

Mass Spectrometry of Terpenes

III. Monoterpene Aldehydes and Ketones

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Twelve monoterpene aldehydes and ketones were investigated in a combined gas chromatograph-mass spectrometer. $m/e = M$ was invariably the parent peak. $m/e = M - 18$ was absent or very small for the ketones and cuminic aldehyde, and thus differed from the alcohols and the two acyclic aldehydes investigated. The interpretation of the fragmentation patterns was more difficult than for the hydrocarbons and the alcohols.

Monoterpene hydrocarbons and alcohols have previously been studied in a combined gas chromatograph-mass spectrometer.^{1,2} The investigations were now extended to include monoterpene aldehydes and ketones, all together twelve compounds. The mass spectra of five ketones have been published by Reed.³ The data presented were, however, neither quite consistent with those obtained in the present study, nor were they as complete, for no information was given on meta-stable ions and besides several m/e peaks in the higher regions were missing.

EXPERIMENTAL

Apparatus. The apparatus and experimental conditions used are described in Part I of this series.¹ Although the transfer system between the chromatograph and the mass spectrometer was kept at 200°C no decomposition seemed to have occurred in the compounds investigated here.

Material. The aldehydes and ketones investigated were obtained from the following sources: citronellal, geranial and cuminic aldehyde from Haarman & Reimer, Germany, pulegone and fenchone from Fluka AG, Switzerland, carvone, piperitone and camphenilone from Light & Co., Ltd., England, methone and camphor from Coleman & Bell Co., USA, piperitenone from Dr. Y.-R. Naves, Givaudan S. A., Switzerland, and thujone from Dr. T. Norin, Stockholm.

The purity of the specimens obtained by separation on the DC column in conjunction with the mass spectrometer in which they were analyzed, was invariably checked by chromatography on polar columns and by infrared spectrophotometry.

RESULTS AND DISCUSSION

The spectra of three monoterpene aldehydes and nine monoterpene ketones are shown in Figs. 1–12. The spectra originally showed peaks at $m/e = 18, 28, 32, 40,$ and 44 , originating from H_2O (partly), N_2 , O_2 , Ar, and CO_2 (partly), respectively. These peaks have been removed. All compounds investigated had the molecule ion $m/e = M$ as parent peak. These together with the three strongest peaks above $m/e = 67$ are given in Table 1 for all compounds investigated. As expected, the general appearance of the spectra did not differ largely from those of the monoterpene alcohols.²

Table 1. Characteristic peaks in the mass spectra of monoterpene aldehydes and ketones.

Monoterpene aldehyde or ketone	Parent peak	Base peak	2nd strongest peak (above $m/e = 67$)	3rd strongest peak (above $m/e = 67$)
Citronellal	154	69	95	81
Geranial	152	69	84	94
Cuminic aldehyde	148	133	105	148
Menthone	154	112	69	139
Pulegone	152	81	152	109
Piperitone	152	82	110	95
Carvone	150	82	108	93
Piperitenone	150	150	107	135
Camphor	152	95	81	108
Thujone	152	81	110	68
Fenchone	152	69, 81	69, 81	80
Camphenilone	138	69	138	72

The meta-stable ions observed as diffuse peaks were studied for breakdown patterns. Some meta-stable ions probably remained concealed owing to masking by large ion peaks and the condition of the spectra studied. Generally speaking, the diffuse peaks for the aldehydes and the ketones were less numerous and weaker than for the alcohols² and even more so than for the monoterpene hydrocarbons.¹

A. Aldehydes. The mass spectra of citronellal, geranial and cuminic aldehyde are presented in Figs. 1–3. No diffuse peaks were observed for these compounds. The cracking patterns of the first two were, as expected, quite similar to each other. The base peak is in both cases $m/e = 69$, which fragment is formed by splitting the bond in allylic position to the double bond or bonds present in the molecules. Both citronellal and geranial easily lose one molecule of water thereby giving rise to a monoterpene hydrocarbon ion, from which several characteristic fragments can be deduced in accordance with the known

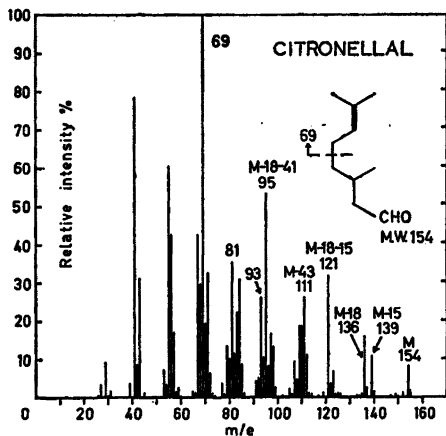


Fig. 1. Mass spectrum of citronellal.

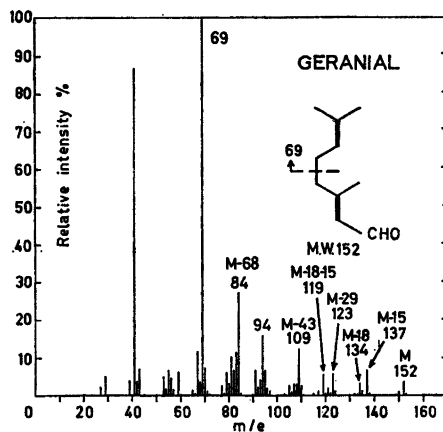


Fig. 2. Mass spectrum of geranial.

breakdown patterns of proper monoterpene hydrocarbons.¹ The alcohols behave similarly, which is indicated by comparing the spectrum of citronellal with that of geraniol.² The interpretation of the fragments $m/e = M - 43$ is not so obvious as they may arise by loss of an isopropyl group or a group $\text{HCO}-\text{CH}_2-$. In the case of cuminic aldehyde (Fig. 3) there seems to be no extra hydrogen atom available for a comparative loss of water on fragmentation as $m/e = M - 18 = 130$ or fragments derived from this ion are not observed. Oxygen can probably be lost only in the form of the aldehyde group as indicated by $m/e = M - 29 = 119$. This peak might also be explained by loss of CH_3-CH_2- , but $m/e = M - 29$ is not generally so high in mass spectra of non-aldehyde monoterpene compounds. The aromatic aldehyde is obviously

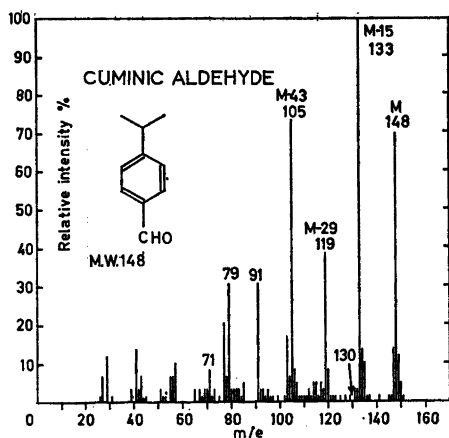


Fig. 3. Mass spectrum of cuminic aldehyde.

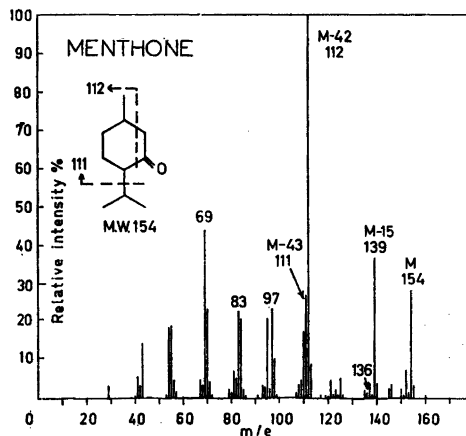


Fig. 4. Mass spectrum of methone.

more stable than the acyclic ones, as revealed by the presence of higher concentrations of ions with large m/e -values. The three or possibly four strongest peaks correspond to fragments containing the aldehyde group indicating the firmness with which it is bound to the aromatic ring. $m/e = 91$ is a common peak in mass spectra of alkylated aromatic compounds.^{1,2} It has been interpreted as the tropylium ion ($C_7H_7^+$).⁴

B. Monocyclic ketones. The mass spectra of menthone, pulegone, piperitone, carvone and piperitenone are shown in Figs. 4–8.

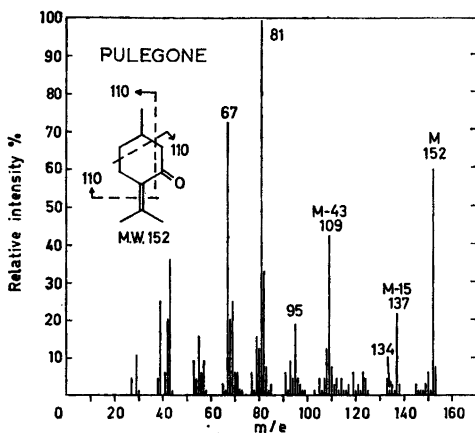


Fig. 5. Mass spectrum of pulegone.

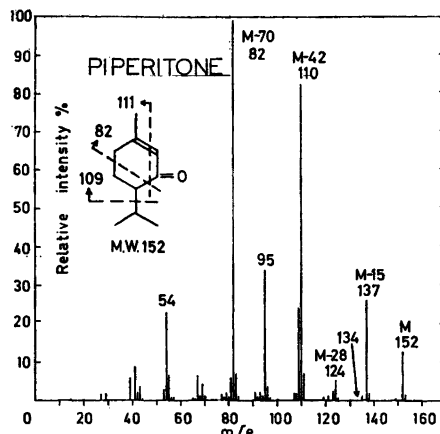


Fig. 6. Mass spectrum of piperitone.

The ketones differ from the aldehydes and the alcohols in that their mass spectra show a very small or no peak at $m/e = M - 18$, corresponding to loss of one water molecule from the parent molecule. This difference is very helpful

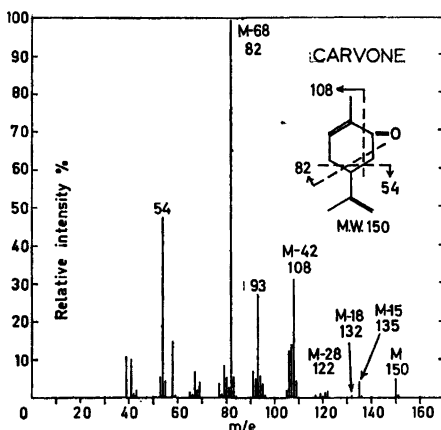


Fig. 7. Mass spectrum of carvone.

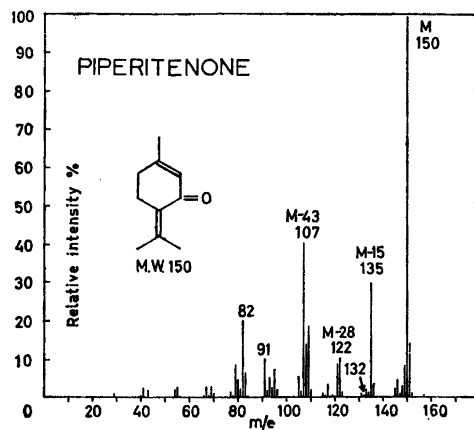


Fig. 8. Mass spectrum of piperitenone.

in the investigation of structures of unknown compounds. Interpretation of the fragmentation patterns of the compounds of this group is very difficult, as very few diffuse peaks were observed. Besides there is another difficulty in that the mass numbers of the fragments $C=O$ and CH_2-CH_2 are both 28. Menthone showed one diffuse peak at 63.0 corresponding to the possible breakdown reaction $112^+ \rightarrow 84^+ + 28$, but it is not possible to attribute definite structures to any of these three fragments. The spectrum of carvone had diffuse peaks at 35.4 and 89.2 corresponding to $82^+ \rightarrow 54^+ + 28$ and $93^+ \rightarrow 91^+ + 2$, respectively. Piperitenone has a spectrum quite different from the other monocyclic ketones investigated. The parent peak is also the base peak, $m/e = M$, which means that this molecule is more stable than the others, probably owing to the conjugated double bond system present. Three diffuse peaks were

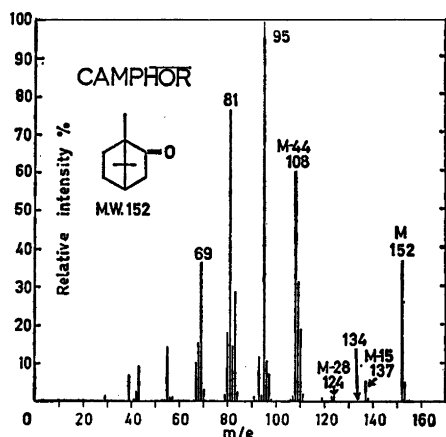


Fig. 9. Mass spectrum of camphor.

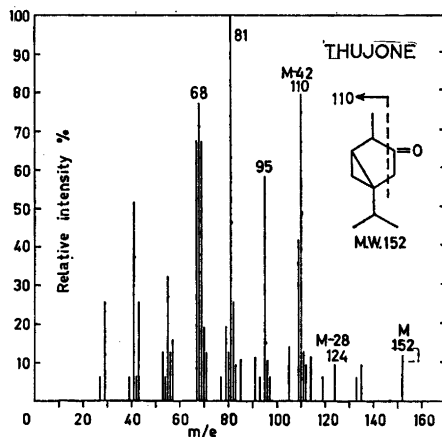


Fig. 10. Mass spectrum of thujone.

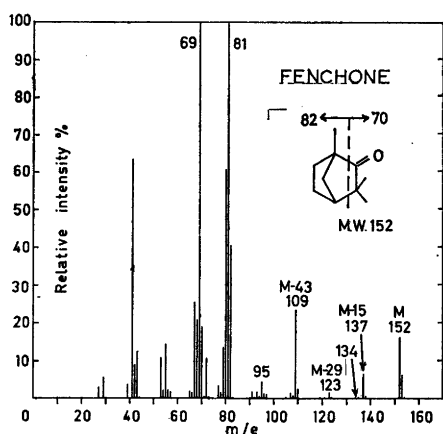


Fig. 11. Mass spectrum of fenchone.

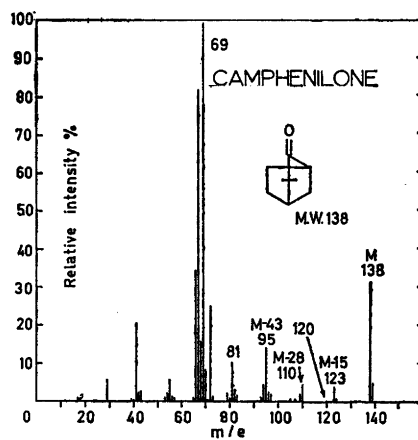


Fig. 12. Mass spectrum of camphenilone.

Table 2. Meta-stable ions of fenchone.

Diffuse peaks <i>*m</i>	Possible break-down reactions
78.1	152 ⁺ → 109 ⁺ + 43
77.1	81 ⁺ → 79 ⁺ + 2
63.1	137 ⁺ → 93 ⁺ + 44
36.7	{ 123 ⁺ → 67 ⁺ + 56
	{ 82 ⁺ → 55 ⁺ + 27
34.5	{ 137 ⁺ → 69 ⁺ + 68
	{ 81 ⁺ → 53 ⁺ + 28
24.3	69 ⁺ → 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 $*m$.

observed, namely at 84.8, 77.3, and 58.4. They may be interpreted as arising according to the following scheme $135^+ \rightarrow 107^+ + 28$, $107^+ \rightarrow 91^+ + 16$ and $107^+ \rightarrow 79^+ + 28$.

C. Bicyclic ketones. The mass spectra of camphor, thujone, fenchone and camphenilone are given in Figs. 9–12. As for the monocyclic ketones $m/e = M-18$ is missing or very weak in these spectra. The spectrum of camphor revealed one diffuse peak at 76.8 corresponding to the breakdown reaction $152^+ \rightarrow 108^+ + 44$. Quite a few meta-stable ions formed were observed in the mass spectrum of fenchone (Table 2), while none were observed in the spectra of the two other compounds investigated.

The mass spectra of monoterpene ketones frequently show the presence of the ion $m/e = M-42$ or $M-44$, while the spectra of the hydrocarbons and the alcohols generally have peaks at $m/e = M-43$, corresponding to a loss of an isopropyl group, or at m/e -values derived from this fragment. It therefore seems likely that the loss of 42 or 44 units from the ketones does not correspond to a loss of an isopropyl group but rather to an oxygen-containing fragment.

Acknowledgement. I feel indebted to Dr. R. Ryhage for placing the combined gas chromatograph-mass spectrometer with technical assistance to my disposal, and to those, mentioned above, who courteously supplied me with specimens of monoterpene aldehydes and ketones.

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Received March 10, 1964.