

Mass Spectral Data for Gas Chromatograph–Mass Spectral Identification of Some Irregular Monoterpenes

William W. Epstein,* Lawrence R. McGee, C. Dale Poulter, and Larry L. Marsh
 Chemistry Department, University of Utah, Salt Lake City, Utah 84112

The mass spectra of 19 irregular monoterpenes as well as the relative gas chromatographic retention times are presented.

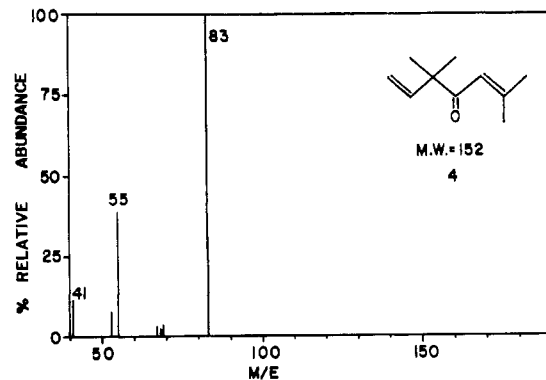
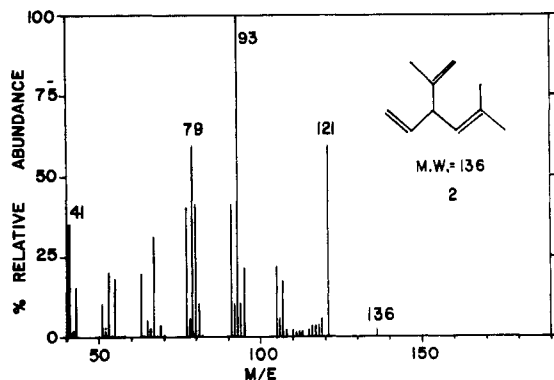
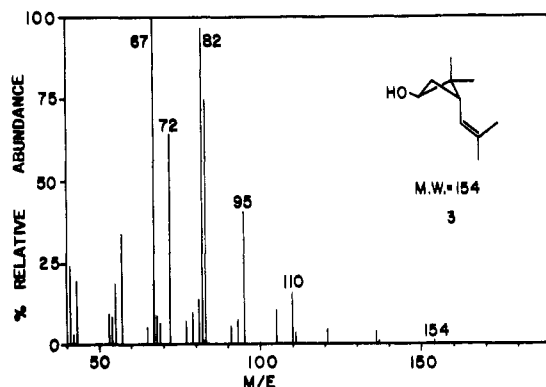
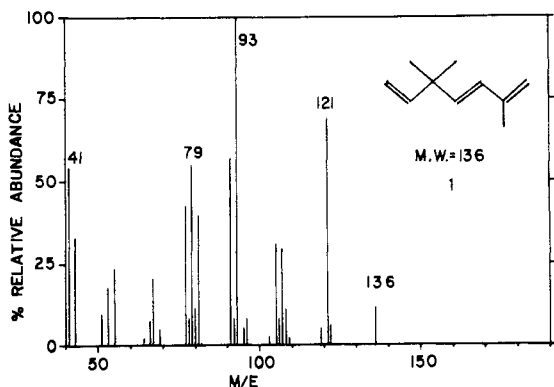
The mass spectra of several non-head-to-tail monoterpenes were recorded as part of a study on the occurrence and biosynthesis of the irregular terpenes (1). The use of combined GCMS in identifying irregular monoterpenes in complex essential oils is greatly facilitated by a comprehensive catalog of the mass spectra of these compounds. Such a catalog is also valuable in pinpointing new compounds for subsequent isolation and identification.

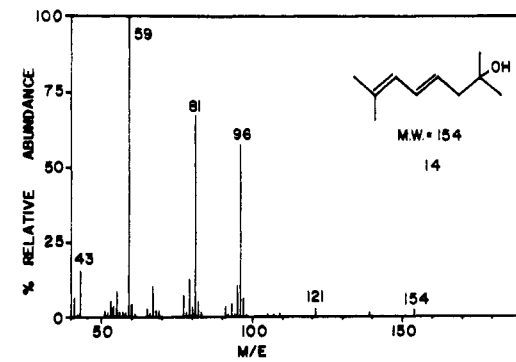
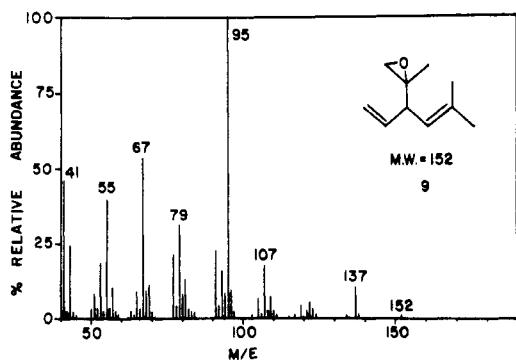
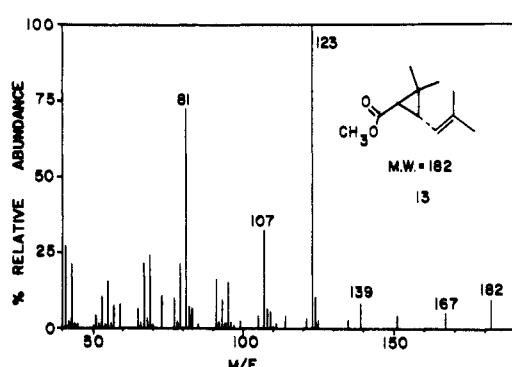
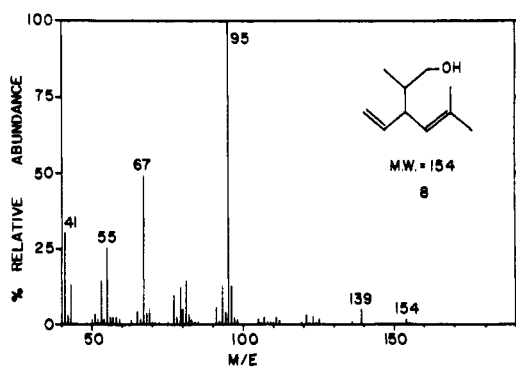
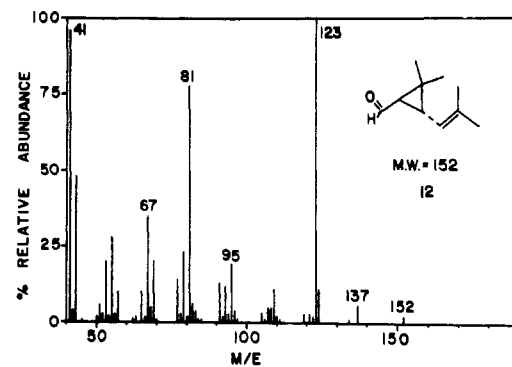
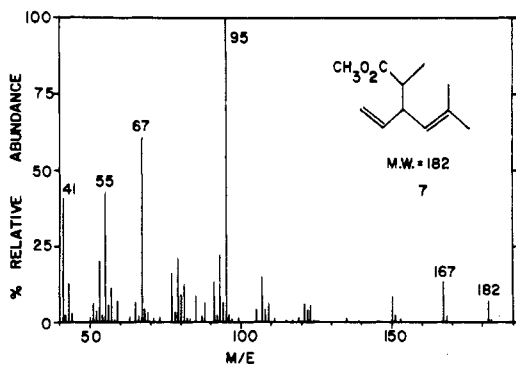
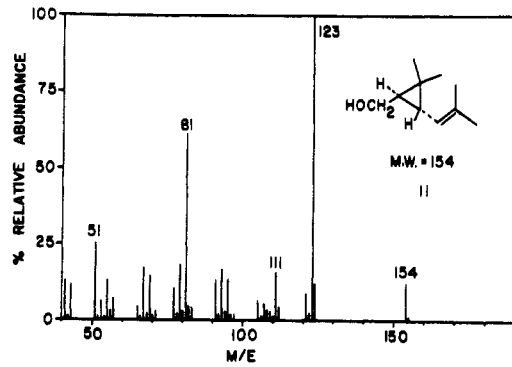
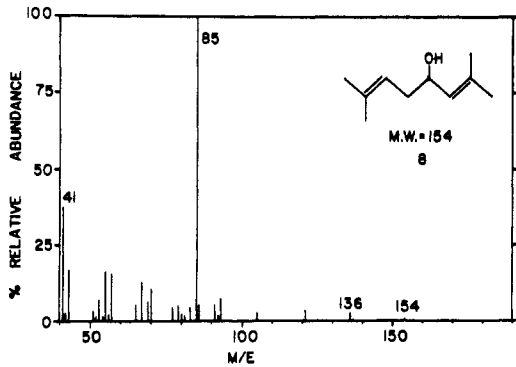
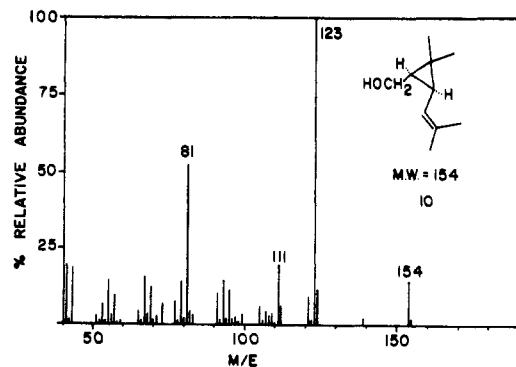
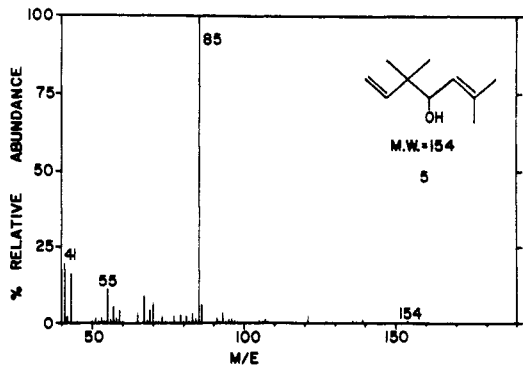
The mass spectra of many regular monoterpenes are available (6, 8). However, only a few mass spectra of irregular monoterpenes, suitable for use in GCMS, have appeared in the literature (4, 5, 7). Therefore we report the mass spectra of 19 irregular monoterpenes, nine synthetic, but possible biosynthetic intermediates, which have not yet been reported from natural sources and ten naturally occurring terpenes. The GC retention

times of these compounds, relative to Yomogi alcohol (16) are included in Table I as a further aid to identification.

Experimental Section

Compounds were isolated from natural sources or synthesized. Details are available elsewhere (2, 3). Mass spectra of each compound were recorded on one or more instruments. In each case the results were usable for positive identification. The mass spectrometers used were an Associated Electronics Inc. MS 30 equipped with a Pye Series 104 gas chromatograph, a Hewlett-Packard Model 5930 equipped with an HP Model 7620 gas chromatograph, and a Perkin-Elmer Model 270 combined GCMS. The first two instruments utilize membrane carrier-gas separators. The last utilizes a fritted-glass carrier-gas separator. The fritted-glass caused some problems with elimination in some of the alcohols. The spectrum of yomogi alcohol (16) reported in ref 4 is an example of this. The alcohol has eliminated and the spectrum displayed actually represents that of the resulting artemesia triene (1). This problem was alleviated by silanizing the





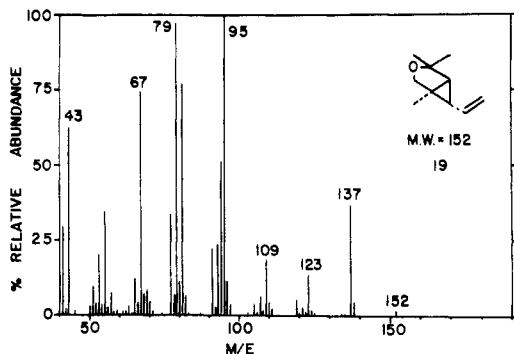
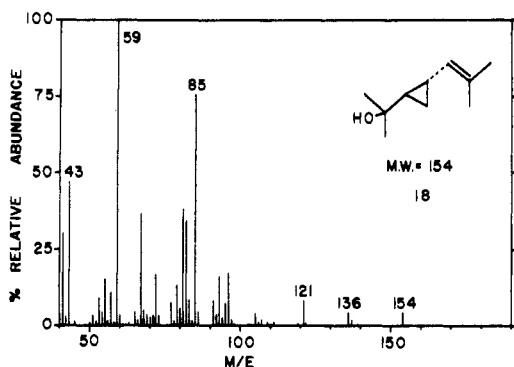
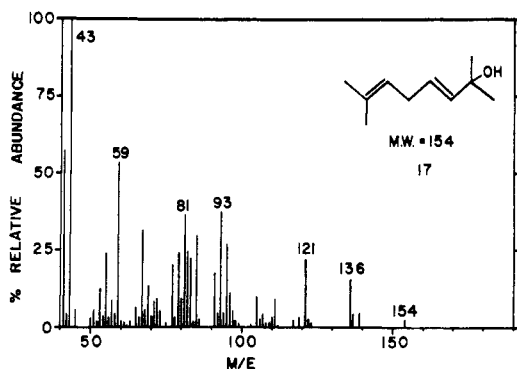
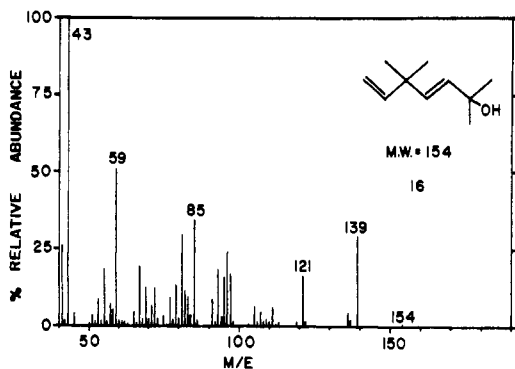
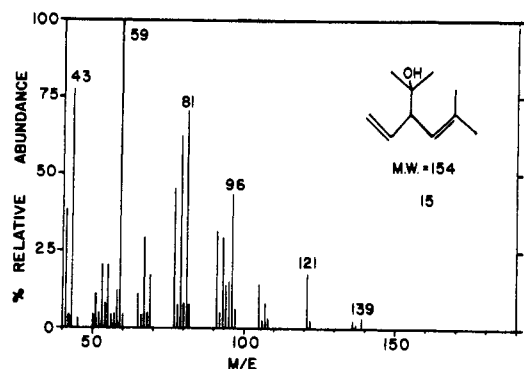


Table I. GC Retention Times Relative to Yomogi Alcohol (16)

Compound	Column		
	30' Carbowax	500' Carbowax	500' OV 101
1 Artemesia triene ^b	...	0.53	0.77
2 Santolina triene ^a	0.37	0.53	0.73
3 <i>trans</i> -2,2-Dimethyl-3-(2'-methyl-1'-propenyl)cyclobutanol ^b	...	3.11	2.03
4 Artemesia ketone ^a	0.95
5 Artemesia alcohol ^a	1.50	1.50	1.42
6 2,7-Dimethyl-2,6-octadien-4-ol ^b	...	3.02	2.27
7 Methyl santolinol ^a	1.20
8 α -Santolina alcohol ^b	2.58
9 Santolina epoxide ^a	0.83
10 <i>cis</i> -Chrysanthemol ^b	2.64	3.03	2.30
11 <i>trans</i> -Chrysanthemol ^a	2.77	3.34	2.30
12 <i>trans</i> -Chrysanthemal ^b	1.56
13 Methyl <i>trans</i> -chrysanthemate ^b	1.59
14 <i>trans</i> -2,7-Dimethyl-4,6-octadien-2-ol ^b	...	2.90	2.30
15 Santolina alcohol ^a	1.00	1.00	1.15
16 Yomogi alcohol ^a	1.00	1.00	1.00
17 <i>trans</i> -2,7-Dimethyl-3,6-octadien-2-ol ^b	...	1.99	1.68
18 <i>trans</i> -2-[2''(2''-Methyl-1''-propenyl)cyclopropyl]propan-2-ol ^b	...	1.96	1.68
19 Arthole ^a	0.57

^a Naturally occurring compounds. ^b Not as yet identified in natural sources.

fritted-glass assembly. The ionization voltage in each case was 70 eV with separator temperature of 150 °C.

Two stainless-steel open-tubular GLC columns (500 ft × 0.03 in. Carbowax 20M and 500 ft × 0.03 in. 95% OV101 5% IGE-PAL) were sufficient to separate compounds 1–19. Most analyses with these columns were done at 100 °C. with carrier-gas flow of 28 ml min⁻¹.

Relative retention times were measured on a Varian Aero-graph Model 1200 gas chromatograph with flame ionization detector. A silanized aluminum column (30 ft × 0.125 in. 10% Carbowax 20M on silanized Chromosorb W 60/80 mesh) was sufficient to separate the naturally occurring compounds except 16 and 17 and is used for the analysis of essential oils. Retention times measured on this column were performed at 145 °C. with carrier gas of 54 ml min⁻¹. The injector temperature was maintained at 190 °C, and the detector temperature at 210 °C.

Literature Cited

- (1) Epstein, W. W., Poulter, C. D., *Phytochemistry*, **12**, 737 (1973).
- (2) Epstein, W. W., et al., unpublished results of this laboratory.
- (3) Marsh, L. L., MS Thesis, University of Utah, Salt Lake City, Utah, 1973.
- (4) Poulter, C. D., Moesinger, S. G., Epstein, W. W., *Tetrahedron Lett.*, 67 (1973).
- (5) References cited in ref 1.
- (6) Stenhagen, E., Abrahamsson, S., McLafferty, F. W., "Atlas of Mass Spectral Data", Vol. 1 and 2, Interscience, New York, N.Y., 1964.
- (7) Thomas, A. F., Willhalm, B., *Tetrahedron Lett.*, 3775 (1964).
- (8) Von Sydow, E., Anjou, K., Karlsson, G., *Arch. Mass. Spectrom. Data*, **1**, 387–495 (1970).

Received for review June 26, 1975. Accepted June 28, 1976. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and NIH (GM 20196 and GM 19557) for support of this research.

Supplementary Material Available: Numerical tables of the data presented in these spectra will appear in Selected Mass Spectral Data of the American Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas.