# Analysis of Carbonyl Flavor Constituents from Grapefruit Oil

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Twenty-two carbonyl compounds were isolated and identified as volatile grapefruit oil constituents. Vacuum distillation, column chromatography, and gas chromatography were used for separation and purification, and identifications were made by infrared spectroscopy and mass spectrometry. Twelve aldehydes were identified as heptanal, octanal, nonanal, decanal, undecanal, dodecanal, neral, geranial, perillaldehyde, citronellal, α-sinensal, and β-sinensal. Nine esters were identified as geranyl acetate, neryl acetate, perillyl acetate, 1,8-*p*-menthadien-9-yl acetate, octyl acetate, decyl acetate, citronellyl acetate, *trans*-carvyl acetate, and 1,8-*p*-menthadien-2-yl acetate. The lone ketone identified was nootkatone. Fourteen of these compounds are being reported for the first time as grapefruit oil constituents.

In the continuing investigation of composition of the various essential oils of citrus fruit and the relationship of composition to flavor and aroma, this laboratory has reported on the terpene hydrocarbons, sesquiterpene hydrocarbons (Hunter and Brogden, 1965), and alcohols (Hunter and Moshonas, 1966) in the volatile fraction of grapefruit oil. The close similarities of these fractions with comparable fractions of orange and tangerine oil indicates that the volatile carbonyl fractions of the various citrus fruit will have the greatest impact on the flavor and aroma which characterizes each citrus fruit.

Researchers have given little attention to the systematic identification of the carbonyl fraction of grapefruit peel oil. Reported carbonyl containing constituents of grapefruit peel oil include citral (Levi and Laughton, 1959), the straight chain saturated aldehydes $C_7$ through $C_{12}$ (Stanley *et al.*, 1961), nootkatone (MacLeod and Buigues, 1964), and geranial and octanal (Attaway *et al.*, 1967).

The present study reports the identification of the aldehydes, ketones, and esters isolated from the volatile fraction of commercial cold-pressed grapefruit oil. The eight previously reported carbonyl constituents have been isolated and identified, as well as 14 compounds never before isolated and identified as constituents of grapefruit peel oil.

## EXPERIMENTAL

**Spectroscopic Measurements.** Mass spectra were obtained with a Bendix Model 3012 (TOF) mass spectrometer, and infrared spectra were obtained on a Perkin-Elmer Infracord Model 137-A.

**Separation Procedure.** Cold-pressed grapefruit peel oil (19 l.) was distilled at 36° C and 1–0.6 mm in a rotary evaporator until most of the terpene hydrocarbons (99% *d*-limonene) were removed. The residue, 1.7 l., was further distilled with a single pass through an Arthur E. Smith Rota Film molecular still operating at a temperature of 105° C and a pressure of 0.7–0.3 mm. A 120-g volatile fraction was collected for further analysis. The molecular still was used because the grapefruit oil would be exposed to 105° C heat for a very short time (7 to 10 sec). These conditions minimize the possibility of decomposition which could occur at higher temperatures or long exposure to heat.

Ten grams of distillate from the molecular still were separated into three fractions on a 1 in. × 15 in. 9° C water-jacketed column containing Fisher Florisil deactivated by addition of 6% water. The fractions were eluted successively with 400 ml of distilled hexane to remove the hydrocarbons, 400 ml of distilled ethyl ether to remove the nonalcoholic oxygen-containing materials, and 400 ml of absolute ethanol to remove the alcohols. The weight of the material of each fraction upon removal of the solvent was as follows: hexane, 6.7 g; ether, 2.2 g; and ethanol, 1.1 g. Most of the carbonyl-containing compounds were in the ether fraction based on the relative intensity of the carbonyl stretching band in the infrared spectrum. However, since infrared analysis also indicated weak carbonyl bands in the other fractions, each of the three fractions was analyzed for carbonyl-containing compounds.

Analysis of the fractions was carried out on an F&M Model 810 gas chromatograph equipped with a thermal conductivity detector and one of the following three columns: a $^3/_8$ in. × 15 ft preparative column packed with 20% Carbowax 20M on 60–80 mesh Chromosorb P which was used to separate a fraction into a number of area cuts; a $^1/_8$ in. by 20 ft analytical column packed with 20% Carbowax 20M on 60–80 mesh Chromosorb P and a 0.25 in. × 20 ft analytical column packed with 10% UCW-98 on 60–80 mesh Chromosorb P. The two analytical columns were used to separate area cuts into the pure components. The helium flow for these columns was 60 ml per min. The oven temperature was programmed from 100 to 225° C at 1° C/min and the injection port and detector temperatures were 275° C.

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**Table I. Compounds Identified in Grapefruit Peel Oil**

| | |
|---|---|
| heptanal | *n*-decyl acetate[a,b] |
| octanal | citronellyl acetate[a] |
| nonanal | *t*-carvyl acetate[a] |
| decanal | 1,8-*p*-menthadien-2-yl acetate[a] |
| undecanal | neral[a] |
| dodecanal | geranial |
| geranyl acetate[a,b] | perillaldehyde[a] |
| neryl acetate[a,b] | citronellal[a,b] |
| perillyl acetate[a] | α-sinensal[a] |
| 1,8-*p*-menthadien-9-yl acetate[a] | β-sinensal[a] |
| *n*-octyl acetate[a,b] | nootkatone |

[a] Isolated and identified as a component of grapefruit peel oil for the first time. [b] Tentatively identified (Kesterson and Hendrickson, 1963).

## RESULTS AND DISCUSSION

Particular care was taken to prevent decomposition and/or rearrangement of compounds by using procedures such as vacuum and molecular still distillation and water-cooled columns for liquid chromatography, all of which kept the heat contact of the oil constituents to a minimum.

The compounds isolated and identified are shown in Table I. Each compound was identified by comparison of its infrared spectrum, mass spectrum, and retention time with those of the known compound. Previously reported carbonyl-containing compounds which were found are heptanal, octanal, nonanal, decanal, undecanal, dodecanal, geranial, and nootkatone. Carbonyl-containing compounds being reported for the first time as grapefruit oil constituents are: geranyl acetate, neryl acetate, perillyl acetate, 1,8-*p*-menthadien-9-yl acetate, *n*-octyl acetate, *n*-decyl acetate, citronellyl acetate, *trans*-carvyl acetate, 1,8-*p*-menthadien-2-yl acetate, neral, perillaldehyde, citronellal, α-sinensal, and β-sinensal. All of these constituents have potent and distinctive odors which probably contribute to the characteristic grapefruit flavor and aroma.

A close comparison of the volatile constituents identified from cold-pressed grapefruit and orange oil shows a great similarity between the terpene hydrocarbons, sesquiterpene hydrocarbons (Hunter and Brogden, 1965), and alcohols (Hunter and Moshonas, 1966) of the two oils.

In the carbonyl-containing constituents one finds notable differences in the qualitative and estimated quantitative make-up of the two oils (Moshonas and Lund, 1969). The major orange oil carbonyls were octanal, nonanal, citronellal, decanal, neral, geranial, carvone, nootkatone, α-, and β-sinensal, as estimated from the relative size of peaks in the gas chromatograms. Due to losses which occur during the separation procedure, as well as the difficulty of quantitative evaluation of some glc peaks, quantitative data cannot be accurately reported. The major grapefruit oil cabonyls are estimated to be geranyl acetate, neryl acetate, octyl acetate, 1,8-*p*-menthadien-2-yl acetate, citronellyl acetate, 1,8-*p*-menthadien-9-yl acetate, decanal, perillyl aldehyde, and nootkatone. This comparison suggests that the carbonyl-containing constituents play the most important role in determining the characteristic flavor and aroma of each citrus fruit.

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