

# MASS SPECTROMETRY IN THE IDENTIFICATION OF COLEOPTERA PHEROMONES

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**Abstract.** Pheromones of Coleoptera comprise nearly all classes of organic chemistry. However, pheromones of different species belonging to the same genera have been found to consist of the same or structurally similar compounds. In this review the mass spectra of pheromones published till 1995 for representatives of 39 genera of Coleoptera are presented. These data can be useful for the identification of yet unknown pheromones of various species of Coleoptera.

**Key words:** pheromones, Coleoptera, mass spectrometry.

## INTRODUCTION

Mass spectrometry is the major tool for the identification of small quantities of substances in natural mixtures such as insect pheromones. The mass spectrometry and main fragmentation pathways of Lepidoptera pheromones were reviewed in 1985 by Struble. In that review mass spectra data concerning moth pheromone components, including saturated and unsaturated C<sub>10</sub>–C<sub>18</sub> aliphatic alcohols, aldehydes, and acetates, are presented [1].

In contrast to Lepidoptera the pheromones of Coleoptera demonstrate a significantly greater variety of structures: their list comprises nearly all the classes of organic compounds from alkenes to heterocycles. Therefore the identification of Coleoptera pheromones is particularly difficult.

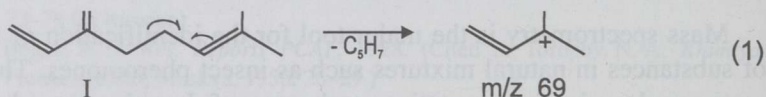
The present review contains data on the main types of chemical structures of Coleoptera pheromones of 39 genera, their mass spectra, and possible fragmentation pathways. This information appears to be useful for the identification of yet unknown pheromone components, especially since related species of the same genus have often structurally similar pheromones.

## MASS SPECTROMETRY OF HYDROCARBONS

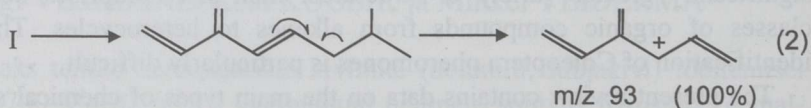
The C-C bond cleavages in hydrocarbons under electron bombardment are high-energy processes, producing highly excited ions, which have a high tendency toward isomerization and rearrangement decompositions. This tendency is reduced by the presence of chain branching and unsaturation. Chain branching causes a decrease in the abundance of the molecular ion ( $M^+$ ) and characteristic increases in the abundance of  $C_nH^+_{2n+1}$  and  $C_n M^+_{2n}$  ions through cleavage and charge retention at the branched carbon with the loss of the largest alkyl group favoured. The addition of a double bond to an alkane increases the abundance of the  $C_nH^+_{2n-1}$  and  $C_n M^+_{2n}$  ion series. Alkene ions exhibit an allylic cleavage, but also show a strong tendency to isomerize through the migration of the double bond [2, pp. 178-189].

Among the pheromone components of *Aleochara* spp. [3] two unsaturated hydrocarbons, *Z*-7-heneicosene and *Z*-7-tricosene, were found. For their identification the methods of PMR, IR-, and UV-spectroscopy were used, because mass spectrometry would lead in this case to double bond migration. The mass spectra of alkenes, especially polyenes, tend to be independent of the double-bond position unless the double bond is highly substituted or a number of double bonds act together. At the same time it is known that the spectra of branched unsaturated alkenes show abundant RCH ions, which appear to arise by initial migration of the double bond away from the position of branching followed by allylic cleavage [2, pp. 178-189].

For example, one of the components of *Agriotes* spp., pheromone myrcene (I, Table 1), exhibits allylic cleavage according to scheme (1), which yields fragments with  $m/z$  67 and  $m/z$  69:



However, the most favoured myrcene fragmentation is allylic cleavage after double bond migration from branching according to scheme (2):



The molecular ion ( $M^+$ ) in alkenes and especially in polyenes is rather abundant; in myrcene, for instance, it makes up 8%, in tetraenes II and III (Table 1) 96 and 55%, respectively. The other peaks ( $m/z$  121, 107, and 79) in the

Mass spectra of hydrocarbon components of Coleoptera pheromones

Genus	Chemical (trivial) name	$M^+$	Fragments (relative abundance, %)	Reference
<i>Agriotes</i>	2-Methyl-6-methylene- 2,7-octadiene (Myrcene) (I)	136	93 (100) 69 (43) 41 (11) 136 (8) 121 (5) 107 (2) 79 (9)	4, 5
<i>Carpophilus</i>	2E,4E,6E,8E-3,5,7-Trimethyl- 2,4,6,8-decatetraene (II)	176	119 (100) 161 (99) 176 (96) 133 (85) 105 (75) 69 (60) 91 (54) 41 (33) 147 (25) 92 (24) 55 (22) 120 (20) 77 (18) 86 (4)	6
<i>Carpophilus</i>	2E,4E,6E,8E-3,5,7-Trimethyl- 2,4,6,8-undecatetraene (III)	190	55 (100) 133 (95) 119 (85) 105 (70) 91 (65) 161 (60) 190 (55) 41 (50) 106 (30) 175 (27) 77 (25) 147 (20)	6

mass spectrum of I must result from allylic cleavage within a resonant structure, produced when the molecule is energized. The same way of fragmentation leads to the largest peak at  $m/z$  55 ( $C_4H_7$ ) and to the elimination of peaks at  $m/z$  175 ( $M^+ - CH_3$ ) in the mass spectrum of tetraene III, fragment at  $m/z$  161 ( $M^+ - CH_3$  in mass spectrum III and  $M^+ - C_2H_5$  in mass spectrum II) as well as at  $m/z$  147, 133, 119, 105, 91, and 77. The exact structures of II and III were proved by Bartlet et al. with the help of mass spectrometry of the products of their hydrogenization [6].

## MASS SPECTROMETRY OF ALCOHOLS

The addition of a hydroxyl group to an alkane lowers the ionization energy, but the abundance of molecular ions decreases despite this stabilization due to an increased ease of decomposition through reactions initiated at the ionized hydroxyl group. Both the radical site and the charge site of the hydroxyl group are intermediate in their capability for reaction initiation, so that the mass spectra

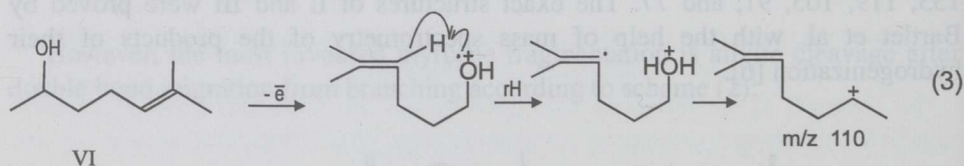
of alcohols exhibit many types of reactions. Tertiary alcohols contain the largest and primary alcohols the smallest total number of oxygen-containing ions in their spectra. In all but the spectra of 1-alkanols,  $\alpha$ -cleavage is the most characteristic reaction [2, pp. 189–195].

### Aliphatic alcohols

The molecular ion  $M^+$  is always weak or undetectable in saturated and monounsaturated alcohols. There is an ion ( $M^+ - 18$ ) due to the loss of water and frequently there is a detectable ion at ( $M^+ - 18 - 28$ ) due to the loss of water and ethylene. The other fragmentations arise from oxygen-containing and hydrocarbon ions. The hydrocarbon ions usually predominate and they often obscure the typical alcohol fragmentations. The mass spectra of these compounds resemble those of the corresponding alkanes with peak groups corresponding to the series  $C_nH_{2n-1}$ ,  $C_nH_{2n}$ , and  $C_nH_{2n+1}$  at 14 mass units ( $CH_2$ ), which decrease in intensity with increasing fragment weight [1]. These series can give evidence of branching or other structural features of the carbon skeleton. The  $C_nH_{2n+1}O^+$  ions that would arise from simple  $\alpha$ -cleavage ( $m/z$  31) and displacement are minor.

In the spectra of alcohols IV–VI (Table 2) the molecular ion is detectable only on unsaturated alcohol VI (6-methyl-5-hepten-2-ol) ( $M^+$  128). The main way of fragmentation of these alcohols is the cleavage of C–C bond at the hydroxyl carbon with elimination of the largest alkyl radical and formation of the ions at  $m/z$  45 ( $CH_3CH=OH$ , 100%) (IV) and at  $m/z$  59 ( $CH_3CH_2CH=OH$ , 100%) (V) together with less abundant fragments with  $m/z$  87 ( $M^+ - CH_3$ ) and 43 ( $C_3H_7$ ) (IV),  $m/z$  101 ( $M^+ - C_2H_5$ ) (V). Decomposition of the largest alkyl radical gives rise to fragments with  $m/z$  69 ( $C_5H_8$ ) and 55 ( $C_4H_7$ ).

There are low abundance peaks at  $m/z$  84 (IV), 112 (V), and 110 (VI) due to the loss of water ( $M^+ - H_2O$ ). Elimination of water is a result of McLafferty rearrangement, when  $\gamma$ -hydrogen atom is transferred by a sterically favourable six-membered ring transition state. For instance, alcohol VI yields an ion at  $m/z$  110 according to scheme (3):



Decomposition of the alkenes that left due to the loss of water eliminates the fragments with  $m/z$  41 ( $C_3H_5$ ), 69 ( $C_5H_9$ ) (IV), 83 ( $C_6H_{11}$ ), 70 ( $C_5H_{10}$ ) (V), 95 ( $C_7H_{11}$ ), and 81 ( $C_6H_9$ ) (VI). In the mass spectrum of alcohol VI the peaks at  $m/z$  85 ( $C_5H_9O$ ) and  $m/z$  71 ( $C_4H_7O$ ) are due to the double bond migration.

## Mass spectra of alcohol components of Coleoptera pheromones

Genus	Chemical (trivial) name	M <sup>+</sup>	Fragments (relative abundance, %)	Reference
<i>Dendroctonus</i>	4-Methyl-2-pentanol (IV)	102	45 (100) 43 (35) 41 (27) 69 (25)	7
<i>Scolytus</i>	4-Methyl-3-heptanol (V)	130	59 (100) 70 (7) 83 (15) 101 (10) 112 (1)	8
<i>Gnathotricus</i>	6-Methyl-5-hepten-2-ol (Sulcatol) (VI)	128	128 110 95 85 81 71 69 55 128 110	9 10
<i>Gnathotricus</i>	3-Methylcyclohexen-2-ol (VII)	112	39 (100) 79 77 91 51 65	11
<i>Anthonomus, Pissodes</i>	(+)-Z-2-iso-Propenyl-1-methylcyclobutanetanol (Grandlure I) (VIII)	154	68 (100) 67 109 121 139 154 68 (100) 109 121 136 139 154	12 13
<i>Anthonomus</i>	Z-3,3-Dimethylcyclohexane- $\Delta^{1,\beta}$ -ethanol (Grandlure II) (IX)	154	69 (100) 93 136 121 154 69 (100) 107 121 136 139 154	12 13
<i>Dendroctonus</i>	2-Phenylethanol (X)	122	91 (100) 92 65	15
<i>Dendroctonus</i>	1-Phenylethanol (XI)	122	79 (100) 107 (94) 77 (43) 43 (35) 122 (33) 51 (27) 78 (22) 73 (18) 50 (10) 91 (9) 80 (9)	7
<i>Chrysopeplus</i>	Methyl ester 6-methylsalicylic acid (XII)	166	166 135 134 107 106 105 77	16
<i>Chrysopeplus</i>	Methyl ester 6-ethylsalicylic acid (XIII)	180	180 148 121 120 105	16
<i>Costelytra</i>	Phenol (XIV)	94	94 66 65 39	17

## Cyclic aliphatic alcohols

The mass spectrum of 3-methylcyclohexen-2-ol (VII, Table 2) shows the complex way of its fragmentation. Instead of  $\alpha$ -cleavage, typical of the cyclic aliphatic alcohols, fragmentation of alcohol VII is accompanied with a loss of water and two hydrogen atoms, followed by "aromatization" of the ring and producing of fragments typical of aromatic compounds, with  $m/z$  39 ( $C_3H_3$ ), 79 ( $C_6H_7$ ), 65 ( $C_4H_4$ ), 51 ( $C_7H_7$ ), and 91 ( $C_7H_7^+ =$  tropyllium ion).

There is a detectable molecular ion ( $M^+$  154) in the mass spectrum of alcohol VIII (Table 2). The main pathway of fragmentation leads to  $m/z$  68 ( $C_5H_8$ ), typical of the cycloalkyl compounds [2, pp. 284–288].

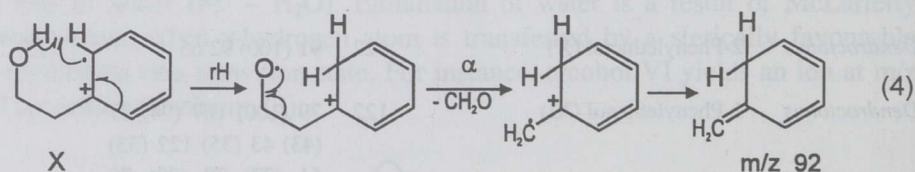
Other peaks in the mass spectrum of alcohol VIII are at  $m/z$  139 ( $M^+ - CH_3$ ), 136 ( $M^+ - H_2O$ ), 121 ( $M^+ - CH_3 - H_2O$ ), and 109 ( $M^+ - CH_2CH_2OH$ ) [12, 13].

A detectable molecular ion ( $M^+$  154) and other ions at  $m/z$  139 ( $M^+ - CH_3$ ), 136 ( $M^+ - H_2O$ ), 121 ( $M^+ - CH_3 - H_2O$ ), and 107 ( $M^+ - CH_3 - CH_3OH$ ) were reported in the spectrum of alcohol IX [12, 13].

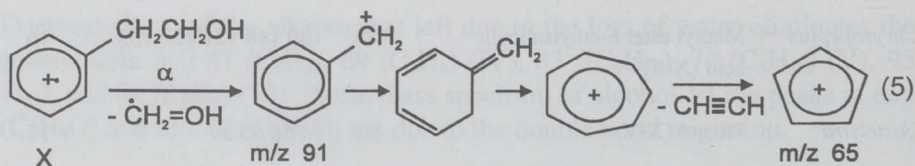
## Benzyl alcohols

Benzyl alcohols and their homologues are a separate class of compounds. As a rule, the molecular ion in their mass spectra is of considerable abundance. The  $\beta$ -cleavage to the ring typical of them yields a peak at  $M^+ - OH$ , while the complex sequence of transformation produces characteristic ions  $M^+ - 1$ ,  $M^+ - 2$ , and  $M^+ - 3$  [14, pp. 51–57].

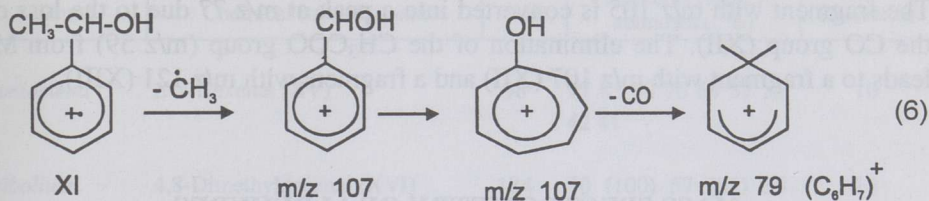
In the mass spectrum of 2-phenylethanol (X, Table 2) the most abundant peak is at  $m/z$  92, which is produced by the McLafferty rearrangement, followed by a transformation according scheme (4):



The main fragmentation pathway of alcohol X leads to the most abundant fragment with  $m/z$  91, which is converted into tropyllium ion and then into the ion  $C_5H_5^+$  ( $m/z$  65) after acetylene elimination by scheme (5):

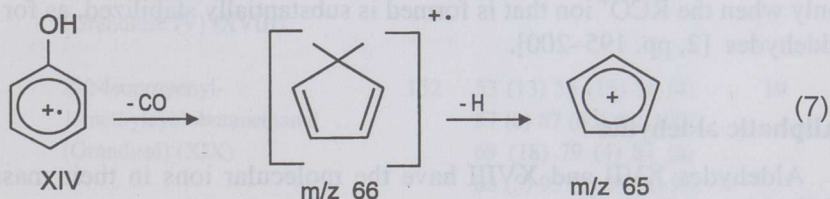


There is an abundant molecular ion ( $M^+$  122, 33%) in the mass spectrum of XI (Table 2) and major peaks at  $m/z$  107 ( $M^+ - CH_3$ ) and  $m/z$  79 ( $M^+ - CH_3 - CO$ ) due to the transformation according to scheme (6):



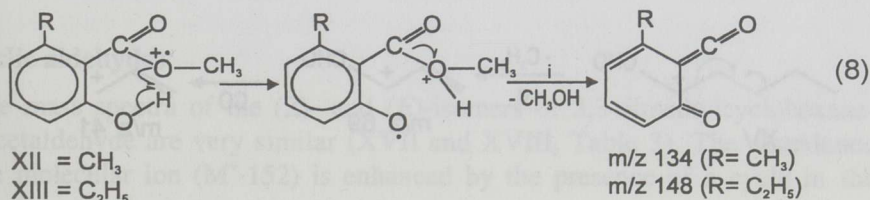
## Phenols

There are detectable molecular ions in the mass spectra of XIV ( $M^+$  94), XII ( $M^+$  166), and XIII ( $M^+$  180) (Table 2). Phenol XIV is converted according to scheme (7) into the fragments with  $m/z$  66 and  $m/z$  65:



The fragment with  $m/z$  39 ( $\text{C}_3\text{H}_3$ ) is typical of mass spectra of aromatic compounds [14, pp. 51–57].

The hydroxyl hydrogen exhibits a high tendency for transfer to a radical site. In a phenol the hydroxyl hydrogen atom can thus act as a ready donor for an ortho effect rearrangement, followed by the elimination of methanol [2, pp. 189–195]. In the mass spectra of methyl salicylates (XII and XIII, Table 2) the fragments with  $m/z$  134 (XII) and 148 (XIII) arise from the  $\text{CH}_3\text{OH}$  elimination due to the ortho effect and the formation of the six-membered ring transition state (see scheme (8)).



The fragments with  $m/z$  106 (XII) and 120 (XIII) are due to the loss of the CO group ( $m/z$  28) in fragments with  $m/z$  134 (XII) and 148 (XIII). The ion at  $m/z$  105 ( $C_6H_5CO^+$ ) in the mass spectra of both methyl salicylates is eliminated from the molecular ions due to the loss of the  $OCH_3^+$  ion, R, and the OH group. The fragment with  $m/z$  105 is converted into a peak at  $m/z$  77 due to the loss of the CO group (XII). The elimination of the  $CH_3COO$  group ( $m/z$  59) from  $M^+$  leads to a fragment with  $m/z$  107 (XII) and a fragment with  $m/z$  121 (XIII).

## MASS SPECTROMETRY OF ALDEHYDES

Addition of a carbonyl group to an alkane substantially lowers the ionization energy. The molecular ion of even higher aldehydes with some degree of chain branching is usually of observable abundance. The characteristic peaks in the spectra of carbonyl compounds provide many types of fragmentation pathways. The  $\alpha$ -cleavage reaction is not very important for aldehydes. The  $CHO^+$  ( $m/z$  29) peak is prominent only for lower aldehydes.

The alternative  $\alpha$ -cleavage, yielding  $(M - H)^+$ , appears to be appreciable only when the  $RCO^+$  ion that is formed is substantially stabilized, as for aromatic aldehydes [2, pp. 195–200].

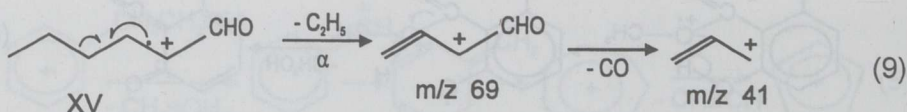
### Aliphatic aldehydes

Aldehydes XVII and XVIII have the molecular ions in their mass spectra ( $M^+$  152) (see Table 3).

The aldehyde group in *E*-2-hexenal (XV) is stabilized by the double bond, and  $\alpha$ -cleavage yields a peak at  $m/z$  97 ( $M^+ - H$ ). *E*-2-Hexenal shows characteristic ion series 41, 55, 69, and 83 due to both  $C_nH_{2n-1}CO^+$  and  $C_nH_{2n-1}^+$  ions, an  $(M^+ - 18)$  peak ( $m/z$  80) from the loss of water, and an  $(M - 28)^+$  peak ( $m/z$  70) from the loss of the carbonyl group.

The fragment  $CH_2=CH-CH=OH^+$  with  $m/z$  57 is eliminated from XV by isomerization through the migration of the double bond, followed by the McLafferty rearrangement, accompanied with  $\alpha$ -cleavage.

Aldehyde XV exhibits allylic cleavage and the formation of fragments with  $m/z$  69 and  $m/z$  41 (scheme (9)):





## Mass spectra of aldehyde components of Coleoptera pheromones

Genus	Chemical (trivial) name	M <sup>+</sup>	Fragments (relative abundance, %)	Reference
<i>Gonioctena</i>	<i>E</i> -2-Hexenal (XV)	98	97 83 80 70 69 57 55 42 41	10
<i>Tribolium</i>	4,8-Dimethyldecenal (XVI)	184	70 (100) 57 (85) 85 (53) 43 (52) 81 (50) 95 (42) 111 (33) 125 (12)	18
<i>Anthonomus</i>	<i>Z</i> -3,3-Dimethylcyclohexane- $\Delta^{1,\alpha}$ -acetaldehyde (Grandlure III) (XVII)	152	137 (100) 109 152 81 69	12
<i>Anthonomus</i>	<i>E</i> -3,3-Dimethylcyclohexane- $\Delta^{1,\alpha}$ -acetaldehyde (Grandlure IV) (XVIII)	152	109 (100) 152 95 81 137	12
<i>Pissodes</i>	<i>Z</i> -2-Isopropenyl- 1-methylcyclobutanethanal (Grandisal) (XIX)	152	53 (13) 55 (15) 56 (4) 57 (8) 67 (60) 68 (100) 69 (18) 79 (4) 81 (8) 83 (5) 93 (7) 95 (4) 96 (5) 97 (5) 107 (2) 108 (37) 109 (22)	19

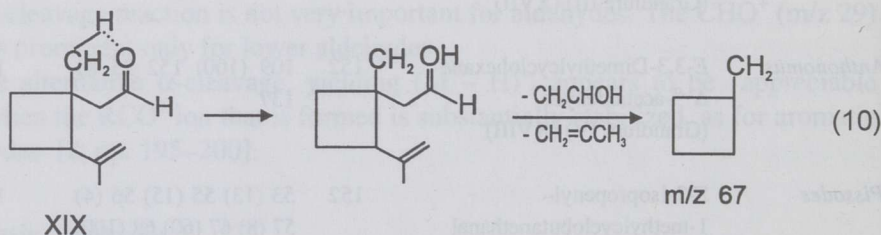
The same rearrangement but associated with the cleavage of the  $\alpha,\beta$ -bonds is typical of branched saturated aldehyde XVI. It is accompanied with the elimination of the ion at  $m/z$  44 ( $\text{CH}_2=\text{CH}-\text{OH}^+$ ) and with the formation of a highly abundant radical  $\text{CH}_2\dot{\text{C}}(\text{CH}_3)(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$  ( $m/z$  140), which can undergo decomposition and eliminate fragments with  $m/z$  125, 111, 95, and 81. The main way of the fragmentation of XVI yields the most abundant fragments with  $m/z$  57 ( $\text{C}_4\text{H}_9$ ), 70 ( $\text{C}_5\text{H}_{10}$ ), and 85 ( $\text{C}_6\text{H}_{13}$ ).

### Alicyclic aldehydes

The mass spectra of the (*Z*)- and (*E*)-isomers of 3,3-dimethylcyclohexane- $\Delta^{1,\alpha}$ -acetaldehyde are very similar (XVII and XVIII, Table 3). The abundance of the molecular ion ( $\text{M}^+$ ·152) is enhanced by the presence of a cycle in the

molecule. The fragment at  $m/z$  137 ( $M^+ - CH_3$ ), which is the main one in the mass spectrum of the *Z*-isomer, is characteristic of both aldehydes. The elimination of the  $CH_3$  group is due to the double bond migration into the cycle of the radical ion. The main way of fragmentation for *E*-isomer is the elimination of the fragment with  $m/z$  109 ( $M^+ - CH_3CO$ ) due to complex rearrangement and migration of the double bond. The presence of a fragment at  $m/z$  69 in the mass spectrum of the *Z*-isomer (its absence in the *E*-isomer) and of a fragment at  $m/z$  96 in the mass spectrum of the *E*-isomer (its absence in the *Z*-isomer) is the result of such fragmentation.

The base peak at  $m/z$  68 ( $C_5H_8$ ) in the mass spectrum of XIX (Table 3) is due to the  $\alpha$ -cleavage of C-C bonds of substituents and the elimination of  $CH_2CHO$  and  $CH_2=C(CH_3)$  groups. The characteristic fragments at  $m/z$  123 ( $M^+ - CHO$ ) and 109 ( $M^+ - CH_2=CHO$ ) are observed in the mass spectrum of XIX. The rearrangement of  $\gamma$ -hydrogen eliminates  $CH_2CHOH$  ( $m/z$  44) and isopropenyl and yields a fragment at  $m/z$  67 according to scheme (10):



## MASS SPECTROMETRY OF KETONES

### Aliphatic ketones

Molecular ions of ketones are usually of observable abundance [14, pp. 61–65; 20], as for example molecular ions of ketones XX–XXII:  $M^+$  128 (5%),  $M^+$  126 (11%), and  $M^+$  254 (0.9%) (Table 4).

Alpha-cleavage at the carbonyl group is characteristic of aliphatic ketones. The base peaks at  $m/z$  57 ( $C_2H_5C=O$ ) in the mass spectrum of XX and at  $m/z$  43 in the mass spectra of XXI and XXII are due to  $\alpha$ -cleavage. The elimination of fragments at  $m/z$  29 ( $C_2H_5$ ) and  $m/z$  99 ( $C_5H_{11}CO$ ) is not favoured by ketone XX. The decomposition of alkyl radical produces a fragment at  $m/z$  43 ( $C_3H_7$ ). The fragment at  $m/z$  86 ( $C_5H_{10}O$ ) is derived from  $\gamma$ -hydrogen rearrangement according to scheme (11):

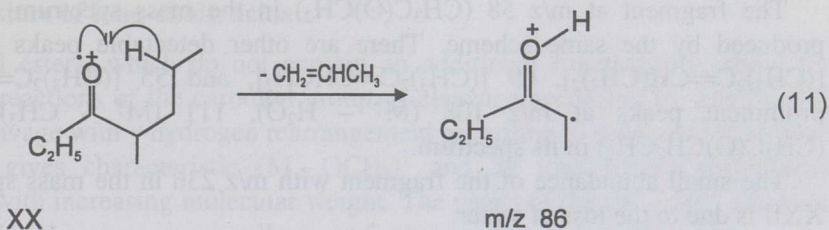


Table 4

Mass spectra of ketones as components of Coleoptera pheromones

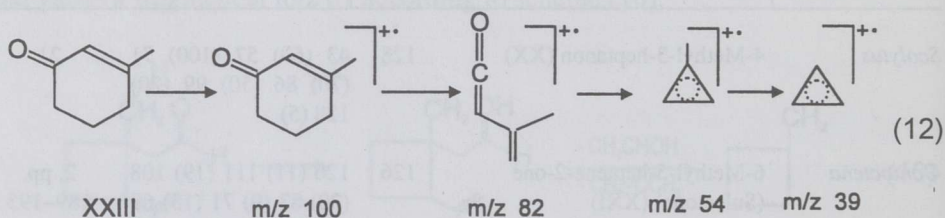
Genus	Chemical (trivial name)	M <sup>†</sup>	Fragments (relative abundance, %)	Reference
<i>Scolytus</i>	4-Methyl-3-heptanon (XX)	128	43 (60) 57 (100) 71 (70) 86 (50) 99 (20) 128 (5)	21
<i>Gonioctena</i>	6-Methyl-5-heptene-2-one (Sulcatone) (XXI)	126	126 (11) 111 (19) 108 (30) 83 (9) 71 (13) 69 (58) 58 (24) 55 (32) 43 (100) 41 (50)	2, pp. 189-195
<i>Diabrotica</i>	6,12-Dimethyl-2-pentadecanone (XXII)	254	43 (100) 58 (82) 59 (38) 71 (42) 85 (24) 95 (13) 97 (8) 109 (10) 110 (15) 123 (3) 137 (2) 151 (1) 165 (1) 196 (3) 211 (2) 236 (6) 254 (0.9)	22
<i>Dendroctonus</i>	3-Methylcyclohexene-2-one-1 (XXIII)	110	82 (100) 67 (10) 54 (35) 39 (45)	23
			82 (100) 39 (60) 54 (50) 26 (20) 41 (13) 110 (24)	24
			82 (100) 39 (56) 54 (35) 110 (34) 27 (23) 53 (16)	25
<i>Dendroctonus</i>	3-Methylcyclohexene-3-one-1 (XXIV)	110	67 (100) 68 (70) 39 (50) 110 (36) 53 (35) 41 (28) 27 (26) 82 (11)	24

The fragment at  $m/z$  58 ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ ) in the mass spectrum of XXI is produced by the same scheme. There are other detectable peaks at  $m/z$  83 [ $(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2$ ], 69 [ $(\text{CH}_3)_2\text{C}=\text{CHCH}_2$ ], and 55 [ $(\text{CH}_3)_2\text{C}=\text{CH}$ ] and prominent peaks at  $m/z$  108 ( $\text{M}^+ - \text{H}_2\text{O}$ ), 111 ( $\text{M}^+ - \text{CH}_3$ ), and 71 ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ) in its spectrum.

The small abundance of the fragment with  $m/z$  236 in the mass spectrum of XXII is due to the loss of water.

### Alicyclic ketones

Cleavage of two bonds of the ring is necessary for fragmentation of cyclic compounds. Alpha-cleavage at the carbonyl group is the same process as for aliphatic ketones. Fragmentation of ketone XXIII proceeds according to scheme (12) [26]:



The mass spectra of XXIV and its isomer XXIII are quite different, may be due to the loss of the fragment with three carbon atoms by XXIV. Further decomposition of the residue of the molecular ion leads to fragments with  $m/z$  67 (100%) and  $m/z$  68 [26].

## MASS SPECTROMETRY OF ACIDS AND THEIR ESTERS

Both the carbonyl oxygen and the saturated oxygen atom of esters can give reaction paths expected from the separate behaviour of these functionalities and, in addition, new reactions apparently due to their combined effects.

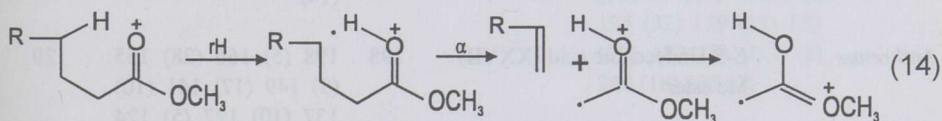
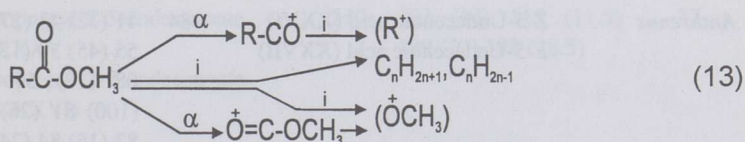
Molecular ions of acids are of small abundance. For esters molecular ions are observable in appreciable abundance;  $\text{M}^+$  increases at higher molecular weights, although it decreases with chain branching [2, pp. 201–205].

The main characteristic ion for acids is  $(\text{CH}_3\text{COOH})^+$  ( $m/z$  60), which is produced by  $\gamma$ -hydrogen rearrangement of the radical ion. The high-molecular-weight  $n$ -aliphatic acids produce two series of ions:  $\text{C}_n\text{H}_{2n+1}^+$  ( $m/z$  29, 43, 57, 71, 85, etc.) and  $\text{C}_n\text{H}_{2n+1}\text{COO}^+$  ( $m/z$  59, 73, 87, etc.). Before spectrum stripping, acids are usually transformed into their methyl esters [14, pp. 66–71].

## Methyl esters of long-chain acids

Methyl esters, which do not contain an additional functionality, show the expected reactions of the carbonyl group:  $\alpha$ -cleavage according to scheme (13) and  $\beta$ -cleavage with  $\gamma$ -hydrogen rearrangement according to scheme (14). Alpha-cleavage gives characteristic  $(M - OCH_3)^+$  and 59 ions whose abundances decrease with increasing molecular weight. The peaks of the  $(M - 59)^+$  alkyl ion and the  $CH_3O^+$  ion are very small except for low-molecular-weight esters.

Further decomposition of the alkyl moiety produces the characteristic  $C_nH_{2n+1}^+$  and  $C_nH_{2n-1}^+$  ion series [2, pp. 201–205]:



A molecular ion ( $M^+$  184) is observable in the mass spectrum of the methyl ester of *Z*-3-decenoic acid (XXV, Table 5).

Alpha-cleavage at the carbonyl group yields the largest  $m/z$  73 ion;  $\beta$ -cleavage with  $\gamma$ -hydrogen rearrangement leads to the ions at  $m/z$  110 ( $C_8H_{14}$ ), 152 ( $M^+ - CH_3OH$ ), and 123 ( $M^+ - CH_3COOH_2^+$ ).

The main peak at  $m/z$  74 [ $CH_2C(OH)=OCH_3$ ] in the mass spectrum of *Z*- and *E*-5-undecenoic acids (XXVI and XXVII, Table 5) is produced by the same  $\gamma$ -hydrogen rearrangement as for the Me ester of XXV. Other ions such as  $m/z$  166 ( $M^+ - CH_3OH$ ), 149 ( $M^+ - CH_3O - H_2O$ ), 137 ( $M^+ - CH_3COOH_2^+$ ), and a series of fragments at  $m/z$  54, 68, 82, 96 and at  $m/z$  67, 81, 95 are observed in their mass spectra. The double bond position at  $C_5-C_6$  of these acids was found by means of diagnostic peaks at  $m/z$  127, 141, and 155 [29].

The determination of the double bond position by the character of mass spectrum is very important in identifying pheromones because of small amounts of their components, which do not give a chance to determine the double bond position by other methods.

Mass spectra of acids and their esters as components of Coleoptera pheromones

Genus	Chemical (trivial) name	M <sup>+</sup>	Fragments (relative abundance, %)	Reference
1	2	3	4	5
<i>Anthrenus</i>	Z-3-Decenoic acid (XXV)	170		
<i>Anthrenus</i>	Z-3-Decenoic acid (XXV) Me ester	184	184 152 123 73 (100)	27
<i>Anthrenus</i>	Z-5-Undecenoic acid (XXVI) E-5-Undecenoic acid (XXVII)	184	41 (32) 43 (27) 54 (20) 55 (45) 59 (15) 67 (23) 68 (18) 69 (29) 74 (100) 81 (26) 82 (20) 83 (16) 84 (24) 87 (13) 95 (13) 96 (30) 97 (12) 98 (11) 124 (38) 166 (14)	28
<i>Anthrenus</i>	E-5-Undecenoic acid (XXVII) Me ester	198	198 (5) 166 (28) 155 (3) 149 (17) 141 (10) 137 (10) 127 (5) 124 (50) 110 (14) 101 (6) 96 (42) 87 (22) 74 (100)*	29
<i>Attagenus</i>	E-3,Z-5-Tetradecadienic acid (XXVIII)	224		
	E-3,Z-5-Tetradecadienic acid (XXVIII) Me ester	238	238 207 206 179 74	30, 31
<i>Trogoderma</i>	Methyl-Z-octadec-9-enoate (Methylolate) (XXIX)	296	264 222 180 87 74 55	32
<i>Acanthoscelides</i>	(-)-Methyltetradeca-E,E-E- 2,4,5-trienoate (XXX)	236	138 (100)	33
<i>Trogoderma</i>	(-)-Z-Methyl-14- methylhexadecen-8-oate (XXXI)	282	251 250	34
<i>Tramiathaea</i>	Ethyldecanoate (XXXII)	200	155 171 157 143 129	35
<i>Xyloterus</i> , <i>Trogoderma</i>	Ethylhexadecanoate (Ethylpalmitate) (XXXIII)	284	239 157 101 88	32

Table 5 (continued)

1	2	3	4	5
<i>Pityogenes</i>	Methyl ( <i>E,Z</i> )(2,4)- decadienoate (XXXIV)	182	182 (19) 151 (18) 135 (1) 122 (10) 113 (28) 112 (29) 111 (100) 97 (25) 93 (20) 87 (8) 82 (28) 81 (100) 80 (10) 79 (51) 67 (51) 66 (41) 65 (25) 59 (45) 53 (39) 41 (42)	36
<i>Dermestes</i>	Isopropyl- <i>Z</i> -5-dodecenoate (XXXV) Isopropyl- <i>Z</i> -7-dodecenoate (XXXVI)	240	102 (14) 115 (11.5) 199 (22) 198 (28.5)	37
<i>Hylobies</i>	Eicosylacetate (XXXVII)	340	43 (100) 97 (96) 55 (93) 61 (87) 69 (74) 54 (72) 83 (64) 111 (43) 125 (32) 139 (17) 153 (10) 182 (8) 252 (8) 280 (18) 205 (5)	38
<i>Hylobies</i>	<i>Z</i> -9-Octadecenylacetate (XXXVIII)	310	55 (100) 83 (63) 97 (53) 69 (52) 43 (20) 109 (19) 123 (16) 137 (7) 61 (7) 152 (5) 250 (5) 222 (1)	38
<i>Cathartus</i>	<i>E</i> -3-Methyl-7-acetoxy- 3-nonen (XXXIX)	198	138 (12) 127 (31) 109 (100) 95 (15) 85 (32) 83 (23) 82 (35) 81 (43) 67 (72) 55 (60) 43 (20) 41 (28)	39
<i>Cathartus</i>	7-Methyl-3-propyl-2( <i>E</i> ),6( <i>E</i> )- nonadienyl acetate (XL)	238	178 (4) 149 (9) 135 (9) 121 (12) 108 (7) 93 (11) 83 (60) 82 (29) 81 (20) 79 (20) 68 (21) 67 (31) 55 (100) 53 (15)	40
<i>Cylas</i>	<i>Z</i> -3-Dodecen-1-yl ( <i>E</i> )- 2-butenolate (XLI)	252	167 (3) 166 (32) 138 (14) 124 (9) 109 (10) 96 (34) 87 (6) 82 (42) 69 (100)	41

1	2	3	4	5
<i>Diabrotica</i>	8-Methyl-2-decanolpropionat (XLII)	242	57 (100) 70 (54) 123 (32) 101 (22) 83 (20) 75 (16) 154 (7) 139 (5)	42
<i>Rhyzopertha</i>	(S)-(+)-1-Methylbutyl (E)-2-methyl-2-pentenoate (XLIII)	184	184 (0.3) 115 (73.6) 97 (100)	43
<i>Rhyzopertha</i>	(S)-(+)-1-Methylbutyl (E)-2,4-dimethyl-2-pentenoate (XLIV)	198	199 (10.5) 129 (100) 111 (96.7) 70 (30.6)	43
<i>Agriotes</i>	E-3,7-Dimethyl-2,6-octadiene- 1-ol-butyrate (Geranylbutyrate) (XLV)	224	155 154 136 121 107 93 71 69 (100) 68 57	44
<i>Agriotes</i>	E-3,7-Dimethyl-2,6-octadiene- 1-ol-isovalerate (Geranylisovalerate) (XLVI)	238	169 154 121 107 93 85 69 (100) 68 57	44
<i>Agriotes</i>	E,E-3,7,11-Trimethyl-2,6,10- dodecatriene-1-ol-acetate (E,E-Farnesylacetate) (XLVII)	264	249 221 204 195 189 175 161 149 147 136 135 121 107 93 81 79 69 (100) 68 67 65	44
<i>Agriotes</i>	E,E-3,7,11-Trimethyl-2,6,10- dodecatriene-1-ol-isovalerate (E,E-Farnesylisovalerate) (XLVIII)	306	238 204 182 172 169 154 137 136 121 109 108 107 98 96 95 94 93 85 (100) 81 80 69 67 57	45
<i>Agriotes</i>	E,E-3,7,11-Trimethyl-2,6,10- dodecatriene-1-ol-butyrate (E,E-Farnesylbutyrate) (XLIX)	292	221 (10.6) 204 (28) 189 (13.5) 161 (27) 136 (40) 121 (24) 119 (30.1) 107 (28.8) 93 (64.4) 71 (11.5) 69 (100)	46
<i>Prostephanus</i>	Isopropyl-(2E)-2-methyl- 2-pentenoate (L)	156	156 (4) 127 (20) 114 (34) 97 (78) 85 (3) 69 (100) 59 (17) 43 (71) 41 (81)	47

\* 20 eV



Since all positional isomers of methyl undecenoates were available, it was attempted to identify the double bond position of the pheromone by comparing the mass spectra of the isomers with the spectrum of the pheromone, using a newly devised fitness index (*FI*). The index (%) was calculated with the help of the following equation:

$$FI = \left( \frac{I}{N} - 1 \right) \times 100,$$

where *I* is the absolute difference between the intensity ratio of every fragment ion pair of an isomer and *N* is the corresponding ratio of the pheromone. The lowest average index value among the isomers indicates the best fit to the pheromone [28].

The mass spectrum of the methyl ester of *E*-3,*Z*-5-tetradecadienoic acid (XXVIII, Table 5) showed the following diagnostic peaks at *m/z*: 238 ( $M^+$ ), 207 ( $M^+ - OCH_3$ ), 206 ( $M^+ - CH_3OH$ ), 179 ( $M^+ - CH_3COO$ ), and 74 ( $CH_2COOCH_3 + H$ ) [31]. In the mass spectrum of the methyl ester of *Z*-9-octadecenoic acid (XXIX, Table 5) the fragments with *m/z* 87 ( $CH_2CH_2COOCH_3$ ), 264 ( $M^+ - CH_3OH$ ), 74 ( $CH_3O=C(OH)CH_2$ ), and 222 ( $M^+ - 74$ ) are observed [32]. The favourable pathway of the fragmentation of the methyl ester *E*-2, *E*-4, *E*-5-tetradeca-2,4,5-trienoic acid (XXX, Table 5), leading to the fragment with *m/z* 138 ( $M^+ - C_7H_{14}$ ), is due to a specific skeleton rearrangement in the alkyl part of the molecule.

Chain branching ester XXXI (Table 5) shows in its mass spectrum diagnostic peaks at *m/z* 251 ( $M^+ - CH_3O$ ) and 250 ( $M^+ - CH_3OH$ ) [34].

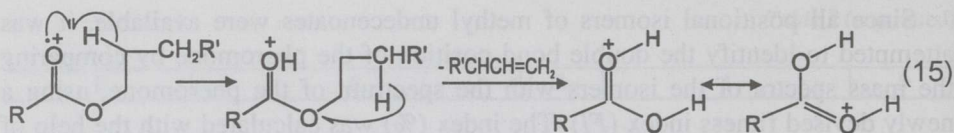
### Ethyl and higher esters of long-chain acids

As it is seen from the mass spectra of esters XXXII–XXXV in Table 5, their way of fragmentation is similar to that of the methyl esters. Characteristic fragments with *m/z* 155 ( $M^+ - C_2H_5O$ ), 171 ( $M^+ - C_2H_5$ ), 157 ( $M^+ - C_3H_7$ ), 143 ( $M^+ - C_4H_9$ ), 129 ( $M^+ - C_5H_{11}$ ), 115 ( $M^+ - C_6H_{13}$ ), and 101 ( $M^+ - C_7H_{15}$ ) are observed in the mass spectrum of XXXII.

McLafferty rearrangement leads to the fragment with *m/z* 88 [ $C_2H_5OC(=OH^+)CH_2$ ] in the decomposition of XXXIII and *m/z* 102 [ $i-C_3H_7OC(=OH^+)CH_2$ ] in the decomposition of XXXV and XXXVI [37].

### Esters of acids with long-chain alcohols

The molecular ion peak of esters  $RCOOR'$  generally becomes relatively small when *R'* is larger than butyl ( $M^+$  184, 0.3%, XLIII) or is absent (Table 5). McLafferty rearrangement eliminates the molecule of acid from the esters and the rearrangement of two hydrogen atoms according to scheme (15) yields the fragments with *m/z* 61, 75, 89, etc. [14, pp. 66–71]:



There is a fragment with  $m/z$  61 ( $\text{CH}_3\text{COOH}_2$ )<sup>+</sup> in the mass spectra of XXXVII and XXXVIII due to the rearrangement (15). Alpha-cleavage at the carbonyl group of the esters yields highly abundant fragments with  $m/z$  43 ( $\text{CH}_3\text{CO}$ ) and produces the characteristic  $\text{C}_n\text{H}_{2n-1}$  ( $m/z$  55, 69, 83, 97) and  $\text{C}_n\text{H}_{2n-1}\text{O}$  ( $m/z$  109, 123, 137) ion series by scheme (13).

McLafferty rearrangement yields peaks at  $m/z$  138 ( $\text{M}^+ - \text{CH}_3\text{COOH}$ ) in the mass spectrum of ester XXXIX and at  $m/z$  154 ( $\text{M}^+ - \text{C}_3\text{H}_7\text{COOH}$ ) in the mass spectrum of ester XLII. The rearrangement of XXXIX by scheme (15) produces in its mass spectrum a peak at  $m/z$  137, the decomposition of which gives peaks at  $m/z$  67, 81, 95, and 109 (100%).

The decomposition of the fragment with  $m/z$  139 ( $\text{M}^+ - \text{CH}_3 - \text{C}_3\text{H}_7\text{COOH}$ ) yields the ions at  $m/z$  83 ( $\text{C}_6\text{H}_{11}$ ) and 70 ( $\text{C}_5\text{H}_{10}$ ) in the mass spectrum of XLII, which contains other peaks at  $m/z$  171 ( $\text{C}_{11}\text{H}_{23}\text{O}$ ), 101 ( $\text{C}_6\text{H}_{13}\text{O}$ ), 155 ( $\text{C}_{11}\text{H}_{23}$ ), 123 ( $\text{C}_9\text{H}_{17}$ ), and 57 ( $\text{C}_4\text{H}_9$ , 100%).

Alpha-cleavage at the carbonyl group in XLIII yields a fragment with  $m/z$  97 ( $\text{C}_6\text{H}_9\text{O}$ ). The rearrangement by scheme (15) leads to a fragment with  $m/z$  115.

The main way of fragmentation of ester XLIV is the complex alkyl transformation, leading to a peak at  $m/z$  129 due to loss of  $\text{C}_5\text{H}_{10}$  group ( $m/z$  70).

## Esters of acids with isoprenoid alcohols

The abundance of the molecular ion decreases with chain branching. There is no  $\text{M}^+$  in the mass spectra of esters XLV–XLIX (Table 5). An allylic type cleavage is favoured for these esters and it leads to a peak at  $m/z$  69 ( $\text{C}_5\text{H}_9$ , 100%) in the mass spectra of XLV–XLVII and XLIX.

The spectra of these esters exhibit characteristic fragments at  $m/z$  136, 121, 107, 93, etc. due to loss of water by the ion at  $m/z$  154 [ $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$ ], which is formed by rearrangements of the radical ion.

## MASS SPECTROMETRY OF MONOTERPENOIDS

Monoterpenoids are a complex family of terpenoids. The observation of their mass spectra leads in many cases to an identification of functional groups. Complete structure assignment by mass spectrometry measurement alone, however, may be achieved only in the most favourable instances.

## Acyclic monoterpenoids

Peak abundances in the mass spectra of acyclic monoterpenoids are to a large extent dependent on the double bond position, being thus related to molecular stability. The presence of oxygenated groups provides an additional directing influence on the fragmentation sequences and the spectra are often more complex than those of the corresponding hydrocarbons. Molecular ions of alcohols are generally of low abundance and may elude detection. In such cases the presence of a hydroxyl group may be demonstrated by the co-occurrence of  $M^+ - 15$  and  $M^+ - 18$  fragments. In addition to the decomposition processes associated with hydrocarbons, aldehydes may give an  $M^+ - 18$  fragment as a result of water elimination and fragments deriving from loss of CHO-function due to  $\alpha$ -cleavage at the carbonyl group [5].

There is a small detectable molecular ion in the mass spectra of alcohols LI-LIV (Table 6). Prominent ions deriving from these alcohols can be attributed to hydrocarbon fragments, and thus peaks are observed at  $m/z$  136 ( $M^+ - H_2O$ ), 121 ( $M^+ - CH_3 - H_2O$ ), 93, and 69 in the spectra of doubly unsaturated alcohols.

The main way of fragmentation of ipsenol (LI) is McLafferty rearrangement, followed by an allylic cleavage with the elimination of the fragment at  $m/z$  68 ( $C_5H_8$ ). The peak of small abundance at  $m/z$  87 in the mass spectrum of LI is due to an allylic cleavage, typical of alcohols. The other peaks at  $m/z$  41, 55, 69, etc. ( $C_nH_{2n-1}$ ), 43, 57, 71, and 85 ( $C_nH_{2n+1}$ ) are the result of rearrangements within a resonant structure, produced when the molecule is energized. The mass spectrum of linalool (LII) is very similar to that of ipsenol (LI).

Decomposition of alcohol LIII is due to allylic cleavage with the elimination of fragments at  $m/z$  57 ( $C_5H_{11}$ ) and 97 ( $M^+ - C_5H_{11}$ ) and rearrangements with the elimination of the ion series  $C_nH_{2n+1}$ ,  $C_nH_{2n}$ , and  $C_nH_{2n-1}$ .

The main peak at  $m/z$  85 ( $C_5H_9O$ ) in the mass spectrum of ipsdienol LIV is due to allylic cleavage at the hydroxyl group. There are characteristic monoterpenoid alcohol fragments in the mass spectrum of LIV:  $m/z$  134 ( $M^+ - H_2O$ ) and 119 ( $M^+ - CH_3 - H_2O$ ).

Rearrangement of LV and LVI by scheme (3) yields fragments with  $m/z$  134 ( $M^+ - H_2O$ ) and 119 ( $M^+ - CH_3 - H_2O$ ), which after double bond migration produce peaks at  $m/z$  105, 91, and 77. According to Silverstein et al. [48] the fragment at  $m/z$  79 (100%) is due to hydrogen rearrangement, followed by the cleavage of the  $C_3-C_4$  bond. The cleavage of the  $C_2-C_3$  bond leads to the ion at  $m/z$  93, which produces fragments at  $m/z$  92 and 91 due to the loss of one and two hydrogen atoms, respectively.

## Bicyclic monoterpenoids

Monoterpenoids containing a cyclohexane ring and an additional double bond produce fragments formed by the double bond or the migration of the  $CH_3$  group to the ring.

## Mass spectra of monoterpenoids of Coleoptera pheromones

Genus	Chemical (trivial) name	M <sup>+</sup>	Fragments (relative abundance, %)	Reference
1	2	3	4	5
<i>Ips</i>	(-)-2-Methyl-6-methylene-7-octene-4-ol (Ipsenol) (LI)	154	38 (4) 39 (37) 40 (12) 41 (70) 42 (10) 43 (66) 44 (18) 45 (26) 51 (6) 53 (25) 55 (6) 57 (17) 58 (7) 66 (5) 67 (35) 68 (100) 69 (64) 70 (5) 71 (8) 79 (6) 85 (15) 87 (10) 121 (2) 136 (2) 154 (1)	48
<i>Ips</i>	3,7-Dimethyl-1,6-octadiene-3-ol (Linalool) (LII)	154	154 (2) 136 (5) 121 (4) 85 (17) 71 (15) 69 (67) 68 (100) 67 (29) 45 (33) 43 (54) 41 (51) 39 (18)	49
<i>Ips</i>	2,6-Dimethyl-5,7-octadiene-4-ol (LIII)	154	57 (45) 67 (11) 69 (13) 79 (14) 85 (60) 93 (17) 95 (5) 97 (100) 98 (10) 121 (3) 154 (3)	50
<i>Ips</i>	(+)-2-Methyl-6-methylene-2,7-octadiene-4-ol (Ipsdienol) (LIV)	152	152 (1) 134 (18) 119 (42) 91 (58) 85 (100) 79 (63) 77 (27) 55 (20) 53 (28) 43 (27) 41 (71) 39 (54) 29 (20) 27 (47)	30
<i>Ips</i>	<i>E</i> -2-Methyl-6-methylene-3,7-octadiene-2-ol (LV)	152	29 (12) 32 (27) 39 (42) 41 (47) 43 (15) 44 (37) 51 (14) 53 (27) 55 (12) 65 (12) 77 (33) 78 (19) 79 (100) 91 (64) 92 (22) 93 (17) 105 (21) 119 (35)	48
<i>Ips</i>	2-Methyl-6-methylene- <i>E</i> -2,7-octadiene-1-ol ( <i>E</i> -Myrcenol) (LVI)	152	134 (10) 119 (17) 93 (65) 79 (35) 67 (20) 43 (100) 29 (35)	51
<i>Ips</i>	<i>Z</i> -2-Pinen-4-ol ( <i>Z</i> -Verbenol) (LVII)	152	137 134 43 (100) 109 152 137 134 119 43 (100)	30 52
<i>Ips</i>	<i>E</i> -2-Pinen-4-ol ( <i>E</i> -Verbenol) (LVIII)	152	134 119 (100) 91	53

Table 6 (continued)

1	2	3	4	5
<i>Dendroctonus</i>	6,6-Dimethyl-2-methylen-bicyclo-/1,1,3/-heptanol-3 ( <i>E</i> -Pinocarveol) (LIX)	152	41 (100) 55 70 92 39 91 27 83 43 41 (100) 92 (87) 55 (85) 91 (75) 39 (69) 70 (63) 43 (50) 27 (48) 83 (48) 81 (46) 53 (45) 137 (3) 134 (42) 119 (28) 152 (1)	54  7
<i>Dendroctonus</i>	6,6-Dimethyl-2-methylol-bicyclo-/1,1,3/-hepten-2 (Myrtenol) (LX)	152	79 (100) 91 41 39 27 77 43 108 93 79 (100) 91 (89) 41 (64) 108 (60) 39 (50) 77 (47) 93 (32) 27 (31) 119 (30) 43 (27) 137 134 152 (19)	54  7
<i>Dendroctonus</i>	6,6-Dimethyl-2-methylal-bicyclo-/1,1,3/-hepten-2 (Myrtenal) (LXI)	150	79 (100) 107 (72) 77 (64) 39 (54) 91 (46) 41 (45) 106 (38) 105 (34) 108 (31) 27 (31) 59 (30) 29 (27) 51 (25) 65 (23) 93 (22) 78 (21) 150 (11)	7
<i>Dendroctonus</i>	6-Hydroxycamphene (LXII)	152	108 (100) 93 (77) 91 (44) 41 (31) 77 (27) 67 (23) 39 (23) 109 (23) 107 (22) 79 (21) 137 134	55
<i>Dendroctonus</i>	6,6-Dimethyl-2-methylen-bicyclo-/1,1,3/-heptanon-3 (Pinocarvon) (LXIII)	150	53 (100) 41 (88) 39 (80) 107 (67) 79 (63) 150 (57) 77 (40) 69 (29) 135 (27) 122 (17) 53 (100) 41 81 39 27 108 79 107 69 53 (100) 41 81 39 27 108	7  54  56
<i>Dendroctonus</i>	1 <i>S</i> ,4 <i>S</i> ,5 <i>S</i> -2-Pinene-4-on (Verbenon) (LXIV)	150	107 (100) 39 27 41 91 150 (72) 107 (100) 135 (84) 91 (64) 80 (58) 79 (46) 108 (43) 39 (36) 41 (34) 67 (30) 77 (27) 95 (27) 105 (26) 109 (26) 82 (21) 53 (20)	54 57

The fragmentation of *cis*- and *trans*-isomers of verbenol (LVII and LVIII, Table 6) depends on the stereochemistry of these structures.

The most abundant peak at  $m/z$  43 in the mass spectrum of LVII is due to complex fragmentation, produced by hydrogen rearrangement and double bond migration, accompanied with the formation of a peak at  $m/z$  109 ( $M^+ - 43$ ).

In the mass spectrum of LVIII the most abundant peak at  $m/z$  119 is due to loss of water, accompanied with the elimination of  $\text{CH}_3$  group ( $M^+ - \text{H}_2\text{O} - \text{CH}_3$ ). Its decomposition with the elimination of  $\text{C}_2\text{H}_4$  leads to a fragment at  $m/z$  91.

Characteristic ions at  $m/z$  134 ( $M^+ - \text{H}_2\text{O}$ ),  $m/z$  119 ( $M^+ - \text{CH}_3 - \text{H}_2\text{O}$ ) and  $m/z$  137 ( $M^+ - \text{CH}_3$ ) are observed in the mass spectrum of *trans*-pinocarveol (LIX, Table 6). The main fragment with  $m/z$  41 ( $\text{C}_3\text{H}_5$ ) is due to  $\alpha$ -cleavage at the hydroxyl group with the elimination of  $\text{CH-OH}$  ( $m/z$  30) [5].

The base peak at  $m/z$  79 ( $\text{C}_6\text{H}_7$ ) in the mass spectrum of myrtenol (LX, Table 6) is due to decomposition within a resonant structure, accompanied with a retro-Diels-Alder reaction. Characteristic peaks at  $m/z$  137 ( $M^+ - \text{CH}_3$ ), 134 ( $M^+ - \text{H}_2\text{O}$ ), 119 ( $M^+ - \text{CH}_3 - \text{H}_2\text{O}$ ), 91, 77 and peaks from the series  $\text{C}_n\text{H}_{2n-3}$  ( $m/z$  53, 39) are observed in the mass spectrum of LX.

The mass spectrum of myrtenal (LXI, Table 6) is similar to the mass spectrum of myrtenol except for peaks at  $m/z$  137 and  $m/z$  134 due to the higher stability of myrtenal.

There are characteristic peaks of monoterpene alcohols at  $m/z$  134 ( $M^+ - \text{H}_2\text{O}$ ) and 137 ( $M^+ - \text{CH}_3$ ) as well as  $\text{C}_n\text{H}_{2n-5}$  ( $m/z$  107, 93, 79) and  $\text{C}_n\text{H}_{2n-3}$  ( $m/z$  67, 39) ion series in the mass spectrum of 6-hydroxycamphene (LXII, Table 6). The base peak at  $m/z$  108 ( $M^+ - \text{CH}_2\text{CHOH}$ ) is due to the cleavage of two bonds of the ring.

High abundances of molecular ions in the mass spectra of bicyclic ketones LXIII ( $M^+$  150, 57%) and LXIV ( $M^+$  150, 72%) are the result of their high stability. Characteristic peaks at  $m/z$  135 ( $M^+ - \text{CH}_3$ ), 122 ( $M^+ - \text{CO}$ ), and 107 ( $M^+ - \text{CH}_3 - \text{CO}$ ) are observed in their mass spectra.

## MASS SPECTROMETRY OF HETEROCYCLIC COMPOUNDS

The peak of the molecular ion of a heterocyclic compound is usually detectable. The main pathway of fragmentation is  $\beta$ -cleavage to the ring. The charge retention by heteroatom not by the  $\pi$ -system of the cycle has an advantage. Ring cleavage in five-membered heterocycles at the carbon-heteroatom bond is not intensive. Beta-cleavage in six-membered heterocycles depends on the position of the substituent. If the alkyl substituent has more than three carbon atoms, the molecule can undergo the  $\gamma$ -hydrogen rearrangement to a heteroatom [14, pp. 90-92].

## Five-membered heterocycles

The molecular ion peak ( $M^+$  144) is detectable in the mass spectrum of pityol (LXV, Table 7). The main way of fragmentation yields a fragment with  $m/z$  59 ( $C_3H_7O$ )<sup>+</sup> by the elimination of the substituent at position 2. The cleavage of C–O bond at a high-weight substituent leads to the ions at  $m/z$  43 ( $CH_3CO$ ), 85 ( $C_5H_9O$ ), and 41 ( $CH_2CH_2CH^+$ ) while the cleavage of the C–O bond at a low-weight substituent leads to the ions at  $m/z$  42 ( $CH_3CHCH_2$ ) and  $m/z$  102 ( $M^+ - CH_3CHCH_2$ ) in the mass spectrum of LXV.

There are characteristic fragments at  $m/z$  225 ( $M^+ + 1$ ), 223 ( $M^+ - 1$ ), 253 ( $M^+ + 29$ ), 265 ( $M^+ + 41$ ), 207 ( $M^+ + 1 - H_2O$ ), 189 ( $M^+ + 1 - 36$ ), and 165 ( $M^+ + 1 - 60$ ) in the mass spectrum of LXVI (Table 7) under chemical ionization [58].

Table 7

Mass spectra of heterocycles as components of Coleoptera pheromones

Genus	Chemical (trivial) name	$M^+$	Fragments (relative abundance, %)	Reference
1	2	3	4	5
<i>Pytogenus</i>	Z-2-(1-Hydroxy-1-methylethyl)-5-methyltetrahydrofuran (Pityol) (LXV)	144	41 (35) 43 (63) 59 (100) 85 (55) 102 (26) 144 (2)	37
<i>Popilla</i>	Z-5-(1-Decenyl)dihydro-2(3H)-furanone (LXVI)	224	225 223 253 265 207 189 165	58
<i>Lasioderma</i>	2,6-Diethyl-3,5-dimethyl-3,4-dihydro-2H-pyran (Anhydrosericornin) (LXVII)	168	41 (46) 43 (54) 55 (58) 57 (42) 69 (42) 86 (31) 99 (100) 111 (12) 125 (19) 139 (15) 153 (4)	59
<i>Dendroctonus</i>	<i>exo</i> -7-Ethyl-5-methyl-6,8-dioxabicyclo-/3,2,1/-octane ( <i>exo</i> -Brevicomine) (LXVIII)	156	43 (100) 85 (21) 114 (20) 41 (17) 86 (9) 68 (11) 98 (10) 156 (0.5) 156 (10) 138 (2) 127 (7) 114 (65) 98 (35) 86 (34) 85 (100) 68 (40) 67 (25)	20 60

Table 7 (continued)

1	2	3	4	5
<i>Dendroctonus</i>	1,5-Dimethyl-6,8-dioxabicyclo-/3,2,1/-octane (Frontalin) (LXIX)	142	142 (17) 114 (6) 112 (8) 100 (49) 72 (88) 43 (100) 142 (17) 112 (29) 100 (92) 72 (100) 58 (23)	61 62
<i>Scolytus</i>	5-Ethyl-2,4-dimethyl-6,8-dioxabicyclo-/3,2,1/-octane (Multistriatin) (LXX)	170	57 (100) 71 (18) 81 (15) 96 (20) 128 (5) 170 (1)	8
<i>Trypodendron</i>	1,3-Dimethyl-2,9-dioxabicyclo-/3,3,1/-nonane (Lineatin) (LXXI)	156	43 (100) 54 (11) 55 (12) 58 (22) 67 (11) 68 (16) 71 (26) 81 (12) 87 (40) 114 (28) 156 (6) 43 55 83 96 107 109 111 125 135 150 153 168	63 64
<i>Pytogenus</i>	2-Ethyl-1,6-dioxaspiro-/4,4/-nonane (Chalcogran) (LXXII)	156	156 (2) 127 (100, 100) 87 (64, 82) 85 (60, 76) 43 (46, 79) 56 (42, 69) 55=57 (38, 60) 41 (31, 51) 97 (30, 35) 42 (28, 42) 69 (29, 30) 98 (26, 35) 81 (20, 22) 39 (16, 19) 73 (11)	65
<i>Cryptolestes</i>	<i>E,E</i> -4,8-Dimethyl-4,8-decadien-10-olide (Ferrilactone I) (LXXIII)	194	194 (2) 127 (90) 99 (89) 68 (100) 67 (85)	66
<i>Cryptolestes</i>	(3 <i>Z</i> ,11 <i>S</i> )-3-Dodecen-11-olide (Ferrilactone II) (LXXIV)	196	196 (10) 178 (2) 167 (1) 136 (60) 110 (70) 95 (60) 82 (90) 81 (100) 67 (95) 54 (80)	66
<i>Oryzaephilus</i>	<i>Z,Z</i> -3,6-Dodecadien-11-olide (LXXV)	194	194 (13) 176 (4) 134 (14) 121 (17) 93 (35) 79 (100)	67
<i>Oryzaephilus</i>	<i>Z,Z</i> -3,6-Dodecadienolide (LXXVI)	194	194 (32) 166 (11) 134 (14) 121 (11) 93 (47) 79 (100)	67
<i>Oryzaephilus</i>	<i>Z,Z</i> -5,8-Tetradecadiene-13-olide (LXXVII)	222	222 (19) 180 (27) 140 (24) 21 (22) 99 (52) 79 (100)	67



## Six-membered heterocycles

The cleavage of a single bond at the  $\beta$ -position to the ring of anhydro-sericornin (LXVII, Table 7) leads to a low-abundance fragment with  $m/z$  153 ( $M^+ - CH_3$ ). The cleavage of a C–O bond yields in its mass spectrum peaks at  $m/z$  139 ( $M^+ - C_2H_5$ ), 41 ( $C_3H_5$ ), 43 ( $C_2H_3O$ ), 55 ( $C_3H_7$ ), 57 ( $C_3H_5O$ ), 69 ( $C_5H_9$ ), 86 ( $C_5H_{10}O$ ), 111 ( $C_7H_{10}O$ ), and 125 ( $C_8H_{13}O$ ). This process and further decomposition produce the main fragment with  $m/z$  99.

## Polycyclic compounds

There are detectable molecular ions ( $M^+$  156 and  $M^+$  142) in the mass spectra of brevicomin (LXVIII) and frontaline (LXIX) (Table 7).

The main pathway of the fragmentation of LXIX is the cleavage of the C–C bond near the heteroatom, which leads to the main fragment with  $m/z$  43 ( $CH_3CO$ ). There are prominent peaks in its mass spectrum at  $m/z$  72 ( $M^+ - C_4H_6O$ ) and 100 ( $M^+ - C_2H_2O$ ) and unstable peaks at  $m/z$  114 ( $M^+ - C_2H_4$ ) and 112 ( $M^+ - CH_2O$ ) [62].

The same way of fragmentation of *exo*-brevicornin (LXVIII) leads to the fragments with  $m/z$  43 ( $CH_3CO$ ) (100%), 85 ( $C_5H_9O$ ), 114 ( $M^+ - C_2H_4O$ ), 41 ( $C_3H_5$ ), 86 ( $C_5H_{10}O$ ), 98 ( $C_6H_{10}O$ ), and 68 ( $C_5H_8$ ).

In the mass spectrum of  $\alpha$ -multistriatin (LXX, Table 7) the following peaks are observed:  $m/z$  71 ( $C_4H_7O$ ), 81 ( $C_5H_5O$ ), 96 ( $C_6H_8O$ ), 128 ( $M^+ - C_2H_2O$ ), 57 ( $C_3H_5O$ , 100%), and  $M^+$  170 (1%).

The radical ion of lineatin (LXXI, Table 7) has the same fragmentation pathway.

## Spiro-compounds

There is a detectable molecular ion ( $M^+$  156, 2%) in the mass spectrum of chalcogran (LXXII, Table 7). The structure of this spiro-compound is very stable, therefore the main way of its fragmentation is the elimination of the  $C_2H_5$  group with the formation of a fragment at  $m/z$  127 (100%).

In its mass spectrum there are fragments at  $m/z$  55 ( $C_3H_3O$ ), 56 ( $C_3H_4O$ ), 57 ( $C_3H_5O$ ), 69 ( $C_4H_5O$ ), 81 ( $C_6H_9$ ), 97 ( $C_6H_9O$ ), and 98 ( $C_6H_{10}O$ ), which are produced by the cleavage of C–O bonds.

There are two patterns of abundance in the mass spectrum of LXXII from the different spectra strippings, which have a good mutual correlation (Table 7).

## Macrolides

There are detectable molecular ions (2–32%) in the mass spectra of macrolides (LXXIII–LXXVII, Table 7).

An allylic cleavage of the ring is the favoured way of the fragmentation of LXXIII, which produces the fragment  $CH_2C(CH_3)=CHCH_2$  ( $m/z$  68, 100%).

The H-rearrangement from methyl to oxygen of the ether part of the molecule, followed by the same allylic cleavage, yields fragments at  $m/z$  67 ( $C_5H_7$ ) and 127 ( $M^+ - C_5H_7$ ).

An elimination of the  $CH_3$  group from LXXIV leads to the fragment at  $m/z$  181 ( $M^+ - CH_3$ ); its decomposition, with the cleavage of the C-C bond and elimination of the  $CH_2$  group, yields a fragment with  $m/z$  167. The H-rearrangement loss of the  $CO_2H$  group by this fragment produces a peak at  $m/z$  136 ( $C_{10}H_{16}$ ).

In the mass spectrum of LXXIV the following other peaks are observed as a result of the decomposition of the fragment  $C_{10}H_{16}$ :  $m/z$  67 ( $C_5H_7$ ), 81 ( $C_6H_9$ ), and 95 ( $C_7H_{11}$ ). A rearrangement of two hydrogen atoms to the saturated oxygen and loss of water eliminate the fragment at  $m/z$  178.

The same way of fragmentation yields the peak at  $m/z$  176 in the mass spectrum of LXXV. The H-rearrangement loss of the  $COOH$  and  $CH_3$  groups leads to the fragments at  $m/z$  134 ( $C_{10}H_{14}$ ), 121 ( $C_9H_{13}$ ), 93 ( $C_7H_9$ ), and 79 ( $C_6H_7$ ) (100%).

The same mass spectra are observed for the macrolides LXXVI and LXXVII. An exception is the loss of the  $CO$  group accompanied with the formation of a peak at  $m/z$  166 in the mass spectrum of LXXVI: the spectrum of LXXVII exhibits two specific fragments with  $m/z$  180 ( $C_{12}H_{20}O$ ) and 140 ( $C_9H_{16}O$ ) due to cleavage of the C-O bond of the ring, followed by the loss of the  $CH_2CO$  group ( $m/z$  180), double bond migration, and allylic cleavage with the elimination of the  $C_3H_4$  group ( $m/z$  140).

## MASS SPECTROMETRY OF COMPOUNDS WITH MIXED FUNCTIONS

The presence of different functional groups and their mutual interference exert additional influence on the fragmentation of the energized molecule.

### Alcohols containing ketogroups

The main way of fragmentation of ketoalcohols (LXXVIII-LXXXII and XCI, Table 8) depends on the presence of a carbonyl group and, to a small degree, on the presence of a hydroxyl group.

There is a detectable molecular ion in the mass spectrum of butanol-1-on-3,  $M^+$  88 (7%) (LXXVIII, Table 8). The fragments with  $m/z$  43 ( $CH_3CO$ ) (100%),  $m/z$  73 ( $M^+ - CH_3$ ), and  $m/z$  45 ( $CH_2CH_2OH^+$ ) in the mass spectrum of LXXVIII are due to the  $\alpha$ -cleavage reaction of the C-C bond near the carbonyl group. The less abundant ion at  $m/z$  70 ( $M^+ - H_2O$ ) depends on the influence of the hydroxyl group.

The complex rearrangements lead to the fragment with  $m/z$  61 ( $CH_3COOH_2^+$ ).

**Mass spectra of compounds with two different functional groups as components of  
Coleoptera pheromones**

Genus	Chemical (trivial) name	M <sup>+</sup>	Fragments (relative abundance, %)	Reference
1	2	3	4	5
<i>Ips</i>	Butanol-1-on-3 (LXXVIII)	88	43 (100) 70 (18) 61 (15) 45 (9) 53 (8) 88 (7) 73 (5)	68
<i>Xyloterus</i>	3-Hydroxy-3-methylbutan-2-on (LXXIX)	102	59 (100) 43 (23) 41 (14) 87 (4) 69 (2) 84 (1) 102 (1)	69
<i>Xylotrechus</i>	2-Hydroxyoctan-3-on (LXXX)	144	39 (32) 41 (75) 43 (98) 45 (78) 55 (71) 71 (98) 83 (63) 99 (100) 101 (30)	70
<i>Lasioderma</i>	4,6-Dimethyl-7-hydroxynonan-3-on (Serricornin) (LXXXI)	186	57 (100) 86 (86) 41 (67) 69 (60) 55 (57) 70 (53) 43 (36) 111 (27) 83 (24) 99 (24) 139 (14) 168 (9) 127 (7) 157 (6)	71
<i>Sitophilus</i>	4-Methyl-5-hydroxy-3-heptanon (Sitofilure) (LXXXII)	144	129 (0.3) 128 (0.3) 115 (1) 97 (3) 86 (18) 70 (5) 69 (3) 57 (91) 29 (100)	72
			115 (71) 97 (45) 87 (75) 70 (40) 57 (100) 43 (35)	73
<i>Sitona</i>	4-Methyl-3,5-heptandion (LXXXIII)	142	142 (4) 113 (10) 86 (30) 57 (100) 55 (16) 44 (12) 41 (8) 29 (74) 27 (25)	74
<i>Agriotes</i>	<i>E,E</i> -2,6-Dimethyl-2,6-octadien-1,8-diol-di(3-methylbutyrate) (LXXXIV)	338	236 134 119 85 (100)	45

Table 8 (continued)

1	2	3	4	5
<i>Xylotrechus</i>	2,3-Octanediol (LXXXV)	146	41 (39) 43 (30) 45 (52) 55 (100) 57 (25) 75 (20) 83 (98) 101 (23)	70
<i>Lasioderma</i>	2,3-Dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-oxobutyl)-4H-pyran-4-one (Serricorone) (LXXXVI)	238	182 (33) 153 (1) 113 (100) 83 (89) 55 (67) 37 (93) 238 (15) 43 (10) 55 (10) 57 (47) 83 (18) 97 (41) 109 (15) 112 (10) 113 (31) 124 (19) 39 (7) 153 (10) 182 (100) 183 (12)	75 76
<i>Ips</i>	2-Hydroxy-4,4,6-trimethyl-2,5-cyclohexadien-1-one (Lanierone) (LXXXVII)	152	152 (27) 137 (28) 124 (50) 123 (17) 110 (12) 109 (100) 91 (16) 81 (18) 79 (21) 53 (19) 43 (14) 41 (18)	77
<i>Lasioderma</i>	2,3-Dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-hydroxybutyl)-4H-pyran-4-one (Serricorol) (LXXXVIII)	240	182 (85) 153 (15) 113 (75) 112 (100) 240 (28) 57 (10) 82 (10) 83 (35) 112 (37) 113 (100) 133 (28) 145 (11) 182 (43) 183 (21)	75 76
<i>Anobiidae</i>	2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-oxobutyl)-4H-pyran-4-one (Stegobion) (LXXXIX)	224	168 139 124 113 112 111 109 97 168 153 139 124 113 97 83 67 57 (100)	78 79
<i>Anobiidae</i>	2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-hydroxybutyl)-4H-pyran-4-one (Stegobiol) (XC)	226	168 (88) 141 (20) 139 (17) 124 (15) 113 (70) 112 (100) 109 (27) 101 (17) 84 (15) 83 (87) 70 (16) 59 (49) 57 (33) 56 (37) 55 (45) 43 (41)	80
<i>Hylotrupes</i>	3-Hydroxy-2-hexanone (XCI)	116	116 (2) 73 (50) 72 (11) 55 (100) 45 (23) 43 (61) 41 (11)	81

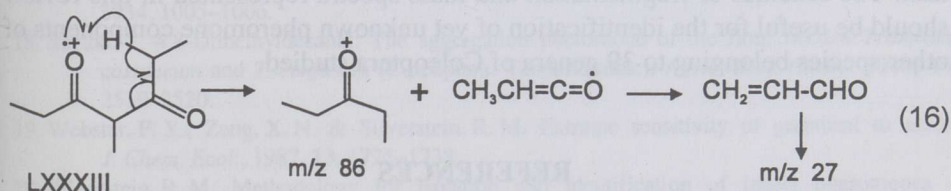
The same  $\alpha$ -cleavage of LXXIX leads to the prominent fragments with  $m/z$  59 ( $M^+ - \text{CH}_3\text{CO}$ ) and  $m/z$  43 ( $\text{CH}_3\text{CO}$ ), as well as to the peaks at  $m/z$  45 ( $\text{CH}_3\text{CH}_2\text{O}$ ), 71 ( $\text{C}_5\text{H}_{11}$ ), and  $m/z$  99 ( $\text{C}_6\text{H}_{11}\text{O}$ ) in the mass spectrum of LXXX.

The most abundant peak at  $m/z$  57 ( $\text{CH}_3\text{CH}_2\text{CO}$ ) in the mass spectrum of LXXXI is due to the same  $\alpha$ -cleavage, as well as the presence of a peak at  $m/z$  157 ( $M^+ - \text{C}_2\text{H}_5$ ), followed by the decomposition with the elimination of the fragments with  $m/z$  83, 69, 55, 41, and 99 ( $M^+ - \text{C}_2\text{H}_5 - \text{C}_3\text{H}_6\text{O}$ ). H-rearrangement to the oxygen of the hydroxyl group leads to the loss of water and the formation of  $M^+ - \text{H}_2\text{O}$  ( $m/z$  168) and  $\text{C}_6\text{H}_{12}\text{O}_2$  ( $m/z$  70). H-rearrangement to the oxygen of the carbonyl group produces a peak at  $m/z$  86 ( $\text{C}_5\text{H}_{10}\text{O}$ ) in the mass spectra of both LXXXI and LXXXII.

The prominent peaks at  $m/z$  29 ( $\text{C}_2\text{H}_5$ ) and  $m/z$  57 ( $\text{CH}_3\text{CH}_2\text{CO}$ ) in the mass spectrum of LXXXII are due to the  $\alpha$ -cleavage, which is a characteristic reaction for ketones as well as for alcohols.

Diketone LXXXIII and ketoalcohol LXXXII have similar structures of their molecules and the same positions of the functional groups. Therefore their mass spectra are very similar as also Table 8 shows.

In the mass spectrum of LXXXIII there are two noticeable abundant peaks: at  $m/z$  86 ( $\text{C}_5\text{H}_{10}\text{O}$ ) due to  $\gamma$ -hydrogen rearrangement and at  $m/z$  27 due to the double bond migration and the elimination of the CHO group according to scheme (16):



## Diols and their esters

The favourable pathway of fragmentation of a diester (LXXXIV, Table 8) is the elimination of the fragment  $\text{C}_5\text{H}_9\text{O}$  ( $m/z$  85), the residue of isovaleric acid. Two McLafferty rearrangements produce a fragment at  $m/z$  236 ( $M^+ - 102$ ) due to the loss of isovaleric acid and at  $m/z$  134 ( $M^+ - 102 - 102$ ) due to the loss of two molecules of isovaleric acid.

The peak at  $m/z$  119 is formed by the secondary fragmentation cleavage of the fragment with  $m/z$  134 due to the loss of the  $\text{CH}_3$  group. The mass spectra of diacetate and dibutanoate of this diol are very similar to the mass spectrum of LXXXIV [4]. Alpha-cleavage of 2,3-octanediol (LXXXV, Table 8) yields fragments with  $m/z$  45 ( $\text{C}_2\text{H}_5\text{O}$ ) and 101 ( $\text{C}_6\text{H}_{13}\text{O}$ ), which leads to the peaks at  $m/z$  41, 55, and 83 due to the loss of water. Other detectable peaks are observed at  $m/z$  43 ( $\text{C}_3\text{H}_7$ ) and 57 ( $\text{C}_4\text{H}_9$ ) in the mass spectrum of LXXXV.

## Substituted six-membered heterocycles

There are detectable molecular ions in the mass spectra of alkyl-substituted pyranes  $M^+$  238 (15%, XXXVI) and  $M^+$  240 (28%, LXXXVIII) (Table 8). The mass spectra of stegobion (LXXXIX) and stegobiol (XC) are very similar.

The  $\gamma$ -hydrogen rearrangement to the saturated oxygen, followed by the loss of  $C_3H_4O$  from stegobion and  $C_3H_6O$  from stegobiol, leads to a fragment with  $m/z$  168. Secondary product ions at  $m/z$  153 and 139 are due to the loss of  $CH_3$  and  $C_2H_5$  groups from the fragment with  $m/z$  168. The main way of fragmentation of stegobion is the  $\beta$ -cleavage of the substituent of the ring, leading to a fragment with  $m/z$  59.

In the mass spectra of stegobion and stegobiol other peaks are observed at  $m/z$  139 ( $M^+ - C_5H_9O$ , LXXXIX;  $M^+ - C_5H_{11}O$ , XC),  $m/z$  124 ( $m/z$  139 -  $CH_3$ ), 112, 85, 84, and 83. Fragmentation of serricorone (LXXXVI) and serricorol (LXXXVIII) is the same as that of LXXXIX and XC.

## CONCLUSION

The pheromones of Coleoptera demonstrate a significant variety of structures. This makes their identification by means of mass spectrometry a complicated task. The schemes of fragmentation and mass spectra represented in this review should be useful for the identification of yet unknown pheromone components of other species belonging to 39 genera of Coleoptera studied.

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# MARDIKALISTE FEROMOONIDE MASSISPEKTROMEETRIA

Katerina LEBEDEVA

Mardikaliste (Coleoptera) feromoonid sisaldavad peaaegu kõiki orgaaniliste ühendite klasse, ent ühesama perekonna liikide feromoonides on avastatud samu või struktuurilt lähedasi aineid. On esitatud kuni 1995. aastani trükitis avaldatud 39 mardikaliste perekonna feromoonide massispektrid ja toodud feromoonide molekulide fragmentatsiooni skeemid.