# CHARACTERISTICS OF THE MASS SPECTRA OF ACETONIDES OF SOME NATURAL COMPOUNDS

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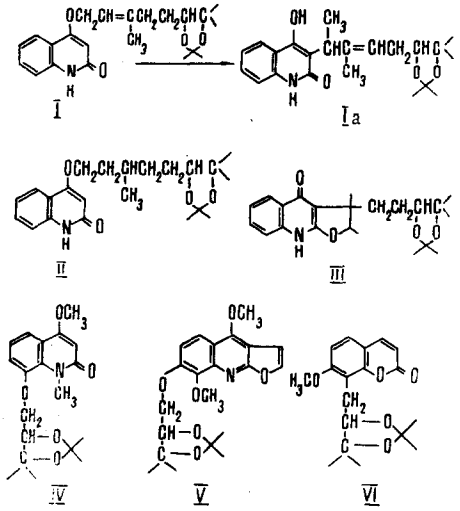
Acetonides in the mass spectra of which a series of fragments characteristic of them appear [1, 2] have been used by Wolff [1] and McCloskey [2] to establish the position of the double bond in the molecules of unsaturated hydrocarbons and fatty acids. Other workers have attempted to use the mass-spectrometric properties of the acetonides for the analysis of sugars [3]. We have resolved to determine the possibility of the identification of the acetonide group from its characteristics, since some natural compounds are isolated in the form of acetonides (alkaloids, coumarins). Although there is no reliable information on whether these acetonides are native or are formed in the process of separation of the substances with the aid of acetone, nevertheless their wide distribution is a sufficient reason for studying the mass-spectrometric properties of these compounds.

As the main subjects we took alkaloids of the genus Haplophyllum, characteristic of which are oxidized isoprenoid links in the side chain. The acetonides of bucharaine (I), dihydrobucharaine (II), and evoxine (V) were obtained from the corresponding alkaloids, and those of bucharamine (III) and foliosidine (IV) were isolated from a mixture of alkaloids [4, 5]. The mass spectrum of the coumarin pranferin, which is the acetonide of meranzin hydrate [6] was used for comparison.



Compounds (I-VI) contain the same structural element, a feature of which is that similar fragments can be detached from it both through the acetonide group ($a_1$ and $a_2$) and through the hydroxyisopropyl group (b). To check this, we obtained the $D_6$-acetonides of bucharaine (I) and of foliosidine (IV).

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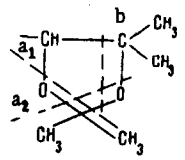


The molecules of the compounds studied are based on a particular heteroaromatic skeleton, in view of which the proportion of fragments with the localization of the charge in the $\pi$-electronic system of the rings must be large. Furthermore, the side chains are added to the nucleus of the molecule in different positions and in different ways: through an ether or a carbon–carbon bond. This fact explains the difference in the stability of the molecular ions of compounds (I-VI) and in the contributions of the processes taking place within the dioxolane ring and adjacent to it.

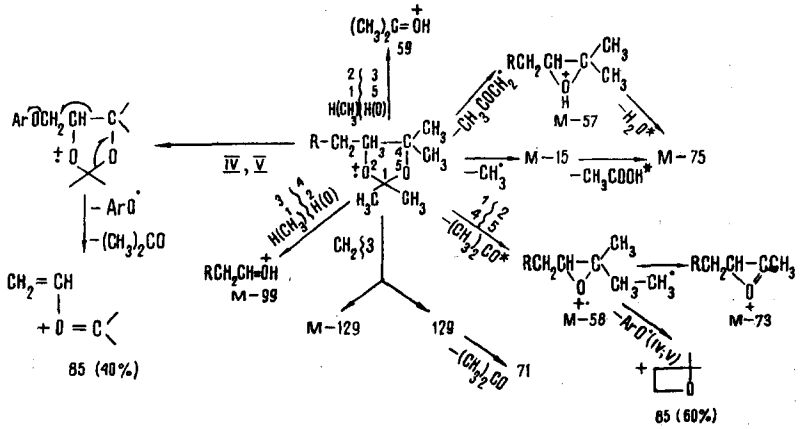
In the present paper we shall consider only the fragments with the charge concentrated mainly in the acetonide group. In spite of the large quantitative differences, a number of fragmentary ions characterizing the acetonide structure of the compounds mentioned can be found in the spectra of (I-VI). The corresponding mass numbers of the ions and intensities as proportions of the total ionic current are given in Table 1.

The most characteristic peaks are those in the region of high mass numbers where ions not corresponding to the decomposition of the acetonide group are almost absent. In contrast to the acetonides of the aliphatic diols studied by Wolff [1], here the peak of the molecular ion is observed. In the acetonides of foliosidine (IV) and evoxine (V), this peak is the maximum peak, which is explained by the high percentage of ions with the charge concentrated in the heteroaromatic system. Only in the acetonide of dihydrobucharaine (II), the molecule of which contains a comparatively long aliphatic chain, is the $M^+$ peak of low intensity, and the M−15 peak is the maximum peak.

According to McCloskey [2], the M−15 ion decomposes in one stage with the ejection of $CH_3COOH$ or in two stages with the ejection of ketene and water. In both cases, this leads to the formation of the M−75 ion. In the spectra that we have studied, the ejection of molecules of acetic acid and water is confirmed by metastable peaks, and the ejection of ketene from the M−15 ion is not confirmed. No m* peaks corresponding to the ejection of 57 amu directly from $M^+$ are observed, either. Nevertheless, regardless of the number of stages as the result of which the M−57 ion is formed, the structure proposed for it by McCloskey [2] does not give rise to objections. In addition to the peak of the M−57 ion, all the spectra show the peak of a M−58 ion which, in the case of compounds (I-III), has an intensity several times greater than the peak of the M−57 ion (see Table 1). The process under consideration consists in the elimination of a molecule of acetone. In the spectrum of the $D_6$ analog of (I), the M−58 peak does not undergo an isotopic shift. Consequently, the acetone molecule is formed only from the acetonide group. The ion produced apparently has the form of an epoxide. With the subsequent detachment of a methyl radical a M−73 ion is obtained. The peak of the M−57 ion in the spectrum of the $D_6$-acetonide of foliosidine (IV) is shifted in the direction of higher mass numbers by one unit, which shows the migration of one deuterium atom from the acetonide group into the charged fragment. This isotopic label is eliminated on the ejection of a molecule of water – the M−75 ion undergoes no shift.

The peak of the M−15 ion in the spectra of the $D_6$-acetonides is shifted mainly by 3 amu. This means that the methyl radical is ejected mainly from the acetonide group. The fraction of the M−15 ions shifted by six units in the $D_6$-acetonide of bucharaine is 3%, and in that of foliosidine 12%. The increase in the contribution of $CH_3$ as compared with $CD_3$ in the latter case is apparently due to the possibility of the detachment of a methyl radical from $C_4$ of the main skeleton.

The M−99 ion corresponds to the M−59 ion in the spectra of diols with a terminal hydroxypropyl group [7] and has the hydrooxonium form. The intensities of the peaks of the M−99 ions far exceed those of the M−59 peaks, which is probably due to the necessity for the simultaneous cleavage of two bonds. As the spectrum of the $D_6$-acetonide of bucharaine shows, the hydrogen atom migrating to the oxygen in this process splits out to approximately equal extents from the terminal and from the acetonide methyl groups.



All the fragments described were formed as the result of the cleavage of bonds of the dioxolane ring. The magnitudes of the contributions of these processes to the total ionic current (Table 1) show the absence of marked quantitative differences on passing from substance to substance (an exception is the intensity of the peak of the M−58 ion). The differences that do exist are due, as shown above, mainly to the different stabilities of the molecular ions. An ion with m/e 59 is also associated with such ions. In the spectra of the $D_6$-acetonides, its peak is shifted to m/e 65 to the extent of 80-90%. Consequently, this ion is formed predominantly from the acetonide grouping. It can be seen from Table 1 that the intensities of the peaks of the ion with m/e 59 depend symbatically on the sum of the intensities of all the peaks in the formation of which the bonds of the dioxolane ring participate, $\Sigma_{acetonide}$ (without the intensity of $M^+$).

In the formation of the other ions given in Table 1, bonds outside the dioxolane ring participate. Their resistance to cleavage depends on the nature of the neighboring bonds, and also on their closeness to the main nucleus of the molecule. Consequently, the intensities of the M−129, and the 129, 85, and 71 m/e, ions vary within wide limits. The first two ions arise by the cleavage of the bond present in the $\alpha$ position to the dioxolane ring. The M−129 ion is the maximum ion in the spectrum of bucharaine acetonide (I). Form (I) cannot explain such a high intensity of this peak. If one bears in mind the fact that bucharaine derivatives undergo the Claisen rearrangement on mass spectrometry [8], we obtain form (Ia) for the acetonide (I). In this form, the heterolytic cleavage of the bond adjacent to the acetonide group is activated by the double bond in the allyl position. The reason for the high intensities of the peaks of the M−129 and 129 peaks in the spectrum of pranferin (VI) is the process, energetically favorable in all respects, leading to the formation of tropylium and oxonium cations. Almost all the other cases of the ions considered are not widespread. By eliminating a molecule of acetone, the ions with m/e 129 may be converted into ions with m/e 71 which undergo no shift in the spectra of the $D_6$-acetonides.

The cleavage of the C−O bond ($\beta$ with respect to the dioxolane ring) is more characteristic for the acetonides (IV) and (V). While the corresponding ions of phenols with the charge in the heteroaromatic system are extremely intense, the ions with the charge in the side chain (m/e 143) scarcely appear. Here, apparently, an acetone molecule and ArO· are eliminated simultaneously, which leads to the appearance of intense peaks of ions with m/e 85. Analysis of the spectrum of the $D_6$-acetonide of foliosidine shows an

TABLE 1. Intensities of the Peaks of the Fragments in the Mass Spectra of the Acetonides (% with respect to the total ionic current)

| Compound | $M^+$ | M−15 | M−57 | M−58 | M−73 | M−75 | M−99 | M−129 | 129 | 85 | 71 | 59 | Σ aceton. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bucharaine acetonides (I) | 371 1,57 | 1,62 | 0,17 | 2,47 | 0,50 | 1,38 | 0,30 | 8,44 | 0,56 | 0,30 | 2,95 | 5,91 | 24,61 |
| Dihydrobucharaine acetonide (II) | 373 0,1 | 4,00 | 0,61 | 3,77 | 0,28 | 3,54 | 1,34 | 0,15 | 0,15 | 0,71 | 2,12 | 2,26 | 18,93 |
| Bucharamine (III) | 371 0,93 | 1,58 | 0,46 | 7,24 | 0,74 | 1,48 | 0,74 | 0,65 | 0,20 | 0,45 | 0,80 | 1,55 | 15,89 |
| Foliosidine acetonide (IV) | 347 5,16 | 1,46 | 0,61 | <0,1 | 0,30 | 0,70 | 0,30 | 0,80 | 0,42 | 5,63 | 2,34 | 2,34 | 15,00 |
| Evoxine acetonide (V) | 387 !5,8 | 3,58 | 0,68 | 0,1 | 0,38 | 0,64 | 0,20 | 3,20 | 0,15 | 4,71 | 0,3 | 4,14 | 18,08 |
| Pranferin (VI) | 1,00 | 2,86 | 3,18 | 0,91 | 0,68 | 2,00 | 0,50 | 12,70 | 7,95 | 0,68 | 3,50 | 10,7 | 45,66 |

approximately 40% shift of the m/e 85 peak to m/e 91. The remaining, nonshifting, fraction of the ions with m/e 85 is formed from the M−58 ions by the splitting out of ArO· as shown in the scheme.

## EXPERIMENTAL

The mass spectra were taken on an MKh-1303 instrument fitted with a system for the direct introduction of the sample into the ion source at a temperature of the inlet tube of 90-110°C at an ionizing voltage of 40 V.

Bucharaine Acetonide (I). A solution of 0.2 g of bucharaine in 20 ml of acetone was treated with three drops of conc. $H_2SO_4$, and the mixture was left for a day. Then the acid solution was neutralized with anhydrous sodium carbonate to give a weakly alkaline reaction. The acetone solution was separated off and distilled. Crystals deposited with mp 158°C (from acetone).

Evoxine acetonide (V), mp 173°C, and dihydrobucharaine acetonide (II), an oil, were isolated similarly. The $D_6$-acetonide of bucharaine with mp 156°C and that of foliosidine with mp 120°C were obtained by using deuteroacetone in place of acetone.

The sample of pranferin was given to us by G. K. Nikonov.

## SUMMARY

The acetonides of alkaloids and coumarins can be identified by their mass-spectrometric properties. The intensity of the fragments characteristic for the dioxolane ring largely depends on the structure of the chain attached to it.

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