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MASS-SPECTROMETRIC DISTINCTION OF LINEAR AND ANGULAR 2,2'-DIMETHYL-3'-OXO-DIHYDROPYRANOCOUMARINS

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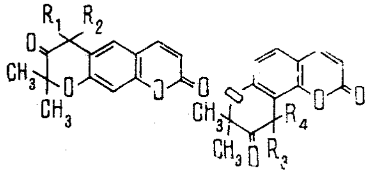
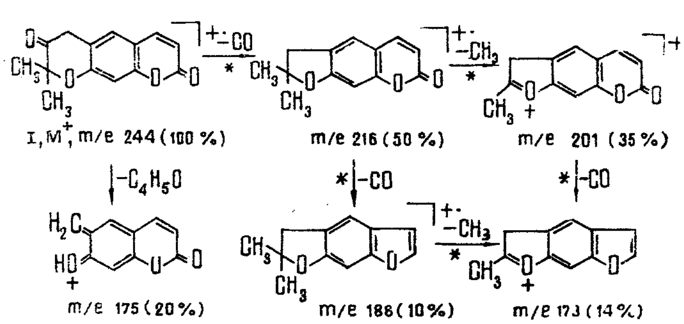
The dissociative ionization of the angular 2',2'-dimethyl-3'-oxo-dihydrocoumarin (II) hasbeen studied previously [1]. We have established a mass-spectrometric difference between this compound and its linear isomer (I). With this aim, we have investigated the mass spectra of substances (I) and (II) and their deuterium analogs (III) and (IV) under identical conditions and energies of the ionizing electrons of 50 and 15 eV.

Compounds (I) and (II) were obtained from natural 3',4'-diacyloxydihydropyramocoumarins [2, 3], which possess a pronounced spasmolytic effect [4] and their presence in plant raw material and in the form of products of the metabolism of the 3',4'-dihydropyranocoumarins when they are used as drugs is not excluded. Because of this, the reliable identification of compounds (I) and (II) by a mass-spectrometric method is required.



I. $R_1=R_2=-H$, II. $R_3=R_4=-H$,
III. $R_1=R_2=-D$, IV. $R_3=R_4=-D$.

The mass spectra of (I) and (II) (Figure 1) contain the peaks of ions with the same m/e values, but the intensities of some ions differ considerably. Since in the case of the fragmentation of the deuterium analogs (III) and (IV) (see Fig. 1) the corresponding ions are displaced by the same number of atomic mass units, at 50 and 15 V compounds (I) and (II) exhibit monotypical fragmentation under the action of electron impact which can be represented for the most characteristic ions in the form of Scheme 1



Scheme 1

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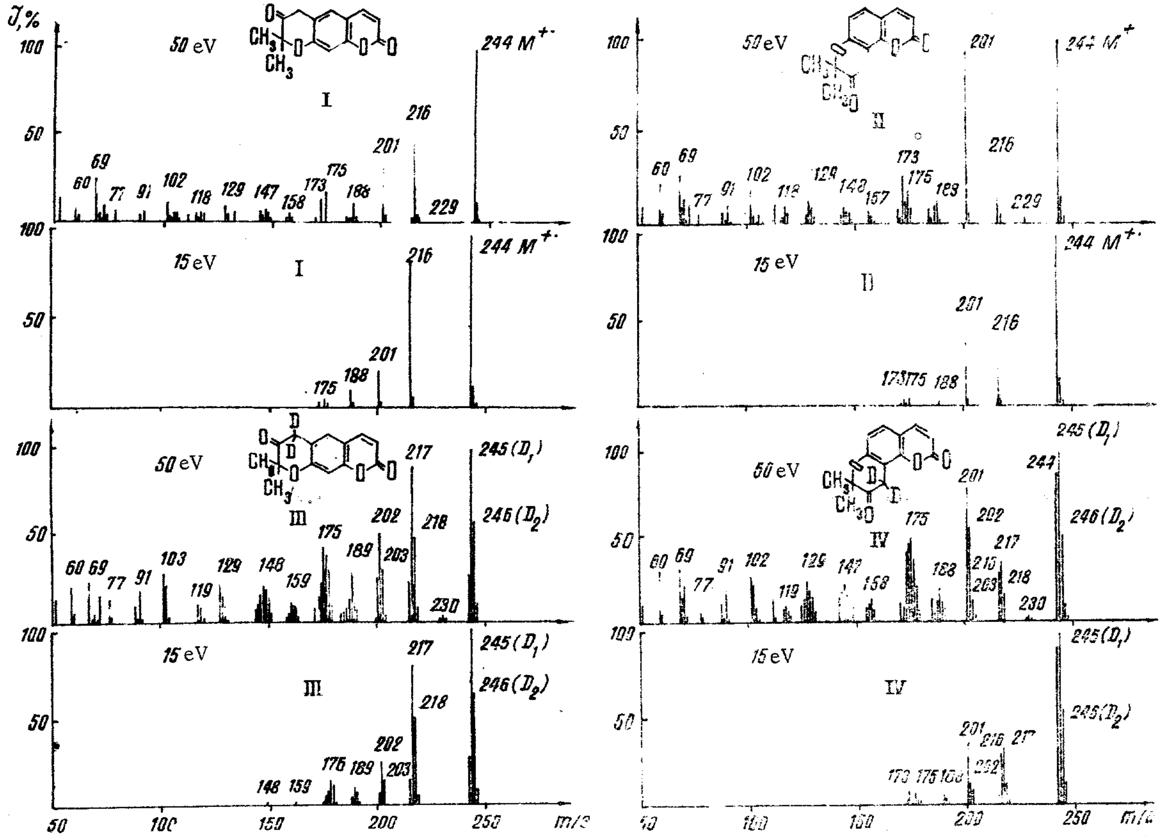
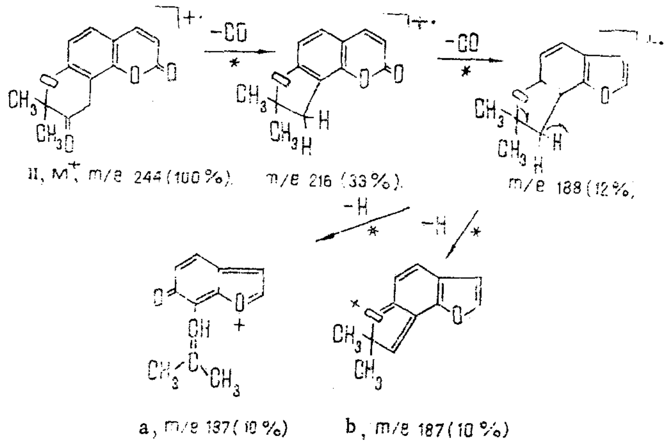


Fig. 1. Mass spectra: 1) 2,2'-dimethyl-3'-oxodihydropyrano-5',6' : 6,7,-coumarin (60°C); II) 2,2'-dimethyl-3'-oxodihydropyrano-5'6' :8,7-coumarin (60°C); III) $[D_2]$-2',2'-dimethyl-3'-oxodihydro-pyrano-5',6' : 6,7-coumarin (60°C); IV) $[D_2]$-2',2'-dimethyl-3'-oxodihydropyrano-5'6' : 8,7-coumarin.

The main difference of the dissociative ionization of the linear 3'-oxo derivative (I) as compared with the mass spectrum of its angular isomer (II) is the increased stability to further fragmentation of the fragment $(M - CO)^{+\cdot}$ with m/e 216, As a result of this, the ratios J_{216}/J_{201} and J_{216}/J_{188} in the mass spectrum of the linear compound (I) are, respectively, 4.0 and 1.9 times higher than in the mass spectrum of compound (II). Furthermore, the linear isomer (I) has a somewhat greater (by a factor of 1.4) stability of the molecular ion $W_{M^{+\cdot}}$, and in the mass spectrum of the deuterium analog (IV) with an increase in the number of D atoms at $C_{4'}$ the probability of the loss of a CH_3 group by the $(M - CO)^{+\cdot}$ ion falls. The presence in the mass spectrum of (I) of a fragment with m/e 187 of considerably lower intensity than in the mass spectrum of (II) must also be observed. Shipchandler and Soine [1], in the case of the decomposition of (II), regarded this fragment as a rearranged fragment formed from ion M^+, although these authors found no metastable transition for this process. It is more likely that this fragment arises from the ion with m/e 188, which is confirmed by the presence in the mass spectrum of (II) of the corresponding metastable peak $m^* = 186$ and by the absence of the ion with m/e 187 in the low-voltage mass spectrum of (II), which shows the fragmentary, and not the rearrangement, nature of this ion [5]. Since the fragment with m/e 187, unlike the ion with m/e 188, shows no ready loss of CH_3 group, it may be assumed that it is present in the more stable form *a*, from which the elimination of a CH_3 radical is less probable than from form b (Scheme 2).



Scheme 2

It must also be observed that the increased stability of the fragment with m/e 216 in the mass spectrum of the linear isomer (I) leads to a decrease in the relative intensities not only of the ions with m/e 201 and 188 but also of the fragment with m/e 173. As a result of this, in the decomposition of substance (I) the relation $J_{173} < J_{175}$ is satisfied, while for the mass spectrum of the angular isomer $J_{173} > J_{175}$. The low-voltage mass spectra do not exhibit a great difference between compounds (I) and (II), which substantially distinguishes their mass spectral behavior from the decomposition of the linear and angular monohydroxy- and monoacyloxydihydropyranocoumarins and -dihydrofurocoumarins [6].

EXPERIMENTAL

The mass spectra of (I-IV) were obtained on a standard MKh-1303 instrument using a system for the direct introduction of the sample into the ion source at ionizing voltages of 50 and 15 V and a temperature of 60°C. The deuterium analogs (II) and (IV) were synthesized by the method of Ermatov et al. [7].

SUMMARY

The mass spectra of linear and angular 2',2'-dimethyl-3'-oxodihydropyranocoumarins and their deuterium analogs have been studied. A basic mass-spectrometric difference between these substances has been found which consists in the greater stability of the fragment $(M - CO)^{+\cdot}$ for the linear isomer than for the angular isomer. A hypothesis has been put forward on the most probable route for the formation of the ion $(M - 2CO - H)^+$ in the mass spectra of the compounds mentioned.

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