

Flavor Evaluation of Concentrated Aqueous Orange Essences

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Commercial aqueous orange essence was compared with several experimental concentrated orange essences for flavor, aroma, and compositional differences. For flavor evaluation, bland aseptically packaged single-strength orange juice samples were flavored with each of the essences and compared with each other and with similar samples flavored commercially with a blend containing orange oils. Samples with concentrated essence containing either 25% or 35% ethanol were preferred over samples with standard commercial essence (15% ethanol). Preferences were also found for samples flavored with aqueous essences containing 15%, 35%, or 40% ethanol, when compared to samples containing flavor fractions with oils. An aroma panel determined a significant difference between a standard commercial essence and each of the concentrated essences. Significant quantitative differences were found for most of the constituents that are common to all essences when concentrated essences were compared to commercial essence. Sixteen components (including six acetals) were identified only in concentrated essences. 1,1-Diethoxypropane and 1,1-diethoxyheptane are reported as orange essence constituents for the first time.

Natural orange essence (aroma) is an aqueous distillate collected from the early stages of the evaporation process used to concentrate orange juice (Johnson and Vora, 1983). The annual production and use of 15-20 million pounds of orange essence make it the most widely used natural flavoring fraction worldwide (Moshonas and Shaw, 1984). Primary use of orange essence is to improve the fresh flavor and aroma of processed orange juice products, particularly frozen concentrate, by contributing a characteristic top-note to these products (Johnson and Vora, 1983). Essence recovery units in the citrus industry are currently adjusted to produce essences with an ethanol content of 15% or less to avoid taxes due to a high ethanol content. The estimated mechanical fold for commercial essences with alcohol content of 15% is 500-fold. However, commercial essence recovery units can be adjusted to produce essence with higher levels of ethanol, resulting in more concentrated essences (Shaw and Moshonas, 1974). Although all essences are concentrated, in this study, essences with an ethanol content of 15% or less will be referred to as commercial essences, and essences with an ethanol content above 15% will be referred to as concentrated essences. The difference in the quantitative composition of these essences alters the aroma and flavor characteristics of processed orange juice products. The more concentrated natural flavoring fractions may have flavor, aroma, and storage characteristics that are superior to commercial aqueous orange essences and thus may be particularly useful for improving the flavor quality of orange juice products in which flavor quality quickly deteriorates.

This paper compares flavor and aroma quality of aseptically packaged single-strength bland orange juice (SSOJ) flavored by each of the experimental concentrated aqueous essences, and those flavored either with commercial essence or with a commercially formulated fraction containing some combination of peel or essence oil and aqueous essence used by most of the citrus processors. Qualitative and quantitative compositional comparisons of commercial and concentrated aqueous essences are also reported in this study.

EXPERIMENTAL PROCEDURES

Aqueous Orange Essences. All essences were prepared from Valencia orange juice extracted from fruit harvested in

April 1987. Redd essence recovery units were used to recover the essences. The amount of each essence added to samples for sensory evaluation was calculated from the estimated mechanical fold as determined from the ethanol content. Essence containing 15% ethanol has an estimated fold of 500 and requires an amount equal to 0.02% of the juice to flavor single-strength juice. For every 5% change in ethanol content there is an estimated 100-fold change (J. D. Johnson, private communication, 1989).

Flavor Evaluations. Samples for the aqueous essence sensory tests were prepared by adding each essence to a base of reconstituted commercially prepared aseptically packaged concentrated Valencia orange juice containing no flavoring materials (evaporator pumpout) and very little orange oil (0.004% v/v). These samples were compared with each other and with commercially flavored aseptically packed orange juice (orange oil, 0.017% v/v, and commercially prepared aqueous essence) obtained from the same juice processed for the experimental samples above. The Brix/acid ratio for all samples was 14.0. 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 judgments (Boggs and Hanson, 1949).

Aroma Evaluations. Triangle difference tests were run on commercial and concentrated experimental aqueous orange essences obtained from commercial citrus essence recovery units. For each test, equal volumes of samples were placed in identical 1-dram vials and presented at room temperature. Each panelist was presented with three samples, two of which were identical, and asked to indicate which sample was different. All flavor and aroma evaluations were carried out in a room with positive pressure, individual booths, and red lighting to mask color differences.

Gas Chromatography (GC). GC data were obtained from three replicate runs of each essence by using a Hewlett-Packard Model 5880A instrument equipped with a flame ionization detector, a 50-m wide-bore (0.031-0.032 mm i.d.) capillary fused silica cross-linked 5% phenylmethylsilicone 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 and then programmed to 200 °C at 6 °C/min and held for 15 min. The threshold was set at 0, peak width at 0.02, and chart speed at 1 cm/min.

Mass Spectra. Identification of constituents was made by gas chromatography-mass spectrometry (GC-MS). A Hewlett-Packard Model 5970 B, MSD, GC-MS was used with a 50-m

Table I. Variations in Relative Amounts of Components Identified in Commercial and Concentrated Aqueous Essences^a

	commercial sample		concentrated sample					
	12% ethanol	15% ethanol	18% ethanol	20% ethanol	25% ethanol	35% ethanol	40% ethanol	50% ethanol
acetaldehyde	0.169	0.152	0.108 ^b	0.123 ^b	0.648 ^b	0.102	0.117 ^b	0.149
methanol	2.894 ^b	2.304	2.484 ^b	2.537 ^b	2.476 ^b	2.350	2.391 ^b	2.171
ethanol	96.930 ^b	96.139	97.399 ^b	97.311 ^b	96.826 ^b	97.549 ^b	97.489 ^b	97.663 ^b
acetone	0.005	0.008	0.003 ^b	0.003	0.009	0.004	0.004	0.009
<i>n</i> -propanol	0.037 ^b	0.045	0.042 ^b	0.041 ^b	0.055 ^b	0.044	0.048 ^b	0.048 ^b
ethyl acetate + 2-methyl-3-buten-2-ol	0.05	0.051	0.043	0.042 ^b	0.062 ^b	0.031 ^b	0.036 ^b	0.055 ^b
2-methyl-1-propanol	0.007 ^b	0.011	0.010	0.009 ^b	0.015 ^b	0.010	0.013 ^b	0.013 ^b
<i>n</i> -butanol	0.009	0.007	0.006	0.005 ^b	0.047 ^b	0.007	0.028 ^b	0.037 ^b
1-penten-3-ol	0.010 ^b	0.003	0.004	0.004	0.003	0.004	0.004	0.007 ^b
ethyl vinyl ketone	0.004	tr	0.002	0.002	0.003	0.002	0.001	0.006
methyl butyrate	tr	tr	0.001	tr	0.002	0.001	0.001	0.002
1,1-diethoxyethane	0.007 ^b	0.002	0.018 ^b	0.016 ^b	0.21 ^b	0.024		
isoamyl alcohol	0.013	0.015	0.021 ^b	0.021 ^b	0.021 ^b	0.022 ^b	0.020 ^b	0.027 ^b
ethyl butyrate	0.029 ^b	0.008	0.017 ^b	0.016 ^b	0.045 ^b	0.023 ^b	0.052 ^b	0.045 ^b
hexanal	0.012 ^b	0.004	0.005	0.003	0.013 ^b	0.006 ^b	0.016 ^b	0.007
<i>trans</i> -2-hexenal	0.036 ^b	0.009	0.018 ^b	0.018 ^b	0.017 ^b	0.017 ^b	0.019 ^b	0.047 ^b
<i>cis</i> -3-hexen-1-ol + <i>trans</i> -2-hexenal	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.004 ^b
<i>n</i> -octanal	0.007	0.009	0.015 ^b	0.009	0.043 ^b	0.030 ^b	0.085 ^b	0.069 ^b
limonene	0.023	0.002	0.003	0.002	0.001	0.005 ^b	0.086 ^b	0.191 ^b
octanol	0.010	0.006	0.009 ^b	0.007	0.016 ^b	0.017 ^b	0.009	0.023 ^b
linalool oxide	0.019 ^b	0.007	0.003 ^b	0.001 ^b	0.008 ^b	0.003 ^b	0.012 ^b	0.018 ^b
linalool	0.080	0.066	0.065	0.058	0.151 ^b	0.123 ^b	0.058	0.061
ethyl 3-hydroxyhexanoate	0.013 ^b	0.003	0.012 ^b	0.013 ^b	0.011 ^b	0.008 ^b	0.004	0.002
<i>cis</i> -2,8- <i>p</i> -menthandien-1-ol	0.005 ^b	0.003	0.003	0.003	0.002 ^b	0.003	0.002 ^b	0.002
terpinen-4-ol	0.014	0.006	0.007	0.008	0.011 ^b	0.008 ^b	0.006	0.020 ^b
α -terpineol	0.013 ^b	0.017	0.017	0.017	0.020	0.025 ^b	0.005 ^b	0.038 ^b
neral	0.003	0.005	0.007	0.008	0.015 ^b	0.015 ^b	0.003 ^b	0.008 ^b
carvone	0.031 ^b	0.002	0.003 ^b	0.002	0.004 ^b	0.003 ^b	0.003 ^b	0.010 ^b
geranial	0.003	0.005	0.006	0.007 ^b	0.016 ^b	0.014 ^b	0.003	0.013 ^b
perillaldehyde	0.002	0.002	0.002	0.001	0.005 ^b	0.003	0.001	0.002

^a Listed as GC area percent values averaged from three replicate runs. ^b Significantly different at the 95% confidence level from values in commercial essence containing 15% ethanol when the three replicate runs for each component were compared.

wide-bore (0.31–0.32 mm), fused silica column of cross-linked 5% phenylmethylsilicone. The initial oven temperature was held at 55 °C for 9 min and then programmed at 7.5 °C/min to 220 °C and held there for 30 min. Injection port and ionizing source were 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 time with those of authentic compounds.

RESULTS AND DISCUSSION

Aqueous commercial and experimental concentrated orange essences obtained from Florida processors were analyzed to determine and compare compositional makeup and evaluate their contribution to flavor and aroma quality when they are used as flavoring fractions. Qualitative and quantitative analyses were accomplished by direct injection of aqueous essence into a gas chromatograph to separate, quantify, and partially characterize individual constituents (Moshonas and Shaw, 1984) followed by mass spectral analysis for final identification.

Table I lists 32 volatile flavor and aroma essence constituents identified that are common to all essence samples evaluated. This table also presents the quantity of each component in each essence and indicates which component levels were significantly different in concentrated essences when compared to the same compounds identified in the commercial essence containing 15% ethanol. Significant quantitative differences were found in many of the compounds compared in all concentrated essences as well as in the commercial essence with 12% ethanol when compared to commercial essence containing 15% ethanol. These quantitative differences in volatile constituents influence both the flavor and aroma of these products (Moshonas and Shaw, 1989). Ethyl butyrate, which is considered to be important to orange flavor (Ahmed et al., 1978), differed significantly in all exper-

Table II. Variations in Relative Amounts of Components Identified Only in Concentrated Aqueous Essences^{a,b}

	% ethanol			
	25	35	40	50
1-ethoxy-1-methoxyethane	ND ^c	ND	ND	0.001
1,1-diethoxypropane	tr	ND	tr	0.001
α -pinene	ND	tr	0.001	0.001
myrcene	ND	ND	ND	0.003
ethyl hexanoate	0.001	0.001	0.003	0.006
ocimene	ND	ND	0.002	0.002
<i>p</i> -cymene	ND	ND	0.001	0.006
1,1-diethoxyhexane	tr	tr	tr	tr
nonanal	0.001	0.001	0.001	0.005
ethyl octanoate	0.002	tr	tr	tr
1,1-diethoxyheptane	0.001	tr	tr	0.022
decanal	0.003	0.003	0.002	0.019
1,1-diethoxyoctane	0.003	0.001	0.035	0.034
1,1-diethoxynonane	ND	ND	0.001	0.002
1,1-diethoxydecane	tr	ND	tr	0.005
valencene	ND	ND	tr	0.005

^a Concentrated essences containing 18% and 20% ethanol did not show detectable levels of these components. ^b Average from three replicate GC runs. ^c ND, not detectable.

imental essences from that of the commercial essence containing 15% ethanol. In addition to significant quantitative differences of constituents common to all aqueous essences, a number of volatile compounds were identified in the concentrated samples, with an ethanol content above 25%, that could not be detected in the commercial sample (Table II). One group of components resulted from the increase in solubility of essence oil components into the aqueous phase as the percentage of ethanol increased. This transfer of constituents occurs naturally during the concentration step before the oil and aqueous phases are separated. This group of compounds included four terpene hydrocarbons, α -pinene, myrcene,

Table III. Aroma Judgments Comparing Commercial Aqueous Orange Essence (15% Ethanol) and Concentrated Essences

concentrated ^a essence, % ethanol	triangle test (24 judgments), no. correct	difference, confidence level, %
18	15	99.9
20	16	99.9
25	18	99.9
35	18	99.9
40	20	99.9
50	22	99.9

^a Evaluated as neat samples.

Table IV. Flavor Preference Judgments Comparing Commercially Flavored and Aqueous Essence Flavored Aseptically Packaged SSOJ

aqueous essence % ethanol	paired test (24 judgments), no. preferred	preference confidence level, %
Commercial Flavor vs Aqueous Essence		
15	17	95 ^a
20	16	NS
25	16	NS
35	19	99 ^a
40	18	99 ^a
50	17	95 ^b
Aqueous Essence (15% Ethanol) vs Concentrated Essence		
25	19	99 ^c
35	17	95 ^c
50	11	NS

^a Preference was for aqueous essence flavored sample. ^b Preference was for commercially flavored sample. ^c Preference was for concentrated essence flavored sample.

ocimine, and *p*-cymene; two aldehydes, nonanal and decanal; two esters, ethyl hexanoate and ethyl octanoate; and one sesquiterpene hydrocarbon, valencene.

A second group of compounds found only in the concentrated essences was a series of acetals (Table II), which are considered artifacts formed from ethanol and straight-chained aldehydes present during processing in the acidic juice medium (Nursten, 1970). 1,1-Diethoxyethane is frequently found in commercial orange essences because of the normally high content of ethanol and acetaldehyde. However, the other seven acetals did not appear until the ethanol content of the essence was at 25% or higher. Acetals identified only in concentrated aqueous orange essences in this study that had been previously reported include 1-ethoxy-1-methoxyethane (Moshonas and Shaw, 1973), 1,1-diethoxyoctane (Moshonas and Shaw, 1984), and 1,1-diethoxyhexane, 1,1-diethoxynonane, and 1,1-diethoxydecane (Nagy, 1989). 1,1-Diethoxypropane and 1,1-diethoxyheptane are now reported as orange essence constituents for the first time. The specific effects of these artifacts on flavor and aroma quality have not been established. When neat samples of commercial essences containing 15% ethanol were compared with each of the concentrated essences or with a commercial essence containing 12% ethanol, an aroma panel determined a significant difference in every test (Table III). Similar results from aroma tests comparing aromas from orange essences produced in the United States and Brazil were found in an earlier study (Moshonas and Shaw, 1990) and were attributed to quantitative differences of the individual components.

Table IV lists the results of flavor evaluations in which the panel compared a bland aseptically packaged orange juice base flavored either with one of the aqueous essences or with a blend used by commercial processors. Of the six aqueous essences tested, the panel indicated significant

preferences for samples flavored with essences containing 15%, 35%, and 40% ethanol and for the commercially flavored juice when compared to juice flavored with essence containing 50% ethanol. Flavor tests comparing aseptically packaged SSOJ flavored with commercial aqueous essence (15% ethanol) and those with essences containing either 25%, 35%, or 50% ethanol showed significant preferences for samples flavored with essence containing 25% and 35% ethanol.

Conclusions. As essence recovery units are adjusted to yield aqueous essences of differing concentrations on the basis of ethanol content, the quantity of individual components common to all essences changes significantly. These quantitative differences result in essences with different flavors and aromas, although they still maintain a topnote fruity flavor that is perceived as contributing to a fresh orangelike flavor. Aseptically packaged orange juice bases flavored solely with individual essences were judged to be as good or better than those that have been commercially flavored with fractions that include peel and essence oils. These oils are known to be the source of oxidation products formed during storage which have an adverse effect on flavor (Durr et al., 1981). This study shows that concentrated aqueous essences could be used as the prime flavoring fraction for orange products, thus eliminating or greatly reducing the oil-rich flavoring materials currently used by the citrus and other industries. An additional advantage of concentrated essences is the great reduction in volume, which makes handling easier while reducing the space necessary for storage.

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Registry No. Acetaldehyde, 75-07-0; methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1; *n*-propanol, 71-23-8; ethyl acetate, 141-78-6; 2-methyl-2-buten-2-ol, 115-18-4; 2-methyl-1-propanol, 78-83-1; *n*-butanol, 71-36-3; 1-penten-3-ol, 616-25-1; ethyl

vinyl ketone, 1629-58-9; methyl butyrate, 623-42-7; 1,1-diethoxyethane, 105-57-7; isoamyl alcohol, 123-51-3; ethyl butyrate, 105-54-4; hexenal, 1335-39-3; *trans*-2-hexenal, 6728-26-3; *cis*-3-hexen-1-ol, 928-96-1; *trans*-2-hexenol, 928-95-0; *n*-octanal, 124-13-0; limonene, 138-86-3; octanol, 29063-28-3; linalool oxide, 60047-17-8; linalool, 78-70-6; ethyl 3-hydroxyhexanoate, 2305-25-1; *cis*-2,8-*p*-methandien-1-ol, 129149-17-3; terpinen-4-ol, 562-74-3; α -terpineol, 98-55-5; neral, 106-26-3; carvone, 99-

49-0; geranial, 141-27-5; perillaldehyde, 2111-75-3; 1-ethoxy-1-methoxyethane, 10471-14-4; 1,1-diethoxypropane, 4744-08-5; α -pinene, 80-56-8; myrcene, 123-35-3; ethyl hexanoate, 123-66-0; ocimene, 29714-87-2; *p*-cymene, 99-87-6; 1,1-diethoxyhexane, 3658-93-3; nonanal, 124-19-6; ethyl octanoate, 106-32-1; 1,1-diethoxyheptane, 688-82-4; decanal, 112-31-2; 1,1-diethoxyoctane, 54889-48-4; 1,1-diethoxynonane, 54815-13-3; 1,1-diethoxydecane, 34764-02-8; valencene, 4630-07-3.