion with m/e 175 in the mass spectra of the linear isomers is approximately 15% more stable than in the mass spectra of the angular isomers. Furthermore, it may be assumed that in the dissociative ionization of compounds with a linear linkage of the dihydropyran or dihydrofuran ring with the coumarin ring the probability of the transition m/e 176 → m/e 175 is higher. This hypothesis is in harmony with the mass spectra of the deuterium analogs of the monohydroxy derivative (XIII-XVI) the hydrogen of the hydroxy groups of which has been replaced by deuterium, where the probability of the elimination of a D atom by the ion with m/e 177 (transition m/e 177 → m/e 175) is considerably higher in the case of the decomposition of the linear isomers than of the angular isomers (approximately threefold). It is not excluded that a similar picture is observed for the transition $M^{+\cdot} \rightarrow$ m/e 175, but it is not possible to give an unambiguous answer to this question on the basis of the mass spectra of (XIII-XVI).

The characteristic features found permit the mass-spectromatic distinction of linear and angular isomers of the series of compounds investigated under standard conditions. Its high sensitivity gives this method a considerable advantage over other methods of analysis, since practically no preparative treatment of the substance under investigation is required; usually the amount eluted from one chromatographic spot is sufficient.

EXPERIMENTAL

The mass spectra of compounds (I-XVI) were obtained on a standard MKh-1303 instrument using a system for the direct introduction of the sample into the ion source at an ionizing voltage of 15 V and at inlet temperature of 90°C (I-VI, XIII-XVI), 80°C (VII-X), and 105°C (XI, XII). The deuterium analogs of the compounds were synthesized by the method of Shipchandler and Soine [6].

SUMMARY

With the aid of the low-voltage mass spectra of 16 compounds belonging to the monohydroxy- and monoacyloxydihydropyranocoumarins and -dihydrofurocoumarins and their deuterium analogs it has been shown the relative intensities of the ions with m/e 176 and 175 is an analytical magnitude both for the dihydropyranocoumarins and the dihydrofurocoumarins which enables linear and angular isomers in these series of substances to be distinguished.

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DITERPENE LACTONES OF Teucrium hyrcanicum

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Species of germander (Teucrium) have long been used in officinal folk medicine as antiflammatory, hypotensive, cholagogic, antihelminthic, etc., agents [1-6]. The species T. polium L. [7], T. Chamaedrys L. [8, 9], and T. viscidum Bl. [10] have been studied chemically to the greatest extent, and from them a number of diterpene lactones with a rearranged labdane skeleton have been isolated.

For the purposes of systematizing the medicinal plants of Armenia, we have begun a chemical investigation of the lactones of the previously unstudied species T. hyrcanicum L. (Hyrcanian germander). From an acetone extract of the plant by chromatography on alumina we isolated four new diterpenoids which we call, by analogy with teucrins A-F [8], teucrins H1-4. Teucrins H1 and H4 are similar in composition and spectra properties to teucrin A, and teucrin H2 to teucrin E. A direct comparison of the melting points of mixtures and the results of chromatography of the substances that we had isolated with samples of teucrins A and E* showed that they were different.

Teucrin H1 (I) is the main component of the total lactones has the composition $C_{19}H_{20}O_6$, and contains a furan ring (coloration with Ehrlich's reagent, and absorption at 3170, 3150, 1605, 1510, and 880 cm^{-1}) that is substituted in the β position (2H, multiplet at 7.43 ppm, and 1H, multiplet at 6.35 ppm; Fig. 1), a hydroxy group (3510 cm^{-1}), and two γ-lactone rings. One lactone is saturated (1770 cm^{-1}), and the other is α,β-unsaturated (1745 cm^{-1} and 217 nm). The presence of two lactone rings is also confirmed by the reaction of (I) with two equivalents of alkali.

A hydroxy group of (I) has a secondary alcoholic nature, as is shown by a downfield shift in the PMR spectra of the signal of the proton geminal to the hydroxy group on acetylation (shift of the broadened one-proton singlet from 4.60 to 5.70 ppm). The spectrum of the acetate contains, in place of the signal of the proton of the hydroxy group (1H, multiplet at 3.38 ppm) the signal of the methyl radical of an acetyl group (3H, singlet at 2.1 ppm). The presence in (I) of a hydroxy group and the position of its signal in the PMR spectrum were confirmed by deuterium exchange.

The molecular composition of the dilactone (I) and the presence in it of a β-substituted furan ring and a secondary methyl group (3H, doublet, J = 7 Hz at 1.35 ppm) enables us to suggest a structural closeness of (I) to teucrin A (II) [8, 9] and, consequently, a biogenetically expected relationship of (I) to the rearranged norlabdane derivatives. The mass and PMR spectra of (I) and its acetate agree well with this hypothesis. In the mass spectrum of (I) there are strong peaks of ions with m/e 95, 94, and 81 which are characteristic for furolactones containing the lactone oxygen in the allyl position to the furan ring [7, 8, 11].

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*Samples of teucrins A and E were kindly provided by D. P. Popa.

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