

Mass Spectrometry of Terpenes

IV. Esters of Monoterpene Alcohols

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Fifteen esters of monoterpene alcohols were investigated in a combined gas chromatograph-mass spectrometer. The ions with m/e -values higher than M less the acyl or acid part were generally of very low intensity resulting in spectra reminiscent of, but still different from, those of monoterpene hydrocarbons or alcohols.

Monoterpene hydrocarbons, alcohols, aldehydes, and ketones have previously been studied in a combined gas chromatograph-mass spectrometer.¹⁻⁴ The investigations were now extended to include esters of monoterpene alcohols, all together fifteen compounds. The mass spectrum of citronellyl acetate has been published before.⁵

EXPERIMENTAL

Apparatus. The apparatus described in Part I of this series¹ has been gradually rebuilt and improved.⁶ The transfer system was kept at a temperature of 100° to 120°C. The chromatography was carried out on 15 % General Electric Silicone Fluid SF96 on silanized Chromosorb W: 3 m glass column of 3 mm inner diameter, helium about 50 ml/min, "on column injection", column temperature between 150° and 180°C depending on the specimen investigated. In order to avoid ionization of helium in the ion source of the mass spectrometer the electron energy was kept at 20-22 eV. With the experimental conditions applied no thermal breakdown occurred.

Material. The sources of the esters investigated were: geranyl acetate from Haarman & Reimer, Germany, bornyl acetate from Theodor Schuchardt, Germany, sabinyl acetate from Professor H. Erdtman, Stockholm. Citronellyl formate, acetate, and propionate, geranyl formate and propionate, neryl acetate and propionate, two isomers of l-carvyl acetate and carvyl propionate, isobornyl acetate and propionate were isolated from various specimens obtained from Fritsche Brothers Inc., USA.

High purity for the analysis was obtained by chromatography on the silicone column. The purity of the fractions actually analyzed was also invariably checked by gas chromatography on two other columns: 10 % butadiol succinate (2 m) and 15 % Carbowax 20 M (2 m), respectively. The identity of the analyzed specimens was regularly checked by infrared spectrophotometry and data on the esters of carveol were supplied by Fritsche Brothers Inc.⁷

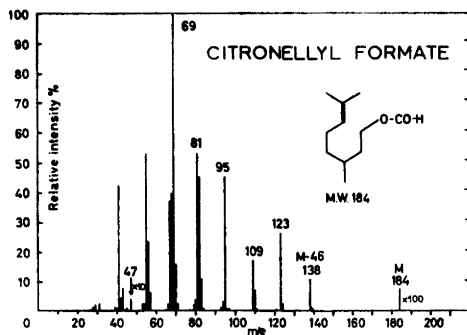


Fig. 1. The mass spectrum of citronellyl formate.

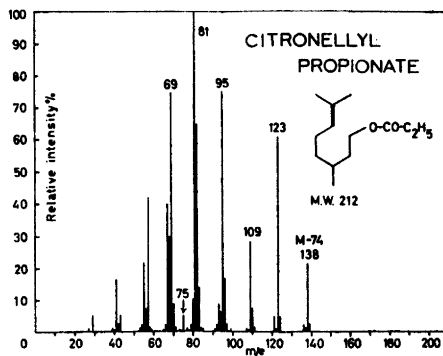


Fig. 2. The mass spectrum of citronellyl propionate.

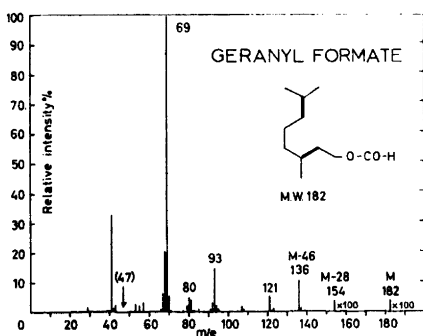


Fig. 3. The mass spectrum of geranyl formate.

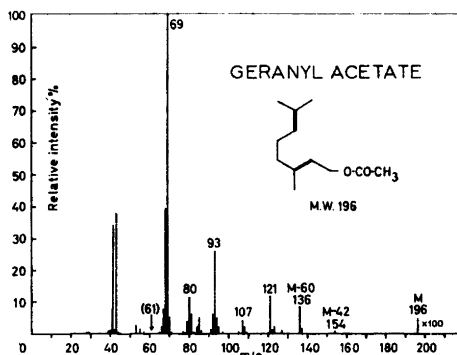


Fig. 4. The mass spectrum of geranyl acetate.

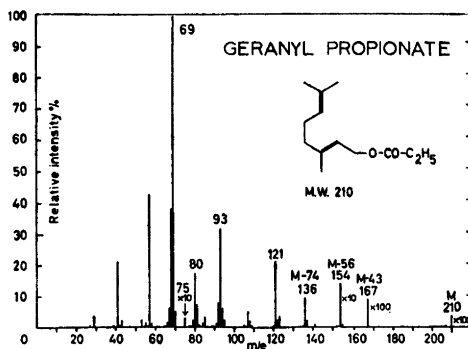


Fig. 5. The mass spectrum of geranyl propionate.

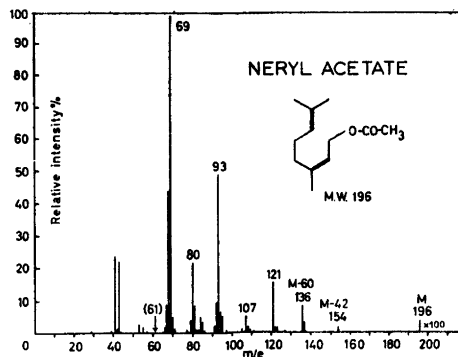


Fig. 6. The mass spectrum of neryl acetate.

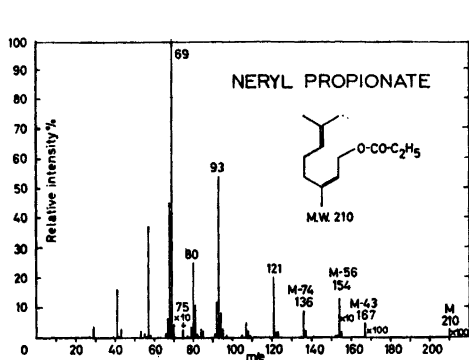


Fig. 7. The mass spectrum of neryl propionate.

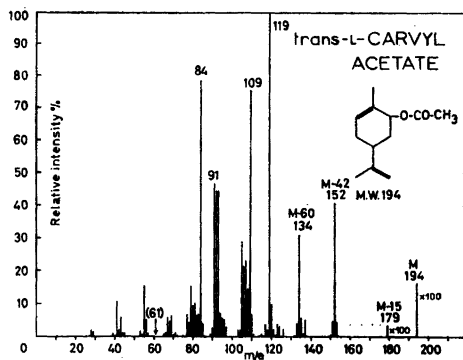


Fig. 8. The mass spectrum of *trans-l*-carvyl acetate.

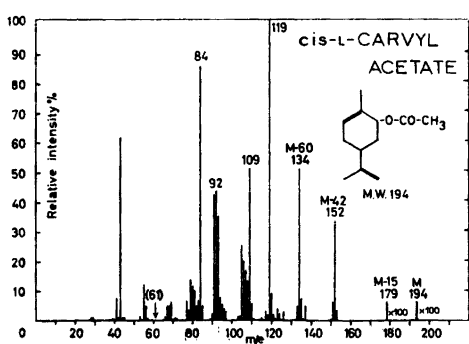


Fig. 9. The mass spectrum of *cis-l*-carvyl acetate.

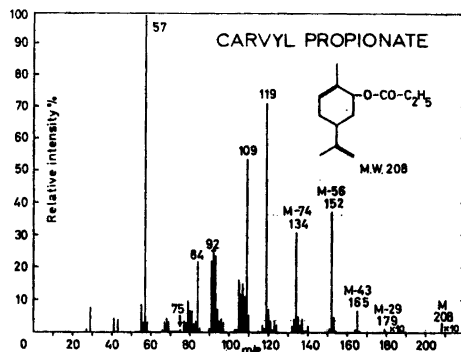


Fig. 10. The mass spectrum of carvyl propionate.

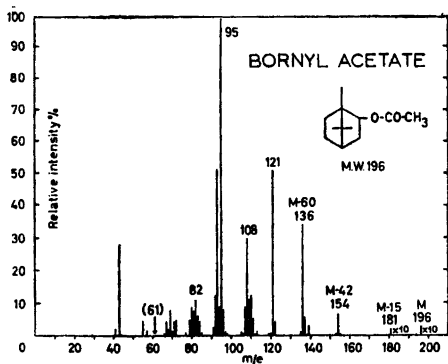


Fig. 11. The mass spectrum of bornyl acetate.

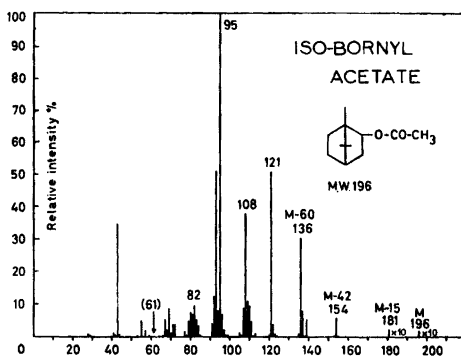


Fig. 12. The mass spectrum of isobornyl acetate.

Table 1. Meta-stable ions of

Diffuse peaks * <i>m</i>	Possible breakdown reactions	Citronellyl			Geranyl		
		formate	acetate	propi- onate	formate	acetate	propi- onate
119.5	154 ⁺ → 136 ⁺ + 18						
115.0	119 ⁺ → 117 ⁺ + 2						
91.1	95 ⁺ → 93 ⁺ + 2	×	×				
89.2	93 ⁺ → 91 ⁺ + 2				×	×	×
86.9	134 ⁺ → 108 ⁺ + 26						
77.2	81 ⁺ → 79 ⁺ + 2	×	×	×			
75.0	152 ⁺ → 107 ⁺ + 45						
69.5	119 ⁺ → 91 ⁺ + 28						
65.3	138 ⁺ → 95 ⁺ + 43	×	×	×			
63.9	136 ⁺ → 93 ⁺ + 43				×	×	×
63.6	93 ⁺ → 77 ⁺ + 16(?)						
52.0	121 ⁺ → 79 ⁺ + 42					×	×
47.5	{ 95 ⁺ → 67 ⁺ + 28 138 ⁺ → 81 ⁺ + 57	×	×	×			
46.3	152 ⁺ → 84 ⁺ + 68						
37.2	121 ⁺ → 67 ⁺ + 54				×	×	×
36.8	123 ⁺ → 67 ⁺ + 56	×	×				
24.4	69 ⁺ → 41 ⁺ + 28	×	×	×	×	×	×

**m* = m_2^2/m_1 , where m_1 and m_2 are the masses of the original and the generated ions,

RESULTS AND DISCUSSION

The spectra of fourteen esters of monoterpene alcohols are shown in Figs. 1–14. 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.

As might be expected the mass spectra of esters of monoterpene alcohols proved very similar to the spectra of the corresponding alcohol² or hydrocarbon,¹ which means that the acyl radical or the acid radical is easily split off. A peak of low intensity corresponding to the molecule ion was, however,

esters of monoterpene alcohols.

Neryl		<i>trans</i> -L-Carvyl acetate	<i>cis</i> -L-Carvyl acetate	Carvyl propionate	Bornyl acetate	Isobornyl		Sabinyl acetate
acetate	propionate					acetate	propionate	
		×	×	×			×	
×	×	×	×		×	×	×	×
		×	×					
		×	×					
×	×				×	×	×	
×	×							
		×	×					
×	×				×	×	×	
×	×							

respectively, giving rise to a diffuse peak at m .

observed in all spectra except three (Figs. 2, 14 and citronellyl acetate). In these three spectra and five others (Figs. 1, 5, 7, 10, and 13) a small but distinct peak was seen at $m/e = 47, 61, \text{ or } 75$, corresponding to formic, acetic and propionic acid plus H^+ , respectively.

The metastable peaks observed are given in Table 1. The data available seem to present little information on the breakdown patterns of the esters of monoterpene alcohols beyond what is known for the alcohols themselves² or the hydrocarbons.¹

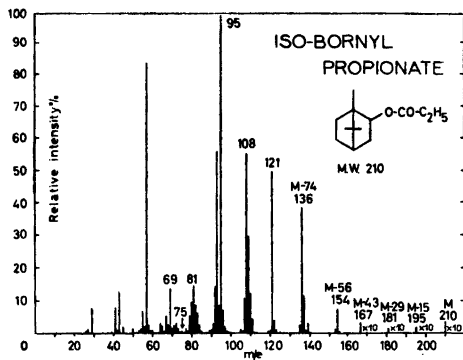


Fig. 13. The mass spectrum of isobornyl propionate.

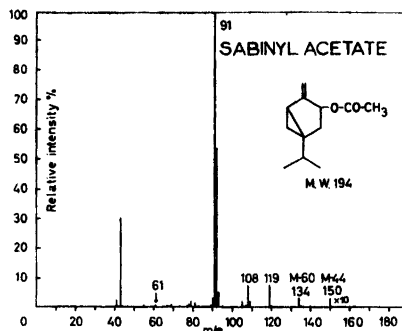


Fig. 14. The mass spectrum of sabinyl acetate.

Although the mass spectra of esters of monoterpene alcohols are similar to those of the alcohols and the hydrocarbons they can thus be recognized as esters by the presence of $m/e = M$ or $m/e = \text{acid} + 1$ or both, after which positive identification can be carried out. In the apparatus used here or with similar arrangements the retention time on the column is also helpful information.

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REFERENCES

1. Ryhage, R. and von Sydow, E. *Acta Chem. Scand.* **17** (1963) 2025.
2. von Sydow, E. *Acta Chem. Scand.* **17** (1963) 2504.
3. von Sydow, E. *Acta Chem. Scand.* **18** (1964) 1099.
4. von Sydow, E. *Acta Chem. Scand.* **18** (1964) 1791.
5. Andersson, J. and von Sydow, E. *Acta Chem. Scand.* **18** (1964) 1105.
6. Ryhage, R. *Anal. Chem.* **36** (1964) 759.
7. Rogers, J.A. *Private communication.*

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