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structural formula

Figure 1: structural formula

Abstract

Full Text

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MASS-SPECTROMETRIC STUDY OF NATURAL FURANOCOUMARINS

(Presented by Academician M. M. Shemyakin, 29 XII 1963)

Continuing our work on the mass-spectrometric study of heterocyclic compounds (¹), we investigated the fragmentation under electron impact of a series of natural furanocoumarins, the individuality of which had been checked chromatographically (²), namely: psoralen (I), bergapten (II), isopimpinellin (III), imperatorin (IV), isoimperatorin (V), prangenin (VI), oxypeucedanin (VII), and fellopterin (VIII):

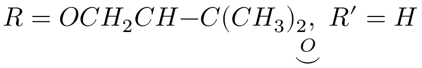
I. $R = R' = H$

II. $R = H,\ R' = OCH_3$

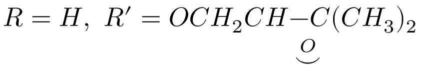
III. $R = R' = OCH_3$

IV. $R = OCH_2CH{=}C(CH_3)_2,\ R' = H$

V. $R = H,\ R' = OCH_2CH{=}C(CH_3)_2$

VI. 

$R = OCH_2CH{-}C(CH_3)_2\underset{\underset{\smile}{O}}{,}\ R' = H$

VII. 

$R = H,\ R' = OCH_2CH\underset{\underset{\smile}{O}}{-}C(CH_3)_2$

VIII. $R = CH_2CH{=}C(CH_3)_2,\ R' = OCH_3$

Taking into account the structural relationship of furanocoumarins and coumarins, it could be expected that their fragmentation would be similar. Earlier (¹) we showed that the mass spectra of coumarins are characterized by the presence of an intense molecular-ion peak (as a rule, one of the largest in

Figure 1. Mass spectra. a —bergapten, b —isopimpinellin

Figure 2: Figure 1. Mass spectra. a —bergapten, b —isopimpinellin

the spectrum), as well as by peaks $M^+ - 28$ and $M^+ - 2 \times 28$, corresponding to onefold and twofold loss of CO.

The spectra of the furanocoumarins proved to be considerably more complex. Only in the spectra of psoralen, bergapten (Fig. 1a), and isopimpinellin (Fig. 1b) is there an intense peak M^+; however, only psoralen shows the fragmentation characteristic of coumarins with successive multiple loss of CO, starting from the molecular ion (peaks with m/e (% Σ): 186(42), 158(27), 130(9.5), and 102(10.1)).

Although the spectrum of bergapten also contains the peak $M^+ - 28$ (m/e 188), its appearance is not due to the main direction of fragmentation. The presence in the spectrum of bergapten of a metastable peak with m/e 150 (calculated 149.6), characterizing the transition m/e 201 → 173, indicates that its fragmentation, analogous to that of coumarins, begins from the fragment with m/e 201 ($M^+ - 15$), and not from the fragment with m/e 188 ($M^+ - 28$).

Similarly to this, the multiple ejection of CO in the mass spectrum of isopimpinellin begins only after the loss of at least one CH_3 group, i.e., from the fragment with m/e 231 ($M^+ - 15$).

The validity of the transitions m/e 216 → 188, 173 → 145, accompanied by elimination of CO, is confirmed by the presence in the spectrum of bergapten of the corresponding metastable peaks with m/e 164 (calculated 163.6) and 122 (calculated 121.5).

In contrast to bergapten and isopimpinellin, the spectra of imperatorin (Fig. 2) and isoimperatorin are characterized by the insignificant intensity of the molecular ion, while in the spectrum of fellopterin the peak M^+ is absent altogether. In the spectra of these compounds the peak $M^+ - 68$ predominates (m/e 202 in the spectra of imperatorin and isoimperatorin and m/e 232 in the spectrum of fellopte-

Fig. 1. Mass spectra. **a** —bergapten, **b** —isopimpinellin

i.e., under the action of electron impact, cleavage of the O—CH_2 bond in the ether grouping occurs first of all.

$$\left[\ \text{structure with O—CHCH=C(CH}_3)_2\ \right]^+ \xrightarrow{-\mathrm{C_5H_8}} \left[\ \text{hydroxyfurocoumarin structure}\ \right]^+$$

m/e 270 m/e 202

Mass spectrum of imperatorin. Molecular weight 270.

Figure 3: Mass spectrum of imperatorin. Molecular weight 270.

Mass spectrum of prangenin. Molecular weight 286.

Figure 4: Mass spectrum of prangenin. Molecular weight 286.

Further fragmentation of imperatorin and isoimperatorin from the ion with m/e 202 is characteristic of coumarins (peaks with m/e 174, 146, 118, and 90). Along with this, it should be noted that their spectra also contain peaks of insignificant intensity with m/e 255 ($M^+ - 15$) and 227 ($M^+ - 15 - 28$).

The fragmentation characteristic of coumarins in fellopterin begins only from the ion with m/e 217 ($M^+ - 68 - 15$), i.e., after loss of the alkyl residues by both ether groups.

A somewhat different type of fragmentation occurs in prangenin (Fig. 3) and oxypeucedanin. Their spectra are characterized by a rather considerable

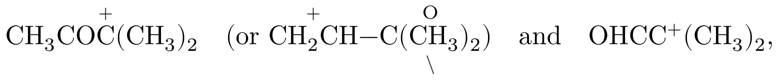
Fig. 2. Mass spectrum of imperatorin

Fig. 3. Mass spectrum of prangenin

by the intensity of the molecular-ion peak, and also by the appearance of the peak of a fragment with m/e 215 ($M^+ - 71$), apparently corresponding to the loss of part of the side chain:

$$\left[\text{ structure, } m/e \text{ 286 }\right]^+ \xrightarrow{-C_4H_7O} \text{ structure, } m/e \text{ 215}$$

In contrast to imperatorin, isoimperatorin, and phellopterin, whose spectra contain peaks with m/e 69, apparently due to the formation of the ion $^+CH_2{-}CH{=}C(CH_3)_2$, in the mass spectra of prangenin and oxypeucedanin, along with this peak, there are intense peaks with m/e 85 ($M^+ - 201$) and 71 ($M^+ - 215$), probably corresponding to side-chain fragments



$$CH_3CO\overset{+}{C}(CH_3)_2 \quad (\text{or } \overset{+}{C}H_2CH{-}C(\underset{\backslash}{\overset{O}{C}}H_3)_2) \quad \text{and} \quad OHCC^+(CH_3)_2,$$

respectively.

Thus, the data obtained make it possible to distinguish with confidence between the methyl, γ,γ-dimethylallyl, and γ,γ-dimethyl-β,γ-epoxypropyl ethers of oxyfuranocoumarins.

In addition, quantitative analysis of the spectra makes it possible to distinguish from one another structural isomers containing an alkoxy group in the 5-position (isoimperatorin, oxypeucedanin) or in the 8-position (imperatorin, prangenin) of the furanocoumarin ring.

Table 1

Analysis of the mass spectra of furanocoumarins

Name	M^+ (%, Σ)	M^+- 15 (%, Σ)	M^+- 68 (%, Σ)	M^+- 84 (%, Σ)	M^+- 71 (%, Σ)	$\frac{M^+}{M^+-15}$	$\frac{M^+}{M^+-68}$	$\frac{M^+}{M^+-84}$	$\frac{M^+}{M^+-71}$
Bergapten	216 (27.2)	201 (8.3)	–	–	–	3.28	–	–	–
Isopimpinellin	246 (13.8)	231 (15.8)	–	–	–	0.87	–	–	–
Isoimperatorin	270 (0.20)	–	202 (5.8)	–	–	–	0.03	–	–
Imperatorin	270 (0.25)	–	202 (18.5)	–	–	–	0.01	–	–
Oxypeucedanin	286 (5.7)	–	–	202 (11.6)	215 (0.6)	–	–	0.49	9.50
Prangenin	286 (5.8)	–	–	202 (23.2)	215 (4.3)	–	–	0.25	1.35

Indeed, from comparison of the ratio of the intensity of the M^+ peaks to m/e 202 (M^+-68 or M^+-84) it is seen (see Table 1) that the stability of the molecular ion in isoimperatorin and oxypeucedanin, which contain an alkoxy group in the 5-position, is considerably higher than in imperatorin and prangenin, which contain an alkoxy group in the 8-position. This is also confirmed by comparison of the intensity ratios of the M^+ peaks to M^+-71 in the spectra of prangenin and oxypeucedanin (see Table 1). By analogy with what has been described above, it may be assumed that the greater stability of the molecular ion in bergapten, as compared with isopimpinellin (the ratio of M^+ to M^+-15 in the former is considerably greater than in the latter), is connected with the presence in the molecule of the latter of an 8—CH_3O group, the demethylation of which under electron impact proceeds considerably more readily than in bergapten, which contains a CH_3O group in position 5.

The mass spectra were recorded on an MX-1303 mass spectrometer, at a temperature of 140—160° and an ionizing voltage of 30 V.

The samples of furanocoumarins investigated in the present work were kindly provided to us by G. A. Kuznetsova (Botanical Institute, Academy of Sciences of the USSR), to whom the authors express their deep gratitude.

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Note: Figure translations are in progress. See original paper for figures.

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