

# Volatiles from Oranges. Oxygenated Compounds Identified by Infrared, Proton Magnetic Resonance, and Mass Spectra

ROY TERANISHI, R. E. LUNDIN, W. H. McFADDEN, T. R. MON, T. H. SCHULTZ, K. L. STEVENS, and JAN WASSERMAN

Western Regional Research Laboratory, Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany, Calif.

Oxygenated compounds were separated from a limonene distillate of orange oil by adsorption on silica, and fractions were analyzed by the combination of open tubular gas chromatography and fast-scan mass spectrometry. Several compounds were isolated by preparative gas chromatography, and the chemical structures were determined by interpretation of infrared, proton magnetic resonance, and mass spectra.

PREVIOUS PAPERS (5, 6, 9) deal with hydrocarbons isolated from orange oil, volatiles from orange juice, and a sesquiterpene aldehyde isolated from orange oil, respectively. Because the distillate, mainly limonene, from cold pressed orange oil has a pleasant aroma, this material was investigated for its oxygenated constituents. This paper describes the separation of the oxygenated compounds from the distillate and the characterization of some of the compounds by infrared (IR), proton magnetic resonance (PMR), and mass spectra (MS).

## Experimental

**Extraction of the Oxygenated Compounds.** The general fractionation scheme used in this series of investigations has been described (9). The distillate (63 kg.) obtained by vacuum distillation of cold pressed oil, Sunkist Growers, was passed through a large divided column (8) of Davison grade 923 silica (7.8 kg.). Limonene was removed from the column with Skellysolve B, which was purified with Alcoa alumina. The oxygenated compounds were eluted from the silica with chloroform and methanol. The fractions were obtained by taking 500-gram cuts, and then each fraction was weighed after the evaporation of the solvent under aspirator vacuum.

**Separation and Analysis.** An infrared spectrum (neat) of each fraction was obtained with a Beckman IR-5 instrument, and fractions with similar spectra were consolidated. Each of the consolidated fractions was analyzed with a programmed temperature open tubular column gas chromatograph, Perkin-Elmer model 226, equipped with a 75-foot, 0.01-inch i.d. column coated with DC 550 silicone oil.

The gas chromatographs used with MS and for preparative work were made in the authors' laboratory. Interesting fractions from the silica column were investigated with an open tubular column gas chromatograph connected to the Bendix Time-of-Flight mass spectrometer Model 12 (3). The PMR spectra were obtained with the Varian Associated model A-60 instrument using carbon tetrachloride as a solvent. For samples too small for conventional single-scan analyses, the multiple scanning technique was employed (2).

## Results and Discussion

The infrared spectra of the representative fractions were analyzed. Although silica separation was used primarily for the isolation of the oxygenated compounds from limonene, inspection of the infrared spectra showed that some fractionation was accomplished.

The open tubular column gas

chromatography-mass spectral analyses of the consolidated fractions not only verified the generalizations from the infrared spectra, but also, these analyses gave detailed information as to the molecular weight and the chemical structure of the various components separated by the open tubular column. Figure 1 shows a chromatogram of a representative consolidated fraction.

Table I. Compounds Identified by GC-MS

GC Peak	Compound
1	Ether <sup>a</sup>
2	n-Heptane <sup>a</sup>
3	Hexanal
4	Hydrocarbon, MW 114 <sup>a</sup>
5	Hydrocarbon <sup>a</sup>
6	Heptanal
7	Hydrocarbon, MW 128 <sup>a</sup>
8	Octanal
9	1,8-Cineole
10	Terpene, alcohol
11	Terpene
12	Nonanal (trace)
13	Linalool
14	Terpenes, MW 152 and 154
15	Isopulegol
16	Neo-isopulegol
17	Terpinen-4-ol
18	Terpene, MW 154
19	Decanal, traces of two other compounds
20	Carvone
21	Citral

<sup>a</sup> From solvents.

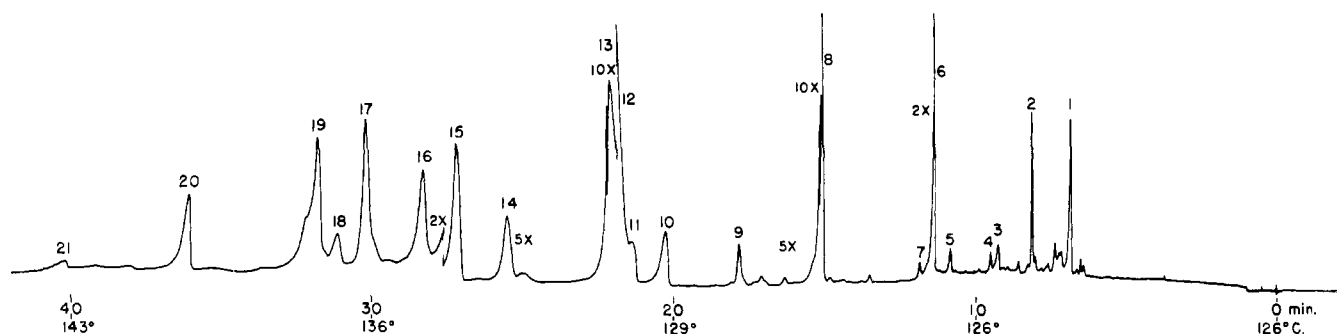


Figure 1. GC-MS analysis of a fraction

200-foot, 0.01-inch i.d. column coated with SF 96(50) silicone oil, programmed temperature

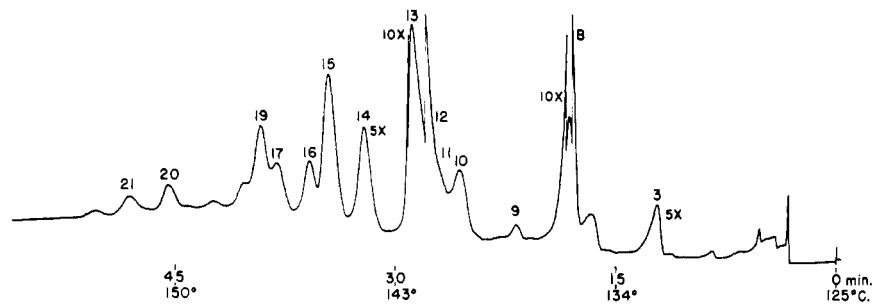


Figure 2. Preparative GC of a fraction

30-foot, 0.5-inch i.d. column packed with 60/70 mesh Chromo G, 4% SF 96(50)<sub>2</sub> silicone oil, programmed temperature

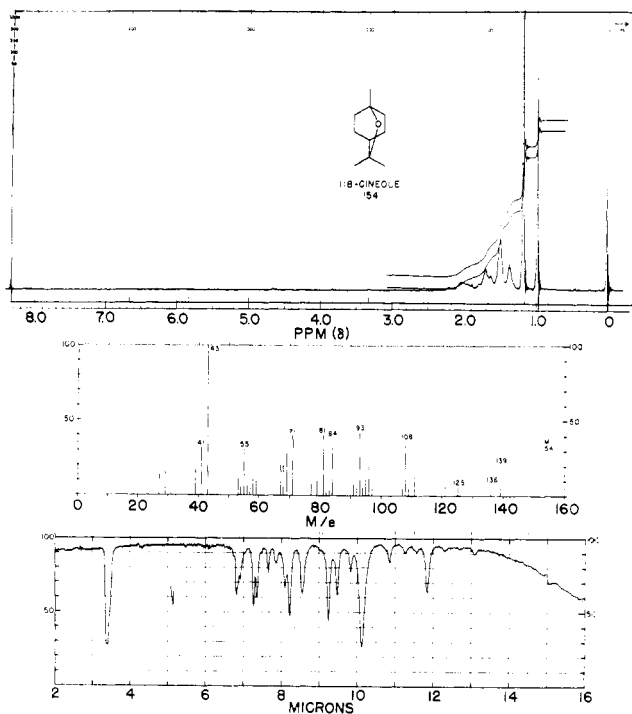


Figure 3. IR, MS, and PMR of 1,8-cineole

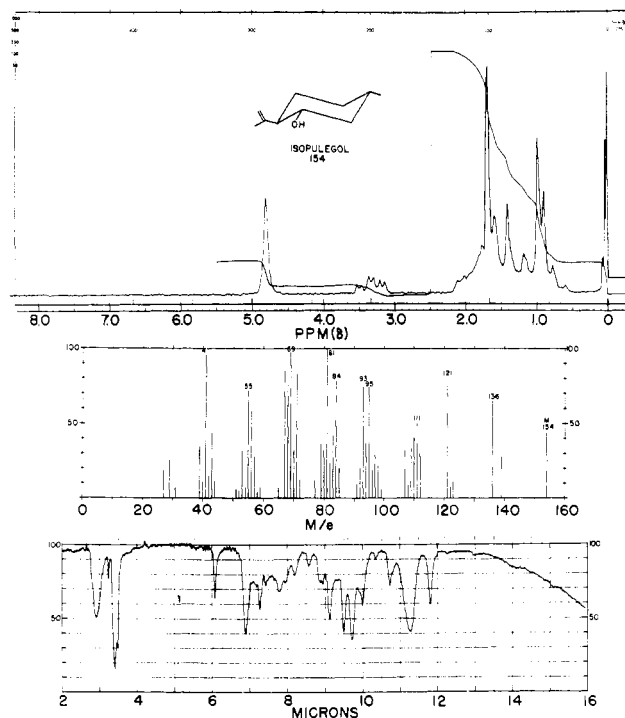


Figure 5. IR, MS, and PMR of isopulegol

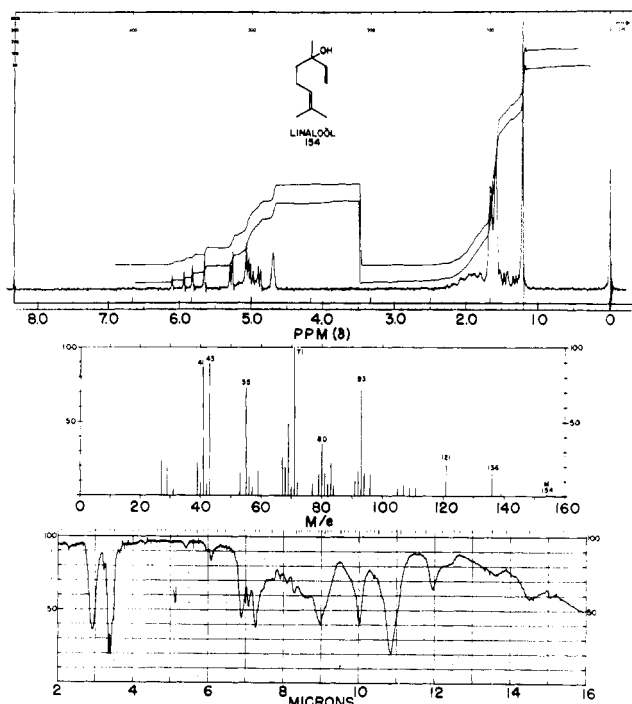


Figure 4. IR, MS, and PMR of linalool

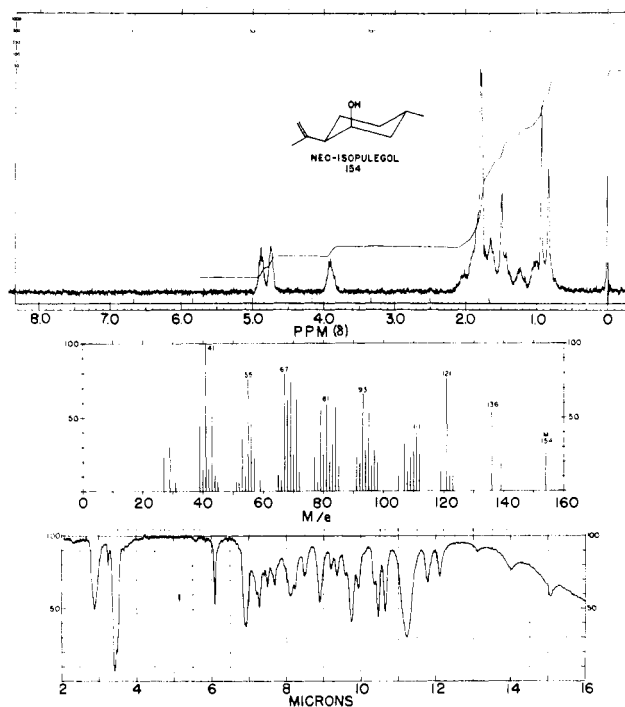


Figure 6. IR, MS, and PMR of neo-isopulegol

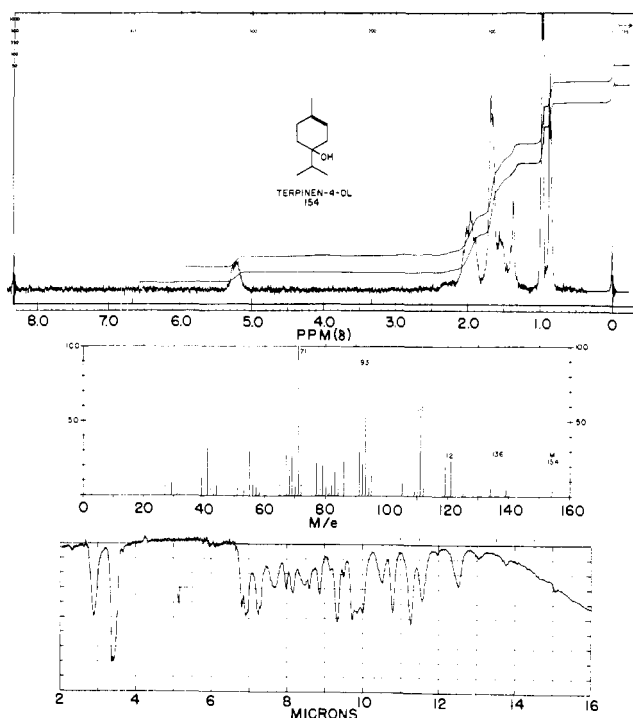


Figure 7. IR, MS, and PMR of terpinen-4-ol

Table I lists the compounds identified by MS and GC retentions. Such data were considered adequate identification for hexanal, heptanal, octanal, nonanal, and decanal in which the MS and GC retentions were compared with authentic samples.

Figure 2 shows the preparative gas chromatographic separation of the consolidated fraction. Obviously, the resolution of the larger, packed column is not so good as with the open tubular column, but sufficient material was obtained for IR and PMR analyses of the constituents not completely identified by MS.

When necessary, further purification was accomplished with a large-bore open tubular column (7).

Figures 3 through 7 show IR, PMR, and MS data of the compounds isolated and purified. Although some of the

spectra are available (7, 10), the authors present the consolidated spectral information in this form for reference in subsequent identification work. Carvone and citral were identified by MS and GC retention times. These compounds will be isolated from orange oil fractions which contain a higher concentration of these compounds, and the spectral data will be reported later.

The isopulegol isolated from orange oil was identical, by IR, MS, and PMR spectra, to the purified material obtained from commercially available isopulegol, predominantly isopulegol but containing all four possible isomers (K and K Laboratories, Inc.). Pickard *et al.* (4) have shown that the cyclization of citronellal yields a mixture of isopulegol and neo-isopulegol and have related these to the known menthols.

Citronellal was not found in these

orange oil fractions, whereas isopulegol and neo-isopulegol were. The ease with which citronellal cyclizes to yield the isopulegols is an indication that such a cyclization might have occurred during the silica chromatography.

Obviously, the ultimate goal of this type of investigation is an evaluation of each of the constituents as to its contribution to the aroma and flavor of oranges. The organoleptic properties of the compounds identified in this work are so well known that there is no need for their description. However, because of these properties, some contribution to the total effect is likely.

#### Literature Cited

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Received for review September 15, 1965. Accepted July 1, 1966. Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable. Fourth in a series on volatiles from oranges.