Volatile Water-Soluble and Oil Constituents of Valencia Orange Juice

Methanol Food.

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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 associated 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, α-terpineol, and a $C_{10}H_{18}O$ alcohol similar to linalool.

Hydrogen sulfide has been reported in green oranges and in orange juice (*1, 18*). Furfural has been detected in orange juice stored in the presence of 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 in the volatile water-soluble and oil fractions from freshly reamed, canned, and stored canned California Valencia orange juices, and represents a continuation of long-term studies on citrus flavoring (*14, 16*).

Water-Soluble Constituents

Experimental

In the preparation of the canned single-strength orange juice used in this study, processing methods followed standard commercial practices. Arrangements were made to purchase the orange juice from a commercial processor, where the oranges were carefully selected to prevent the inclusion of soft and rotten fruit, and thoroughly washed. Total soluble solids in the juice was 13.8%, and total 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 mixing tank. One third of the juice was quick-frozen for delivery to the laboratory for immediate analysis, while the remaining juice was pasteurized at 92° C. (198° F.) and filled directly into 46-ounce citrus enamel-lined cans. After being filled and sealed, the cans were cooled to approximately 38° C. (100.4° F.) by passage through a cold water tank before being packed in cartons. The following volumes of orange juice were distilled and studied individually: 3000 gallons of freshly reamed juice, 2500 gallons of freshly canned juice, and 1520 gallons

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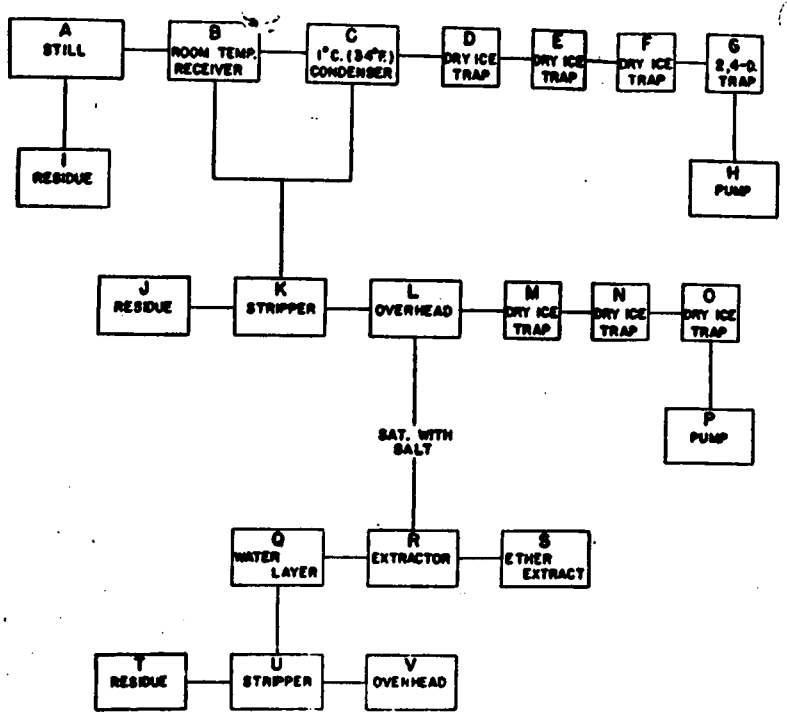

Figure 1. Flowsheet for separation of volatile constituents from orange juice

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 lost its volatile oil less readily than grapefruit juice (*16*), so it was necessary to distill 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 external 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 trap acetaldehyde. The condensate from the room temperature, *B*, and refrigerated receivers, *C*, was pumped to a stainless steel stripping column, *K*, in order to concentrate the volatile water-soluble materials. The stripping 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 order to recover the volatile water-soluble material, *V*. This 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 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-naphthyloxide (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 (3 years)
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_6H_7COOH	0.1	0.1	0.7
Other acids	0.1	...	...

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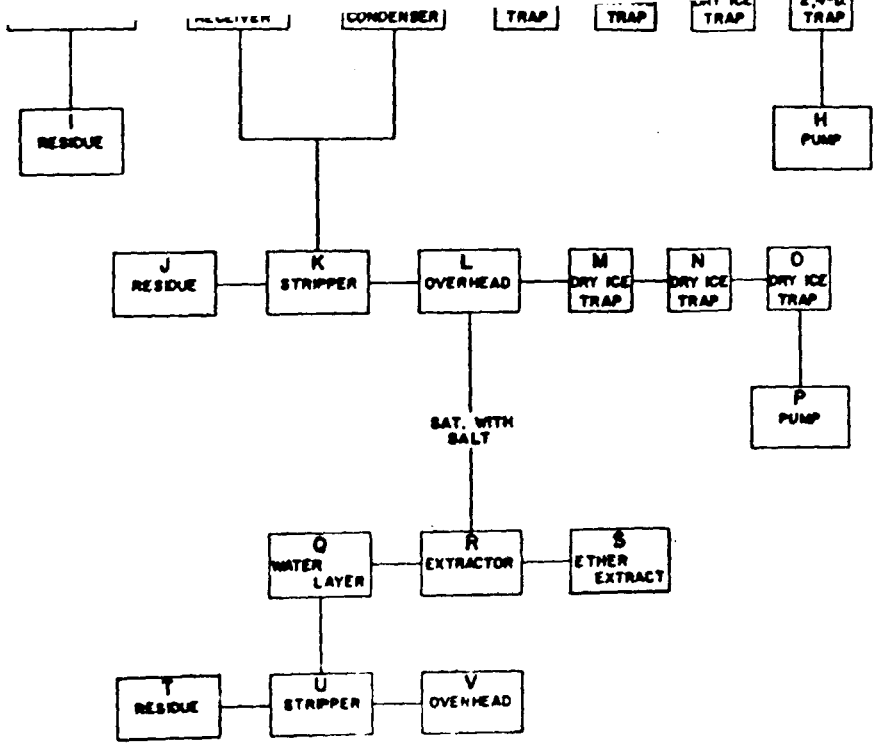

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