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## Flavor and Compositional Comparison of Orange Essences and Essence Oils Produced in the United States and in Brazil

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One commercial sample of each of aqueous orange essence and orange essence oil from Brazil was compared with three samples of each product produced in Florida. Brazilian and U.S. products were qualitatively identical, but minor quantitative differences were found. Sensory panels noted aroma differences between aqueous essences and essence oils produced in the United States and Brazil; similar aroma differences were found between these products produced by two different U.S. suppliers. When the products were used to flavor frozen concentrated orange juice (evaporator pumpout), however, no flavor differences were noted between any of the aqueous essences or essence oils.

The most widely used natural flavoring fractions for enhancing the fresh flavor and aroma of processed orange juice, particularly frozen concentrate, are aqueous orange essence and essence oil. Compositional flavor and aroma studies have shown that these fractions contribute fresh flavor top notes to processed juice products (Moshonas and Shaw, 1983). These two important byproducts are collected as the distillate from the second stage of an evaporator during concentration of freshly expressed orange juice (Johnson and Vora, 1983). Aqueous essence is separated from essence oil to produce a flavor fraction that is predominately a water-ethanol solution containing most of the volatile flavor constituents of fresh juice. Essence oil also contains some of the volatile components found in the juice but is largely made up of volatile components found in peel and juice oils. It differs greatly from the peel oil, however, in that it lacks the higher boiling compounds present in peel oil. Worldwide demand for orange juice products continues to increase, resulting in the need by the U.S. citrus industry to import large quantities of Brazilian frozen concentrate, aqueous essence, and essence oil in order to meet the demand of their domes-

tic and foreign markets. Brazil is expecting a record harvest of 250 million boxes (10 200 000 MT) of oranges for the 1989-1990 season while Florida's crop is expected to be 140 million boxes (5 700 000 MT), down from the high of 212 million boxes (8 700 000 MT) for the 1979-1980 season. (Florida Citrus Processors Assn., 1989).

The essence fractions used for flavoring have direct bearing on the quality of orange products to which they are added. This report compares flavor quality, aroma, and compositional profiles of aqueous essences and essence oils produced in the United States with those imported from Brazil.

### EXPERIMENTAL SECTION

Commercial aqueous orange essences and essence oils were obtained from citrus processing plants in the United States and in Brazil. Although typical commercial orange essences and essence oils are obtained from processing more than one cultivar, the major source of aqueous essence and essence oil in the United States is the Valencia cultivar and in Brazil it is the Pera cultivar. Since processors blend many samples to produce a uniform product, these are typical samples produced by each of the four processors.

**Flavor Evaluations.** Samples for the aqueous essence sensory tests were prepared by adding 3.3 mL (0.33%) of each essence to a 1-L base of reconstituted commercially prepared orange concentrate containing no flavoring materials (evaporator pumpout) and very little orange oil (0.004% v/v). Samples for the essence oil sensory tests were prepared by adding 190  $\mu$ L (0.019%) of oil to 1 L of reconstituted concentrate described above. An experienced 12-member flavor panel was used for paired comparison preference tests, with each member being given two presentations for a total of 24 judgements (Boggs and Hanson, 1949).

**Aroma Evaluations.** Triangle tests were run on aqueous orange essence, and paired comparison tests were run on essence oils obtained from oranges grown and processed in the United States and in Brazil. For each test, equal volumes of samples were placed in identical 5-mL screw-capped vials and presented at room temperature. The panel consisted of 12 experienced members, each of whom made two determinations. For triangle tests each panelist was presented with three samples, two of which were identical, and members were asked to indicate which sample was different. For paired comparison tests, each member was given two samples and asked to indicate whether the samples were the same or different.

**Gas Chromatography (GC).** GC data were obtained with a Hewlett-Packard Model 5880A instrument equipped with a flame ionization detector, a 50-m wide-bore (0.31–0.32-mm i.d.) capillary fused silica cross-linked 5% phenylmethyl silicone column (Hewlett-Packard, Avondale, PA), and a capillary inlet system fitted with a split line that allows the helium flow to be split at 100:1. Helium flow through the column was 1.5 mL/min. Injection port and detector temperatures were 275 °C. The column temperature was held at 60 °C for 4 min, then programmed to 200 °C at 6 °C/min, and held there for 15 min. The threshold was set at 0, peak width at 0.02, and chart speed at 1 cm/min. Aqueous essence samples (1.0  $\mu$ L) and essence oil samples (0.2  $\mu$ L) were injected manually.

**Mass Spectra.** Identification of constituents was made by gas chromatography–mass spectrometry (GC–MS). A Hewlett-Packard Model 5970B, MSD, GC–MS was used with a 50-m wide-bore (0.31–0.32-mm) fused silica column of cross-linked 5% phenylmethyl silicone. The initial oven temperature was held at 55 °C for 9 min, then programmed at 7.5 °C/min to 220 °C, and held there for 30 min. These GC–MS programming conditions gave GC retention times about equal to those for the GC cited above. Injection port and ionizing source were kept at 275 °C, and the transfer line was kept at 280 °C. Mass units were monitored from 25 to 350 at 70 eV. Mass spectral matches were made by comparison of mass spectra and retention times with those of authentic compounds.

## RESULTS AND DISCUSSION

Aqueous orange essences and essence oils obtained from oranges processed in the United States and Brazil were analyzed and compared for compositional, flavor quality, and aroma differences. Aqueous essences from both countries were qualitatively and quantitatively analyzed by a method in which the characteristic volatile flavor and aroma constituents were separated and characterized from direct injection of whole essences into a gas chromatograph (Moshonas and Shaw, 1984) followed by mass spectral analyses. Table I lists 30 volatile flavor and aroma compounds identified in aqueous essences and the quantity of each component. Table II lists 29 compounds identified in orange essence oils produced in the United States and in Brazil and the quantity of each component. Analysis shows that qualitative compositions of the aqueous essences and essence oils from the United States and Brazil were identical. In addition to the identified compounds, a number of trace constituents that could not be positively identified were compared by GC–MS analysis and found qualitatively identical. These data also show that any qualitative compositional changes that may occur during the production of aqueous essences and

**Table I. Variations in Relative Amounts<sup>a</sup> of Components Identified in Aqueous Orange Essences Produced in the United States and Brazil**

compound	source of sample			
	United States			Brazil
	A	B	C	
acetaldehyde	0.152	0.619	0.601	0.586
methanol	2.304	2.339	1.857	3.366 <sup>b</sup>
ethanol	96.139	95.637	96.445	94.239 <sup>b</sup>
acetone	0.008	0.014	0.012	0.014
1-propanol	0.040	0.045	0.042	0.047
ethyl acetate + 2-methyl-3-buten-2-ol	0.054	0.081	0.067	0.083
2-methylpropanol	0.011	0.012	0.013	0.008 <sup>b</sup>
1-butanol	0.004	0.005	0.004	0.009 <sup>b</sup>
1-penten-3-ol	0.004	0.007	0.004	0.015 <sup>b</sup>
ethyl vinyl ketone	0.009	0.009	0.007	0.021 <sup>b</sup>
methyl butyrate	0.002	0.001	0.002	0.002
1,1-diethoxyethane	0.014	0.044	0.074	0.007
isoamyl alcohol	0.022	0.023	0.024	0.022
ethyl butyrate	0.019	0.037	0.042	0.055
hexanal	0.010	0.010	0.009	0.031 <sup>b</sup>
<i>trans</i> -2-hexenal	0.015	0.029	0.018	0.032
<i>trans</i> -2-hexenal + <i>cis</i> -3-hexen-1-ol	0.002	0.001	0.001	0.005
octanal	0.009	0.010	0.007	0.007
limonene	0.002	trace	0.001	0.001
octanol	0.007	0.007	0.003	0.015
linalool oxide	0.006	0.003	0.002	0.001
linalool	0.079	0.076	0.049	0.143 <sup>b</sup>
ethyl 3-hydroxyhexanoate	0.004	0.010	0.011	0.004
terpinen-4-ol	0.009	0.007	0.007	0.005
$\alpha$ -terpineol	0.015	0.020	0.011	0.033 <sup>b</sup>
neral	0.002	0.001	0.001	0.001
geranial	0.002	0.001	0.001	0.001
perillaldehyde	trace	trace	trace	trace

<sup>a</sup> Listed as GC area percent values. <sup>b</sup> Significantly different at the 95% confidence level from values in all the U.S. samples.

essence oils are common to essence recovery units in both countries.

Quantitative compositional comparisons between the Brazilian aqueous essence and the U.S. aqueous essence samples showed significant differences in 9 of the 27 components quantified (Table I). Of the significant differences between the Brazilian and all U.S. samples noted in Table I, the slight increase in  $\alpha$ -terpineol in the Brazilian sample is the most noteworthy.  $\alpha$ -Terpineol is formed in citrus products by acid-catalyzed hydrolysis of limonene, and an increase in this alcohol may indicate slightly more heat treatment of the Brazilian product during processing (Slater and Watkins, 1964).

A Brazilian essence oil sample was compared qualitatively and quantitatively with three essence oils produced in the United States (Table II). Just as was found for aqueous essences, no qualitative differences but several quantitative differences were detected between the two samples. 1,1-Diethoxyethane, which was at a higher level in two U.S. samples, is an artifact formed during processing (Coleman and Shaw, 1971). Several components known to be important to orange flavor, ethyl butyrate, octanal, decanal, and neral (Ahmed et al., 1978), were significantly higher in the U.S. samples than in the Brazilian sample. The optimum levels for these compounds in orange juice have not been established, however. Several oxidation products of the main orange oil component, *d*-limonene, were higher in two of the three U.S. samples, including *cis*-2,8-*p*-menthadien-1-ol, *trans*-carveol, and carvone. Elevated levels of these three compounds indicated that some oxidation of the sample has probably occurred.

**Table II. Variations in Relative Amounts<sup>a</sup> of Compounds Identified in Orange Essence Oil Produced in the United States and Brazil**

compound	source of sample			Brazil
	United States			
	A	B	C	
methanol	0.007	0.001	0.002	0.001
ethanol	0.698	0.025	0.210	0.020 <sup>b</sup>
acetone	0.004	0.004	0.001	trace
ethyl acetate	0.006	0.008	0.004	0.002
1,1-diethoxyethane	0.026	0.010	0.001	0.004 <sup>b</sup>
ethyl butyrate	0.111	0.188	0.080	0.057 <sup>b</sup>
hexenal	0.007	0.016	0.014	0.007
$\alpha$ -pinene	0.529	0.467	0.398	0.493
sabinene	0.266	0.315	0.203	0.358 <sup>b</sup>
myrcene	1.800	1.750	1.790	1.833
octanal	0.291	0.267	0.330	0.216 <sup>b</sup>
$\alpha$ -phellandrene	0.017	0.027	0.033	0.036 <sup>b</sup>
ocimene	0.045	0.058	0.048	0.145 <sup>b</sup>
limonene	93.230	92.141	92.113	95.037 <sup>b</sup>
unknown	0.158	0.116	0.147	0.133
octanol	0.033	0.045	0.119	0.071 <sup>b</sup>
linalool	0.370	0.517	0.539	0.500
nonanal	0.052	0.041	0.049	0.035 <sup>b</sup>
ethyl 3-hydroxyhexanoate	0.055	0.035	0.009	0.020 <sup>b</sup>
cis-2,8-p-menthadien-1-ol	0.104	0.087	0.013	0.038 <sup>b</sup>
citronellal	0.071	0.075	0.040	0.066
decanal	0.258	0.225	0.340	0.175 <sup>b</sup>
$\alpha$ -terpineol	0.040	0.054	0.067	0.051
trans-carveol	0.060	0.036	0.005	0.019 <sup>b</sup>
neral	0.080	0.089	0.096	0.061 <sup>b</sup>
carvone	0.182	0.093	0.044	0.066 <sup>b</sup>
geranial	0.074	0.095	0.122	0.048 <sup>b</sup>
perillaldehyde	0.033	0.033	0.031	0.029
valencene	0.938	1.909	2.032	0.244 <sup>b</sup>

<sup>a</sup> Listed as GC area percent values. <sup>b</sup> Significantly different at the 95% confidence level from values in all the U.S. samples.

**Table III. Sensory Evaluation of U.S. and Brazilian Aqueous Orange Essences and Orange Essence Oils**

samples compared	% confidence level of	
	aroma panel (difference)	flavor panel (preference)
AOE <sup>a</sup> (U.S. A) vs AOE (Brazil)	99.9	N.S.
AOE (U.S. A) vs AOE (U.S. B)	99.9	N.S.
OEO <sup>b</sup> (U.S.) vs OEO (Brazil)	95.0	N.S.
OEO (U.S. A) vs OEO (U.S. B) <sup>c</sup>	95.0	N.S.

<sup>a</sup> AOE = aqueous orange essence. <sup>b</sup> OEO = orange essence oil. <sup>c</sup> Essence oils from two different U.S. suppliers.

Results of aroma and flavor panel tests of aqueous orange essences and essence oils are shown in Table III. The aroma panel determined a significant difference when U.S.-produced aqueous essences were compared with either Brazilian essence or with essences from different U.S. processors. Significant differences were also determined when the aroma of an essence oil produced in the United States was compared with either Brazilian oil or with an oil from a different U.S. processor. Since the specific flavor and aroma constituents identified were identical in all aqueous essences, the differences found in the

aroma of each essence are determined by the varying quantities of each component. Quantitative differences of the individual compounds in essence oil would also account for the differences the panel determined in these aromas.

Use of these aqueous essences and essence oils to flavor citrus juices to determine flavor preference afforded results somewhat different from those found when aromas of the pure flavor fractions were judged in difference tests. A flavor panel determined no significant flavor preference when U.S.-produced aqueous essences were compared with either Brazilian essence or U.S. essences produced in different processing plants. Many panel members noted that although they could detect a difference in flavor, all aqueous essences added a fresh orange flavor "top-note" to juice, which precluded a significant preference. Similar flavor results were determined from flavor tests that compared juices flavored with orange essence oils produced in the United States and in Brazil (Table III).

Although the quantitative differences of aqueous essence and essence oil constituents do produce different flavors and aromas, they all have a top-note fruity flavor that is perceived as contributing to a fresh orange-like flavor and aroma. Orange essences in the United States are blended to produce a more uniform flavoring fraction. This study suggests that the blending procedure can be extended to include Brazilian orange aqueous essences and essence oils without adversely affecting the flavor or aroma quality.

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