Analysis of Volatile Flavor Constituents from Grapefruit Essence

Manuel G. Moshonas and Philip E. Shaw*

Thirty-two volatile flavor compounds were identified as aqueous grapefruit essence constituents after extraction of the aqueous essence with methylene chloride and ether, and separation of the extracted components by gas-liquid chromatography. In addition to the major extracted constituent, ethanol, there were 14 other alcohols, six aldehydes, four esters, two ethers, *d*-limonene, acetal, nootkatone, and two other ketones. Twenty-three of these compounds are being reported for the first time as grapefruit juice constituents.

During the concentration of citrus juices, an aqueous condensate is collected that is referred to as "essence." This essence has a pleasant aroma characteristic of the fresh fruit and, in the case of orange essence, has become an important flavor enhancement material for orange products. Many of the volatile flavor components of orange essence have been isolated, identified, and reported in a number of publications (Wolford *et al.*, 1962, 1967; Schultz *et al.*, 1964, 1967).

Grapefruit essence currently can be collected in commercial essence recovery units, but so far it has not been widely used to enhance the flavor of grapefruit products. However, the consumer acceptance of orange essence and the availability of grapefruit essence for addition to grapefruit products indicate the need for information on the flavor constituents in grapefruit essence. The only previous report on volatile grapefruit juice constituents was that of Kirchner *et al.* (1953a,b). The present paper describes the separation and identification of 32 volatile flavor constituents of aqueous grapefruit essence. Twenty-three of these are being reported for the first time as grapefruit juice components.

EXPERIMENTAL

Anhydrous grapefruit 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 grapefruit essence was saturated with sodium sulfate, extracted with three 400 ml portions of distilled methylene chloride, and concentrated by distillation through a Vigreux column to give a sample of anhydrous essence. The residual water solution was extracted with three 400 ml portions of distilled ethyl ether in order to remove the ethanol. The ether extract was dried over anhydrous sodium sulfate and the ether was removed under reduced pressure.

Fruit and Vegetable Products Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture, Winter Haven, Fla. 33880

The individual essence constituents were separated on an F and M Model 810 gas chromatograph using a thermal conductivity detector and containing a 1/8-in. × 20-ft column packed with 20% Carbowax 20M on 60 to 80 mesh Gas-Chrom P. The oven temperature was programmed from 80 to 225° C at 1° C per min with a helium flow of 30 ml per min. When separation of individual components was not complete, the mixed components were rechromatographed on a 1/4-in. × 20-ft column packed with 10% of the nonpolar liquid phase UC W-98 (Applied Science Lab. Inc., State College, Pa.) on 60 to 80 mesh Gas Chrom P. For all runs, the injector temperature was 250° C and the detector temperature was 280° C. Injection volume was 20 μl. Fractions were either collected in short capillary tubes for infrared and mass spectral analysis, or were run into the mass spectrometer from the gas chromatograph. Mass spectra were obtained with either the Bendix Model 3012 (TOF) or the CEC type 21-490 mass spectrometer, and infrared spectra on a Perkin-Elmer Infracord Model 137 spectrometer.

RESULTS AND DISCUSSION

Gas chromatographic analysis of the ether extract shows this fraction to be mostly ethanol. Small quantities of methanol and acetal were also isolated. Separation of the components extracted from the grapefruit essence with methylene chloride is shown by the chromatogram in Figure 1. Identifications of acetaldehyde, methanol, ethanol, acetone, acetal, and ethyl acetate were made by comparison of 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.

Peaks 3 and 22 shown in Figure 1 are each mixtures of two constituents. Using the UC W-98 column, ethyl acetate and methylene chloride were separated from peak 3 and α-terpineol and neral from peak 22.

Of the 32 flavor constituents (Figure 1) isolated from grapefruit essence, 12 were considered major and 20 minor by indications of relative amounts by the gas chromatogram.

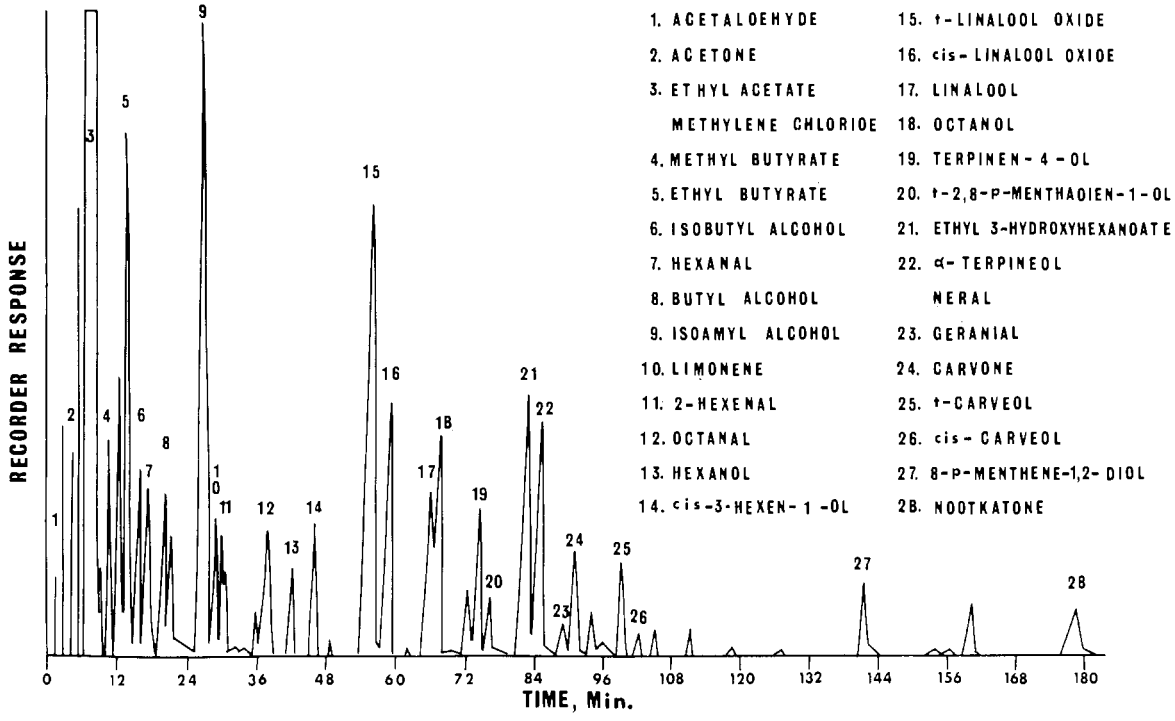

Figure 1. Chromatogram of nonaqueous grapefruit essence

Major constituents were ethanol, acetal, ethyl acetate, ethyl butyrate, isoamyl alcohol, *cis*- and *trans*-linalool oxide (tetrahydrofuran series, Felix *et al.*, 1963), linalool, *n*-octanol, α-terpineol, ethyl 3-hydroxyhexanoate, and terpinen-4-ol. Compounds identified in smaller quantities were methanol, acetaldehyde, acetone, methyl *n*-butyrate, isobutyl alcohol, *n*-hexanal, *n*-butyl alcohol, *d*-limonene ($[\alpha]^{29°\,C}_{D}$ + 112° C [C 1.07 in EtOH]), 2-hexenal, *n*-octanal, *n*-hexanol, *cis*-3-hexen-1-ol, *trans*-2,8-*p*-methadiene-1-ol, neral, geranial, carvone, *cis*- and *trans*-carveol, 8-*p*-menthene-1,2-diol, and nootkatone. These components all have distinctive aromas which may contribute to the characteristic grapefruit aroma. Nootkatone, however, is one of those most characteristic of grapefruit odor.

Among the volatile constituents of grapefruit juice reported by Kirchner *et al.* (1953a,b) were nine of the compounds identified here. These included acetaldehyde, methanol, acetone, and ethanol as volatile water soluble constituents and limonene, carvone, linalool, α-terpineol, and 3-hexen-1-ol as volatile oil constituents of grapefruit juice. In their volatile oil fraction, carveol, linalool oxide, and citral were also reported. Recent advances in gas-liquid chromatography have made possible the further separation of these into *cis*- and *trans*-carveol, *cis*- and *trans*-linalool oxide, and neral and geranial. Several minor and trace constituents remain to be characterized but this report covers the major, and probably most important components.

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