

# CANNING AND STORAGE EFFECTS

## Volatile Water-Soluble and Oil Constituents of Valencia Orange Juice

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The nature of the chemical changes in the water and oil constituents of the volatile flavoring material of fresh, freshly canned, and stored canned California Valencia orange juices has been investigated. Acetic, propionic, isovaleric, and traces of butyric acid were found in the stored juice. There was a decreased acetaldehyde content and traces of diacetyl. A  $C_6H_8O_2$  unsaturated acid previously found in grapefruit juice was present in all three orange juices. Twenty-nine compounds from the oil fraction were identified and their amounts determined in each of the three juices. Analyses were made by chromatographic techniques when possible. The major changes in the oil fraction of orange juice on canning and storage were loss in total volatile oil, conversion of hydrocarbons to alcohols, and loss in esters, aldehydes, and terpene aliphatic alcohols. The predominant off-flavor of stored canned orange juices appears to arise from the non-volatile precursors.

THE VOLATILE FLAVORING CONSTITUENTS of orange juice have been considered in this study to be materials that can be removed from the juice by distillation methods. These include low-boiling organic constituents and high-boiling oils, the latter being removed as aqueous azeotropes.

If these volatile constituents are removed from the juice by distillation at atmospheric pressure, the recovered fraction has an odor strongly suggesting that its composition has been considerably altered in the process. If they are removed at reduced pressures and correspondingly lower temperatures, the aroma of the recovered fraction resembles more closely the aroma of the original juice. The lower the temperature of distillation the more closely the volatiles resemble the original fruity aroma.

A citrus juice from which a portion of the water has been removed by distillation shows a definite change in flavor, and it was early recognized that the aroma of orange juice was associated with the volatile fraction (10). It was also shown that the flavor of orange juice is largely lost by evaporation, but that this loss may be partly overcome by the addition of fresh juice to the concentrate to restore flavor and aroma (22).

The flavor of a concentrated orange juice which has been restored to its original strength by the addition of pure water tastes insipid and is lacking in orange character (27). It is generally recognized that the flavor and aroma of fresh orange juice, as well as certain off-flavors of the processed juice, are associ-

ated with the volatile fractions (2, 4, 11). These fractions consist of constituents soluble and insoluble in water; whereas some of the aroma resides in the water-soluble fraction (10, 16, 23), most of the characteristic flavor and aroma of citrus juices is considered to be in the volatile, sparingly water-soluble, oil fractions (14, 16, 23, 27).

The method of extraction of the juice from the fruit results in the incorporation of some peel oil into the juice, but the juice itself contains some oil present in the juice sacs. In experiments in which fruit was carefully peeled and washed, appreciable amounts of oil were recovered from the juice sacs (2, 4, 23, 27). Globules of oil have been demonstrated by histological studies on the juice sacs of various citrus fruits (6, 26).

Orange juice has been investigated extensively, particularly as regards changes in the composition of the volatile fractions resulting from heating and storage. Hall and Wilson (10) investigated the volatile materials obtained from 10,000 gallons of fresh California Valencia orange juice.

They reported the following constituents: acetone, acetaldehyde, ethyl alcohol (0.018% on separate sample), formic acid, citronellal, caprylic acid as ester, acetic acid as ester, formic acid as ester, isoamyl alcohol, phenyl ethyl alcohol, possibly geraniol,  $\alpha$ -terpineol, and a  $C_{10}H_{18}O$  alcohol similar to linalol.

Hydrogen sulfide has been reported in green oranges and in orange juice

oxygen (24), and seasonal acetaldehyde and alcohol contents of orange juice have been determined (32).

This paper reports the isolation and identification of the constituents of the volatile water-soluble and oil fractions from freshly reamed, canned, and stored canned California Valencia orange juice and represents a continuation of long-term studies on citrus flavoring (14).

### Water-Soluble Constituents

#### Experimental

In the preparation of the canned strength orange juice used in this study, the processing methods followed standard commercial practices. Arrangements were made to purchase the oranges from a commercial processor, who selected oranges were carefully selected to prevent the inclusion of soft and rotten fruit and thoroughly washed. Total solids in the juice was 13.8%, and citric acid (as citric acid) was 1.26%.

The juice, obtained from an automatic citrus juice extractor, was screened and run into a large stainless steel storage tank. One third of the juice was frozen for delivery to the laboratory for immediate analysis, while the remainder of the juice was pasteurized at 92° C. (195° F.) and filled directly into 46-ounce enamel-lined cans. After being cooled and sealed, the cans were cooled to approximately 38° C. (100.4° F.) and passed through a cold water tank before being packed in cartons. The total volumes of orange juice were determined by weighing the juice and

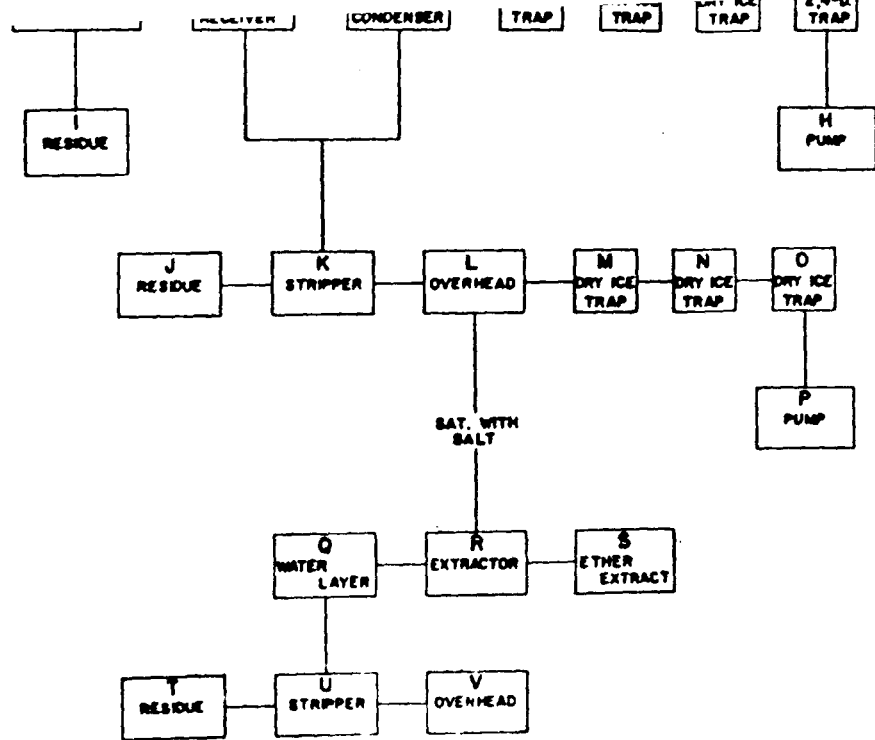


Figure 1. Flowsheet for separation of volatile constituents from orange juice

of stored canned juice held at room temperature for 3 years.

A flowsheet describing separation of the volatile material from the juice appears in Figure 1. The frozen, fresh Valencia orange juice (3000 gallons) was thawed by running through a Seprosieve into a warm water-jacketed kettle equipped with a stirrer, and then fed directly into the evaporator, *A*, while still cold. Distillation was carried out at 40 mm. of mercury absolute, with the evaporator contents maintained below 45° C. (113° F.) at all times, until 75% of the juice had distilled. The evaporator was heated by steam at 8-pound gage pressure (112° C., 233.6° F.). [It was found by test runs that orange juice distills its volatile oil less readily than grapefruit juice (16), so it was necessary to still off 75% of the juice before essentially all of the oil was removed.] The still was a long vertical-tube, natural-circulation, vacuum evaporator with an internal vertical-liquid separator. The vapors passed from the top of the evaporator through two water-cooled stainless steel condensers into flask, *B*, at room temperature. This flask was connected to the vacuum pump, *H*, through another condenser, *C*, refrigerated with a 1° C. (34° F) brine system, and a series of traps, *D, E, F*, maintained at -78° C. (-108° F.) with dry ice and alcohol. A trap, *G*, containing 2,4-dinitrophenylhydrazine in sulfuric acid was inserted just ahead of the pump to detect acetaldehyde. The condensate from the room temperature, *B*, and refrigerated receivers, *C*, was pumped to a stainless steel stripping column, *K*, in

column was also operated under vacuum with a 1° C. (34° F.) condenser and refrigerated receiver, *L*, connected through a series of dry ice traps, *M, N, O*, to the vacuum pump, *P*, in order to collect the volatiles. By this means the evaporator distillate was reduced to 150 gallons. The distillate was saturated with salt and extracted with diethyl ether in a continuous extractor, *R*, under a pressure of 360.7 mm. of mercury absolute. Ether used in this work was anhydrous analytical grade containing not more than 0.01% alcohol. Prior to use it was checked to make sure no peroxides were present. Approximately 5 gallons of ether were used to each 1000 gallons of juice. The water layers in the various cold traps were separated from the oils, saturated with salt, and extracted with ether. All of the ether-extracted water fractions were then combined, freed of excess salt and ether, and concentrated in the stripping column to 5 gallons in

soluble material, *V*. This concentrate was then carefully fractionated on Podbielniak Hyper-Cal column, and the resulting fractions were systematically examined by microtests for carbonyl compounds, alcohols, esters, acids, and sulfur and nitrogen compounds.

The combined ether extracts of the water-layer condensates from the evaporation of the juice were freed of ether by distillation on the Hyper-Cal column. Low-boiling alcohols present in this fraction were fractionally distilled on this column. The combined oil layers from the condensers, *B, C*, the cold traps, *D, E, F, M, N, O*, and the oil remaining after removal of the low-boiling alcohols from the ether extract, were analyzed.

The freshly canned juice and the juice that had been stored for 3 years were distilled in a similar manner.

As the residue, *M*, from stripping the evaporator distillate from stored juice was acidic, a portion was worked up to determine which acids were present. Thirty gallons of the residue were neutralized with sodium hydroxide and evaporated to dryness, and 4.76 grams of sodium salts were recovered. From a similar treatment of 58 gallons of residues from fresh juice, and 14 gallons from freshly canned juice there were obtained 1.28 and 0.7 grams of sodium salts. This material was converted to the *p*-phenylphenacyl esters (7) for chromatographic separation and identification of the acids (17).

Table I gives the approximate amounts of the compounds found in the volatile water-soluble fractions of the three juices.

### Results and Discussion

**Carbonyls.** A crystalline 2,4-dinitrophenylhydrazone (melting point 167.5° C.) was identified as that of acetaldehyde by a mixed melting point with a known sample. It was also identified by the dimedone derivative (melting point 143° C.), and by the preparation of ethylidene di-2-naphthyl oxide (melting point 173° C.).

Table I. Volatile Water-Soluble Constituents of Fresh, Freshly Canned, and Stored Canned Valencia Orange Juices

	Mg. per Kg. of Juice		
	Fresh	Freshly canned	Stored canned
Acetaldehyde	3.0	3.0	0.8
Furfural	Trace	Trace	5.1
Acetone	Trace	Trace	Trace
Diacetyl	...	...	Trace
Ethyl alcohol	380	550	484
Methanol	0.8	Present	62
Hydrogen sulfide	Trace	Trace	None
Acetic acid	2.8	5.8	18.6
Propionic acid	...	...	0.1
Butyric acid	...	...	Trace
Isovaleric acid	...	...	0.4
C <sub>6</sub> H <sub>5</sub> COOH	0.1	0.1	...

## CITRUS FLAVORING

# Volatile Water-Soluble Constituents of Grapefruit Juice

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The nature of the chemical changes taking place in the volatile water-soluble flavoring constituents of grapefruit juice resulting from canning and storage has been investigated. There is only a small difference in the composition of the fresh and the freshly canned juices but these differ greatly from the stored juice. The freshly canned juice has a small amount of volatile acids and a trace of furfural not present in the fresh juice. The stored juice has a considerable increase in the volatile acids, methanol, and furfural. The lack of hydrogen sulfide in the freshly canned juice is taken to be due to deaeration before canning, and its reappearance in the stored juice as evidence of the breakdown of some sulfur compound in the juice. The volatile acids found in the freshly canned and stored juice were acetic and two unsaturated acids with the empirical formula  $C_6H_8O_2$ . A trace of a fourth acid was found in freshly canned juice in too small an amount to be identified.

THE FLAVORING CONSTITUENTS OF FRUITS have not been extensively investigated, and in only a few studies have the flavoring compounds been isolated and identified in an exhaustive manner (4, 5, 7-10, 17). Little work has been done on the chemistry of the flavoring constituents in canned fruit juices, and scarcely anything is known of the effect of the canning process on these constituents (1, 3, 11, 16).

The following investigations on grapefruit juice (*Citrus paradisi* Macfadyen) were carried out to determine the chemical nature of the volatile constituents in fresh juice, and particularly the effect of canning and storage on these constituents. Canned grapefruit juice develops an off-flavor on standing, which is distinct from the cooked flavor produced during the canning process. Although the exact nature of the constituents in the juice that produce flavor deteriorations is unknown, the flavor characteristics of this juice are due primarily to the volatile compounds which, if removed by vacuum distillation, leave the residue tasting merely sweet and sour. Therefore, it was desired to begin these studies by determination of the

volatile flavoring constituents in fresh, freshly canned, and stored canned juices.

This paper is a report on the isolation and identification of the volatile water-soluble constituents obtained from 2760 gallons of freshly reamed Marsh seedless grapefruit juice, 2470 gallons of freshly canned grapefruit juice, and 2470 gallons of stored canned juice.

In order to assure comparable juice throughout the experiment, each batch of fruit was divided into two lots, one for studies of fresh juice and the other for studies of the freshly canned and storage juices. The canned juice for the storage work was held at room temperature (27° to 32° C.; 80° to 90° F.) for 4 years to develop storage off-flavors. This long period was selected because it was suspected that the total amount of change in the flavoring constituents would be small. Table I gives the approximate amounts of the compounds found in the volatile water-soluble fractions of the three juices.

### Experimental Work

Mature orchard-run Marsh seedless grapefruit [total soluble solids 11.74%, total acid (as citric acid) 1.30%] that had been hand sorted to remove soft

and damaged fruit was used in these studies. Two shipments of fruit were received per week, so that none of the fruit was stored for more than 2 days. The fresh fruit was stored at room temperature.

Juice from freshly hand-reamed grapefruit (2760 gallons) was charged into the evaporator in 10-gallon batches. The distillation was carried out at 40 mm. of mercury absolute, with the evaporator contents maintained below 45° C. (113° F.) at all times, until 50% of the juice had distilled over. The evaporator was heated by steam at 8 pounds' gage pressure (112° C. 233.6° F.). (It was found by a test run in which the distillate was collected in 10% lots, that essentially all of the volatile fractions were distilled off by the time the 50% point was reached.) The evaporator, a long vertical-tube, natural circulation, vacuum evaporator with a external vapor-liquid separator, had capacity under the above conditions of 10 gallons of distillate per hour. The vapors passed through two water-cooled stainless steel condensers into a flask at room temperature. This flask was connected to the vacuum pump through another condenser, refrigerated to 1° C. (34° F.) with an ethylene glycol system and then through a series of traps main-

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Summary of Volatile Water-Soluble Constituents of Fresh, Freshly Canned, and Stored Canned Grapefruit Juice

(Mg. per kg. of juice)

	Fresh Juice	Freshly Canned Juice	Stored Canned Juice
Acetaldehyde	1.45	0.33	0.6
Acetone	None	None	0.1
Furfural	None	Trace	8.2
Ethyl alcohol	400	400	460
Methanol	0.2	0.2	23
Acetic acid	None	1.9	23.3
Acid A (C <sub>6</sub> H <sub>8</sub> O <sub>2</sub> )	None	4.8	2.9
Acid B (C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> )	None	1.9	1.6
Acid C	None	Trace	None
Hydrogen sulfide	Trace	None	Trace

maintained at -78° C. (-108° F.) with dry ice and alcohol. The efficiency of this trapping system was checked by adding liquid air traps between the vacuum pump and the rest of the system. As the liquid air traps yielded only a trace of acetaldehyde and carbon dioxide, and in the case of the fresh juice a trace of hydrogen sulfide (15), they were eliminated in the regular runs, and replaced by a trap containing 2,4-dinitrophenylhydrazine in sulfuric acid to trap the acetaldehyde.

The condensate from the room-temperature receiver was kept at 3° C. (37.4° F.) until material had been collected for several days. The combined condensate was then further concentrated by returning it to the evaporator and taking off half of it as distillate under the same conditions as the original juice. This operation was repeated until the total volume of condensate from the room temperature receiver had been reduced to 175 gallons. This material was then saturated with sodium chloride and extracted in a continuous extractor with diethyl ether. (All ether used in this work was anhydrous analytical grade ether containing not more than 0.01% alcohol. Prior to use it was distilled from alkaline ferrous sulfate to remove peroxides. A total of 15 gallons of ether was used for each type of juice.) The water layers in the traps were separated from the oils which they contained, saturated with salt, and then extracted with ether. All of the ether-extracted water fractions were then combined, freed of excess salt and ether, and concentrated in the vacuum evaporator to 8 gallons for the recovery of the alcohol fraction. The alcohol in this alcohol-water solution was recovered by fractionation on a Podbielniak Hyper-Cal column.

The canned juice for both the freshly canned and stored studies was extracted and canned commercially. It was de-aerated at room temperature by flowing over a series of disks in a tank held at 97 mm. of mercury absolute. The juice was pasteurized at 88° C. (190.4° F.) by

directly into 46-ounce plain tin cans without previous cooling. After filling and sealing, the cans were cooled by a water spray to approximately 38° C. (100.4° F.) before being packed in cases. One half (2470 gallons) of this canned juice was then distilled in the same manner as the fresh juice.

The stored juice was distilled in the same manner as the fresh and freshly canned juices, except that the water-cooled condensate from the circulating evaporator was put through a stainless steel stripping column in order to concentrate the volatile water-soluble materials. In this manner the evaporator distillate was reduced to 140 gallons. This was then saturated with salt and extracted with ether. After removal of the salt and excess ether, the water layer was further concentrated to 4.3 gallons on the stripping column to recover the water-soluble material that was present. This volatile water-soluble concentrate was then carefully fractionated on a Podbielniak Hyper-Cal column, and the resulting fractions were systematically examined by microtests for carbonyl compounds, alcohols, esters, acids, and sulfur and nitrogen compounds.

The combined ether extracts of the water-layer condensates from the evaporation of the juice were freed of ether by distillation on the Podbielniak Hyper-Cal column. Any alcohols present in this fraction were fractionally distilled on this column. In the case of the stored-juice material, the oil remaining after the removal of ether and alcohol was extracted with sodium bisulfite to remove the large amount of furfural which was present.

Since the residue from the stripping of the evaporator distillate was acidic, 54.95 gallons (208 liters) of this residue were neutralized with sodium hydroxide. On evaporation of the neutralized solution, 14.27 grams of sodium salts were obtained. This material was converted to the *p*-phenylphenacyl esters (6) for separation and identification of the acids (14).

## Results and Discussion

**Aldehydes** Acetaldehyde was identified in the fresh juice fraction as a crystalline 2,4-dinitrophenylhydrazone melting at 167° C.; a mixed melting point with a known sample was not depressed.

Analysis. Calculated for C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>O<sub>4</sub>, N 24.95. Found, N 24.84. Fresh juice contained 1.45 mg. of acetaldehyde per kg. based upon analysis with 2,4-dinitrophenylhydrazine.

Acetaldehyde was determined in the distillate from the freshly canned juice and the stored juice in the same manner. The values for these were 0.33 and 0.6

juice fraction by a test with *p*-toluidine acetate. A trace of this aldehyde was found in the water-soluble freshly canned juice fraction by means of the same test; a small amount of the purified aldehyde was isolated from one of the oil fractions of the same juice. It was positively identified by the formation of a semicarbazone melting at 190-191° C. (corrected). A mixed melting point with a known sample of furfural semicarbazone was not depressed.

Analysis. Calculated for C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>, N 27.44. Found, N 27.01.

The preferred melting point for this derivative in the literature appears to be 203° C. (12). However, no analyses were found for a semicarbazone melting at this temperature, and Wolff (18) also reported a melting point of 190° C. for the semicarbazone of furfural, which yielded the theoretical values of carbon and hydrogen on analysis. A 2,4-dinitrophenylhydrazone was also prepared and melted at 224-226° C. The preferred melting point for this derivative is 229° C. (12).

The large quantity of furfural (8.2 mg. per kg. of juice) in the stored juice was isolated from the ether extract of the water distillate by means of the bisulfite addition product.

Acetone was found only in the stored juice in the amount of 0.1 mg. per kg. of juice. This was present in one of the alcohol fractions. It was identified as the 2,4-dinitrophenylhydrazone melting at 125-127° C. The melting point was not depressed when the derivative was mixed with a known sample of acetone 2,4-dinitrophenylhydrazone.

**Alcohols** Ethyl alcohol was identified in all three juice fractions as the crystalline 3,5-dinitrobenzoate melting at 92.3-93° C. Mixed melting points with a known sample did not show a depression. The fresh juice contained a minimum of 400 mg. of ethyl alcohol per kg., the freshly canned juice 400 mg. per kg., and the stored juice 460 mg. per kg.

Analysis. Calculated for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>, C 44.99; H 3.36. Found, C 44.92; H 3.31.

Methanol was detected in the distillate from all three juices. It was also identified by means of its 3,5-dinitrobenzoate, which melted at 107° C. Mixed melting points with a known sample were not depressed.

The methanol in the stored juice was separated by careful fractionation of the volatile fraction taken from the stripping column. The absolute amount of this methanol was determined by the refractometer method (19).

Because of the smaller quantities of methanol present in the fresh and the

contained 0.2 mg. of methanol per kg. of juice and the stored juice, 23 mg. per kg.

**Acids** As acidic material was found in the residue from the stripping column run of the stored juice and a small amount in the freshly canned juice, a sample of fresh juice was rechecked for the presence of volatile acids. The distillate from fresh grapefruit juice was neutral.

The *p*-phenylphenacyl esters obtained from the acids in the stripper residue of the stored juice were separated by chromatographic adsorption on silicic acid (14). The major portion of this was found to be the derivative of acetic acid, representing 23.3 mg. of acetic acid per kg. of juice. The melting point of the ester was 110–112° C. and a mixed melting point with *p*-phenylphenacyl acetate gave no depression.

A *p*-phenylphenacyl ester melting at 76–77° C. was obtained. This analyzed for the derivative of an unsaturated acid with a formula of  $C_6H_8O_2$ . Its unsaturated nature was further confirmed by a positive fluorescein-bromine test on a chromatostrip (13).

Analysis. Calculated for  $C_{20}H_{18}O_3$ , C 78.40; H 5.92. Found, C 77.20; H 6.04. This acid was present to the extent of 1.6 mg. per kg. of juice.

The *p*-phenylphenacyl ester of a second unsaturated acid melted at 120–126° C. It, too, analyzed for the derivative of an unsaturated acid with a formula of  $C_6H_8O_2$ . The acid was present to the extent of 2.9 mg. per kg. of juice.

nor sorbic acid, as evidenced by the melting points of the *p*-phenylphenacyl esters.

A small quantity of acetic acid was found in the ether extract of the freshly canned grapefruit distillate. As a further check on the acidic material, the distillate from a sample of freshly canned juice was neutralized and evaporated to dryness. The *p*-phenylphenacyl esters prepared from this were resolved into four derivatives. The acetic acid derivative represented 1.9 mg. of acid per kg. of juice. The two unsaturated acids found in the stored juice were also present in the freshly canned juice in the amounts of 1.4 mg. (76–77° C. melting derivative) and 4.8 mg. (120–126° C. melting derivative) per kg. of juice. A fourth acid was present in too small a quantity to be identified.

#### Acknowledgment

The authors wish to acknowledge the cooperation of A. J. Haagen-Smit and Glen Swinehart of the California Institute of Technology in the elementary analyses.

#### Literature Cited

- (1) Blair, J. S., Godar, E. M., Masters, J. E., Riester, D. W., *Food Research*, **17**, 235 (1952).
- (2) Boos, R. N., *Anal. Chem.*, **20**, 964 (1948).
- (3) Boyd, J. M., and Peterson, G. T., *Ind. Eng. Chem.*, **37**, 370 (1945).
- (4) Coppens, A., and Hoejenbos, L., *Rec. trav. chim.*, **58**, 675 (1939).
- (5) *Ibid.*, p. 680.
- (6) Drake, N. L., and Brotinsky, J., *J. Am. Chem. Soc.*, **52**, 3715 (1930).

G., Deasy, C. L., and Prater, A. N., *J. Am. Chem. Soc.*, **67**, 1646 (1945).

- (9) Haagen-Smit, A. J., Kirchner, J. G., Prater, A. N., and Deasy, C. L., *Ibid.*, **67**, 1651 (1945).
- (10) Hall, J. A., and Wilson, C. P., *Ibid.*, **47**, 2575 (1925).
- (11) Henry, R. E., and Clifcorn, L. E., *Canning Trade*, **70**, 7 (1948).
- (12) Hopkins and Williams Research Laboratory, "Organic Reagents for Organic Analysis," p. 121, Brooklyn, N. Y., Chemical Publishing Co., 1946.
- (13) Kirchner, J. G., Miller, J. M., and Keller, G. J., *Anal. Chem.*, **23**, 420 (1951).
- (14) Kirchner, J. G., Prater, A. N., and Haagen-Smit, A. J., *Ind. Eng. Chem., Anal. Ed.*, **18**, 31 (1946).
- (15) Kirchner, J. G., Rice, R. G., Miller, J. M., and Keller, G. J., *Arch. Biochem.*, **25**, 231 (1950).
- (16) Nolte, A. J., and von Loesecke, H. W., *Food Research*, **5**, 457 (1940).
- (17) White, J., *Ibid.*, **15**, 68 (1950).
- (18) Wolff, L., *Ann.*, **394**, 101 (1912).
- (19) Woodman, A. G., "Food Analysis," 4th ed., p. 511, New York, McGraw-Hill Book Co., 1941.

Received for review March 13, 1953. Accepted June 4, 1953. Presented before the Division of Agricultural and Food Chemistry at the 123rd Meeting of the AMERICAN CHEMICAL SOCIETY, Los Angeles, Calif. Work initiated under a cooperative agreement with the Desert Grapefruit Industry Committee, Inc., and continued on funds provided by the Research and Marketing Act of 1946. The mention of special instruments or materials throughout this paper does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.