MASS SPECTRA OF SOME DERIVATIVES OF AMORPHIGENIN

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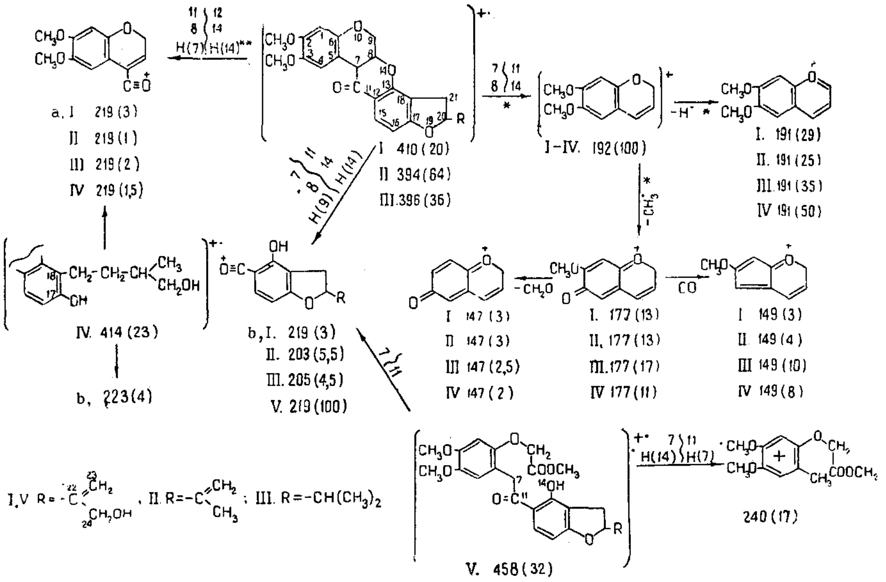
The mass spectra of a number of rotenoid derivatives has been described in the literature [1] but not that of amorphigenin, the complete chemical structure of which has been established comparatively recently [2, 3]. In this paper, we give information on the fragmentation of amorphigenin (I) and rotenone (II) and their reduction products—22,23-dihydrorotenone (III) and tetrahydroamorphigenin (IV)—and of methyl amorphigenate (V), 7,8-dehydroamorphigenin (VI), and 7,8-dehydrorotenone (VII).

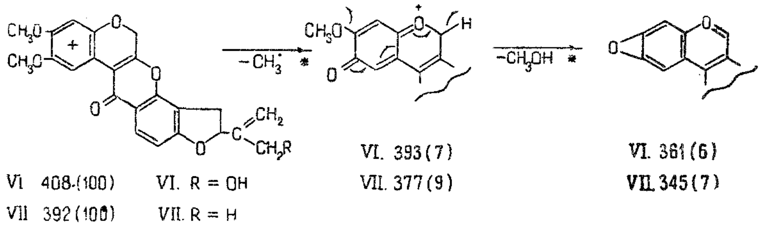
The main feature of the mass spectra of the compounds mentioned is the dependence of the nature of the decomposition on the degree of unsaturation of the skeleton at $C_{(7)}$ and $C_{(8)}$. For compounds with an ordinary $C_{(7)}$—$C_{(8)}$ bond (substances I–IV) the intensity of M^+ is fairly high but it does not represent the maximum peak (Scheme 1). The maximum peak, with m/e 192, is formed by the cleavage of the bonds of the γ-pyrone ring [1]. Ions which are less intense but are extremely important for deducing the structure of the compounds studied arise with the localization of the charge on the oxygen of the carbonyl of the γ-pyrone. Depending on which of the α-ruptures takes place ($C_{(11)}$—$C_{(12)}$ or $C_{(7)}$—$C_{(11)}$), either the benzopyran or the benzofuran part of the skeleton of the molecule is charged, giving ions of type a and type b, respectively. The spectra of compounds I–IV contain peaks of ions of both types, while for amorphigenin (I) the ions and b have the same masses (m/e 219). In order to check this hypothesis, we deuterated amorphigenin with CD_3OD and obtained a shift in the 219 peak by one mass unit (to the extent of almost 50%). Consequently, the probabilities of the formation of an ion with m/e 219 from the benzopyran and benzofuran parts are approximately equal. In the spectra of substances II–IV, the ions a and b appear separately, in complete harmony with the structure of the side chain attached to the dihydrofuran ring.



Scheme 1. Decomposition of the molecules of I–V. *Metastable transitions; **)H(m) ⌇ H(n) denotes the transfer of a proton from atom m to atom n.

Under the influence of electron impact, the molecule of the ester V also undergoes cleavage of the $C_{(7)}-C_{(11)}$ bond. The ion with m/e 219 corresponds to the ion b of amorphigenin and has the maximum intensity in the spectrum. In this case the ions with 239 and 240 amu, produced without (239) and with (240) the migration of a proton (from the hydroxyl) belong to type a.

The mass spectra of dehydroamorphigenin (VI) and dehydrorotenone (VII) differ substantially from the mass spectra of compounds I–IV. The introduction of a double bond into the 7, 8-position greatly increases the stability of the molecule; M^+ becomes the maximum peak and indications of the cleavage of the bond of the skeleton practically disappear, with the exception of low-intensity peaks of type b: 219 for VI and 203 for VII. It is interesting that a characteristic feature of these spectra is the formation of the ions M − 47 in two stages, apparently as shown in Scheme 2.



Scheme 2. Decomposition of the molecules of VI and VII

The molecules of amorphigenin (I) and of dehydroamorphigenin (VI) also split off the side chains in the form of prop-1-en-3-ol, and give the ion M − 58, more common in the doubly-charged form. This is particularly characteristic of the dehydro derivative VI in the spectrum of which the corresponding peak, (M − 58)/2, corresponds to 12.5% of the maximum peak.

The appearance in the mass spectra of the peaks of the ion M − 1 and M − 2 corresponds to the mobility of the hydrogens at $C_{(7)}$ and $C_{(8)}$ (compounds I–IV). These peaks are absent from the spectra of compounds VI and VII. In addition to this, the proton at $C_{(7)}$ probably favors the tautomerism of the rotenoids in view of which in the mass spectrum of deuterated amorphigenin there is a partial shift of a number of peaks by two mass units.

In all the spectra studied, apart from that of compound V, there are peaks of the ions M − 15, M − 30, M − 31, and M − 43, which are characteristic for hydroxymethylene- and methoxy-containing compounds.

EXPERIMENTAL

The mass spectra were taken on a standard MKh-1303 instrument fitted with a system for the direct introduction of the substance into the ion source at 100–120° C with an ionizing voltage of 40 V.

CONCLUSIONS

The mass spectra of seven rotenoid compounds have been studied. The appearance of the main fragments in the mass spectra of the rotenoid is due to the cleavage of the bonds of the γ-pyrone ring. The molecules of the 7, 8-dehydro-derivatives are more stable to electron impact.

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