# RECOVERING VOLATILE FLAVOR COMPOUNDS FROM ORANGE ESSENCE OIL

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*Abstract.* **Two means were studied for separating volatile flavor components from orange essence oil by vacuum distillation. (a) Ethanol was added to Valencia orange essence oil and the resulting solution distilled to afford a water-soluble volatile fraction with a strong essence-like aroma. Upon gas chromatographic analysis of this fraction, 16 volatile components were identified, including one, diacetyl, not previously reported in orange essence oil. Most of the identified components are believed to contribute to the essence-like aroma of the oil. A taste panel judged that this volatile fraction contributed a desirable essence-like flavor in orange juice at its approximate threshold of 17 ppm. (b) Folded essence oil was prepared by distilling orange essence oil and blending the fractions more-volatile and less-volatile than limonene. When the folded oil in single-strength orange juice was compared to whole essence oil in the same juice, a taste panel could differentiate the two samples, but neither was judged to have more essence-like aroma and flavor. Both methods for separating volatile flavor components permit recovery of the D-limonene for separate marketing.**

Orange essence oil is the oily layer separated from aqueous essence when vapors from the first stage of an evaporator used to produce frozen concentrated orange juice are condensed in an essence recovery unit (2). The aroma of essence oil is similar to that of aqueous essence and cold-pressed orange oil combined. Because essence oil lacks the carotenoids and other high-boiling components that help stabilize cold-pressed oil (3),it usually is blended with cold-pressed oil to increase its storage stability.

The components of essence oil that are more volatile than the main component (D-limonene) are primarily responsible for the essence-like aroma of the oil (3, 8). These volatile components, when concentrated, might be useful in flavoring citrus products such as high-density concentrates and instant orange juice powders. In such products, concentrated "fresh" (essence-like) flavor fractions are advantageous since they do not appreciably increase the water or oil content of the product.

Volatile components of essence oil were concentrated by low pressure distillation, but D-limonene was still the main compound in the distillate (3). The presence in essence oil of several percent of a compound lower-boiling than D-limonene (such as ethanol) might minimize the quantity of D-limonene in the volatile distillate. In a recent study, distillation of a tangerine essence oil containing about 2 percent ethanol furnished a potent, water-soluble fraction of the most volatile components suitable for flavoring orange products (4).

The present study reports two distillation procedures for obtaining concentrated flavor fractions from orange essence oil: (a) a water-soluble flavor fraction from orange essence oil previously treated with ethanol, and (b) folded orange essence oil. The flavor potential of each fraction was evaluated in single-strength orange juice.

## Experimental

Valencia orange essence oil collected commercially (9) was obtained from a local citrus plant and stored at -5°F until needed.

### *Distillation Procedures*

A. *Separating water-soluble volatiles.* Absolute ethanol (7.25 g) was added to 390 g (460 ml) of Valencia orange essence oil and the resulting solution was distilled in a rotary evaporator (Büchi Rotavapor R, Type KRV 45/65, Rinco Instruments, Inc., Greenville, IL) to which a condenser cooled with chilled (9°C) water and two liquid nitrogen traps were attached in series.

Distillation at 2.7-3.3 mm Hg and a bath temperature of 26-33°C was continued until condensate began to appear on the chilled water condenser (5-10 min.). At that point, the first liquid nitrogen trap contained 8.56 g of material (essence oil volatiles). The second liquid nitrogen trap and chilled water condenser contained no distillate. Liquid nitrogen trap condensate was analysed by gas liquid chromatography described below.

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References to specific commercial products do not constitute endorsement.

B. *Preparing Folded Essence Oil.* Distillation of 438 g of orange essence oil (without added ethanol) in a rotary evaporator at 2.5 mm Hg and 55°C afforded 5.37 g of condensate in the first liquid nitrogen trap, 400 g of chilled water condensate and 28.1 g of pot residue (3). The liquid nitrogen trap condensate and pot residue were combined to yield a folded essence oil representing 7.6% of the original oil by weight. This was used in taste evaluation studies.

*Glc Analyses.* Essence oil water-soluble volatiles were analyzed on a Hewlett-Packard Model 7624A gas chromatograph using both polar and nonpolar stainless steel columns 0.20 in. i.d. by 20 ft. long. The polar column was packed with 20% Carbowax 20M and the nonpolar column with 20% UCW-98, both on 60- to 80-mesh Gas Chrom P. Temperature programming conditions were: 70°C isothermally for 28 min., then raised to 90°C at 30°C per min. and programmed at 2°C per min. to 225°C. Injection port temperature was 280°C, thermal conductivity block temperature was 285°C and He flow was 100 ml per min.

*Taste Panel Studies.* Two taste panel methods were used: (A) threshold determination by triangulation and (B) essence-like flavor preference by paired comparison.

Essence oil volatiles were evaluated in high quality juice reconstituted from frozen concentrated orange juice to which cold-pressed orange oil, but no aqueous essence, had been added. Folded essence oil was compared to whole essence oil by adding each to samples of a high quality frozen concentrated orange juice "evaporator pumpout" to which no cutback juice or cold-pressed orange oil had been added, and then reconstituting to single-strength juice. Taste panels were conducted as follows:

(A) *Triangulation tests* were employed for threshold level and folded oil strength determinations using 12 experienced tasters with two presentations each (1). In each presentation, the panelist was asked to select the one sample of the three that was different. To determine the threshold of detection, a relatively high level (83 ppm) of the volatile fraction in orange juice was used initially to acquaint the taste panel with the flavor being studied. Then, successive levels were approximately halved (41, 17 and 8 ppm) until the panel no longer could detect the different sample. For folded oil strength determinations, single-strength juice with 0.015% (150 ppm) whole Valencia orange essence oil was compared with juice flavored with 0.003% (30 ppm) folded essence oil (5-fold oil).

(B) *Paired comparison tests* for essence-like flavor evaluations were conducted with two presentations each to six panelists experienced in detecting essence added to orange juice (1). In each presentation, the panelist was asked to select from a pair the one sample that had "more essence-like aroma and flavor." For essence oil volatiles the level in the experimental sample was 17 ppm. For folded essence oil compared to whole essence oil, the levels were the same as used in the triangulation test (30 ppm and 150 ppm, respectively).

## Results and Discussion

When orange essence oil, with 1.83% of added absolute ethanol, was distilled under reduced pressure it yielded an anhydrous, water-soluble, volatile fraction having a pleasant, essence-like aroma. The water-solubility and the essence-like aroma made this fraction an attractive potential flavor fraction for orange products. To evaluate its potential, studies were made of both its approximate flavor threshold in orange juice and its contribution of "essence-like" flavor to juice. In the threshold determination, the 17 ppm level was the lowest which the panel could detect (17 of 24 judgments, or >99% significant) (6). In the essence-like flavor evaluation, all 12 judgments selected the sample containing the volatile fraction as having more essence-like character.

The presence in this water-soluble volatile fraction of a blend of components believed responsible for the essence-like character of essence oil was confirmed by glc analysis. Table 1 lists the components identified along with their retention times on both polar (20M) and nonpolar (UCW-98) columns. For each compound, mass spectra and retention times were compared with those for authentic samples. Quantities of components present in this volatile fraction are listed in Table 1 as area percent values, and were determined by integrating peak areas under the glc curve obtained using a polar column. Of the 16 components identified, all but one had been identified previously in orange essence oil and several were shown to be important to the essence-like aroma of the oil (3, 8). Diacetyl, the one component not found previously in essence oil, is believed to contribute to the aroma and flavor of orange essence, but is difficult to isolate and identify from aqueous essence.

Our method for concentrating the most volatile components in essence oil offers advantages over alternate methods considered. Essence oil

TABLE 1. VOLATILES FROM ETHANOL-TREATED ORANGE ESSENCE OIL

| Compound | Retention time (min) 20M | Retention time (min) UCW-98 | Area % 20M |
|---|---|---|---|
| Hexane | 3.5 | | 0.03 |
| Acetaldehyde + Heptane | 5.5 | | 0.01 |
| Acetone | 10 | | 0.03 |
| Ethyl acetate | 14 | 7 | 0.6 |
| Ethanol | 19 | 3 | 78.5 |
| Methyl butyrate + Diacetyl | 26 | 16 | 0.01 |
| Ethyl vinyl ketone | 31 | 13 | 0.01 |
| Ethyl butyrate + α-Pinene | 32.5 | 24, 44 | 0.6 |
| Hexanal | 37.5 | 41 | 0.04 |
| Sabinene | 42 | 48 | 0.15 |
| Myrcene | 45 | 49 | 0.3 |
| D-Limonene | 51 | 54 | 19.6 |
| Octanal | 56 | | 0.1 |

can be extracted with a large volume of a polar solvent, as for cold-pressed citrus oils (5), but the procedure is long and concentration of the solvent causes loss of volatiles that should be retained. Low-pressure distillation of essence oil, as reported previously (3, 8), affords a concentrated volatile fraction with an essence-like aroma. That fraction which is insoluble in water, cannot be added directly to single-strength orange juice. Furthermore, its high D-limonene content limits its addition to juices containing cold-pressed oil because an undesirably high oil level might result.

Flavor recovery by the present method is difficult to determine because, when added to orange juice, essence oil contributes peel oil-like as well as essence-like flavor. Present analyses show that the higher boiling components in essence oil (3) are absent in the volatiles from ethanol vacuum distillation. Thus no peel-oil-like flavors should be present, and none were noted by the taste panel.

A significant finding in the present study is that when orange essence oil was treated with a small volume of ethanol and the volatile flavor components removed by low temperature distillation, the D-limonene remained and could be marketed separately. Possibly a low water-to-oil ratio from an oil recovery unit could raise the ethanol content in the aqueous fraction (7) and thus provide an oil fraction similar in composition to the ethanol-treated oil reported here. A low water-to-oil ratio also can cause a decrease in total organic components collected (7).

Another means of concentrating the flavor components in essence oil utilized both the volatile and nonvolatile minor components. Folded orange essence oil was prepared by low-pressure distillation of essence oil followed by blending the fractions more-volatile and less-volatile than D-limonene. This folded oil represents only 7.6% by weight of the oil and, in preliminary taste panel tests, was about five times as potent as whole essence oil in flavoring orange juice. In a triangulation test comparing single-strength juice flavored with either 0.015% essence oil or 0.003% folded essence oil (5-fold oil) both samples had acceptable flavors, but the panel could distinguish between the two samples (15 of 24 judgments, or 99% significance) (6). In a paired comparison test a panel, experienced in detecting essence added to orange juice, had no significant preference for one sample as having more essence-like aroma and flavor. Thus, a folded essence oil with an acceptable flavor can be prepared from essence oil by distillation and most of the D-limonene can be recovered and marketed separately. The folded essence oil prepared by this method is more potent as a flavoring agent (five times) than the starting essence oil, but not in proportion to the fold (12 times) indicating that a significant amount of the flavoring components still remain in the D-limonene fraction. However, this folding procedure should increase its storage stability and its addition to citrus products will not raise the oil level as much as would whole essence oil.

Both concentrated fractions described herein contribute essence-like flavor to orange juice, and each has advantages for specific uses. Water-soluble essence oil volatiles would be recommended for adding directly to single-strength juices, drinks, concentrates, or instant orange juice powder where flavoring is needed without noticeably affecting the oil or water content. Folded essence oil would be useful for blending with cold-pressed oil to yield an oil with essence-like character. Also, folded essence oil might be added to concentrate or instant orange juice powder where both heavy oil-like and light essence-like flavor character are needed with considerably less increase in oil content than if whole essence oil were used.

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# EQUIVALENT COLOR SCORES FOR FLORIDA CONCENTRATED ORANGE JUICE FOR MANUFACTURING AND CANNED ORANGE JUICE

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*Abstract.* **Visual color scores and Citrus Colorimeter Citrus Red and Citrus Yellow readings were obtained on 3,629 samples of concentrated orange juice for manufacturing and 416 samples of canned orange juice produced in 9 commercial plants during the 1969-70 season. Although a regression equation derived from a statistical analysis of this data failed to discriminate between juices having a weak or a strong yellow color, it was found that the Color Scores of samples, which included both red and yellow color components, could be adjusted to reflect the correct color classification. Equivalent Color Scores were found to agree well with reported visual scores for both canned orange juice and concentrated orange juice for manufacturing. A few misclassified samples appeared at all color levels indicating that there was no bias in this method toward juices of deep, medium or pale color.**

The importance of color in juices (1) was brought out in a consumer survey test at the New York World's Fair where it was found that juice enhanced by the addition of artificial color was reported to have, "better body," be "sweeter," and have "more flavor" than juice reconstituted from the same concentrate without added artificial color.

The premium Florida product, Frozen Concentrated Orange Juice (FCOJ), must have a rich deep orange color. Only choice midseason and late season oranges, predominantly 'Pineapple' and 'Valencia' varieties respectively, produce juice of this color.

Traditionally, light colored juices from early varieties of fruit have been used by the processor to prepare concentrated orange juice for manufacturing (COJFM) or canned orange juice (COJ). In recognition of this difference in color quality, the citrus industry has given additional score points to pale orange colored products. To extend the usefulness of the Citrus Colorimeter from the measurement of FCOJ to all orange juice products, it was necessary to develop a method of measuring the color of these products.

The purpose of this paper is to compare objective and subjective color scores obtained from concentrated orange juice for manufacturing and canned orange juice. A method of relating colorimeter readings obtained from COJFM and COJ products to their respective visual scores is presented.

## Materials and Methods

During past years, Florida Frozen Concentrated Orange Juice has been scored for color with plastic standard comparator tubes developed by the USDA and the citrus processors. There are 6 tubes in use (5). They have been selected as being the best visual match for the range of colors found in orange juice varying from pale yellow to deep orange. The Hunterlab Citrus Colorimeter (HCC) (3), which is capable of measuring translucent orange juice color in values that can be related accurately to subjective color scores has been successfully applied to the measurement of Florida FCOJ. Huggart, Wenzel and

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