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METASTABLE-ION MASS SPECTRA OF INSECT PHEROMONES

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The laws of the fragmentation of the metastable molecular and key fragmentary ions of mono- and dienic alcohols, acetates, aldehydes, hydrocarbons, and epoxy compounds forming components of the pheromones of the turnip, tomato, and bollworm moths and other pests of agricultural crops are discussed, and the use of the laws found in the identification of compounds of this class has been demonstrated.

Chemical substances participating in inter- and intraspecies interactions are material carriers of signal information. One of the classes of such substances includes the sex pheromones-highly active compounds secreted by specialized glands of sexually mature females for attracting males [1-8].

The successful development of the investigation of pheromones and their use for keeping down the numbers of insects harmful for agricultural crops has required the development of new sensitive methods and methodological approaches in the study of their structure and identification.

Recently, wide use has been made for the identification of pheromones of spectral methods of investigation such as UV, IR, and NMR spectroscopy and mass spectrometry. With the aid of UV spectroscopy it is easy to establish the presence in pheromone molecules of a conjugated dienic system absorbing at λ 232 nm with an extinction coefficient of 18,000. The presence of functional groups (hydroxy, carboxy, ester) is established reliably with the aid of UV spectroscopy. NMR spectroscopy is used most frequently for determining the geometry of double bonds and epoxy groups in pheromone molecules [9, 10].

The most sensitive and informative method of identifying pheromones and establishing their structures is mass spectrometry, which is used frequently in combination with gas chromatography and a computer data-processing system [11-19]. At the present time, the mass spectrometry of metastable ions is being widely used as a sensitive and specific method for the structural investigation and identification of various classes of organic compounds [20-23]. We were the first to use this method for the study of pheromones [24]. The methods of the direct analysis of daughter ions (DADI) and metastable defocussing (MD) in combination with low- and high-resolution mass spectrometry undoubtedly increase the possibilities of electron-impact mass spectrometry – the most widely used method of identifying the components of insect pheromones.

An advantage of the DADI and MD methods is the possibility of establishing a genetic link between the ions arising on the breakdown of molecular and fragmentary ions. The absence of genetic links between the groups of ions determined indicates the presence of impurities in the specimen under study. The detection of impurities and the determination of the origins of ions connected with the components of the impurities permits their analysis without preliminary separation [21-23].

Investigations that we have carried out with the use of the mass spectrometry of the metastable ions of pheromones and their precursors has shown the promising nature of such an approach both in the determination of the components and in the establishment of the *m/z* values of the molecular ions of compounds unstable to electron impact.

In this paper the results are generalized of an investigation of the electron-impact mass spectra and the metastable-ion mass spectra of products of intermediate stages of the synthesis of pheromones (1-8), and of the cis- and trans-monoenic alcohols and their acetates (9-24), the monoenic aldehydes (25-30), the ketone (29), the dienic alcohols and acetates (31-37), the mono-, di-, and trienic hydrocarbons (39-45), and the epoxy compounds (46-51) that are components of pheromones of insects of the order Lepidoptera and others. The names and structural formulas of the compounds studied are given in Table 1.

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TABLE 1. Products and Components of the Sex Pheromones of Some Species of Lepidoptera

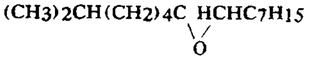
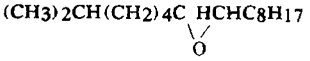
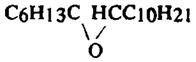
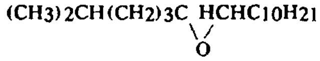
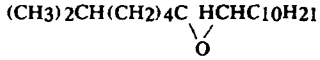
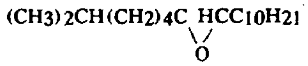
	Name	Structure	Mol. mass
1.	Diethyl sebacate	$C_2H_5OOC(CH_2)_8COOC_2H_5$	258
2.	Decane-1,10-diol	$HO(CH_2)_{10}OH$	174
3.	10-Chlorodecan-1-ol	$HO(CH_2)_{10}Cl$	192
4.	Hex-1-yne	$C_4H_9C{\equiv}CH$	82
5.	Hexadec-11-yn-1-ol	$C_4H_9C{\equiv}C(CH_2)_{10}OH$	238
6.	1,1-Diethoxypentan-5-ol	$(C_2H_5O)_2CH{-}(CH_2)_4OH$	176
7.	Tetradec-5E-enoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_2CH_2COOH$	226
8.	Ethyl tetradec-7Z-enonate	$CH_3(CH_2)_5CH{=}CH(CH_2)_4CH_2COOC_2H_5$	204
9.	Dec-5Z-en-1-ol	$C_4H_9CH{=}CH(CH_2)_4OH$	156
10.	Dec-5Z-en-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_4OCOCH_3$	198
11.	Dec-5E-en-1-ol	$C_4H_9CH{=}CH(CH_2)_4OH$	156
12.	Dec-5E-en-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_4OCOCH_3$	198
13.	Dodec-3E-en-1-yl acetate	$CH_3(CH_2)_7CH{=}CHCH_2CH_2OCOCH_3$	226
14.	Dodec-7Z-en-1-ol	$C_4H_9CH{=}CH(CH_2)_6OH$	184
15.	Dodec-7Z-en-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_6OCOCH_3$	226
16.	Dodec-10E-en-1-yl acetate	$CH_3CH{=}CH(CH_2)_9OCOCH_3$	226
17.	Tetradec-11Z-en-1-ol	$C_2H_5CH{=}CH(CH_2)_9CH_2OH$	212
18.	Tetradec-11Z-en-1-yl acetate	$C_2H_5CH{=}CH(CH_2)_9CH_2OCOCH_3$	254
19.	Tetradec-9Z-en-1-ol	$C_4H_9CH{=}CH(CH_2)_7CH_2OH$	212
20.	Tetradec-9Z-en-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_8OCOCH_3$	254
21.	Hexadec-11Z-en-1-ol	$C_4H_9CH{=}CH(CH_2)_9CH_2OH$	240
22.	Hexadec-11Z-en-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_9CH_2OCOCH_3$	282
23.	Hexadec-11E-en-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_9CH_2OCOCH_3$	282
24.	Heneicos-6Z-en-11-ol	$C_{10}H_{21}CH(OH)(CH_2)_3CH{=}CH(CH_2)_4CH_3$	310
25.	Tridec-3E-enal	$CH_3(CH_2)_8CH{=}CH{-}CH_2{-}CHO$	196
26.	Hexadec-7Z-enal	$C_8H_{17}CH{=}CH(CH_2)_4CH_2CHO$	238
27.	Hexadec-9Z-enal	$C_4H_9(CH_2)_2CH{=}CH(CH_2)_7CHO$	238
28.	Hexadec-11Z-enal	$C_4H_9CH{=}CH(CH_2)_9CHO$	238
29.	Heneicos-6Z-en-11-one	$C_{10}H_{21}CO(CH_2)_3CH{=}CH(CH_2)_4CH_3$	308
30.	Dodeca-8E,10E-dien-1-ol	$CH_3CH{=}CH{-}CH{=}(CH_2)_7OH$	182
31.	Dodeca-7E,9Z-dien-1-yl acetate	$C_2H_5CH{=}CH{-}CH{=}CH(CH_2)_6OCOCH_3$	224
32.	Dodeca-5Z,7Z-dien-1-yl acetate	$C_4H_9CH{=}CH{-}CH{=}CH(CH_2)_4OCOCH_3$	224
33.	Tetradeca-9Z,11E-dien-1-yl acetate	$C_2H_5CH{=}CH{-}CH{=}CH(CH_2)_8OCOCH_3$	252
34.	Tetradeca-9Z,12E-dien-1-yl acetate	$CH_3CH{=}CHCH_2CH{=}CH(CH_2)_8OCOCH_3$	252
35.	Hexadeca-7Z,11Z-dien-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_2CH{=}CH(CH_2)_6OCOCH_3$	280
36.	Hexadeca-7Z,11E-dien-1-yl acetate	$C_4H_9CH{=}CH(CH_2)_2CH{=}CH(CH_2)_6OCOCH_3$	280
37.	Octadeca-3E,13Z-dien-1-yl acetate	$CH_3(CH_2)_3CH{=}CH(CH_2)_8CH{=}CH(CH_2)_2OCOCH_3$	308
38.	Nonadeca-3Z,6Z,9Z-triene	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_8CH_3$	262
39.	Nonadeca-6Z,9Z-diene	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_8CH_3$	264
40.	Eicosa-3Z,6Z,9Z-triene	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_9CH_3$	276
41.	Eicosa-6Z,9Z-diene	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_9CH_3$	278
42.	Heneicosa-3Z,6Z,9Z-triene	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_{10}CH_3$	290
43.	Heneicosa-3Z,6Z-diene	$CH_3CH_2CH{=}CHCH_2CH{=}CH(CH_2)_{13}CH_3$	292
44.	Heneicosa-6Z,9Z-diene	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_{10}CH_3$	292
45.	Tricos-9Z-ene	$CH_3(CH_2)_{12}CH{=}CH(CH_2)_7CH_3$	322
46.	2-Methyl-(Z)-7,8-epoxypentadecane	 $(CH_3)_2CH(CH_2)_4\underset{\diagdown\,O\,\diagup}{C\quad H}CHC_7H_{15}$	240
47.	2-Methyl-(Z)-7,8-epoxyhexadecane	 $(CH_3)_2CH(CH_2)_4\underset{\diagdown\,O\,\diagup}{C\quad H}CHC_8H_{17}$	254

TABLE 1 (continued)

	Name	Structure	Mol. mass
48.	(Z)-7,8-Epoxyoctadecane	 $\underset{\diagdown O \diagup}{C_6H_{13}C\;HCC_{10}H_{21}}$	268
49.	2-Methyl-(Z)-6,7-epoxy-heptadecane	 $\underset{\diagdown O \diagup}{(CH_3)_2CH(CH_2)_3C\;HCHC_{10}H_{21}}$	268
50.	2-methyl-(Z)-7,8-epoxy-octadecane	 $\underset{\diagdown O \diagup}{(CH_3)_2CH(CH_2)_4C\;HCHC_{10}H_{21}}$	282
51.	2-Methyl-(E)-7,8-epoxy-octadecane.	 $\underset{\diagdown O \diagup}{(CH_3)_2CH(CH_2)_4C\;HCC_{10}H_{21}}$	282

Mass Spectra of Compounds (1-8)

Substances (1-8) are the products of intermediate stages of the synthesis of hexadec-11Z-en-1-ol (21) and its acetate (22), of hexadec-11Z-enal (28), and of dec-5E-en-1-ol (11) and its acetate (12), which are components of the pheromones of the bollworm moth and other insects.

In an investigation of these compounds a dual aim was followed. In the first place, these compounds differ in the size of the molecules, the variety of functional groups, and the numbers of double and triple bonds, and therefore it was of interest to reveal the influence of these factors in the mass spectra and in the spectra of the metastable molecular and other key fragments. In the second place, the use of the spectral characteristics found could play an important role in the monitoring of intermediate stages of the synthesis of the pheromones.

In the mass spectrum of diethyl sebacate (1) we have detected the peak of the molecular ion with *m/z* 258 (2%) while the line of maximum intensity corresponds to the peak of an ion with *m/z* 213 (100%) arising through the splitting out of an ethoxy group from the molecular ion.

In the DADI spectrum of the ion with *m/z* 213 the peaks of ions with *m/z* 195, 185, 166, 158, and 129 appear. The first two ions show the splitting out of water and carbon monoxide molecules; the formation of the ion with *m/z* 158 is due to the simultaneous occurrence of two processes involving the cleavage of different bonds – the splitting out of ketene ($CH_2{=}C{=}O$) through the cleavage of the C_2-C_3 bond and of a methyl radical from the ethoxy group. The peak of a rearrangement ion with *m/z* 166 in the mass spectrum of (1) had a high intensity, this ion being genetically linked with ions having *m/z* 212 and 213 as is shown by its MD spectrum and the DADI spectrum of the ion with *m/z* 213. On its formation from the ion with *m/z* 258 (M^+), two water molecules are split out. Such ejection can be explained rationally starting from structure (1) and is characteristic for the M^+ ions of dibasic fatty acids. The ion with *m/z* 129 in the DADI spectrum of the ion with *m/z* 213 corresponds to a C_5-C_6 cleavage with the retention of the charge on the ester part of the ion.

Although the DADI spectrum of the ion with *m/z* 213 lacks the peak of an ion showing the formation of a fragment with *m/z* 171 from it, in the MD spectrum of the latter an intense peak of a precursor ion with *m/z* 213 appears. In addition, in this spectrum there are the peaks of ions with *m/z* 185, 212, and 258. In the spectra of the metastable ions with *m/z* 166 and 171 the peaks of ions with *m/z* 138 and 125 appear.

The following stage of the synthesis is the production of the decanediol (2) by the reduction of (1) with $LiAlH_4$ in absolute ether. A study of the mass spectrum of (2) has shown that the reaction takes place without the formation of by-products. The mass spectrum of (2) lacks the M^+ peak with *m/z* 174. In the region of high masses the peak appears of an ion with *m/z* 156, corresponding to the splitting out of one molecule of water. The dehydration ion with *m/z* 156 is capable of losing another water molecule, thereby confirming the presence of two hydroxy groups in the (2) molecule.

The metastable defocusing spectrum of the ion with *m/z* 138 definitively shows that the precursors of this ion are ions with *m/z* 156 and 174 (M^+). An ion with *m/z* 110 is formed directly from M^+ by the loss of two molecules of water and one of ethylene. The DADI spectrum of this ion includes the peaks of ions with *m/z* 96, 95, 83, 68, and 67, arising by the splitting out of C_nH_{2n} and C_nH_{2n+1} groups.

In the mass spectrum of 10-chlorodecan-1-ol (3) the weak peak of the $(M - 18)^+$ ion with *m/z* 174 is observed (here and below, the values of *m/z* for the chlorine-containing fragments are taken for ^{35}Cl). The following peak of an ion with *m/z* 146 arises with the splitting out of an ethylene molecule. Then the latter, as can be seen from its DADI spectrum, breaks down into ions with *m/z* 118 (ejection of ethylene), 110 (splitting out of an HCl molecule) 104, 84, and 68 (breakdown of the chain).

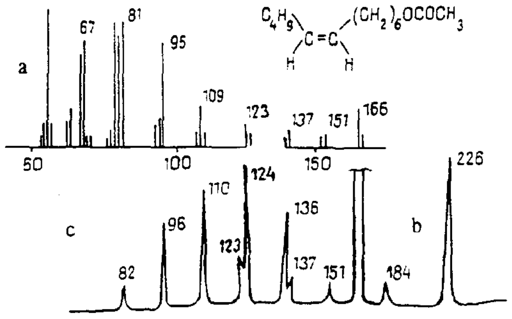


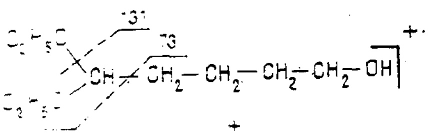
Fig. 1. Mass spectrum of the acetate of dodec-cis-7-en-1-ol (15) (a), the MD spectrum of fragment Φ of substance (15) (b), and the DADI spectrum of fragment Φ of substance (15) (c).

The purity of hex-1-yne (4) has been confirmed by its mass spectrum, in which the M^+ peak with *m/z* 82 is shown. Extremely unusual is the peak of an ion with *m/z* $(M - 1)^+$ having a high intensity (48%). The maximum intensity in spectrum (4) is possessed by the peak of an ion with *m/z* 67 $(M - 15)^+$. A peak corresponding to the splitting out of an ethyl radical also has a high intensity. In all these ions, the positive charge is localized on the triple bond.

The mass spectrum of the product of the following stage of the synthesis of hexadec-11-yn-1-ol (5) is characterized in the region of high-mass numbers by low-intensity peaks of ions with *m/z* 238 (M^+) (0.3%), 196 (1%), 179 (8%), and 166 (8%). In the DADI spectrum of M^+ (5), the maximum intensity corresponds to the peak of the dehydration ion $(M-H_2O)^+$ with *m/z* 220.

Then in this spectrum appear the peaks of ions with *m/z* 196, 182, 166, 152, 138, 124, and 110 with almost equal intensities. The formation of these ions fully confirms the structure of (5). 5,5-Diethoxypentan-1-ol (6) exhibits a low stability to electron impact. The relative intensity of the M^+ peak of this compound in its mass spectrum amounts to 2%. A distinguishing feature of the mass spectrum of (6) is the absence from it of the peak of the dehydration ion $(M-H_2O)^+$ that is characteristic for alcohols. The peak of a fragmentary ion in the high-mass region of the spectrum with *m/z* 131 corresponds to the splitting out of an ethoxy radical. Another fragmentary ion, with *m/z* 100, the peak of which has the maximum intensity is also formed on the cleavage of the bond at the tertiary carbon atom, as shown below.

In the DADI spectrum of the ion with *m/z* 103, the peak of an ion with *m/z* 73 appears, showing the elimination of an ethylene molecule from an ethoxy substituent.



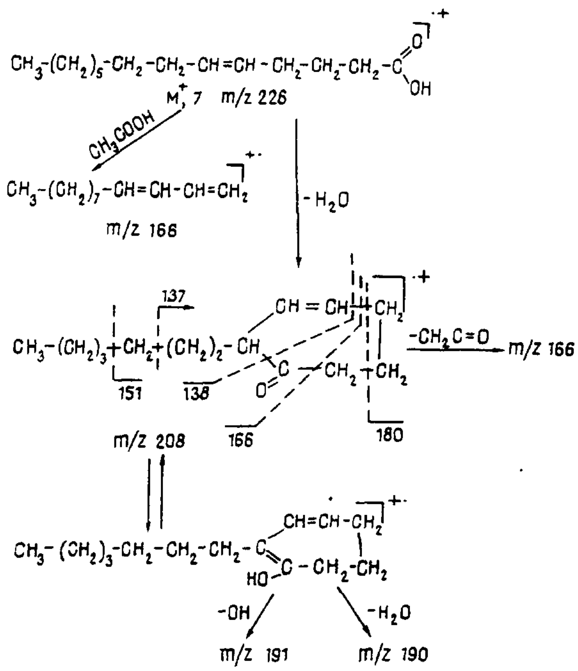
$\overset{+}{M}$, 6

Thus, characteristic for the mass spectra of the alcohols that we have studied, (2), (3), (5), and (6), is an extremely low intensity or the complete absence of the peaks of molecular ions and of other fragmentary ions in the high-mass region, which considerably complicates the identification of such compounds from their mass spectra.

The application of the mass spectrometry of metastable ions to the study of such compounds permits a genetic link between the intense and weak fragmentary ions going as far as the molecular ions to be established and thereby enables information to be obtained on the accurate *m/z* values of the metastable fragmentary and molecular ions that is necessary for their reliable identification. On electron impact, tetradec-5E-enoic acid (7) exhibits the peak of the molecular ion, *m/z* 226, with a considerable intensity. The peaks of the dehydration ion with *m/z* 208 and of ions with *m/z* 166 and 164 are the most intense in the high-mass region. Then follow groups of peaks of ions the intensities of which rise with a decrease in their *m/z* values.

In the DADI spectrum of M^+ for (7), the peaks of ions with *m/z* 208, 190, 183, 166, 153, 129, 127, and 113 are observed. The ions with even values of *m/z* 208, 190, and 166, which are rearrangement ions, arise on the loss of one molecule of water, two molecules of water, and a molecule of acetic acid, respectively. The remaining ions, with odd values of *m/z*, are formed in the direct breakdown of the chain, and the intensities of their peaks are inferior to those of the peaks of the rearrangement ions.

One of the hydrogen atoms of the chain participates in the formation of the dehydration ion. Depending on the position of the carbon atom the hydrogen of which takes part in this process the formation of dehydration ions with cyclic structures of different sizes is possible. On the basis of the structure of (7), we assume the formation of a seven-membered structure from this ion (Scheme 1) which is confirmed to a certain degree by its DADI spectrum.



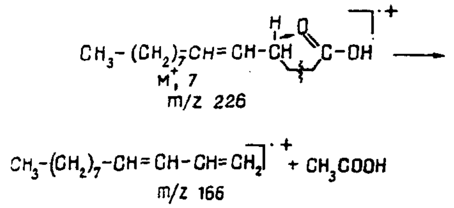
Scheme 1. Fragmentation of the M^+ and the dehydration ions from tetradec-5E-enoic acid.

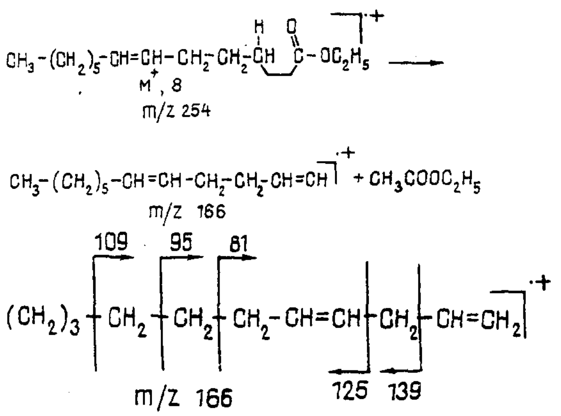
The DADI spectrum of the dehydration ion with *m/z* 208 contains the peaks of ions with *m/z* 191, 190, 180, 166, 151, 138, 137, 126, 125, 113, and 98. The first two ions arise by the splitting out of a hydroxyl radical and a water molecule, respectively. The ions with *m/z* 180, 166, and 138 are formed on the breakdown of the seven-membered ring. The ejection of a hydroxyl ion and of a water molecule from the dehydration ion takes place from its enolic tautomeric form. The ions arising on the breakdown of the alkyl chain are represented in the spectrum by peaks with *m/z* 151 (ejection of a butyl radical) and 137 (ejection of a pentyl radical) (see Scheme 1). We are the first to have detected the splitting out of two molecules of water from the molecular ion of an unsaturated fatty acid. This phenomenon may possibly take place with other acids, as well. The absence of information on the mass spectra of metastable molecular and dehydration ions has not permitted this to be detected previously.

As compared with the corresponding acid (7), the ethyl tetradec-7Z-enoate (8) has a lower stability to electron impact. In the high-mass region of the mass spectrum of (8) the peak of the molecular ion with *m/z* 254 (8%) and the peaks of ions with *m/z* 221, 209, 208, 166, and a number of others appear.

On the breakdown of the metastable molecular ion, fragmentary ions appear with *m/z* 225, 209, 208, 193, 181, 166, 151, and 140. The first three ions are formed on the splitting out of ethyl and ethoxyl radicals and of a molecule of ethanol, respectively.

The ion with *m/z* 208 in the spectrum of compound (8) is analogous to the dehydration ion of the acid (7) with *m/z* 208. In the DADI spectrum of M^+ for (8) it arises through the elimination of ethyl alcohol from the M^+ ion. The simultaneous occurrence of the splitting out of an ethanol molecule and a methyl radical leads to the formation of an ion with *m/z* 193. An analogy between the DADI spectra of the M^+ ions for (7) and (8) consists in the fact that in them the peaks of a rearrangement ion with *m/z* 166 (a McLafferty ion) appear to equal degrees. While in the DADI spectrum of M^+ for (7) this ion arises through the splitting out of a molecule of acetic acid, in the case of the DADI spectrum of M^+ (8) it is the result of the splitting out of a molecule of ethyl acetate, as shown below.





The proposed structure of the rearrangement ion with *m/z* 166 for substance (7) is shown by the presence in the total DADI spectrum of the peaks of ions with *m/z* 139, 138, 125, 109, 95, 83, and 82, the pathways for the formation of which are given below.

In each of these ions, the positive charge is localized predominately on the double bond. As is shown by the MD spectrum of the ion with *m/z* 160 that is characteristic for the mass spectrum of compound (7), its precursors are, in addition to the molecular ion, ions with *m/z* 184 and 208. However, the intensities of the peaks of the latter indicate that they make only a small contribution to the formation of the ions with *m/z* 166. Thus, these facts show the high possibilities of the mass spectrometry of the metastable ions in establishing the mechanism of rearrangement processes taking place under the action of electron impact and their use in the identification of compounds unstable to electron impact [25].

Mass Spectra of Compounds (9)-(29)

The monoenic alcohols and acetates (9)-(24), and the aldehydes (25)-(28) with different numbers of carbon atoms and positions and configurations of the double bonds in the chain are components of the pheromones of the majority of Lepidoptera. Characteristic for the mass spectra of these compounds, regardless of the size of the molecule and the position of the double bond, is an extremely low intensity or a complete absence of the peak of the molecular ion M^+.

In the high-mass regions of the spectra of the alcohols and aldehydes the peaks of the dehydration ions $(M-H_2O)$ appear, and in the case of the acetates those of the $(M-CH_3COOH)^+$ ions. The mass spectra of the alcohols and of the acetates corresponding to them have similar patterns. This is connected with the fact that on the elimination of a molecule of water from an alcohol and of a molecule of acetic acid from the M^+ ion of its acetate one and the same ion Φ is formed, the further breakdown of which takes place both through direct cleavage of the $C-C$ bonds, leading to the formation of bonds with odd values of *m/z* and also by the cleavage of these bonds accompanied by the migration of a hydrogen atom to the charged part. The ions formed in this process and the neutral fragments split out have even masses.

This breakdown leads to the appearance of groups of peaks of pairs of ions differing from adjacent pairs by 14 mass units. With an approach to the region of low masses the intensities of the peaks of these ions rise, as can be seen from the mass spectrum of the acetate of dodec-7Z-en-1-ol given for illustration (Fig. 1). In the high-mass region of this spectrum the M^+ peak with *m/z* 226 is absent and the Φ fragment $(M-CH_3-COOH)^+$ with *m/z* possesses an appreciable intensity. In a series of groups ion peaks, those with odd masses (peaks of ions with *m/z* 137, 123, 109, 95, 81, and 67) stand out by their intensities.

The same pattern is observed for the spectra of the other alcohols and acetates. The *m/z* value of the Φ fragment in the mass spectrum of such compound is insufficient by itself for it to be assigned to a product of the breakdown of M^+ for the alcohol or the acetate or to the M^+ peak of an individual substance. Identification of a substance by the methods of mass spectrometry begins with the detection of the peak of the molecular ion. Where necessary, its elemental composition is determined. The absence of information about the molecular ion greatly complicates identification and the determination of the structure of a substance under investigation by electron-impact mass spectrometry.

As our investigation has shown [24-26], such a restriction can be successfully overcome with the aid of the mass spectrometry of metastable ions. This is demonstrated for typical compounds below. In spite of the low intensities of the peaks of the Φ ions in the spectra of the alcohols and their acetates that we have studied, in the metastable defocusing (MD)

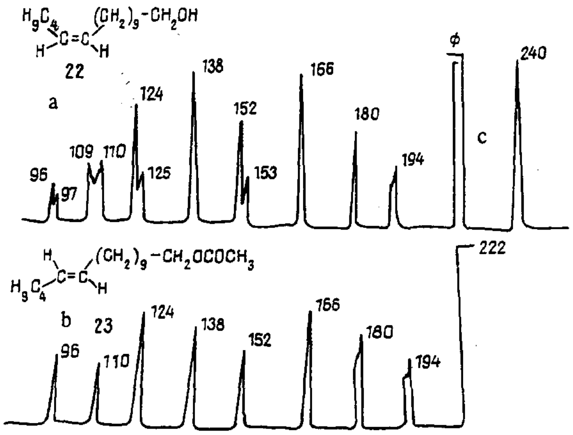
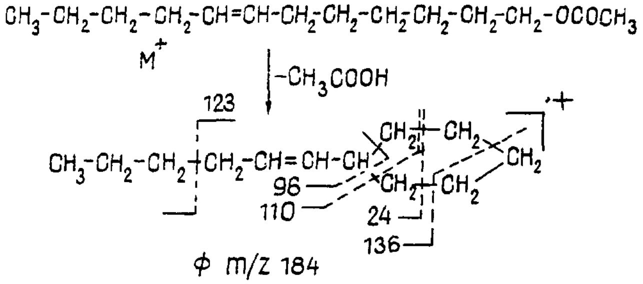


Fig. 2. DADI spectra of the Φ fragment with *m/z* 222 arising from the M^+ ions of hexadec-11E-en-1-ol (22) (a) and of hexadec-11E-en-1-yl acetate (23) (b), and the MD spectrum of the Φ fragment (c).

spectra of the acetates very intense peaks of the maternal ions appear. If an alcohol under study contains a minor amount of its acetate or, conversely, the acetate is accompanied by the alcohol, the MD spectrum of fragment Φ shows two peaks corresponding to the M^+ peaks of the alcohol and of its acetate, the relative intensities of which reflect their quantitative ratio. As an illustration to what has been said, we give the MD spectrum of the Φ ion $(M-CH_3COOH)^+$ with *m/z* 166 for compound (15) (Fig. 1b) which shows the peaks of ions with *m/z* 184 and 226 (M^+) of low and high intensity, respectively. The first of them reveals the presence of the alcohol in the form of a minor impurity in its acetate.

Such a high sensitivity and accuracy of the MD spectra permit the detection and identification of minor components of pheromone that might have been overlooked previously. Interest in the minor components of pheromones is due to the fact that they, even if present in inconsiderable amount, impart high specificity and efficacy to the pheromones. It is for this reason that pheromones the compositions of which have been made up without taking the minor components into account do not exhibit the expected efficacy in field trials.

The DADI spectrum of fragment Φ of compound (15) is characterized by the peaks of ions with *m/z* 151, 137, 136, 124, 123, 110, 96, and 82. It must be emphasized that the intensities of the peaks of ions with even *m/z* values predominate considerably over those with odd *m/z* values (Fig. 1c). In the formation of an ion with an even *m/z* value the cleavage of two bonds or the occurrence of a rearrangement process with the migration of a hydrogen atom from one part of an ion to another is necessary. In the final account, these processes determine the structure of the Φ fragment. This fragment may have different structures, depending on the position in the chain of the hydrogen atom participating in the elimination of a molecule of water or of acetic acid. Judging from ring strain, the participation in this process of the hydrogen atom at C_6, leading to the formation of a six-membered ring, as shown below, appears to us to be most probable. Ions with even *m/z* numbers are obtained through the breakdown of the six-membered ring of the Φ fragment.



An increase in the length of the chain of a monoenic alcohol or its acetate does not cause an appreciable change in its mass spectrum. It must be mentioned that in the spectra of the Φ fragments of monoenic alcohols and acetates the most intense peaks correspond to the cleavage of allyl and vinyl bonds, and this, to a certain degree, shows the positions of the double bonds in the chains.

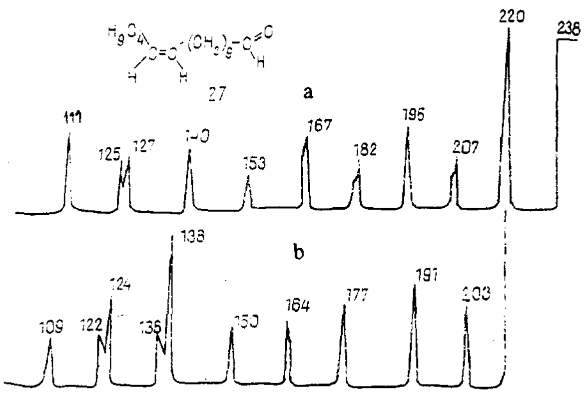


Fig 3. DADI spectrum of M$^+$ for hexadec-9Z-enal with *m/z* 238 (a) and of the dehydration ion with *m/z* 220 (b).

As is known, the cis- and trans-configurations of an isolated double bond of an aliphatic alcohol or acetate are not distinguished in their electron-impact mass spectra. A comparative study of the DADI spectra of the Φ fragments arising from the M$^+$ ions of the cis- series [dec-5Z-en-1-ol (9), dodec-7Z-en-1-ol (14), tetradec-11Z-en-1-ol (17), tetradec-9Z-en-1-ol (19), and hexadec-11Z-en-1-ol (21) and their acetates (10, 15, 18, 20, 22)] and of the trans- series [dec-5E-en-1-ol (11), dec-5E-en-1-yl acetate (12), dodec-3E-en-1-yl acetate (13), dodec-10E-en-1-yl acetate (16), and hexadec-11E-en-1-yl acetate (23)] has shown that there are some differences between them. They consist in the fact that, as mentioned above, the DADI spectra of the Φ fragments of the cis- series contain peaks with even and odd values of *m/z*, i.e., some peaks are doublets. At the same time, the DADI spectra of the Φ fragments of the trans- series consist mainly of isolated singlets with even *m/z* values.

As an example, Fig. 2 gives the DADI spectrum of fragment Φ of hexadec-11E-en-1-yl acetate (23). If this spectrum is compared with the DADI spectrum of the Φ fragment formed from M$^+$ of hexadec-11Z-en-1-ol (Fig. 2), it can be observed immediately that the first consists of singlet peaks and the second contains a number of doublets. An unambiguous explanation of this difference between the spectra of the cis- and trans- series requires a more detailed study of the process of breakdown using model labeled compounds. But the differences that we have detected in these spectra can be used for the preliminary evaluation of the assignment of such compounds to a definite series.

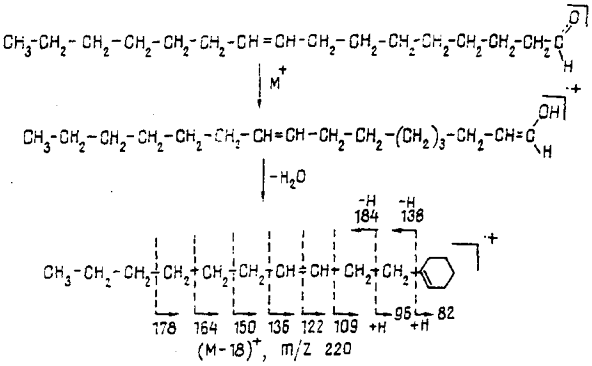
In acetylenic alcohols, the triple bond greatly lowers the stability of the molecular ion to electron impact. For these, no splitting out of a molecule of water is observed. The stability of the molecular ions of primary monoenic alcohols and their acetates is greatly reduced, but the elimination of a molecule of water takes place to a considerable degree, which leads to the appearance in their mass spectra of dehydration ions the MD spectrum of which clearly shows a high-intensity peak of the molecular ion.

In secondary monoenic alcohols fragmentation takes place mainly through the cleavage of bonds adjacent to the carbon atom bearing the hydroxy group. The spectra of these compounds lacks the peaks of both molecular and dehydration ions. In the monoenic ketones, the molecular ions are more stable than the M$^+$ ions of secondary alcohols.

The M$^+$ ions of the monoenic aldehydes (25)-(28) exhibit even greater stability. We have described features of the mass spectra and metastable-ion spectra of these aldehydes using hexadec-9Z-enal (27) as an example. In the mass spectrum of this compound the M$^+$ peak with *m/z* 238 appears with a low intensity, and the intensity of the peak of the dehydration ion (M − 18) with *m/z* 220 is twice as great (2.5 and 5%, respectively). The peaks of other ions in the region with *m/z* values of 220-240 have extremely low intensities.

In the DADI spectrum of M$^+$ for (27) (Fig. 3a) the splitting out of a molecule of water appears as dominant over other breakdown processes. In order of the degree of occurrence, the dehydration process is followed by the formation of a (M − 43)$^+$ ion with *m/z* 195 (splitting out of a propyl radical and, possibly, of a methyleneformyl radical). The peaks of the other ions, even though they have a low intensity, nevertheless bear information on the number of methylene units and the position of the double bond. In the spectrum of this compound, peaks of ions with *m/z* 153, 140, and 127 arising on the cleavage of the double bond and the bonds closest to it have a broadened form as compared with the peaks of the other ions (Fig. 3b). In the identification of M$^+$ for compound (27) by the mass spectrometry of metastable ions, additional information can be obtained from the DADI spectrum of its dehydration ion with *m/z* 220, the peak of which is fairly intense in the mass spectrum. In the DADI spectrum of this ion there is a number of peaks of ions differing in the *m/z* values from their closest neighbors by 14 (cleavage of a bond between methylene groups) and by 13 (cleavage of a double bond) mass units.

In the formation of the dehydration ion from the M^+ ion of compound (27), the elimination of a molecule of water possibly takes place from the enolic tautomic form of M^+, with the capture of one hydrogen atom from the chain. The participation of the hydrogen at the C_3, C_4, C_5, and C_6 atoms, leading to the formation of hydration ions with different sizes of the unsaturated ring in the process of eliminating a water molecule, is not excluded. On the basis of ring strain, it may be assumed that the most suitable is the formation of a six-membered cyclic form of the dehydration ion, as shown below.



The breakdown of the metastable dehydration ion takes place over practically all the bonds of the chain, with the exception of the ring bonds. The DADI spectrum of this ion shows peaks with even *m/z* values of 82, 96, 122, 124, and 136, arising on the simple cleavage of C–C bonds in the ions. On the formation of the ions with *m/z* 124 and 138, the charge is localized in the acyclic part of the molecule, and in the other cases in the cyclic part. Ions with even *m/z* values are formed on the cleavage of vinyl bonds (ions with *m/z* 82, 136, and 138) and allyl bonds (ions with *m/z* 96, 124, and 150). The cleavage of the double bond in this dehydration ion also leads to the formation of an ion with the even *m/z* value of 122.

Thus, the metastable-ion spectra of the M^+ ion and of the dehydration ion of hexadec-9Z-enal (27), which is a component of insect sex pheromones, have a specific pattern reflecting both the number of methylene units and the position of the isolated double bond in the chain and can serve as a reliable criterion for the identification of this compound in a mixture.

Mass Spectra of Compounds 30-36

We have studied the mass spectra and metastable-ion spectra of the M^+ ions of several key fragmentary ions of a dienic alcohol — dodeca-8E,10E-dien-1-ol (30) – and of dienic acetates — dodeca-7E,9Z-dien-1-yl acetate (31), dodeca-5Z,7Z-dien-1-yl acetate (32), tetradec-9Z,11E-dien-1-yl acetate (33), tetradeca-9Z,12E-dien-1-yl acetate (34) hexadeca-7Z,11Z-dien-1-yl acetate (35), hexadeca-7Z,11Z-dien-1-yl acetate (36), and octadeca-3E,13Z-diene-1-yl acetate (37) the molecules of which differ by the numbers of carbon atoms in the chain (C_{12}–(30-32); C_{14}–(33, 34); C_{16}–(35, 36); and C_{18}–(37)) and by the positions and configurations of the double bonds – all these compounds forming components of the majority of pheromones (see Table 1).

Analysis of the mass spectra of these compounds shows that the most stable are the molecular ions of compounds with the E,E-configuration of the double bonds. The M^+ ions possessing the lowest stability are those of compounds of the Z,Z-series. The stability of the M^+ ions of compounds with mixed (Z,E; E,Z) configurations of the double bonds are intermediate between these two series.

While the intensity of the M^+ ion of compound (30) with E,E-configuration of the double bonds amounts to 55%, the intensity of the peak of the Φ fragment with *m/z* 164 of compound (33) with the Z,E-configuration of the double bonds is 6%, and the intensity of the peak of its Φ fragment with *m/z* 192 is 10%.

In the mass spectrum of compound (32) with the Z,Z-configuration of the double bonds, a M^+ peak is totally absent. The peak of the Φ fragment with *m/z* 164 appears (20%) in the region of high masses in the spectrum of this compound. A common feature of the spectra of these compounds is the presence of ions with *m/z* 135, 121 and 107, and a number of other fragments.

The breakdown of the metastable molecular ion of compound (30) is directed predominately to the formation of a dehydration ion with *m/z* 164 the intensity of the peak of which is two orders higher than the intensities of the other ions. It shows the presence of other ions with m/z 136, 122, 97, and 82, arising on the cleavage of C−C bonds. The intensity of the Φ fragment $(M-CH_3COOH)^+$ with m/z 192 in the DADI spectrum for the M^+ ion of compound (33) is far lower than that of the ions with m/z 164, 149, 136, 122, 91, and 82. It follows from these facts that the higher the intensity of M^+ in the DADI spectrum the lower is the intensity of the peak of the Φ fragment. The ratio of the intensities of the M^+ and Φ ions depends on the configurations of the double bonds, the E,E-configuration imparting greater stability to the ions than the Z,E-, E,Z-, and Z,Z-configurations. However, for a quantitative estimation, experiments must be performed on a large number of model compounds differing by the length of the chain, the positions of the double bonds in the chains, and their geometries.

The structural differences of compounds 30 and 33 due to the positions and configurations of the double bonds are also reflected in the DADI spectra of their Φ fragments. The DADI spectra of the Φ fragments of dienic alcohols and acetates can be used for obtaining additional information on the structures of the molecular ions. Furthermore, from the MD spectra of the Φ fragments it is possible to determine with high accuracy the m/z values of the molecular ions that are absent from the mass spectra (27).

Mass Spectra of Compounds 38-45

The hydrocarbons (38-45) are components of the pheromones of certain flies. These compounds have in a $C_{18}-C_{23}$ chain one (45), two (39, 41, 43, and 44) or three (38, 40, and 42) double bonds with the cis-configuration. The molecules of these compounds possess a fairly high stability to electron impact, which is reflected in their mass spectra by the presence of molecular ions having high intensities. The mass spectrum of tricos-9Z-ene (45) is characterized in the high-mass region by ions with m/z 332, M^+ (40%), 293 $(M - 29)^+$, 251 $(M - 71)^+$, and other low-intensity ions. With an approach to the low-mass region, the intensities of the peaks rise, the greatest intensity corresponding to ions with odd m/z values. The position of the double bond is not reflected in the mass spectrum, since an isolated double bond plays no essential role in the fragmentation process.

The DADI spectrum of the M^+ ion of compound (45) with m/z 322 consists of ions with m/z values differing from the closest ions by·14 mass units. In this spectrum, ions with m/z 294, 293, 280, 165, 251, and 252 show the splitting out of allyl radicals (ions with odd m/z values) and of alkene molecules (ions with even m/z values. Other ions, with m/z 237, 233, 209, 195, and 181, have a singlet form. The mass spectrum of compound (45) and the DADI spectrum of its M^+ ion do not reflect the position of the isolated double bond in the chain.

In the high-mass region of the mass spectrum of a hydrocarbon with two double bonds − heneicosa-3Z,6Z-diene (43) − peaks of rearrangement ions with m/z 264, 236, 222, 162, 126, 110, and 96 are easily singled out. An ion with m/z 46 has the maximum intensity. Judging from the mass spectrum of (43), in the fragmentation of M^+ a breakdown takes place at the double bond. Rearrangement ions are formed mainly on the cleavage of its vinyl bonds.

When the double bonds move further into the chain of the molecule − in heneicosa-6Z,9Z-diene (44) as compared with heneicosa-3Z,6Z-diene (43) − the intensities of the rearrangement ions so reflected to a certain degree in the DADI spectra of their molecular ion. The DADI spectrum of M^+ for compound (43) shows that fragmentation begins with splitting out of a propyl radical. The majority of rearrangement ions with even m/z values appear in the form of singlets, which are always more intense than in the case of ions with odd m/z values. Rearrangement ions are usually formed on the cleavage of vinyl bonds, which, to some extent, shows the positions of the double bonds.

In the mass spectrum of a compound with three double bonds − heneicosa-3Z,6Z,9Z-triene (42) − the intensity of the molecular ion with m/z 290 is not very high (14%). The intensities of other ions in the high-mass region are also low, the ions with odd m/z values being more intense, although the maximum intensity corresponds to the peak of a rearrangement ion with m/z 108.

Thus, the number and positions of the double bonds in the hydrocarbon chain substantially affect the pattern of the mass spectrum and the DADI spectrum of the molecular ions of mono-, di-, and trienic hydrocarbons. In the majority of cases the formation of rearrangement ions from their M^+ ions is determined by the positions of the double bonds.

Mass Spectra of Compounds (46)-(51)

The epoxy compounds (46)-(51) are found fairly frequently as components of the pheromones of various insect species. We have studied the mass spectra of 2-methyl-(Z)-7,8-epoxypentadecane (46), 2-methyl-(Z)-7,8-epoxyhexadecane (47),

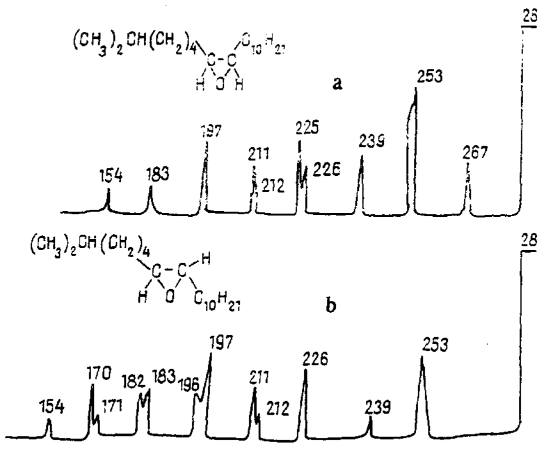
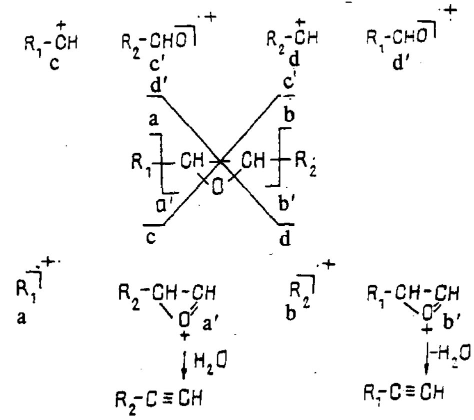


Fig. 4. DADI spectra of M^+ for the isomeric compounds (50) (a) (cis- isomer) and (51) (b) (trans- isomer).

(Z)-7,8-epoxyoctadecane (48), 2-methyl-(Z)-6,7-epoxyheptadecane (49), 2-methyl-(Z)-7,8-epoxyoctadecane (50), and 2-methyl-(E)-7,8-epoxyoctadecane (51) (see Table 1).

Characteristic for the mass spectra of these compounds is a low intensity of the molecular ion. The main directions of the breakdown of the M^+ ions of the compounds are: a) fragmentation of the alkyl chains; b) breakdown of the epoxide ring; and c) cleavage of the α-bonds (in relation to the epoxide oxygen). In each form of breakdown there is the possibility of the production of two types of ions – not containing oxygen (ions of types *a*, *b*, *c*, and *d*) and oxygen-containing (ions of types *a'*, *b'*, *c'*, *d'*). The revelation of these ions is important in determining the structures of epoxy compounds (see Scheme 2). The oxygen-containing ions, in their turn, may have the structures of oxonium ions (*a'*, *b'*) or aldehydes (*c'*, *d'*). The difference in the *m/z* values of the oxonium ions and M^+ harbors information on the position of the epoxide region in the molecule. These facts are also confirmed by the *m/z* values of the ions of types *c'* and *d'*.

A comparison of the intensities of the peaks of fragments a (19%) and *c* (8%) in the mass spectra of the epoxides (46)-(51) shows that the intensity is always greater for the heavy fragment.



Scheme 2. Fragmentation of the M^+ ions of the epoxy compounds (46)-(51):

46. $R_1 = (CH_3)_2CH(CH_2)_4$; $R_2 = C_7H_{15}$
47. $R_1 = (CH_3)_2CH(CH_2)_4$; $R_2 = C_8H_{17}$
48. $R_1 = C_6H_{13}$; $R_2 = C_{10}H_{21}$
49. $R_1 = (CH_3)_2CH(CH_2)_3$; $R_2 = C_{10}H_{21}$
50. $R_1 = (CH_3)_2CH(CH_2)_4$; $R_2 = C_{10}H_{21}$
51. $R_1 = (CH_3)_2CH(CH_2)_4$; $R_2 = C_{10}H_{21}$

Among the key fragments in the mass spectra of compound (50) and (51) are those of types *a'* with *m/z* 183 and *b'* with *m/z* 141.

It must be mentioned that in the DADI spectrum of the fragment with *m/z* 183 from compound (50) the number of doublet peaks has increased in comparison with the DADI spectrum of its molecular ion. Characteristic for these spectra are the maximum intensity of the peak of an ion with *m/z* 123 (elimination of water) and the breakdown of the side-chain with the ejection of neutral molecules of alkenes (propene, isobutene, and isopentene).

In the high-resolution mass spectra of substances (50) and (51) the peak of the ion with *m/z* 141 is split, forming a doublet with accurate *m/z* numbers of 141.1270 (found) 141.1278 (calculated), and 141.1632 (found) 141.1622 (calculated), which correspond to the elemental compositions of $C_9H_{17}O$ and $C_{10}H_{21}$ ions, the intensity of the oxygen-containing component of the doublet being three times higher.

The main direction of the breakdown of metastable ions of types *c'* and *d'* is the elimination of a molecule of water from them, which is reflected in their DADI spectra. The peak of the dehydration ion $(M - 18)^+$ has the maximum intensity.

The metastable defocusing spectra of the ions of type *c'* with *m/z* 152 from compounds (50) and (51) differ both by the numbers of peaks shown and by their intensities. The precursors of fragment *c'* from compound (50) (cis- isomer) are ions with *m/z* 170, 194, 207, 263, and 282 (M^+). Ions with *m/z* 179, 208, 265, and 282 (M^+) appear as parents of fragments *c* for the trans- isomer (51). Judging from their intensities, all these ions participate to the same degree in the formation of fragment *c'*. In the case of the cis- isomer, the main source of appearance of fragment *c* is the molecular ion.

Thus, under the action of electron impact, the epoxy compounds that we have studied give metastable molecular and fragmentary ions of types *a-d* and *a'-d'*, the breakdown of which takes place very specifically. From the spectra of the metastable ions it is possible to determine reliably the position of the epoxide bridge in the chain. A similarity has been detected between reactions in which two molecules of aldehydes are formed from olefins on ozonolysis and the breakdown of the epoxy ring under the action of electron impact.

The formation of ions of types *c'* and *d'* with aldehydic structures is shown by the DADI spectra of the molecular ions of compounds isomeric with respect to the configurations of the epoxide ring (in the first, those with the cis-, and in the second, those with the trans- configuration). Such stereochemical differences do not appear in their mass spectra: the intensities of the peaks of the molecular ions and other key fragments are practically identical. Certain differences are observed in a comparison of the DADI spectra of their molecular ions (Fig. 4a, b). The DADI spectrum of M^+ for (50) contains an ion with *m/z* 267, corresponding to the splitting out of a methyl radical, while in the DADI spectrum of M^+ for (51) there is an ion with *m/z* 253 (the splitting out of an ethyl radical). These spectra contain ions with the same *m/z* values, such as 239, 226, 225, 211, 197, and 183 but the intensities of each of them in the spectra under comparison differ considerably. The very greatest difference in the DADI spectrum of M^+ for the trans- isomer (51) consists in the appearance of numerous ions split into doublets (212, 211, 197, 196, 183, 182, 171) which shows the occurrence of rearrangement processes competing with ordinary breakdown.

In the DADI spectrum of M^+ for the cis- isomer (50), only one doublet is observed, with *m/z* values of 225 and 226, corresponding to the splitting out of a propyl radical and a propylene molecule. In both spectra, as the bonds undergoing cleavage approach the epoxide ring the intensities of the fragments formed decrease.

The mass spectra of the cis- and trans- isomers of epoxides (46)-(51) do not differ appreciably, while in the DADI spectra of their molecular ions appreciable differences are observed, and this will in the future provide the possibility of determining the configuration of epoxide rings [28].

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