Analysis of Volatile Flavor Constituents from Tangerine Essence

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Aqueous tangerine essence was extracted with methylene chloride and ether. The extracted components were separated by gas chromatography and analyzed by mass spectrometry and infrared spectroscopy. Thirty-four volatile compounds were identified as tangerine juice essence constituents for the first time. There were 18 alcohols, five aldehydes, four esters, four ethers, two ketones, and limonene.

The aqueous condensate collected from the distillate when citrus juices are concentrated is rich in volatile flavor components and is generally known as aqueous essence. In the case of orange juice, aqueous essence can be added back to the juice concentrate to give it a fresher fruit flavor and aroma (Wolford and Attaway, 1967). This widely used aqueous essence from orange juice has been analyzed both by Wolford *et al.* (1962; Wolford and Attaway, 1967) and Schultz *et al.* (1964, 1967). Aqueous grapefruit essence was analyzed by Kirchner *et al.* (1953; Kirchner and Miller, 1953), and more recently by Moshonas and Shaw (1971).

Tangerine essence can also be collected in commercial essence recovery units; however, at the present time it is generally not collected. Its value for flavor and aroma enhancement of citrus products is not known. However, its availability, ease of collection, and possible use as a flavoring material for citrus products indicate the need for information on its flavor constituents.

There has been no previous investigation of volatile tangerine juice constituents. The present paper describes the isolation and identification of 34 flavor constituents from aqueous tangerine juice essence.

EXPERIMENTAL

Aqueous tangerine essence was obtained from a commercial plant in Florida producing 100-fold essence by fractionating and condensing vapors from the first stage of the evaporator. Anhydrous tangerine essence was obtained by the methylene chloride extraction method of Wolford *et al.* (1962). This method does not extract the ethanol which might otherwise interfere with subsequent glc analysis. A 1400-ml sample of commercial aqueous tangerine essence was saturated with sodium sulfate, extracted with three 400-ml portions of distilled methylene chloride, and concentrated by distillation to give a sample of anhydrous essence. Then three 400-ml portions of ethyl ether were used to extract the ethanol from the residual water solution. The ether extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The methylene chloride and ether extracts were each analyzed by gas chromatography.

The glc analyses were made on an F&M Model 810 gas chromatograph using a thermal conductivity detector and equipped with a $^1/_4$-in. × 20-ft column packed with 20% Carbowax 20M on 60- to 80-mesh Gas Chrom P. The oven temperature was programmed from 80° C to 225° C at 1° C per min with a helium flow of 60 ml per min. When separation of individual components was not complete, the mixture was collected and rechromatographed on a $^1/_4$-in. × 20-ft column packed with 10% of the nonpolar liquid phase UCW-98 (Applied Science Lab., Inc., State College, Pa.) on 60- to 80-mesh Gas Chrom P. For all runs, the injection temperature was 250° C and the detector temperature was 280° C. Injection volume was 25 μl. Fractions were either collected in short capillary tubes for infrared and mass spectral analysis, or were run into the mass spectrometer directly from the gas chromatograph. Mass spectra were obtained with either the Bendix Model 3012 (TOF) or the CEC Model 21-490 mass spectrometer equipped with a Becker-Ryhage jet separator, and infrared spectra on a Perkin-Elmer Model 137 spectrophotometer.

RESULTS AND DISCUSSION

Glc separation of the components extracted from tangerine essence with methylene chloride is shown by the chromatogram in Figure 1. Identity of peaks on the glc chromatogram (Figure 1) is listed in Table I. Identifications of acetaldehyde, acetone, methanol, ethanol, 1,1-diethoxyethane, ethyl acetate, and methyl butyrate were made by comparing the mass spectra and retention times with those of known compounds. The remaining constituents were identified by comparison of infrared spectra, mass spectra, and retention times with those of known compounds.

The glc analysis of the ether extract shows a large quantity of ethanol as was also found in the comparable extract of grapefruit essences (Moshonas and Shaw, 1971). Small quantities of acetaldehyde, methanol, and acetone were also found in this fraction.

All of the compounds listed are being reported as tangerine essence constituents for the first time. Thymol, piperitenone, 1,8-*p*-menthadiene-9-ol, and 1,1-ethoxymethoxyethane are constituents which have not been previously found in any of the citrus fruit essences. However, thymol and 1,8-*p*-

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Table I. Identity of Tangerine Essence Constituents from the Gas Chromatogram (Shown in Figure 1)

1. Acetaldehyde	15. Hexanol
2. Acetone	16. *cis*-3-Hexen-1-ol
3. 1,1-Ethoxymethoxyethane	17. *trans*-Linalool oxide[b]
4. 1,1-Diethoxyethane	18. *cis*-Linalool oxide[b]
Ethyl acetate	19. Linalool
Methylene chloride[a]	Octanol
5. Methyl butyrate	20. Terpinene-4-ol
6. 2-Methyl-3-buten-2-ol	21. *trans*-2,8-*p*-Methadien-1-ol
7. Ethyl butyrate	22. Ethyl 3-hydroxyhexanoate
8. Isobutyl alcohol	23. α-Terpineol
9. Hexanal	24. Citronellol
10. Butanol	25. Nerol
11. 1-Penten-3-ol	26. Perillaldehyde
12. Isopentyl alcohol	27. Piperitenone
13. Limonene	28. 1,8-*p*-Menthadien-9-ol
2-Hexenal	
14. Octanal	29. Thymol

[a] Solvent. [b] Tetrahydrofuran series; Felix *et al.* (1963).

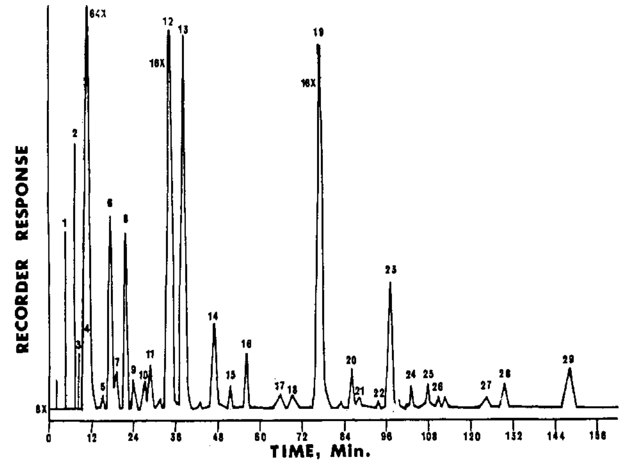

Figure 1. Chromatogram of nonaqueous tangerine essence

menthadiene-9-ol have been identified as constituents of tangerine peel oil by Hunter and Moshonas (1966) and thymol was found in tangerine peel and leaf oils by Attaway *et al.* (1967). The 1,1-ethoxymethoxyethane was only recently identified as a citrus component and reported in grapefruit essence oil by Coleman *et al.* (1972).

Due to losses which occurred during the separation procedure, quantitative data cannot be accurately reported. The glc analysis indicates the major tangerine essence constituents to be ethanol, methanol, acetaldehyde, acetone, ethyl acetate, 1,1-diethoxyethane, 2-methyl-3-buten-2-ol, isobutyl alcohol, isopentanol, octanal, *cis*-3-hexene-1-ol, linalool, terpinene-4-ol, α-terpineol, and thymol.

Although all of the isolated constituents have potent and distinctive odors, no one compound was found to have a characteristic tangerine odor. Several minor and trace constituents remain to be characterized but this report covers the major and probably the most important compounds.

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