Mass Spectrometry of Terpenes

I. Monoterpene Hydrocarbons

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Seventeen monoterpene hydrocarbons — acyclic, monocyclic and bicyclic — were investigated in a combined gas chromatograph-mass spectrometer. All compounds gave rise to characteristic peaks at $m/e = $ M, M-15, M-43 and 80. The metastable ions formed were studied allowing certain conclusions on the decomposition pattern. The isopropyl group is generally easily split off both in an one-step reaction directly from the molecule ion and in one or more two-step decompositions. Although the differences between the spectra in the bicyclic group are not very large, all compounds investigated have their characteristic mass spectrum and can easily be distinguished from each other.

Two short papers on the mass spectrometry of monoterpenes have been published.[1,2] The spectra are, however, not published in detail, and the formation of metastable ions is not discussed. The purity of the specimens investigated is not given. As information about the mass spectra of mono- and sesqui-terpenes were needed for other studies, a systematic survey has been started using a combined gas chromatograph-mass spectrometer, which simplifies mass spectrometric investigations of compounds generally available only in contaminated form.

EXPERIMENTAL

Apparatus. The gas chromatograph used was a standard Perkin-Elmer model 116 equipped with a thermistor detector. The mass spectrometer was an Atlas CH 4 modified in respect of the speed of scanning and of the possibility of measuring and recording total ion current as described by Ryhage.[3] The technique and mechanics of the combination of the instruments will be described later.[4] A molecular separator is included in the sample introducing line into the spectrometer in order to concentrate the gas mixture with regard to the specimen to be analyzed. The technique enables at present determination of specimens of the order of 10 μg. The combination system is, however, still under development.

Method. Gas chromatography was done on a silicone column: 10 % Dow Corning Silicone Oil 200 on Embacel Kieselguhr (60—100 mesh, acid washed) 3.9 m 1/4″ column, 50 ml He/min, temperature 110°C. Depending on the availability of specimens the sample sizes introduced varied between 0.1 and several mg.

In order to avoid ionization of helium in the ion source of the mass spectrometer the electron energy was kept at 20 eV. The temperature of the ion source was 250°C. The pressure in the mass spectrometer tube around the ion source was 10^{-5} mm Hg, and the pressure in the ionization chamber was of the order of 10^{-4} mm Hg.

The fractions of the specimen to be analyzed are first recorded in the thermistor detector of the gas chromatograph in the usual manner. When a component reaches the ion source of the mass spectrometer, it becomes ionized and a constant fraction of the total ion current is measured and recorded on a separate recorder in order to facilitate scanning of the mass spectrum at the moment when the concentration of the specimen is highest. The rate of scanning is variable and can be as high as about 300 m/e units per second. This amounts to a double recording of the gas chromatogram, which, however, is necessary owing to the time delay in the gas transfer system.

The temperature of the transfer system can be varied depending on the compounds studied. The high temperature (200°C) is preferable, because it enables a more rapid transport from the chromatograph to the ion source of the mass spectrometer. However, some of the compounds investigated here decompose at 200°C and show more fragments in the spectrum after electron bombardment than when the compound is not thermally decomposed. These compounds were, therefore, run with the gas transfer system at 100°C.

Material. The monoterpene hydrocarbons investigated were obtained from the following sources: *allo*-ocimene from the Glidden Co., USA, β-ocimene from Givaudan S.A., Switzerland, myrcene, *p*-cymene, α-pinene, β-pinene and camphene from Light & Co., Ltd., England, α-terpinene, γ-terpinene, α-phellandrene, β-phellandrene and car-3-ene from Dragoco, Germany, *l*-limonene from Fluka AG, Switzerland, sabinene from Dr. T. Norin, Stockholm, and α-fenchene and santene from Professor N. J. Toivonen's collection, Finland.

High purity for the analysis was obtained by chromatography on the silicone column. The purity of the fractions actually analyzed was invariably also checked by gas chromatography on a polar column: 10 % sucrose acetate isobutyrate and 5 % N,N,N′,N′-tetrakis-(2-hydroxypropyl) ethylene diamine on Embacel Kieselguhr (60 — 100 mesh, acid washed), 3.9 m 1/4″ column, 50 ml He/min, temperature 100° or 110°C. The identity of the analyzed specimens was regularly checked by infrared spectrophotometry. β-Ocimene was separated into two fractions, which have been identified as the X and Y forms according to Klouwen and ter Heide [5] and Farnow and Porsch.[6]

RESULTS AND DISCUSSION

The spectra of seventeen monoterpene hydrocarbons are shown in Figs. 1—17. All spectra originally showed peaks at m/e = 18, 28, 32, 40, and 44, originating from H_2O, N_2, O_2, Ar and CO_2. These peaks were removed. The spectra have some common features. They all show the molecule ion as well as peaks at M-15 and M-43, although of different intensities. The peak m/e = 80 is small but significant for all monoterpene hydrocarbons investigated (except *p*-cymene).

The metastable ions observed as diffuse peaks were studied with regard to possible breakdown patterns (see Tables 1—4). Owing to the quality of the spectra and to the possible masking by large ion peaks, some metastable ions remained concealed.

All compounds investigated, except *p*-cymene and santene, have strong diffuse peaks at m/e = 63.8 and 89.2 corresponding to the breakdown reactions $136^+ \rightarrow 93^+ + 43$ and $93^+ \rightarrow 91^+ + 2$, respectively (*cf.* Tables 1—4). The first one corresponds to the loss of the isopropyl group, which is characteristic for this kind of compounds. The reaction $93^+ \rightarrow 91^+ + 2$ is not so obviously interpreted. However, it is interesting to compare it with the formation of a tropylium ion $C_7H_7^+$ from alkylbenzenes.[7]
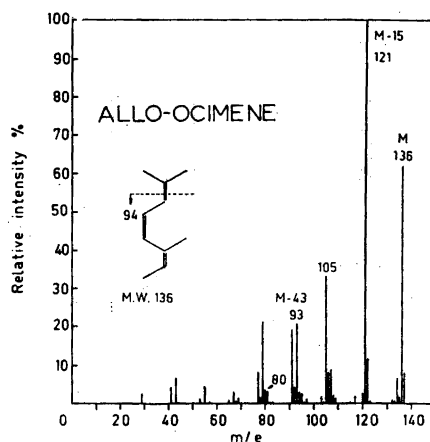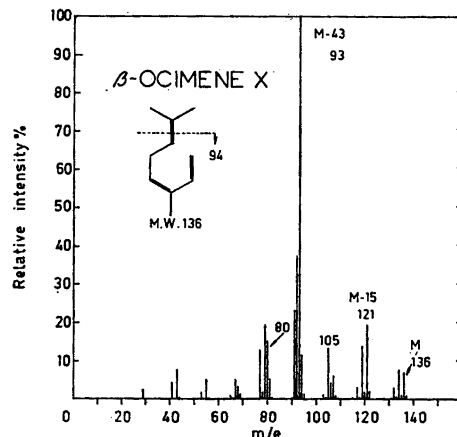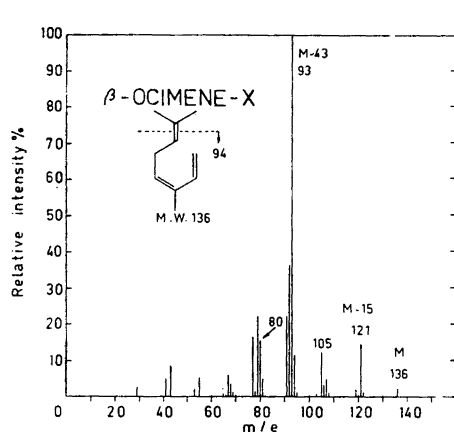
Fig. 1. The mass spectrum of allo-ocimene.

Fig. 2A. The mass spectrum of β-ocimene X.

Fig. 2B. The mass spectrum of thermally decomposed β-ocimene X.

The results will be given and discussed in accordance with the general structure of the compounds.

A. Acyclic

The spectra of *allo*-ocimene, β-ocimene X and Y, respectively, and myrcene are presented in Figs. 1—4 and the corresponding diffuse peaks in Table 1. The cracking patterns are quite different from each other. *Allo*-ocimene has the most intense molecule ion $m/e = 136$, which means that this molecule is more stable than the others. This stability is due to the conjugated double bond system, which is not present in the three other acyclic hydrocarbons. The branching methyl groups can, however, easily be lost, as revealed by the base peak $m/e = 121 = $ M-15. Table 1 shows that *allo*-ocimene produces
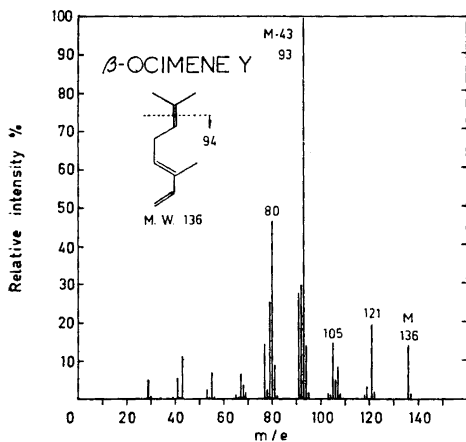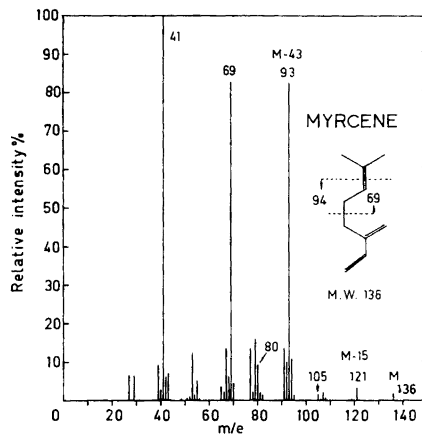
Fig. 3. The mass spectrum of β-ocimene Y.   Fig. 4. The mass spectrum of myrcene

more kinds of metastable ions than the other acyclic hydrocarbons, partly because of the presence of large amounts of ions with large m/e values (136 and 121). $m/e = 93$ is produced both from the molecule ion directly, and from $m/e = 121 = $ M-15. $m/e = 91$, which is also common for most monoterpene hydrocarbons, is at least partly formed from $m/e = 93$, as has been indicated.

As expected, the spectra including the diffuse peaks are very similar for β-ocimene X and β-ocimene Y, respectively, the only difference between the molecules being a *cis-trans* isomerism. These structures are not stabilized by a conjugated double bond system and are therefore more decomposed. The base peak is $m/e = 93 = $ M-43, which has been formed from the molecule ion and from the ion $m/e = 121$ (*cf*. Table 1). The only prominent difference between the spectra of the X and the Y forms is the intensity of the peak at $m/e = 80$ compared with the surrounding peaks.

Table 1. Metastable ions of acyclic monoterpene hydrocarbons.

Diffuse peaks *m	Break down reaction	allo-ocimene	β-ocimene X	β-ocimene Y	myrcene
107.8	$136^+ \rightarrow 121^+ + 15$	×			
101.2	$105^+ \rightarrow 103^+ + 2$	×	×	×	
89.2	$93^+ \rightarrow 91^+ + 2$	×	×	×	×
71.5	$121^+ \rightarrow 93^+ + 28$	×	×	×	
63.8	$136^+ \rightarrow 93^+ + 43$	×	×	×	×
59.6	$105^+ \rightarrow 79^+ + 26$	×			
24.3	$69^+ \rightarrow 41^+ + 28$				×

Note. * $m = m_2^2/m_1$, where m_1 and m_2 are the masses of the original and the generated ions, respectively, giving rise to a diffuse peak at *m.
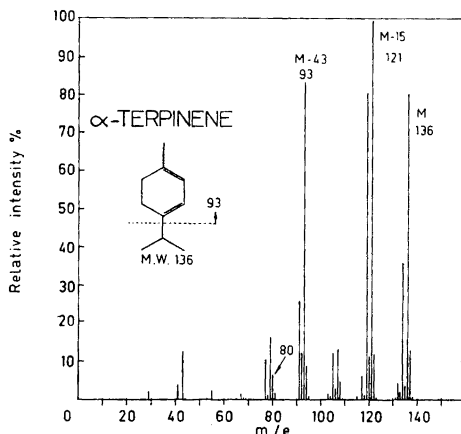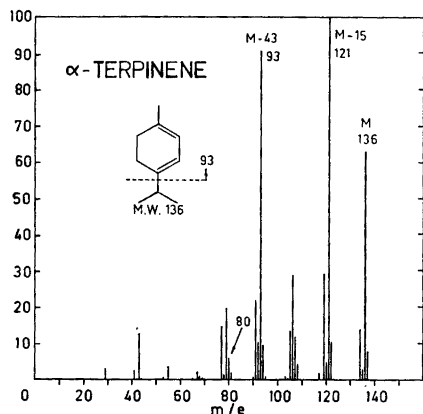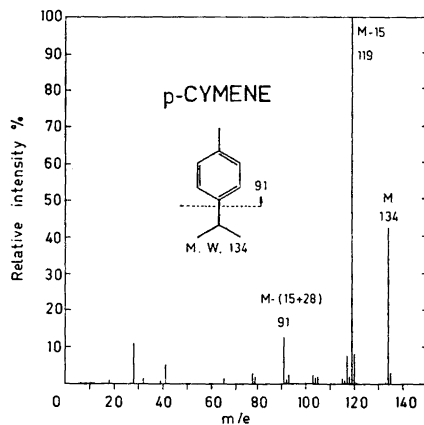
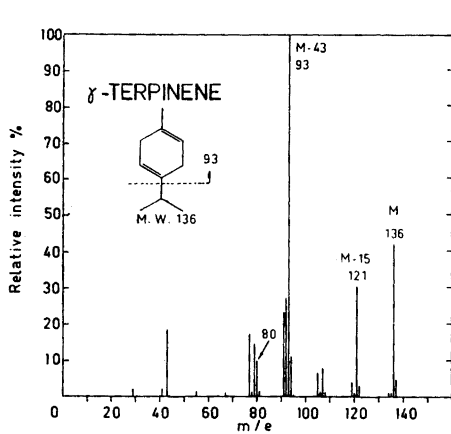Fig. 5. The mass spectrum of p-cymene.
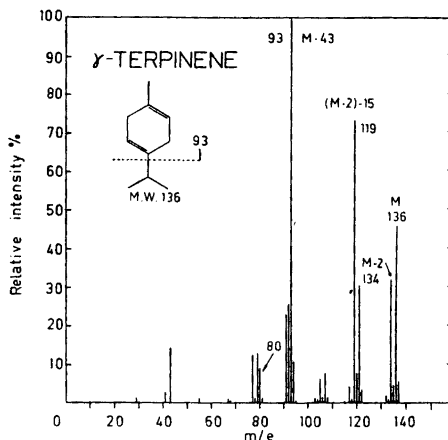

Fig. 6A. The mass spectrum of a-terpinene.

Fig. 6B. The mass spectrum of thermally decomposed a-terpinene.

Myrcene is obviously the most easily decomposed compound of this group. $m/e = 93$ is probably formed from the molecule ion (cf. Table 1). The bond linking the two isoprene units is in allylic position to two double bonds resulting in a fragmentation giving rise to a strong $m/e = 69$. The presence of a diffuse peak at 24.3 indicates the formation of the ion of $m/e = 41$ from one of $m/e = 69$.

B. Monocyclic

The spectra of p-cymene, a-terpinene, γ-terpinene, a-phellandrene, β-phellandrene and limonene are given in Figs. 5—10 and the corresponding diffuse peaks in Table 2.

Except for limonene, all spectra in this group have their most intense peaks at higher m/e-values ($m/e = 93$ and above), indicating a certain stability of the ring system.

Fig. 7A. The mass spectrum of γ-terpinene.

Fig. 7B. The mass spectrum of thermally decomposed γ-terpinene.
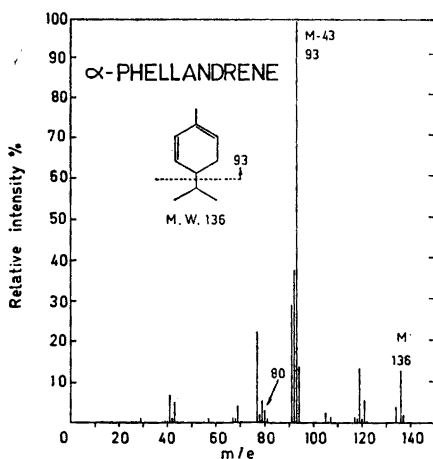
Fig. 8A. The mass spectrum of a-phellandrene.
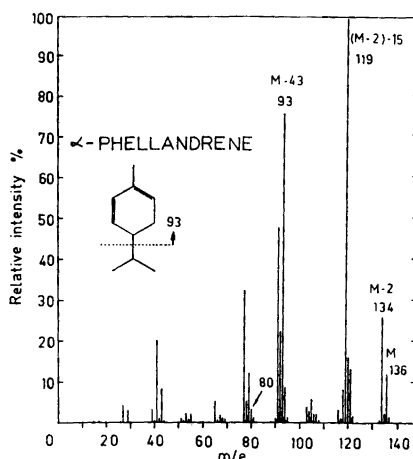
Fig. 8B. The mass spectrum fo thermally decomposed a-phellandrene.

p-Cymene, being an aromatic hydrocarbon, gives large peaks at $m/e = 134 = M$, $m/e = 119 = M-15$ (base peak) and $m/e = 91 = M-43$. It is interesting to note that in this case there are diffuse peaks corresponding to $134^+ \rightarrow 119^+ + 15$ and to $119^+ \rightarrow 91^+ + 28$ but not to $134^+ \rightarrow 91^+ + 43$. It is likely, therefore, that $m/e = 91$ is formed in more than one step from the molecule ion. $m/e = 80$ is missing in the spectrum of p-cymene.

The spectra of a-terpinene and γ-terpinene are presented in Figs. 6A and 7A. Both compounds have two double bonds in the ring, but the bonds differ in their positions. a-Terpinene has strong peaks at $m/e = 136 = M$,
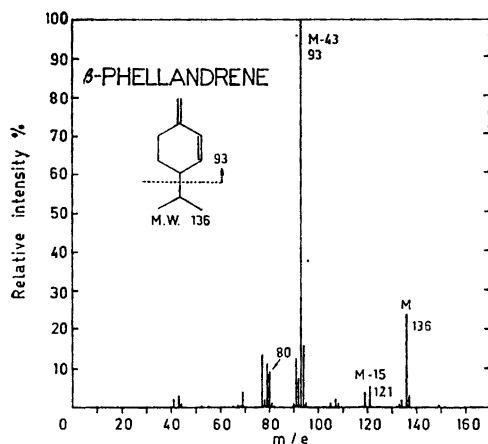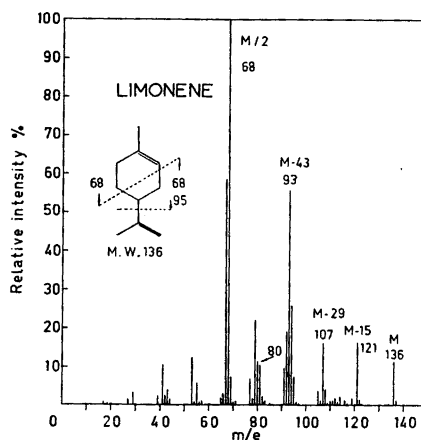
Fig. 9. The mass spectrum of β-phellandrene.

Fig. 10. The mass spectrum of limonene.

$m/e = 121 = M-15$ (base peak) and $m/e = 93 = M-43$. γ-Terpinene has the same strong peaks but of different intensities (base peak $m/e = 93 = M-43$). $m/e = 93$ is formed not only directly from the molecule ion, but also from $m/e = M-15 = 121$, as indicated from the decomposition of the metastable ions (Table 2).

The spectra of α- and β-phellandrene (Figs. 8A and 9) are dominated by $m/e = 93 = M-43$. A comparison with other peaks in the spectrum and with other spectra in this group indicates that this fragment is more easily formed from the phellandrenes than from any other monocyclic hydrocarbon in-

Table 2. Metastable ions of monocyclic monoterpene hydrocarbons.

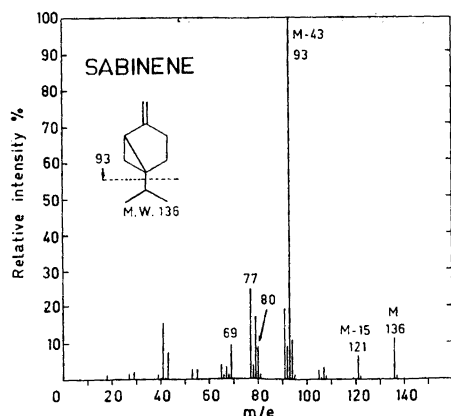| Diffuse peaks *m	Break down reaction	p-cymene	a-ter-pinene	γ-ter-pinene	a-phel-landrene	β-phel-landrene	limo-nene
117.2	$121^+ \rightarrow 119^+ + 2$		×	×			
115.2	$119^+ \rightarrow 117^+ + 2$	×	×	×	×		
107.6	$136^+ \rightarrow 121^+ + 15$		×	×		×	
105.8	$134^+ \rightarrow 119^+ + 15$	×					
101.2	$105^+ \rightarrow 103^+ + 2$		×				
89.2	$93^+ \rightarrow 91^+ + 2$	×	×	×	×	×	×
75.1	$79^+ \rightarrow 77^+ + 2$	×	×	×	×	×	×
71.5	$121^+ \rightarrow 93^+ + 28$		×	×			×
69.6	$119^+ \rightarrow 91^+ + 28$	×					
66.4	$93^+ \rightarrow 79^+ + 14$					×	
64.9	$136^+ \rightarrow 94^+ + 42$					×	
63.8	$136^+ \rightarrow 93^+ + 43$		×	×	×	×	×
46.6	$91^+ \rightarrow 65^+ + 26$	×					

Note. See Table 1.
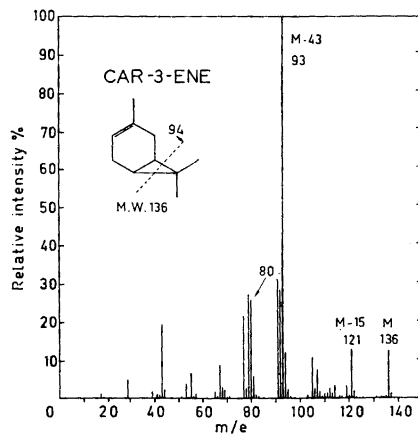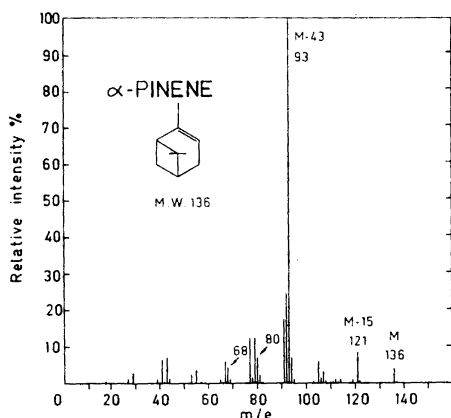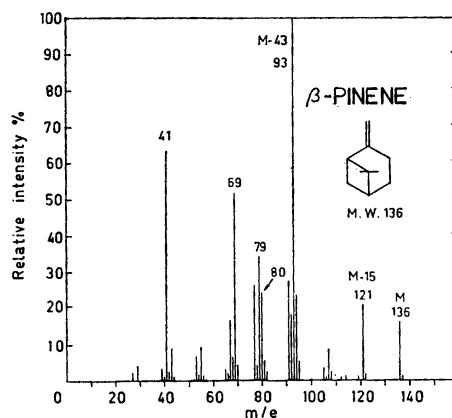
Fig. 11. The mass spectrum of sabinene.

Fig. 12. The mass spectrum of car-3-ene.

Fig. 13. The mass spectrum of a-pinene.

Fig. 14. The mass spectrum of β-pinene.

vestigated. The two conjugated double bonds and the binding of the iso-propyl group in allylic position to one of them may provide the explanation.

Diffuse peaks arising from the decompositions $136^+ \rightarrow 94^+ + 42$ and $94^+ \rightarrow 79^+ + 15$ are found for β-phellandrene but not for α-phellandrene.

The spectrum of limonene (Fig. 10) has peaks at $m/e = 136 = M$, $m/e = 121 = M\text{-}15$, $m/e = 107 = M\text{-}29$ and $m/e = 93 = M\text{-}43$. The last one is formed through two different mechanisms, directly from the molecule ion, but also from $m/e = 121$, as can be seen in Table 2. The base peak for limonene is $m/e = 68 = \frac{1}{2} M$, which has been pointed out by Gilchrist and Reed.[2] This peak corresponds to one isoprene unit.
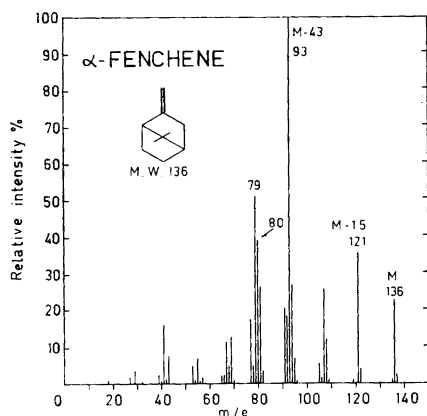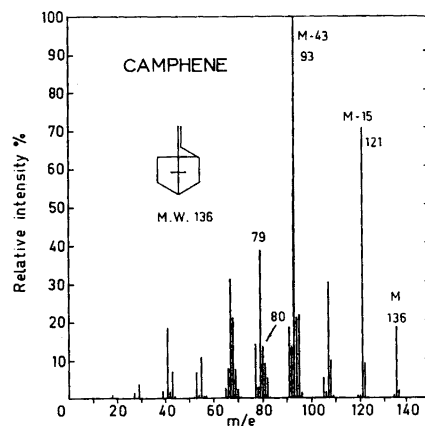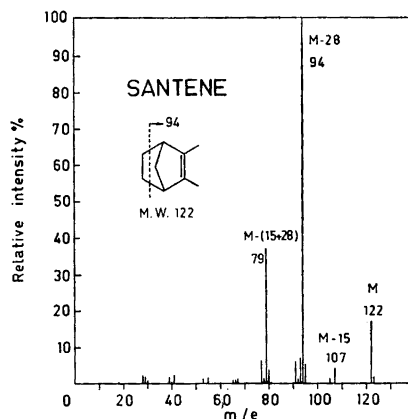
Fig. 15. The mass spectrum of a-fenchene.

Fig. 16. The mass spectrum of camphene.

Fig. 17. The mass spectrum of santene (C_9H_{14}).

C. Bicyclic

The mass spectra of sabinene, car-3-ene, α-pinene, β-pinene, α-fenchene, camphene and santene (C_9H_{14}) are shown in Figs. 11—17, and the corresponding diffuse peaks are given in Tables 3 and 4.

The base peak for all bicyclic hydrocarbons investigated is at $m/e = 93$ (santene $m/e = 79$). As seen from Table 3, in all cases this fragment can be formed both in a one-step decomposition directly from the molecule ion ($136^+ \rightarrow 93^+ + 43$) as well as in a two-step reaction $136^+ \rightarrow 121^+ \rightarrow 93^+$ but not $136^+ \rightarrow 108^+ \rightarrow 93^+$. As expected, santene is an exception, as there is no isopropyl group in the molecule. In santene $m/e = 79$ is formed (Table 4) both from $122^+ \rightarrow 94^+ \rightarrow 79^+$ and from $122^+ \rightarrow 107^+ \rightarrow 79^+$ but not directly $122^+ \rightarrow 79^+ + 43$. (The diffuse peak for $122^+ \rightarrow 107^+ + 15$ at $m^* = 93.9$ is very likely masked by $m/e = 94$). These differences in behaviour indicate

Table 3. Metastable ions of bicyclic monoterpene hydrocarbons.

Diffuse peaks * m	Break down reaction	sabinene	car-3-ene	a-pinene	β-pinene	a-fen-chene	cam-phene
107.6	$136^+ \rightarrow 121^+ + 15$	×	×		×	×	
103.3	$107^+ \rightarrow 105^+ + 2$				×	×	
89.2	$93^+ \rightarrow 91^+ + 2$	×	×	×	×	×	×
84.3	$136^+ \rightarrow 107^+ + 29$	×			×	×	
75.1	$79^+ \rightarrow 77^+ + 2$	×	×	×	×	×	×
71.5	$121^+ \rightarrow 93^+ + 28$	×	×	×	×	×	×
66.4	$93^+ \rightarrow 79^+ + 14$	×				×	
63.8	$136^+ \rightarrow 93^+ + 43$	×	×	×	×	×	×
59.6	$105^+ \rightarrow 79^+ + 26$					×	
58.3	$107^+ \rightarrow 79^+ + 28$					×	
51.6	$121^+ \rightarrow 79^+ + 42$						×
46.6	$91^+ \rightarrow 65^+ + 26$	×			×		
37.0	$121^+ \rightarrow 67^+ + 54$	×			×		
24.3	$69^+ \rightarrow 41^+ + 28$				×		

Note. See Table 1.

Table 4. Metastable ions of santene.

Diffuse peaks * m	Break down reaction	santene
89.2	$93^+ \rightarrow 91^+ + 2$	×
72.5	$122^+ \rightarrow 94^+ + 28$	×
67.4	$95^+ \rightarrow 80^+ + 15$	×
66.4	$94^+ \rightarrow 79^+ + 15$	×
63.0	$67^+ \rightarrow 65^+ + 2$	×
58.3	$107^+ \rightarrow 79^+ + 28$	×

Note. See Table 1.

that $m/e = 93$ for all proper monoterpene hydrocarbons is formed by loss of the isopropyl group.

Although the spectra of the bicyclic hydrocarbons are quite characteristic of the different compounds, they all show the same general pattern. Because of the complexity of the different structures involved, it is not advisable to make any detailed postulates as to how the various kinds of molecules decompose. However, it is reasonable to believe, which has already been pointed out, that the isopropyl group is the first part of the molecule to break off in one-step reaction as well as in one or two two-step reactions.

D. Thermal decomposition

β-Ocimene, a-terpinene, γ-terpinene and a-phellandrene (but not β-phellandrene) were thermally decomposed when the gas transfer system between the chromatograph and the mass spectrometer was kept at a temperature close

to 200°C. The spectra so obtained are shown in Figs. 2B, 6B, 7B and 8B. An interesting common feature is the occurrence of large peaks at m/e = M-2 and (M-2)-15 and small peaks at m/e = M-4 and (M-4)-15. No other new fragments of significant size seem to be formed, and it is important to note that the relative intensities of the fragments originating from the thermally nondecomposed molecules are unchanged, which makes an identification quite feasible even if some thermal decomposition has occurred.

The difference in behaviour between the monocyclic terpenes α-terpinene, γ-terpinene and α-phellandrene on one side and β-phellandrene and *l*-limonene on the other might be due to the fact that the first three contain two double bonds in the ring and thus by loss of two hydrogens give rise to compounds with a stable aromatic ring. The two other compounds have only one double bond in the ring. In this connection it is interesting to compare the relative intensities of m/e = 134, 119 and 91 from *e.g.* α-terpinene (Fig. 6B) with those from *p*-cymene (Fig. 5). The similarity might indicate the correctness of the suggested explanation. Another indication is the existence of diffuse peaks at m/e = 105.8 and 69.6 for thermally decomposed α- and γ-terpinene and α-phellandrene. These peaks are also found in the mass spectrum of *p*-cymene.

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