MASS-SPECTROMETRIC STUDY OF THE PHEROMONE OF THE COTTON BOLLWORM AND ITS PRECURSORS

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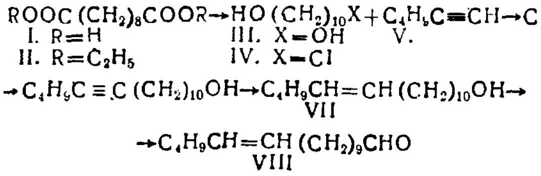
The structures of the products of intermediate stages of the synthesis of the sex pheromone hexadec-11Z-enal that are labile to electron impact have been studied with the aid of low-resolution mass spectrometry and metastable ions.

Hexadec-11Z-enal is the main component of the sex pheromone of the cotton bollworm Heliothis armigera, a dangerous pest of the cotton plant [1, 2]. In view of the wide use of this compound for signaling an invasion of the pest, the task of monitoring the intermediate stages of its synthesis is becoming urgent [3]. We have used the method of mass spectrometry for this purpose. The synthesis of hexadec-11Z-enal is performed by the following scheme: the esterification of sebacic acid (I) with ethanol gives its diester (II), which is reduced with lithium tetrahydroaluminate to decane-1,10-diol (III). By the action of hydrochloric acid under conditions of continuous extraction with toluene, (III) is converted into 10-chlorodecan-1-ol (IV). The alkylation of hex-1-yne with the chlorohydrin (IV) gives hexadec-11-yn-1-ol (VI) which is then reduced stereoselectively to hexadec-11Z-en-1-ol (VII). Oxidation of the alkenol (VII) with pyridinium chlorochromate gives the required aldehyde (VIII).



$$\underset{\substack{\text{I. } R=H\\ \text{II. } R=C_2H_5}}{ROOC(CH_2)_8COOR} \rightarrow \underset{\substack{\text{III. } X=OH\\ \text{IV. } X=Cl}}{HO(CH_2)_{10}X} + \underset{\text{V.}}{C_4H_9C\equiv CH} \rightarrow C$$
$$\rightarrow C_4H_9C\equiv C(CH_2)_{10}OH \rightarrow \underset{\text{VII}}{C_4H_9CH=CH(CH_2)_{10}OH} \rightarrow$$
$$\rightarrow \underset{\text{VIII}}{C_4H_9CH=CH(CH_2)_9CHO}$$

Scheme 1

In the mass spectrum of diethyl sebacate (II), the peak of the molecular ion with m/z 258 (2%) is observed, while the line with the maximum intensity corresponds to the peak of an ion with m/z 213 (100%), which arises through the splitting out of an ethoxy group from the molecular ion.

In the DADI (direct analysis of daughter ions) spectrum [4, 5] the peaks of ions with m/z 195, 185, 166, 148, 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 148 is due to the simultaneous occurrence of two processes, involving the breakage of different bonds – the splitting out of ketene ($CH_2C{=}O$) through cleavage of the $C_2{-}C_3$ bond and that of a methyl radical from an ethoxy group (Fig. 1, A). The peak of a rearrangement ion with m/z 166 in the mass spectrum of (I) has a high intensity; this ion is genetically linked with ions having m/z 212 and 213, as is shown by its MD (metastable defocusing) spectrum and the DADI spectrum of the m/z 213 ion. In its formation from the M^+ ion with m/z 258 two molecules of ethanol are split out. It is rational to explain this ejection on the basis of structure (I), and it is characteristic for M^+ of esters of dibasic acids. An ion with m/z 129 in the DADI spectrum of the ion with m/z 213 corresponds to the cleavage of the $C_5{-}C_6$ bond with retention of the charge in the ester moiety of the ion.

Although in the DADI spectrum of the ion with m/z 213 there is no peak of an ion showing the formation from it of a fragment with m/z 171, in the MD spectrum of the latter an intense peak of a precursor ion with m/z 213 appears. Furthermore, in this spectrum there are also the peaks of ions with m/z 185 (8%), 212 (6%), and 258 (2%). The peaks of ions with m/z 138 and 125 appear in the DADI spectra of the metastable ions with m/z 171 and 166.

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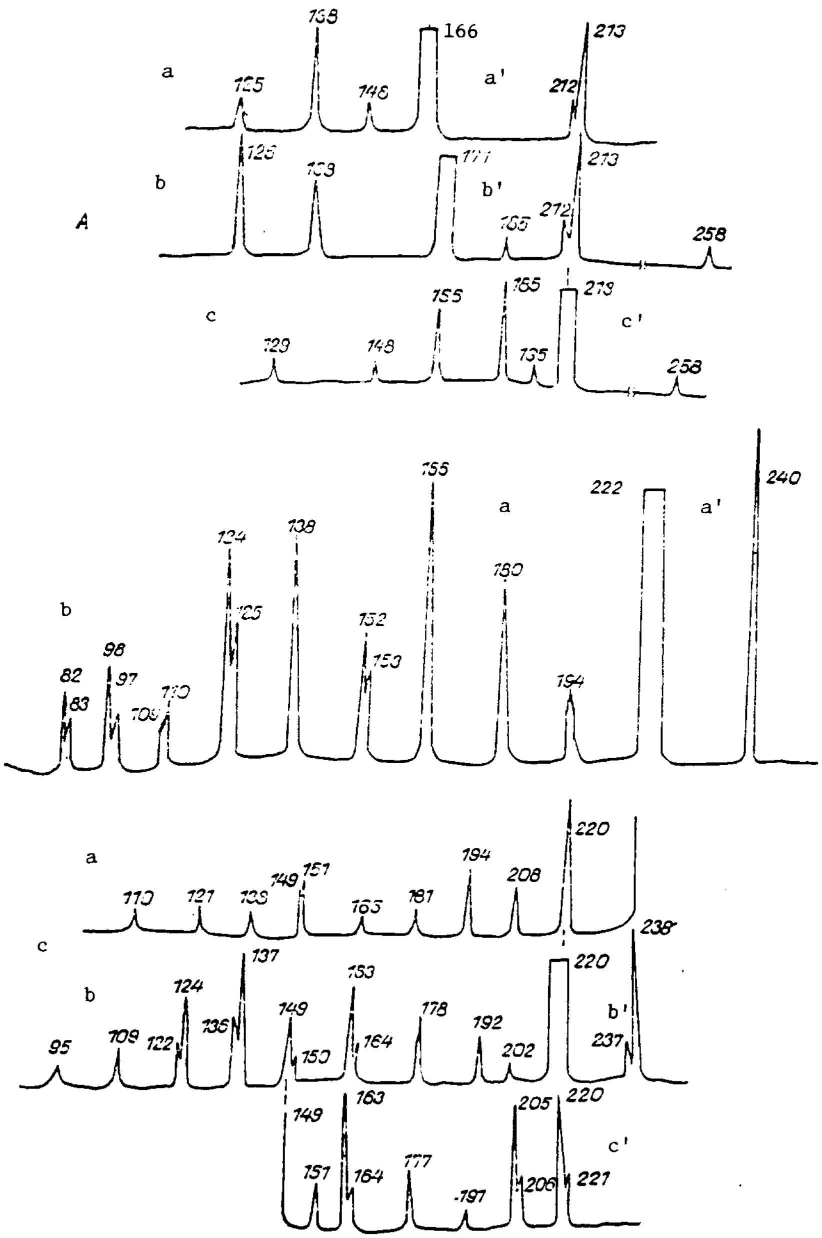


Fig. 1. Spectra of ions with the m/z values given: A) DADI of m/z 166 (a); MD of m/z 166 (a'); DADI of m/z 171 (b) MD of m/z 171 (b'); DADI of m/z 213 (c); MD of m/z 213 (c') of diethyl sebacate; B) DADI of m/z 222 (a); MD of m/z 222 (a') of hexadec-11Z-en-1-ol; C) DADI of m/z 238 (a); DADI of m/z 220 (b); MD of m/z 220 (b'); MD of m/z 149 (c') of hexadec-11Z-enal.

The following stage of the synthesis is the production of decanediol by the reduction of (II) with $LiAlH_4$ in absolute ether. A study of the mass spectrum of (III) has shown that the reaction takes place without the formation of by-products.

The mass spectrum of compound (III) lacks the M^+ peak with m/z 174. In the high-mass region the peak of an ion with m/z 156 (1%) corresponding to the loss of one water molecule appears. The dehydration ion with m/z 156 is capable of losing another water molecule, which confirms the presence of two hydroxy groups in the molecule of (III). The metastable defocusing spectrum of an ion with m/z 138 definitively shows that ions with m/z 156 and 174 (M^+) are precursors of this ion. An ion with m/z 110 is also formed directly from M^+ by the loss of two water molecules and a molecule of ethylene. The DADI spectrum of this ion contains 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 (IV) a weak peak of an ion $(M - 18)^+$ with m/z 174 (1%) can be detected (here and below the masses of the chlorine-containing fragments have been taken for ^{35}Cl). The following peak of an ion with m/z 146 (12%) arises through the splitting out of a molecule of ethylene. Then this ion, as is obvious from its DADI spectrum, breaks down into ions with m/z 118 (ejection of ethylene), 110 (splitting out of a molecule of HCl), 104, 84, and 68 (chain degradation).

The purity of the hex-1-yne (V) was confirmed by recording its mass spectrum, in which the M^+ peak (17%) with m/z 82 was detected. Extremely unusual is the peak of the $(M - 1)^+$ ion (48%), which has a high intensity. In the mass spectrum of (V) the peak of an ion with m/z 67 $(M - 15)^+$ has the maximum intensity. 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 a triple bond.

The mass spectrum of the next stage of the synthesis – hexadec-11Z-en-1-ol (VI) – is characterized in the region of high masses by low-intensity peaks of ions with m/z 238 (M^+) (0.3%), 196 (1%), 179 (6%), and 166 (8%). In the DADI spectrum of the M^+ ions of (VI), the most intense peak corresponds to a dehydration ion $(M - H_2O)^+$ with m/z 220.

Then the peaks of ions with m/z 196, 182, 166, 152, 138, 124, and 110 of almost equal intensity appear in this spectrum. The formation of these ions completely confirms structure (VI).

The stereospecific hydrogenation of the triple bond in (VI) forms hexadec-11Z-en-1-ol (VII). The mass spectra and the DADI spectra of the M^+ ions of these compounds differ considerably. Thus, the mass spectrum of (VII) lacks the M^+ peak with m/z 240. In this spectrum the peaks of a dehydration ion with m/z 222 of considerably intesnity appear in the region of high masses, while in the case of (VI) a different pattern has been observed – the presence of the M^+ peak and the absence of the peak of a dehydration ion. The MD spectrum of the ion with m/z 222 shows an intense peak of an ion with m/z 240 corresponding to the molecular ion of hexadec-11Z-en-1-ol (Fig. 1, B). The absence of the peaks of the molecular ions is characteristic for the mass spectra of monoenic alcohols and their acetates. The molecules of such compounds possess a low stability under electron impact. Usually, under the action of electron impact they readily lose molecules of water (monoenic alcohols) and of acetic acid (acetates of monoenic alcohols) [5].

The study of the processes involved in the formation of metastable ions substantially expands the possibilities of mass spectrometry, since the detection of the molecular ion and the determination of its mass and elementary composition are necessary prerequisites for establishing the structure of an unknown compound being studied that is unstable under electron impact.

On the other hand, the absence not only of the peak of the molecular ion but also of the peaks of other ions of appreciable intensity in the high-mass region makes the mass spectra of monoenic alcohols and their acetates relatively uninformative. In such cases, extremely valuable information on the structure of the initial compound can be obtained from the DADI and MD spectra of the $(M - 18)^+$ and $(M - 60)^+$ ions.

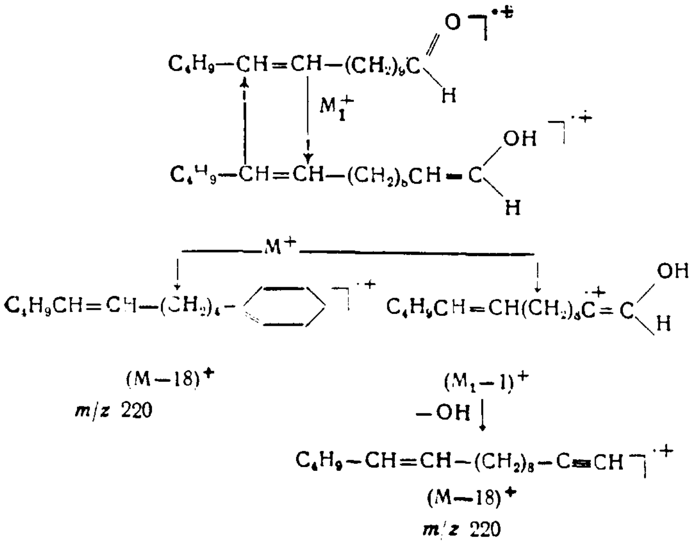
The DADI spectrum of the dehydration ion with m/z 222 from alcohol (VII) (Fig. 1, B) contains two types of ions – ions with even mass numbers (194, 180, 166, 152, 138, 124, 110, 96, and 82) and ions with odd mass numbers (153, 125, 109, 97, and 83). The first type of ions arises on the rupture of two bonds, and the second on the rupture of one bond. An important point in the interpretation of the spectrum of a dehydration ion is the determination of the position of the hydrogen atom in the chain that participates in the process of splitting out water. Usually, hydrogen atoms from various positions participate in the elimination of water from the M^+ ions of alcohols. Position 6 is considered to be the most preferred. Then a six-membered ring, having the least strain, is formed. Ions of the first type arise mainly through the breakdown of this six-membered ring (the ions with m/z 194, 180, 166, and 152).

The formation of the ion with m/z 152 may be accompanied by the splitting out of a methyl radical from the other end of the chain, as the result of which an ion with m/z 137 arises. When allyl and vinyl bonds are cleaved the hydrogen atom migrates (ions with m/z 96 and 82). All these facts and also the absence from the mass spectrum of the peaks of foreign ions confirm the purity of the compound obtained and its structure.

The final reaction product, hexadec-11Z-enal (VIII), as compared with the alcohol (VII), shows an increased resistance to electron impact, which is reflected in the considerable intensity (20%) of the M^+ peak with m/z 238. The peak of a dehydration ion with m/z 220 also has a high intensity (30%).

In the DADI spectrum of M^+ the peak of a dehydration ion possesses the maximum intensity. In this spectrum the peaks of other ions, corresponding to the cleavage of the methylene units of the chain, have a low intensity (Fig. 1, C).

In the MD spectrum of the dehydration ion (Fig. 1, C) the peaks of two precursor ions appear with m/z 238 (M^+) and 237 $(M - 1)^+$, which shows both a one-stage and a two-stage occurrence of the dehydration process: $M^+ \xrightarrow{-H_2O} (M - 18)^+$ and $M^+ \xrightarrow{-H} (M - 1)^+ \xrightarrow{-OH} (M - 18)^+$. A necessary prerequisite for the occurrence of these processes is the automerization of the molecular ion into the enolic form, as is shown in scheme 2.



Scheme 2

In the one-stage route of formation of the ion with m/z 220 from the tautomeric form of the molecular ion M^+ (VII) the participation of various hydrogen atoms, beginning from position 2 and ending with a more remote position, leading to structures of dehydration ions with different ring sizes, is possible. On the basis of ring strain, the formation of a six-membered ring appears most likely to us. To a certain degree, this is confirmed by the DADI spectrum of the ion with m/z 220 (Fig. 1, C), which contains the peaks of ions with m/z 192, 178, and 164 (arising on the breakdown of the ring) and 178 and 163 (formed from the linear part). As can be seen from its DADI spectrum, the fragmentation of the dehydration ion takes place through the cleavage of the bonds of the linear moiety with retention of the charge of the cyclic moiety.

EXPERIMENTAL

The spectra were taken on a Varian MAT-311 instrument at an energy of the ionizing electrons of 70 eV and an accelerating voltage of 3 kV, with an evaporator temperature of 25-30°C. In the DADI spectra the mass of each daughter ion was calculated from the formula:

$$m_2 = m_1 \frac{E_1}{E_0},$$

where m_1 is the mass of the maternal ion; m_2 is the mass of the daughter ion; E_1 is the strength of the electric field at which m_2 was recorded; and E_0 is the initial electric field strength.

In the MD spectrum, the mass number of the maternal ion was determined from the formula

$$m_1 = m_2 \cdot \frac{V_1}{V_0},$$

where V_0 represents the initial values of the accelerating voltage at which the daughter ion m_2 was recorded; and V_1 is the accelerating voltage at which the maternal ion m_1 was recorded.

The values of E_1 and E_0 and of V_1 and V_0 were recorded on a digital voltmeter with an accuracy of ±0.5 V.

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