STUDY OF NATURAL COUMARINS BY MASS SPECTROSCOPY

I. Mass Spectra of Kamolone and Kamolol

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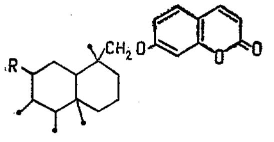
The isolation of kamolone and kamolol, new terpenoid coumarins from Ferula penninervis, Rgl. et Schmalh., and the determination of their structure has been reported previously [1, 2].

In this paper we give the results of a study of the fragmentation under the action of electron impact of kamolone (I), kamolol (II), [D$_3$]kamolone (III), [D]kamolol (IV), acetylkamolol (V), and the diol (VI).

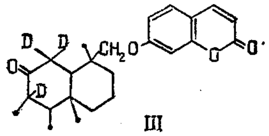


I R=O=

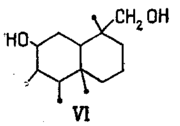
II R=-OH

IV R=-OD

V R=-O-C-CH$_3$ $\overset{\|}{\text{O}}$

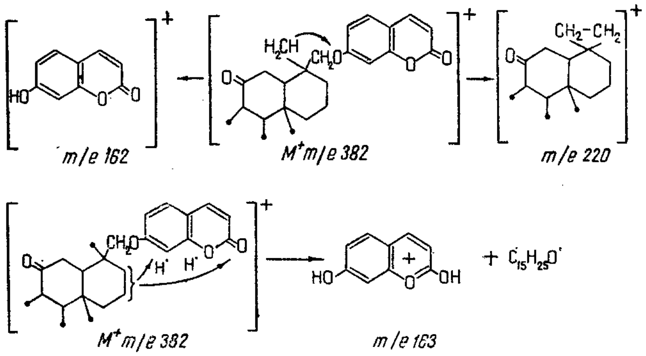


III



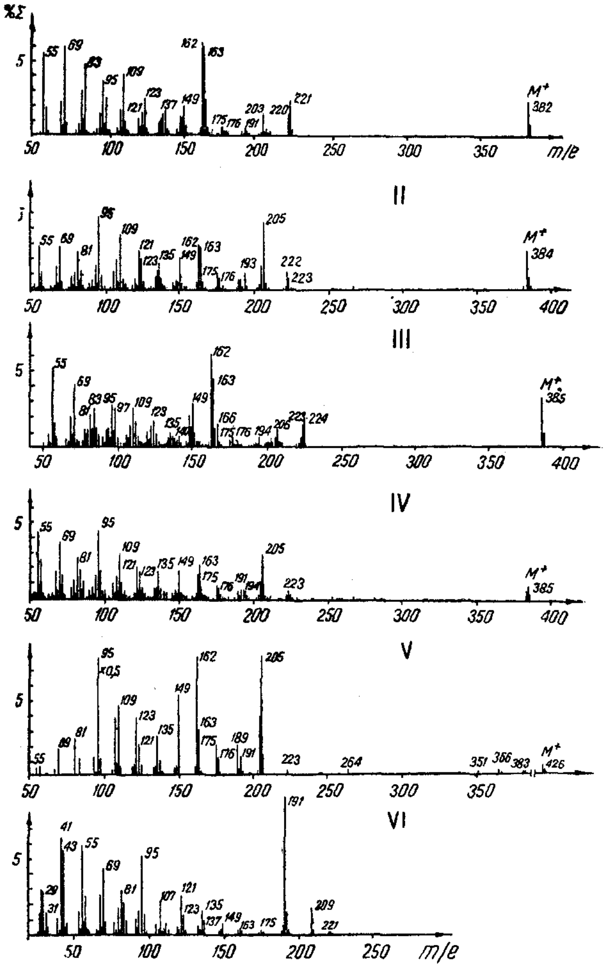
VI

The mass spectra of all the compounds (figure) except VI contain molecular peaks of moderate intensity. The strongest peaks in the mass spectra of the compounds studied are those with m/e 162 and 163, which probably belong to the molecular and protonated ions of umbelliferone. The formation of these fragments apparently takes place in the manner shown below (the decomposition of kamolol is shown).



That the fragments with m/e 162 and 163 belong to the coumarin part of the molecule of the compounds studied is confirmed by the absence of a shift for them in the mass spectrum of [D$_3$]kamolone. In the mass spectrum of [D]kamolol, the peaks with m/e 162 and 163 change their relative intensities, which may be explained by the migration (approximately 25%) of hydrogen from the hydroxyl in the cleavage of the ether bond and the appearance of umbelliferone and protonated umbelliferone. As a result, some of the ions with m/e 162 and 163 increase their mass by one unit. This also leads to the observed change in intensities. The structure of the ion with m/e 220 shown in the scheme is only one of the possible structures. We assume that in the formation of this ion the transfer of hydrogen from the terpene part of the molecule to the coumarin part takes place from the neighboring gem-methyl group.

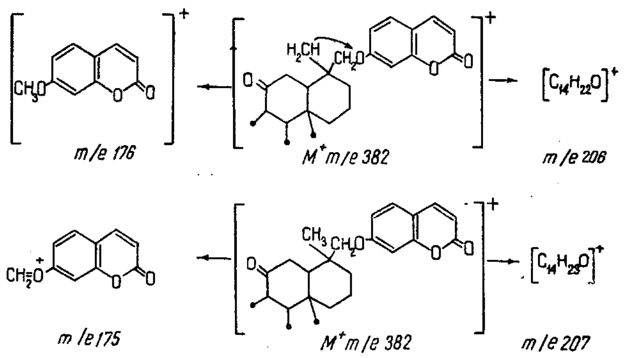
The terpene part of the molecule of kamolone is a substituted β-decalone and on fragmentation exhibits the properties typical for the mass spectra of β-decalone [3]. The elimination of water from the fragments with m/e 221 and 220 leads to peaks with m/e 203 and 202, which can be seen in the mass spectrum of [D$_3$]kamolone in the region three mass units higher. The fragment with m/e 191 in the mass spectrum of [D$_3$]kamolone is also shifted by three mass units. Therefore, the formation of the ion with m/e 191 is possibly the result of the successive elimination of two methyl groups from the fragment with m/e 221.



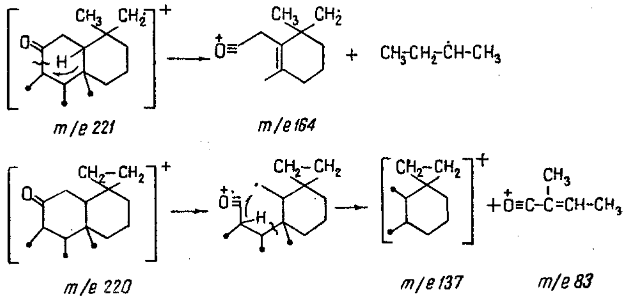
Mass spectra of kamolone (I), kamolol (II), [D_3]kamolone (III), [D]kamolol (IV), acetylkamolone (V), and the diol (VI).

In the mass spectrum of kamolol, the fragment with m/e 223 belongs to the terpene part of the molecule. A proof of this is the shift of its peak in the mass spectrum of [D]kamolol by one mass unit. Because of the loss of a molecule of water from the ion with m/e 223, a fragment with m/e 205 appears. The latter does not undergo a shift in the mass spectrum of [D]kamolol, which shows the elimination of the hydroxyl hydrogen in the water molecule. The fragment with m/e 193 in the mass spectrum of [D]kamolol increases its mass by one unit. It is apparently formed from the fragment with m/e 223 by the successive loss of two methyl groups.

The mass spectra of all the compounds studied have peaks of medium intensity with m/e 175 and 176. Since these fragments do not undergo shifts in the mass spectra of [D_3]kamolone and [D]kamolol and possess a very low intensity in the mass spectrum of the diol, we may assume that they are due to α-cleavage with respect to the oxygen atom of the ether bond with and without transfer of hydrogen from the terpene part of the molecule to the coumarin part. A possible route for their formation is shown for the kamolone molecule.



In the formation of the fragment with m/e 176, the transfer of hydrogen may probably take place from various positions of the terpene part of the molecule. In the mass spectrum of [D_3]kamolone, in the region of high masses the fragments with m/e 164 are shifted by two mass units and those with m/e 137 by three mass units. This permits a scheme for their formation to be proposed.



The mass spectrum of kamolol acetate contains, in addition to peaks common to the mass spectrum of kamolol, peaks of fragments due to the presence of the acetyl group in the molecule of this compound. The intensities of these peaks are low, but their very presence in the mass spectrum of kamolol acetate characterizes the possible routes of decomposition of its molecular ion thanks to the presence of the acetyl group. As a result, the mass spectrum of kamolol acetate has fragments with m/e 384 ($M^+ - CH_2{=}C{=}O$), 383 ($M - CH_3{-}C{=}O$), 367 ($M^+ - CH_3COO$), and 366 ($M^+ - CH_3COOH$). In its turn, the expulsion of a methyl group in the further decomposition of the fragment with m/e 366 gives an ion with m/e 351, and the dissociation of the molecular ion of kamolol acetate at the ether bond with the transfer of hydrogen from the terpene part of the molecule to the coumarin part leads to the formation of an ion with m/e 264 ($M^+ - 162$).

The mass spectrum of the diol does not contradict the structure of the terpene part of kamolol given previously [1]. The appearance of its main fragments with m/e 209 and 191 can be explained by fragmentation typical for dihydric alcohols: $M^+ - CH_2{=}OH$ and $M^+ - CH_2{=}OH - H_2O$.

The reason for the absence of the molecular ion from the mass spectrum of the diol is that α-cleavage with the formation of oxonium ions $CH_2{=}\overset{+}{O}H$ takes place very intensively at tertiary and quaternary atoms [4].

EXPERIMENTAL

The mass spectra were taken on a standard MKh-1303 instrument at an ionizing voltage of 70V with a sample temperature of 100-120° C and an inlet system providing for the entry of the sample into the ion source.

CONCLUSIONS

The mass spectra of six compounds have been obtained: kamolone, kamolol, [D_3]kamolone, [D]kamolol, kamolol acetate, and the terpene diol derived from kamolol. The fragmentation of these compounds under the action of electron impact have been discussed. The mass spectra of kamolone and kamolol agree well with the structures provided for them previously.

REFERENCES

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