

Mass Spectrometry of Terpenes

II. Monoterpene Alcohols

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Nineteen monoterpene alcohols were investigated in a combined gas chromatograph-mass spectrometer. Compared with monoterpene hydrocarbons, the mass spectra of the alcohols are generally more complex and less like each other. The parent peak in all cases except three is $m/e = M$. The presence of the hydroxyl group is always revealed by the occurrence of $m/e = M - 18$ or fragments derived from this ion. The meta-stable ions observed as diffuse peaks were studied for possible breakdown patterns.

Seventeen monoterpene hydrocarbons were studied in a combined gas chromatograph-mass spectrometer.¹ The investigation has now been extended to include monoterpene alcohols since systematic information on the mass spectra of these compounds were required for other investigations. Some information on mass spectra of monoterpene alcohols has recently been published. α -Terpineol and terpinene-4-ol are described as giving quite different mass spectra² owing to the site of the hydroxyl group. The mass spectrum of 1-borneol is given by Reed.³ Various data are, however, still missing, *e.g.*, meta-stable ions formed.

EXPERIMENTAL

Apparatus. The apparatus used and the experimental conditions proper applied are described in Part I of this series.¹ Like some monoterpene hydrocarbons, some of the alcohols investigated decompose thermally at 200°C, and in these cases the transfer system between the chromatograph and the mass spectrometer was kept at a lower temperature or 100°C.

Material. The monoterpene alcohols investigated were obtained from the following sources: β -citronellol, linalool, menthol and borneol from Haarman & Reimer, Germany, geraniol and nerol from Fluka AG, Switzerland, lavandulol from Givaudan S. A., Switzerland, thymol from E. Merck AG, Germany, carvacrol, cuminyl alcohol, isopulegol, terpinen-4-ol and fenchyl alcohol from Light & Co., Ltd., England, carveol and isoborneol from Fritsche Brothers Inc., USA, α -terpineol from Th. Schuchardt, Germany, sabinol from Professor H. Erdtman, Stockholm, and thujyl alcohol and neo-isothujyl alcohol from Dr. T. Norin, Stockholm.

A high degree of purity for analysis was obtained by chromatography on the silicone column. The purity of the fractions actually analyzed was also invariably 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 specimens analyzed was regularly checked by infrared spectrophotometry.

RESULTS AND DISCUSSION

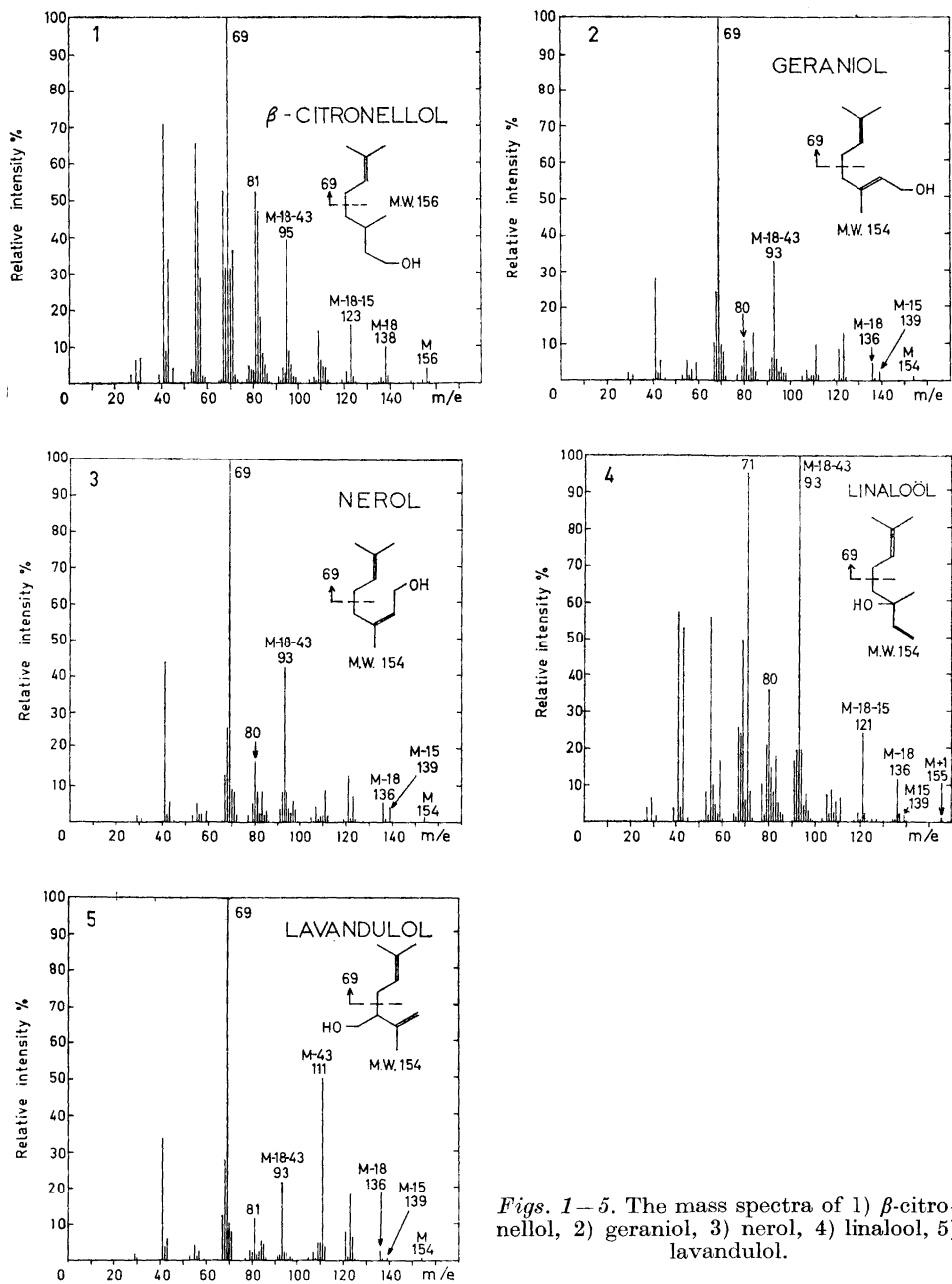
The spectra of nineteen monoterpene alcohols are shown in Figs. 1–19. Six of them are in pairs stereoisomers namely geraniol and nerol, thujyl alcohol and neo-isothujyl alcohol, borneol and isoborneol. The spectra originally showed peaks at $m/e = 18, 28, 32, 40,$ and 44 , originating from H_2O (partly), $N_2, O_2, Ar,$ and CO_2 , respectively. These peaks have been removed.

Compared with the monoterpene hydrocarbons,¹ the mass spectra of the alcohols are generally more complex and less like each other owing to the influence of the polar hydroxyl group and its position in the structure. Variations in the hydrocarbon skeleton occur in both groups of compounds.

The parent peak is mostly $m/e = M$, in two cases it is $M-15$ and in one case $M+1$. The intensity of the parent peak is generally much lower than for the hydrocarbons.

Table 1. Characteristic peaks in the mass spectra of monoterpene alcohols.

Monoterpene alcohol	Base peak	2nd strongest peak	3rd strongest peak	Strong peaks around $m/e = 70$ and 80
β -Citronellol	69	41	55	69, 81, 82
Geraniol	69	93	41	69, 80, 84
Nerol	69	41	93	69, 80
Linalool	93	71	41, 55	71, 80
Lavandulol	69	111	41	69, 81
Thymol	135	150	91	(79)
Carvacrol	135	150	91, 107	(79, 82)
Cuminyl alcohol	135	107, 150	107, 150	79
Carveol	119	134	91	69, 82, 84
α -Terpineol	59	93	81, 121	67, 68, 81
Isopulegol	69	55, 81	55, 81	69, 81
Terpinen-4-ol	71	93	43, 111	71, 86
Menthol	71	81	95	71, 81
Sabinol	81	109, 110	109, 110	67, 69, 81
Thujyl alcohol	93, 95	93, 95	43	67, 70, 81
Neo-isothujyl alcohol	93	121	136	67, 69, 81
Borneol	95	110	93, 139	69, 82
Isoborneol	95	93, 110	93, 110	69, 71, 82
Fenchyl alcohol	81	80	43	69, 72, 81



Figs. 1–5. The mass spectra of 1) β -citronellol, 2) geraniol, 3) nerol, 4) linalool, 5) lavandulol.

The presence of the hydroxyl group is always revealed by the occurrence of $m/e = M-18$ or fragments derived from this ion. In cases where $m/e = M$ is missing, the occurrence of $m/e = M-15$ and $M-18$, simultaneously, indicates the presence of a monoterpene alcohol and makes it possible to calculate M . The three strongest peaks and certain peaks around $m/e = 70$ and 80 are given in Table 1.

The meta-stable ions observed as diffuse peaks were studied for breakdown patterns (see Tables 2-5). Owing to the quality of the spectra and to the possible masking by large ion peaks some meta-stable ions remained concealed.

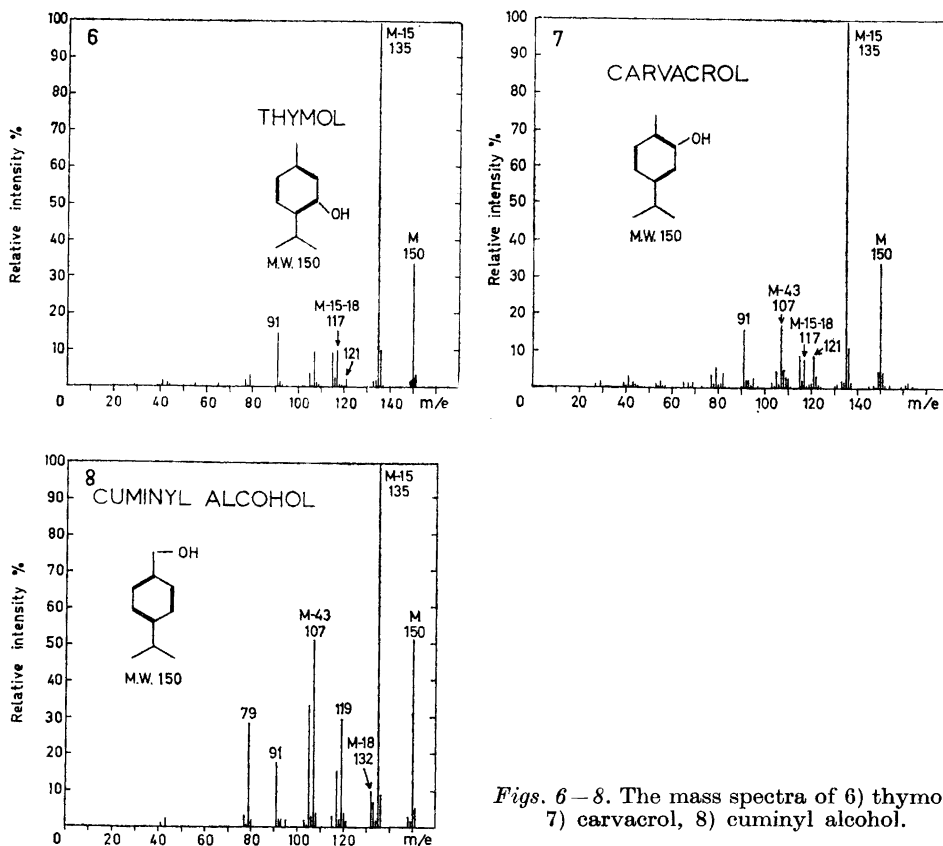
Generally speaking, the diffuse peaks for the alcohols are less numerous and weaker than for the hydrocarbons which should be expected in view of the decomposing influence of the hydroxyl group. Fairly many of the diffuse peaks are the same as for the hydrocarbons, which means that they originate from ions that have lost one molecule of water and are thus monoterpene hydrocarbon ions with structures resembling or identical with those of the hydrocarbons investigated.¹ These peaks are 89.2, 75.0, 66.5, 63.8, and 24.3, corresponding to the following breakdown reactions: $93^+ \rightarrow 91^+ + 2$, $79^+ \rightarrow 77^+ + 2$, $93^+ \rightarrow 79^+ + 14$ (or $136^+ \rightarrow 95^+ + 41$), $136^+ \rightarrow 93^+ + 43$ and $69^+ \rightarrow 41^+ + 28$, respectively.

A. Acyclic. The spectra of β -citronellol, geraniol, nerol, linalool and lavan-dulol are given in Figs. 1-5 and the corresponding diffuse peaks in Table 2. With the exception of the tertiary alcohol linalool these compounds have the parent peak at $m/e = M$ and they have $m/e = 69$ as the base peak. The latter fragment is formed by splitting the bond in allylic position to the double bond or bonds present in the respective molecules. Linalool has $m/e = M + 1$ as the parent peak and $m/e = M-18-43 = 93$ as the base peak. With the possible exception of linalool the mass spectra of these compounds are typical of acyclic compounds, the peaks with the higher intensities being at lower m/e -values. From the mass spectra including the appearance of diffuse peaks it can be seen that the strong peaks belong to one or the other of two groups, one containing the hydroxyl group, the other consisting of a hydrocarbon skeleton only. In the case of geraniol, for instance, $m/e = M$, 139 and 111 belong to the former group and $m/e = 136$, 121 and 93 to the latter, which peaks also

Table 2. Meta-stable ions of acyclic monoterpene alcohols.

Diffuse peaks * m	Breakdown reaction	β -Citro-nellol	Geraniol	Nerol	Linalool	Lavan-dulol
89.2	$93^+ \rightarrow 91^+ + 2$		×	×	×	×
78.1	$111^+ \rightarrow 93^+ + 18$		×	×		×
37.2	$121^+ \rightarrow 67^+ + 54$					
	$81^+ \rightarrow 55^+ + 26$	×	×	×		×
36.6	$123^+ \rightarrow 67^+ + 56$	×				
24.4	$69^+ \rightarrow 41^+ + 28$		×	×		×

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 .



Figs. 6–8. The mass spectra of 6) thymol, 7) carvacrol, 8) cuminyll alcohol.

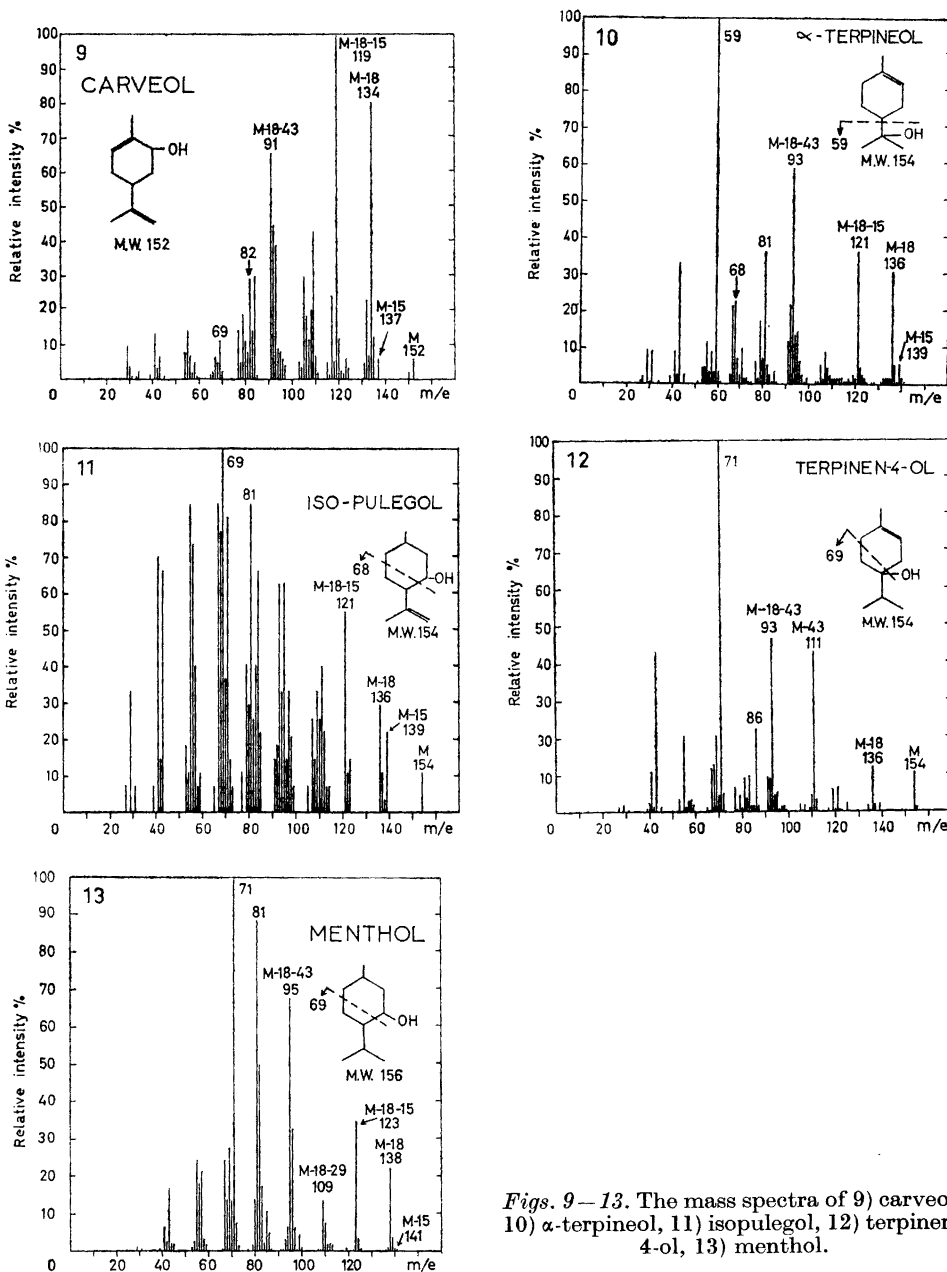
are common in the mass spectra of proper monoterpene hydrocarbons. As expected, the spectra of geraniol and nerol do not differ substantially from one another, these compounds being *cis-trans* isomers.

B. Aromatic. The spectra of thymol, carvacrol and cuminyll alcohol are given in Figs. 6–8 and the diffuse peaks in Table 3. These compounds are

Table 3. Meta-stable ions of aromatic monoterpene-like alcohols; cf. Table 1.

Diffuse peaks * <i>m</i>	Breakdown reaction	Thymol	Carvacrol	Cuminyll alcohol
121.3	150 ⁺ → 135 ⁺ + 15	×	×	×
118.1	150 ⁺ → 132 ⁺ + 18			×
113.3	117 ⁺ → 115 ⁺ + 2	×	×	×
101.5	135 ⁺ → 117 ⁺ + 18	×	×	×
84.5	135 ⁺ → 107 ⁺ + 28	×	×	
61.0	135 ⁺ → 91 ⁺ + 44	×	×	

much more stable than the acyclic compounds as revealed by the presence of high concentrations of ions with large m/e -values. The two strongest peaks in each case, *i.e.* $m/e = M$ and $M-15$, indicate the firmness with which the



Figs. 9–13. The mass spectra of 9) carveol, 10) α -terpineol, 11) isopulegol, 12) terpinen-4-ol, 13) menthol.

hydroxyl group is bound. As a matter of fact, most stronger peaks correspond to fragments containing the hydroxyl group, particularly in thymol and carvacrol, where the hydroxyl group is attached to the ring. Nevertheless, $m/e = 91$ is present in all three cases. It is interesting to compare with the formation of a tropylium ion $C_7H_7^+$ from alkylbenzenes.⁴

C. Monocyclic (non-aromatic). The mass spectra of carveol, α -terpineol, isopulegol, terpinen-4-ol and menthol are given in Figs. 9–13. The diffuse peaks belonging to the last two are listed in Table 4. No diffuse peaks were recorded for the first three compounds. With the exception of carveol these alcohols have their base peak in the lower m/e -area. As expected, the non-aromatic ring system is broken down much more easily than the aromatic ring in the previous group of compounds, placing the monocyclic non-aromatic alcohols in roughly the same stability range as the acyclic ones. The structure of carveol is obviously stabilized, as revealed by the higher concentrations of fragments of $m/e = 134, 119$ and 91 (Fig. 9). It is interesting to compare these fragments and their relative intensities with those from *p*-cymene¹ possibly indicating the similarity of the structure of *p*-cymene and the structure of the fragment formed from carveol by loss of one molecule of water.

Table 4. Meta-stable ions of two monocyclic monoterpene alcohols; cf. Table 1.

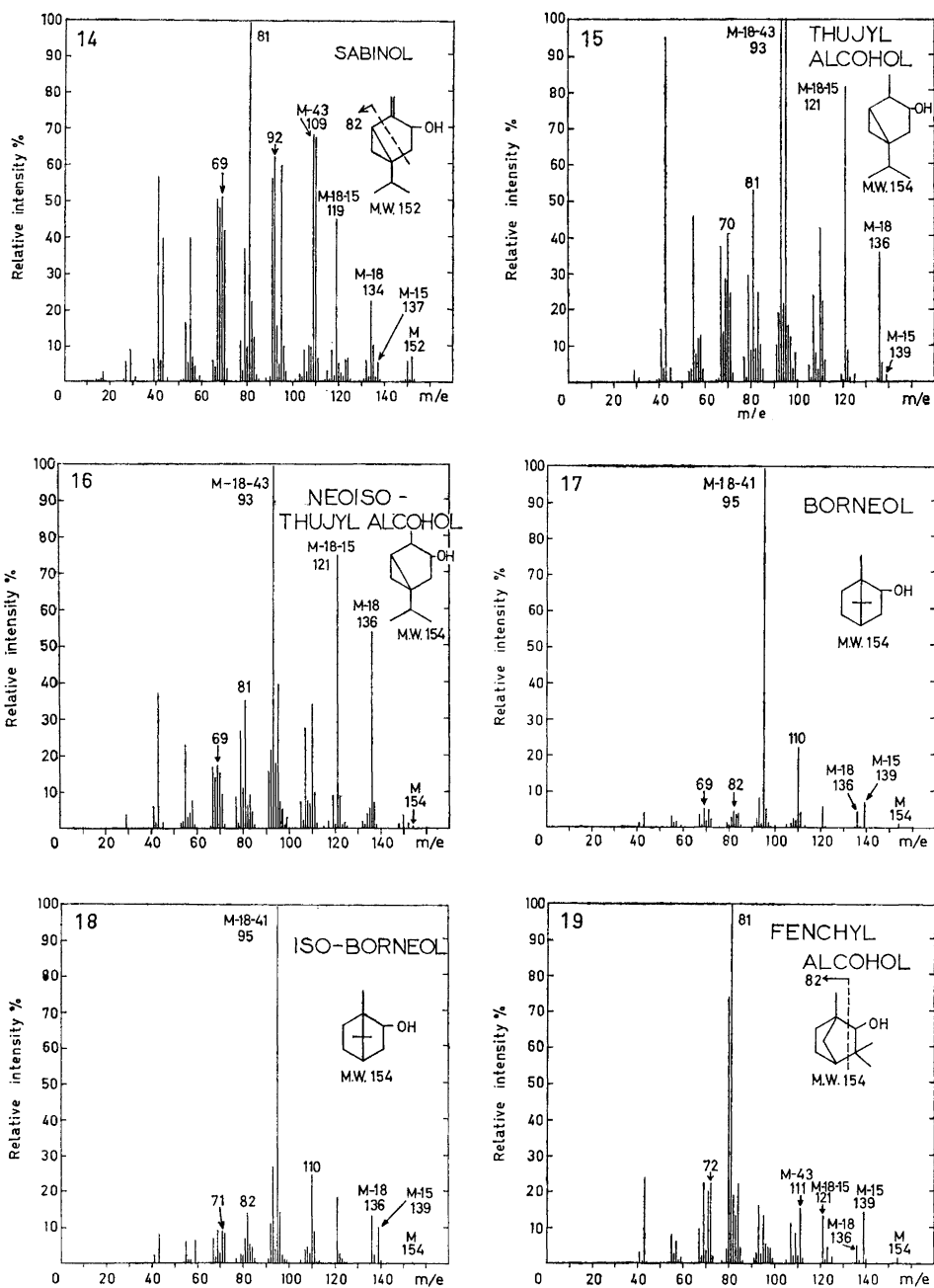
Diffuse peaks * m	Breakdown reaction	Terpinen-4-ol	Menthol
107.5	141 ⁺ → 123 ⁺ + 18		×
91.2	95 ⁺ → 93 ⁺ + 2		×
89.2	93 ⁺ → 91 ⁺ + 2	×	
76.8	81 ⁺ → 79 ⁺ + 2		×
65.5	138 ⁺ → 95 ⁺ + 43		×
63.8	136 ⁺ → 93 ⁺ + 43	×	
58.7	86 ⁺ → 71 ⁺ + 15	×	
47.6	138 ⁺ → 81 ⁺ + 57		×
36.6	123 ⁺ → 67 ⁺ + 56		×

The base peak $m/e = 59$ for α -terpineol (Fig. 10) is characteristic for this compound being the only one studied with the hydroxyl group attached to the isopropyl group.

D. Bicyclic. The mass spectra of sabinol, thujyl alcohol, neo-isothujyl alcohol, borneol, isoborneol and fenchyl alcohol are given in Figs. 14–19 and the diffuse peaks in Table 5. In pairs, four of these compounds are stereoisomers. As to thujyl alcohol, the isomerism will be described by Norin.⁵

The base peak for these compounds is in the upper half of the appropriate m/e -region. In the case of the thujyl alcohols and the borneols the similarity in this respect with the bicyclic hydrocarbons is obvious¹ indicating the ease with which the hydroxyl group is lost.

The mass spectra of the borneols are presumably very much like each other, although there are differences. On the other hand, the spectra of the thujyl



Figs. 14–19. The mass spectra of 14) sabinol, 15) thujyl alcohol, 16) neo-isothujyl alcohol, 17) borneol, 18) isoborneol, 19) fenchyl alcohol.

Table 5. Meta-stable ions of three bicyclic monoterpene alcohols *cf.* Table 1.

Diffuse peaks * m	Breakdown reaction	Sabinol	Thujiyl alcohol	Neo-iso-thujiyl alcohol	Fenchyl alcohol
89.2	93 ⁺ → 91 ⁺ + 2		×	×	
78.0	111 ⁺ → 93 ⁺ + 18				×
77.0	81 ⁺ → 79 ⁺ + 2	×			
75.0	79 ⁺ → 77 ⁺ + 2		×	×	
74.1	121 ⁺ → 95 ⁺ + 26				×
66.5	{ 93 ⁺ → 79 ⁺ + 14		×		
63.8	{ 136 ⁺ → 95 ⁺ + 41		×		
	{ 136 ⁺ → 93 ⁺ + 43		×	×	

alcohols differ markedly in two respects, $m/e = 43$ and 95 being much more intense in thujiyl alcohol than in neoisothujiyl alcohol.

Like most of the alcohols, except the aromatic ones, the mass spectra of the bicyclic alcohols generally have the hydroxyl-free fragments in much higher concentrations than those still containing the hydroxyl group. This is also evident from the diffuse peaks, which are rarely produced by reactions involving a hydroxyl group (see Tables 2–5).

E. Thermal decomposition. As was the case with some monoterpene hydrocarbons, certain alcohols were thermally decomposed when the gas transfer system between the chromatograph and the mass spectrometer was kept at a temperature around 200°C. These were geraniol, nerol, lavandulol, cuminyll alcohol, borneol, isoborneol and fenchyl alcohol. The decomposition is manifested by the occurrence of extra peaks added to the spectra originating from the thermally non-decomposed molecules. These new peaks occur at positions two or four units lower than some of the original peaks in the upper m/e -region. They are generally much weaker for the alcohols than for the hydrocarbons.¹ The intensities of the original peaks are not influenced very much by the occurrence of these extra peaks, which means that an identification is quite feasible even if some thermal decomposition has occurred.

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