

## Quantitative Composition Studies of Water-Soluble Aromatics from Orange Peel

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Quantitative analyses were carried out on water-soluble aromatic solutions made from orange peel oil centrifuge effluent by steam stripping and concentration in a fractionating column at atmospheric pressure under various conditions. The variables studied were the percentage vaporization in the stripper (*i.e.*, the amount stripped from the feed) and the relative amounts of water and oil in the condensate from the fractionating column. Quanti-

tative data were obtained for 20 volatile compounds in the aqueous layer of the product. The yield of the volatile components was not influenced in any predictable manner by the percentage vaporization, but was found to be directly proportional to the ratio of water to oil in the product. Generally, lesser ratios of water to oil resulted in an aqueous product higher in content of organics.

The preparation of aqueous solutions of volatile compounds from orange peel for use in the flavor enhancement of citrus products has been previously described (Veldhuis *et al.*, 1972). The qualitative analysis of these solutions of water-soluble aromatics prepared from various parts of the orange fruit (Veldhuis *et al.*, 1972; Moshonas *et al.*, 1972) revealed that most of the compounds derived from the juice can also be obtained from the peel.

In citrus processing plants, a favorable source of aromatic materials of this type is the aqueous discharge stream from cold-pressed peel oil mills. When the peel has been pressed in screw presses and the oil-peel-juice emulsion has been washed from this pressed peel, it is transferred to centrifuges where the top layer (predominantly cold-pressed orange oil) is separated from the lower layer (predominantly water with small amounts of residual oil). This aqueous stream, commonly referred to as peel oil desludger effluent, provides a considerable problem in waste disposal due to the residual oil in it. Studies by Veldhuis *et al.* (1972) indicate this material may be used as a source of flavor enhancement materials.

As previously described (Veldhuis *et al.*, 1972), the apparatus for preparing such solutions consists of a steam stripper into which the aqueous peel extract is fed and the volatile aromatics are stripped with steam and a fractionating column, where the volatile material from the stripper is concentrated to give a two-phase product: an oil layer (96% limonene) and an aqueous layer containing water-soluble aromatics.

Information was needed on the relative influence of variables involved in the preparation of such solutions. Two of the major conditions expected to influence composition and quantity of this aqueous solution of volatiles were percentage vaporization and ratio of water to oil in the final product. Percentage vaporization refers to the amount stripped from the feed material, as described by Veldhuis *et al.* (1972). The relative amounts of water collected with the oil as final product could be regulated by the temperature of a reflux condenser. Since most of the aroma and flavor-enhancing components in orange juice are water-soluble to some extent, it was likely that the relative organic composition of a given product would depend upon the ratio of water/oil when collected. To determine these effects, experiments were required encompassing a variety of operating conditions.

Glc-mass spectrometer combined analysis has made both qualitative and quantitative analysis of these aroma solutions

much more efficient. An extraction-glc procedure for the minor constituents (Wolford *et al.*, 1962) combined with a glc method for methanol, ethanol, and acetaldehyde offered advantages for the analysis of these products. After these three dominant components were separated, the remainder of the aroma components could be analyzed separately, free from interference from the relatively large quantities of methanol and ethanol. Analyses were made on some of the principal components of aqueous aromatics made under different conditions.

## EXPERIMENTAL

**Preparation of Aroma Solutions.** The feed was heated to 212°F and injected into a steam stripping unit (Veldhuis *et al.*, 1972) where a portion of the feed was vaporized. Percentage vaporization (*i.e.*, amount of feed stripped off) was controlled by pressure of the steam being injected. The volatile mixture of oil and water was directed into a 3-in. diameter glass packed column equipped with a reflux condenser and a reboiler. The product condensed from this column was varied by changing the cooling water through the reflux condenser. Organic material left in the column reboiler was negligible, as determined by measuring chemical oxygen demand (Dougherty, 1968) on samples of this material.

## ANALYSIS

**Apparatus.** A gc-mass spectrometer system was used consisting of a Loenco Model 160 gas chromatograph (Loenco Inc., Altadena, Calif.) equipped with a flame ionization detector coupled to a CEC 21-490 mass spectrometer (Consolidated Electrodynamics, Pasadena, Calif.).

## PROCEDURE

A 300-ml sample of aqueous layer saturated with Na<sub>2</sub>SO<sub>4</sub> was extracted three times with 100-ml portions of methylene chloride. For quantitative analyses the combined extracts were concentrated to about 4 ml by distillation through a Vigreux column at atmospheric pressure.

For qualitative analysis, a portion of the partially concentrated extract was further concentrated by distillation and 8 μl of this concentrate was used for the gc-ms analysis on each of three 1/8-in. × 5-ft stainless steel columns packed with 5% of the liquid phases Carbowax 20M, stabilized diethylene glycol succinate (Analabs C6) and OV-101 on 70/80 Anakrom ABS. The operating conditions were as follows: helium flow rate, 37 ml/min; temperatures (°C), injection port 220, detector 220, manifold 230, source 230, column 80-200 @ 2°C/min. Identification was made by a comparison of re-

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Table I. Glc Analysis of Water-Soluble Aromatics from Orange Peel

Compound	Retention time, min		
	Carbowax 20M	DGS	OV-101
Methanol <sup>a</sup>	1.1		
Acetaldehyde <sup>a</sup>	1.6		
Ethanol <sup>a</sup>	3.5		
Linalool	24.0	21.0	19.0
$\alpha$ -Terpineol	28.5	30.1	27.7
<i>cis</i> -3-Hexene-1-ol	13.3	12.3	6.2
Limonene	7.4	4.6	13.6
<i>n</i> -Octanal	10.5	9.1	11.4
1-Hexanol	12.6	10.1	6.2
1-Octanol	24.4	19.2	17.6
<i>trans</i> -2-Hexenal	8.2	7.6	5.2
Terpinene-4-ol	27.2	24.8	25.3
<i>n</i> -Hexanal	4.5	4.0	3.8
Geraniol	42.8	36.5	35.5
Neral	32.3	31.3	32.3
<i>cis</i> -Carveol	43.3	41.9	32.2
<i>trans</i> -Linalool oxide	18.2	17.1	16.8
<i>n</i> -Amyl alcohol	7.3	6.5	3.5
1-Pentene-3-ol	5.5	4.2	2.6
<i>cis</i> -Linalool Oxide	19.7	18.3	10.4

<sup>a</sup> Retention times on Porapak (min). DGS = Diethylene glycol succinate.

Table II. Analysis of Water-Soluble Aromatics from Peel with Increasing Amounts Stripped from the Feed

Compound	Amount stripped off, %	Yield, mg $\times 10^{-2}/100$ g			
		13.6	17.4	19.5	22.2
Methanol	600	750	670	670	
Acetaldehyde	63	44	58	47	
Ethanol	350	330	260	340	
Linalool	45	40	29	25	
$\alpha$ -Terpineol	10.1	12.9	10.9	7.7	
<i>cis</i> -3-Hexene-1-ol	7.5	5.0	4.5	4.9	
Limonene	20	10.8	8.4	21	
<i>n</i> -Octanal	3.5	2.5	2.3	2.1	
1-Hexanol	4.8	2.8	2.2	2.9	
1-Octanol	4.6	6.4	4.8	2.1	
<i>trans</i> -2-Hexenal	2.9	2.5	2.6	2.2	
Terpinene-4-ol	1.88	1.49	1.40	1.18	
<i>n</i> -Hexanal	2.3	1.81	1.59	2.7	
<i>trans</i> -Linalool oxide	0.36	0.169	0.27	0.29	
<i>n</i> -Amyl alcohol		0.54		0.59	

tention times and mass spectra with those of known essence constituents.

The same columns and conditions were used for the quantitative analysis, using the less concentrated samples. Methanol, ethanol, and acetaldehyde were determined using 4- $\mu$ l injections of the aqueous aroma solution on a 1/8-in.  $\times$  5-ft stainless steel column packed with 50/80 mesh Porapak Q (Waters Associates, Inc., Framingham, Mass.) column at 120°C. Percentages were based on relative peak areas determined by planimeter. For partially resolved peaks, either triangulation or perpendicular drop methods were used (Westerburg, 1969), depending on the relative size of the peaks.

The instrument was calibrated by injecting a series of known concentrations of linalool in methylene chloride, or of methanol, ethanol, and acetaldehyde in water on each column under the above conditions and plotting peak areas *vs.* concentration. The concentration of linalool or of methanol, ethanol, or acetaldehyde in a sample was then determined by reference to the curve. The concentrations of other components, usually lower in concentration, were calculated from the product of the peak area relative to linalool and the relative

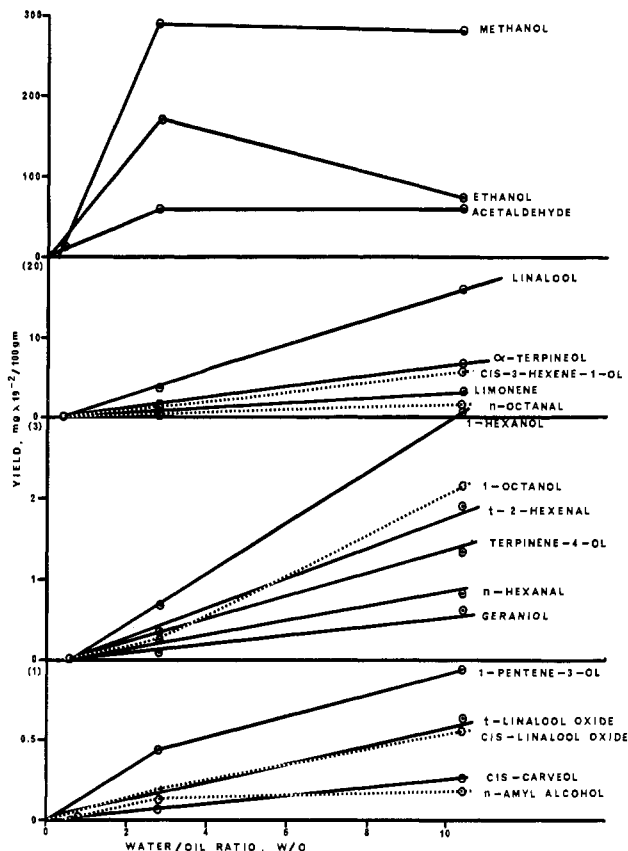


Figure 1. Yield of water-soluble aromatics as a function of water to oil ratio

peak area response factor ( $P_L$ ). In order to calculate  $P_L$  for a given compound, mixtures of known relative amounts of linalool and the compound were injected and the relative peak areas determined. The response factor was equated to the area of the linalool peak per unit weight of linalool divided by the area of the compound peak per unit weight of the compound.

## RESULTS AND DISCUSSION

From a total of 120 compounds isolated from the aroma solution, a quantitative estimate was obtained for 20. These are shown in Table I and they accounted for over 90% of the total peak area appearing in the glc traces. Methanol, ethanol, and acetaldehyde were the major constituents, with linalool,  $\alpha$ -terpineol, limonene, and *cis*-3-hexene-1-ol generally predominating among the remainder of the aroma components. Linalool and  $\alpha$ -terpineol had previously been identified as the most prominent volatile constituents of orange peel (Swift, 1961; Moshonas *et al.*, 1972). Glc retention times are also shown in Table I. Peak area response factors vary according to the configuration of the particular flame ionization detector (Novaks *et al.*, 1970) and thus are not shown. This table gives the elution sequence of these components on three different columns, and thus might serve as an aid in identification. It is also interesting to note the qualitative similarity of these aqueous peel volatiles to orange essences. All of these components have been previously reported in orange essence (Wolford *et al.*, 1962).

Composition of stripped volatiles remained about the same with increasing amounts of stripped products. Table II shows results from four runs where percent vaporization varied from 13.6 to 22.2. The water/oil ratio was held at 22.

Table III. Analysis of Water-Soluble Aromatics from Peel As Water/Oil in Product Increases

Ratio water/oil in product	Yield, mg $\times 10^{-2}/100$ g						
	Series A		Series B				
	2.6	6.2	0.5	0.9	2.2	3.6	5.8
Compound							
Methanol	370	440	310	300	540	380	570
Acetaldehyde	47	38	22	50	45	48	46
Ethanol	230	230	240	390	570	460	390
Linalool	6.9	11.0	0.56	1.60	3.5	10.2	15.5
$\alpha$ -Terpineol	2.7	4.6	0.074	0.177	2.05	3.3	8.1
<i>cis</i> -3-Hexene-1-ol	2.8	3.8	1.35	1.84	2.1	5.0	7.3
Limone	1.25	3.3	0.28	0.79	0.46	2.1	2.3
<i>n</i> -Octanal	0.86	2.6	0.24	0.41	0.56	0.57	1.98
1-Hexanol	0.66	1.07	0.44	0.63	0.93	1.54	2.4
1-Octanol	0.37	0.87	0.075	0.103	0.35	0.96	1.51
<i>trans</i> -2-Hexenal	0.92	2.04	0.31	0.42	0.74	1.16	2.3
Terpinene-4-ol	0.37	0.49	0.024	0.094	0.27	0.49	0.78
<i>n</i> -Hexanal	0.52	1.17	0.191	0.33	0.50	0.64	1.56
Geraniol						0.45	0.94
Neral	0.50						
<i>trans</i> -Linalool oxide	0.159	0.39					0.32
<i>n</i> -Amyl alcohol	0.43	0.54	0.21	0.052	0.25	0.30	0.88

Yields ranged from about  $0.002 \times 10^{-2}$  mg/100 g of feed for *trans*-linalool oxide to about  $0.4 \times 10^{-2}$  mg/100 g of feed for linalool and acetaldehyde. No discernible trends could be detected in the yield data; some variations were observed, but these were apparently random. These data imply that as more product is steam stripped from the feed, the various organic components continue to come off at about the same rates. They also give an indication of yields to be expected.

There was an increase in yield in nearly all components as the water to oil ratio was increased as shown by analyses of product from peel in Table III. The percent vaporization was held at 11 for these. In Sample A as water/oil increased from 2.6 to 6.2, yield of most components nearly doubled. Acetaldehyde slightly decreased and ethanol did not change. In sample B all components increased considerably as the W/O ratio increased from 0.5 to 5.8. With the exception of ethanol and acetaldehyde, which only increased slightly, all other components increased as much as two to more than ten times.

These increases are further emphasized in Figure 1, which is a plot of yield vs. water to oil ratio for another series of three runs with water to oil ratios of 0.4, 2.8, and 10.4. A roughly linear relationship was found between yield and ratio of water to oil for 16 of the measured components. Methanol, ethanol, acetaldehyde, and *n*-amyl alcohol are exceptions in that the concentrations leveled off at water to oil ratios of less than 3. The influence of relative solubilities may explain these exceptions. The different organic components would be expected to be present in the water layer in amounts relative to their individual solubility distribution coefficients between water and *d*-limonene (principal component of the oil layer). For

the less water-soluble compounds the amount in the water layer should increase linearly over a very wide range of water/oil ratios. On the other hand the more water-soluble components would be expected to level off at lower ratios of water to oil, *i.e.*, methanol, ethanol, and acetaldehyde would be expected to level out at relatively low water/oil ratios as found. Thus, it has been shown that both relative and total amounts of these aroma solution components can be increased or changed through control of the conditions under which they are produced, and a highly influential factor is the ratio of water/oil. Also, it is possible to predict the approximate relative proportions of these components which might be obtained under a given set of conditions, making it more possible to control the composition of the solution of water-soluble aromatics as required.

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