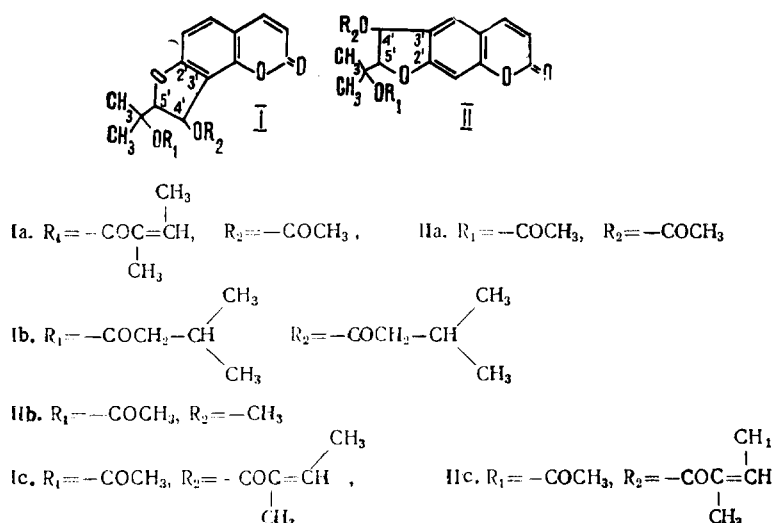


# A MASS-SPECTROMETRIC STUDY OF ANGULAR AND LINEAR DIACYLOXYDIHYDROFUROCUMARINS

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We have previously [1] discussed the mass spectra of peucenidin (Ia), smyrniorin (IIa), athamantin (Ib), libanotin (Ic), and smyrnioridin (IIc) [2-5] in order to determine the positions of the acyl residues in the peucenidin molecule. In the present paper we give the results of a more detailed analysis of the mass spectra of these compounds and also the product of the mild methanolysis of smyrnioridin (IIb) in order to establish the main routes of fragmentation and to determine the structural characteristics in the mass spectra of angular and linear diacyloxydihydrofurocoumarins, to which classes the compounds investigated belong.

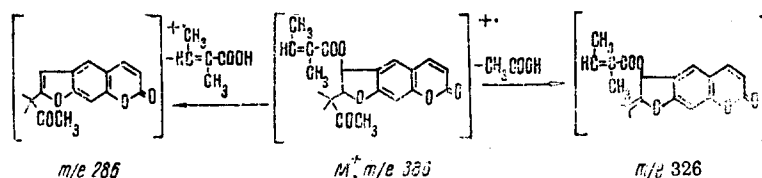


It can be seen from the table, which gives the masses of the main ions observed in the mass spectra of compounds (Ia, b, c) and (IIa, b, c), that on electron impact they all give a molecular ion of appreciable intensity (0.6-8.0% of the peak of the maximum ion). Thus, the molecular weights of compounds of this class can always be firmly established.

The acyl residues on the tertiary and secondary alcoholic groups are readily detected in the mass spectra obtained from the presence in them of the peaks of the ions formed by the loss of molecules of acid by the mechanism of the McLafferty rearrangement [6]. As a result, the ions  $M^+ - R_1\text{OH}$  and  $M^+ - R_2\text{OH}$  arise; their production can be represented by Scheme 1 given for compound (IIc) as example.

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Scheme 1

The acids  $R_1OH$  and  $R_2OH$  are probably split off as a consequence of the transfer of a hydrogen atom from position 5' to the oxygen atom of the acyl residue and the formation of a multiple bond in the residual ion. Consequently, the mass spectra of the compounds under consideration permit the molecular weights of the acids corresponding to their acyl groups to be determined. Compound (Ic) with the angular position of the dihydrofuran ring, containing the larger acyl residue at the  $C_4'$  carbon atom, splits off from the 4' position not the acid but the acid residue, giving an ion with  $m/e$  287, while the substance (Ia) isomeric with it but having the smaller acyl at  $C_4'$  and the linear compound (IIc) with the larger acyl at  $C_4'$  split off predominantly the acid from position 4', forming the ions with  $m/e$  326 and 286, respectively. The presence of the ion  $M^+ - RO$  with a greater intensity than that of the ion  $M^+ - ROH$  (where R is the larger of the two acyl radicals present) in the mass spectrum of a furocoumarin under investigation shows the angular position of the dihydrofuran ring and the presence of the larger acyl residue R at the  $C_4'$  carbon atom.

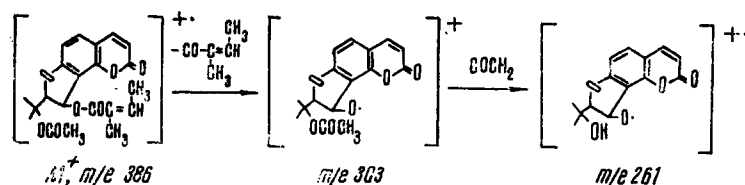
In addition to this, the molecular ions of the angular compounds (Ia, b, c) readily lose the larger acyl residue with the subsequent ketene decomposition of the resulting ion  $M^+ - R$  (Scheme 2). We have not observed this type of process in the mass spectra of the linear analogs.

In the mass spectra of substances (Ia, b, c) and (IIa, c) the ions with  $m/e$  244, 243 and 223, 227 are very important for structural-analytical purposes. From their mutual intensities it is possible to determine the positions of the acyl residues in the molecules both of the angular and of the linear compounds. In compounds (Ia), (IIa), and (Ib), each of which contains the larger acyl radical or one with an equal number of carbon atoms on the tertiary carbon atom, the relative intensities of the ions mentioned satisfy the inequalities  $I_{244} > I_{243}$  and  $I_{229} > I_{227}$ . For substances (Ic) and (IIc) with the acyl group having the larger number of carbon atoms on the  $C_4'$  carbon atom, these inequalities are reversed. The preceding paper in this

TABLE 1. Main Fragments and Their Relative Intensities in the Mass Spectra of the Diacyloxydihydrofurocoumarins in the Region of High and Moderate Masses

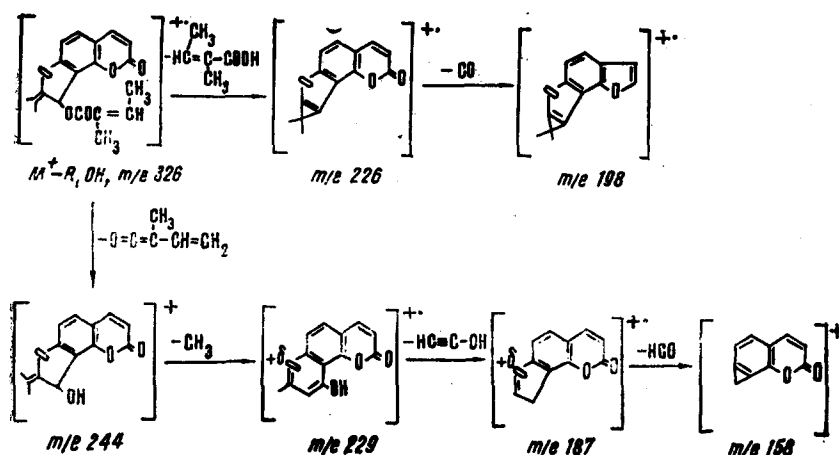
| Compound | Mass numbers $m/e$ (relative intensities, %) |              |              |              |              |              |              |              |              |              |              |
|----------|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Ia       | 386<br>(0,6)                                 | 326<br>(0,7) | 311<br>(3,0) | 303<br>(1,0) | 287<br>(1,4) | 286<br>(5,5) | 271<br>(1,5) | 261<br>(1,4) | 244<br>(18)  | 243<br>(11)  | 229<br>(26)  |
|          | 228<br>(4,5)                                 | 227<br>(15)  | 226<br>(8,2) | 213<br>(3,6) | 198<br>(3,1) | 191<br>(4,5) | 187<br>(4,0) | 186<br>(5,1) | 158<br>(5,8) | 83<br>(100)  |              |
|          |  |              |              |              |              |              |              |              |              |              |              |
| Ib       | 430<br>(3,3)                                 | 328<br>(4,2) | 313<br>(2,1) | 261<br>(3,3) | 245<br>(5,5) | 244<br>(19)  | 243<br>(11)  | 230<br>(6,5) | 229<br>(37)  | 228<br>(6,7) | 227<br>(25)  |
|          | 226<br>(16)                                  | 213<br>(7,0) | 198<br>(7,6) | 191<br>(3,5) | 187<br>(9,2) | 186<br>(6,7) | 158<br>(6,2) | 57<br>(100)  |              |              |              |
|          |  |              |              |              |              |              |              |              |              |              |              |
| Ic       | 386<br>(7,0)                                 | 326<br>(1,5) | 311<br>(6,0) | 303<br>(1,5) | 287<br>(3,5) | 286<br>(2,3) | 271<br>(1,5) | 245<br>(5,5) | 244<br>(10)  | 243<br>(14)  | 229<br>(20)  |
|          | 288<br>(14)                                  | 227<br>(4,5) | 226<br>(28)  | 213<br>(13)  | 196<br>(19)  | 191<br>(2,0) | 187<br>(14)  | 186<br>(6,0) | 158<br>(12)  | 83<br>(100)  |              |
|          |  |              |              |              |              |              |              |              |              |              |              |
| IIa      | 346<br>(5,0)                                 | 287<br>(0,8) | 286<br>(3,3) | 271<br>(5,5) | 245<br>(2,5) | 244<br>(5,0) | 243<br>(2,3) | 229<br>(23)  | 228<br>(10)  | 227<br>(17)  | 226<br>(19)  |
|          | 213<br>(19)                                  | 198<br>(6,2) | 191<br>(14)  | 187<br>(14)  | 186<br>(6,0) | 158<br>(5,0) | 57<br>(100)  |              |              |              |              |
|          |  |              |              |              |              |              |              |              |              |              |              |
| IIb      | 318<br>(8,0)                                 | 259<br>(1,0) | 258<br>(3,0) | 245<br>(2,5) | 244<br>(15)  | 243<br>(100) | 229<br>(3,0) | 228<br>(3,2) | 227<br>(10)  | 213<br>(2,0) | 205<br>(5,5) |
|          | 189<br>(3,3)                                 | 187<br>(9,0) | 186<br>(3,2) | 175<br>(3,5) | 158<br>(3,0) |              |              |              |              |              |              |
|          |  |              |              |              |              |              |              |              |              |              |              |
| IIc      | 386<br>(1,3)                                 | 326<br>(2,2) | 311<br>(3,5) | 287<br>(0,3) | 286<br>(1,3) | 271<br>(1,0) | 245<br>(3,0) | 244<br>(3,8) | 243<br>(4,5) | 229<br>(11)  | 228<br>(8,0) |
|          | 227<br>(24)                                  | 226<br>(17)  | 213<br>(11)  | 198<br>(4,5) | 191<br>(1,7) | 187<br>(12)  | 186<br>(9,5) | 158<br>(6,5) | 83<br>(100)  |              |              |
|          |  |              |              |              |              |              |              |              |              |              |              |

issue [1] gives a scheme of the formation of the fragments with  $m/e$  244, 243 and 229, 227, and an explanation of the observed relationship between the intensities of these ions and the positions of the acyl groups.



Scheme 2

The results of a comparison of the mass spectra of the diacyloxydihydrofurocoumarins with the mass spectra of the diacyloxydihydropyranocoumarins [7] show that the mass-spectrometric method of analysis easily permits these two classes of compounds to be distinguished. Although the latter form very complex mass spectra in the region of high mass numbers, in the region of moderate mass numbers they differ substantially by the relative intensities of the ions with  $m/e$  229 and 227. Thus, in the mass spectra of the diacyloxydihydropyranocoumarins the ion with  $m/e$  229 has a considerably greater intensity (more than twice as great) as the ion with  $m/e$  227, while in the mass spectra of the diacyloxydihydrofurocoumarins the intensity of the ion with  $m/e$  229 exceeds that of the ion with  $m/e$  227 by a factor of not more than 1.5 or even has a lower intensity than the latter. Furthermore, in the region of moderate mass numbers the mass spectra of the diacyloxydihydrofurocoumarins contain ions with  $m/e$  198 and 158, which are not found in the mass spectra of the dihydropyranocoumarins isomeric with them. The formation of fragments important for structural-analytical purposes can be represented by Scheme 3, shown for compound (Ic) as example.



Scheme 3

Thus, the features studied in the mass spectra of the diacyloxydihydrofurocoumarins well reflect the structural characteristics of these compounds and can be used successfully for structural and analytical purposes.

## EXPERIMENTAL

The mass spectra of compounds (Ia, b, c) and (IIa, b, c) were taken on a modified MKh-1303 instrument at an ionizing potential  $U = 50$  V at temperatures of 105°C (Ia), 90°C (IIa), 83°C (Ib), 126°C (Ic), 90°C (IIc), and 80°C (IIb) (the inlet system provides for the introduction of the sample into the ion source). The samples of smyrniorin, smyrnioridin, and the product of the alkaline methanolysis of smyrnioridin were kindly given to us by A. A. Savina.

## SUMMARY

The mass spectra of six compounds belonging to the class of angular and linear 4'-acyloxy-5'-(1-acyloxy-1-methylethyl)- and 4'-methoxy-5'-(1-acyloxy-1-methylethyl)dihydrofurocoumarins have been obtained. It has been shown that from the mass spectra of this class of compounds it is possible to deter-

mine the molecular weights of the acids corresponding to the acyl radicals that they contain, the position of attachment of the dihydrofuran ring to the coumarin ring, and the positions of the acyl residues, and also to distinguish this class of substances from the class of diacyloxydihydropyranocoumarins isomeric with it.

#### LITERATURE CITED

1. P. I. Zakharov, P. B. Terent'ev, G. K. Nikonov, A. I. Ban'kovskii, N. D. Antonova, and A. P. Prokopenko, *Khim. Prirodn. Soedin.*, 271 (1972).
2. A. P. Prokopenko, *Zh. Obshch. Khim.*, 34, 4111 (1964).
3. A. A. Savina, G. K. Nikonov, and M. E. Perel'son, *Khim. Prirodn. Soedin.*, 592 (1969).
4. A. P. Prokopenko, *Khim. Prirodn. Soedin.*, 215 (1965).
5. A. A. Savina, M. E. Perel'son, and G. K. Nikonov, *Khim. Prirodn. Soedin.*, 165 (1970).
6. F. W. McLafferty, *Advan. Mass Spectrometry*, 1, 353 (1959).
7. P. I. Zakharov, P. B. Terent'ev, G. K. Nikonov, and A. I. Ban'kovskii, *Khim. Prirodn. Soedin.*, 704 (1971).