

## Distribution of Aqueous Aroma Components in the Orange

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Aqueous aroma solutions from various parts of Valencia oranges were analyzed by extraction with methylene chloride followed by glc analysis of the anhydrous solution and individual component identification by mass and infrared spectra. The compounds ethyl 3-hydroxyhexanoate and valencene were only found in the aqueous aroma solution from the interior of the fruit, while linalool was one of

the most prominent aroma components from the peel. The other identified components generally were similar to those in commercial orange juice essence, with the exception of 1,8-*p*-menthadiene-9-ol, *p*-menthane-1,2-diol, and *tert*-2,8-*p*-menthadiene-1-ol which had not been previously identified as orange essence constituents.

Orange juice and processed products contain chemical components derived from all the different parts of the fruit. Little has been reported on the parts of the orange which may serve as sources for different chemical components which influence aroma and flavor. Previous reports on oil-soluble components affecting flavor have been mostly limited to studies of cold-pressed peel oil, and those on the water-soluble aroma components have been generally limited to essences stripped from fresh juice.

Previous work on the analysis of orange juice essence (Wolford *et al.*, 1962, 1963; Wolford and Attaway, 1967; Schultz *et al.*, 1964, 1967) has resulted in the identification of over 100 compounds. The essence used for these studies was the aqueous layer obtained from the distillation of orange juice and was analyzed by the extraction of the aqueous essence with an organic solvent, followed by high-resolution glc analysis of the concentrated anhydrous essence solution. The organic portion of the essence was found to consist principally of ethanol, with smaller amounts of other volatile organic compounds, amounting, in total, to approximately one-hundredth of the ethanol concentration. Ethyl butyrate, limonene, and linalool were found to be the most abundant constituents after ethanol. These three were found to be present in considerably larger amounts than any of the other constituents, with the exception of ethyl 3-hydroxyhexanoate, which was reported in an earlier study (Schultz *et al.*, 1964) to be one of the major essence constituents.

In related studies on orange peel as a source of water-soluble aroma for citrus products (Veldhuis *et al.*, 1972), several concentrated samples of aroma solutions from various parts of the fruit were obtained. The relative chemical composition of these might provide evidence of the relative importance of different fruit parts to quality of orange products. These aroma solutions were analyzed for major components and compared. This is a report of that study.

## EXPERIMENTAL

The raw materials serving as sources for the aroma samples were fractions of Florida Valencia orange obtained from various citrus processing plants. The following sources were used for obtaining aqueous aroma solutions: flavedo; albedo; whole peel (albedo plus flavedo); peeled fruit (interior of fruit with sections and membranes intact but with albedo, flavedo, and rag removed); single strength orange juice (SSOJ)

obtained by commercial processing techniques and centrifuge effluent (aqueous discharge from oil centrifuges) from a commercial peel oil mill, after separation of the oil layer. In addition to these six fractions, a sample of commercial orange juice essence was analyzed.

Aqueous aroma solutions were prepared from the different fruit parts as follows: flavedo, albedo, whole peel, or peeled fruit were ground in a Fitz mill Model D comminuting machine (W. J. Fitzpatrick Mfg. Co., Chicago, Ill.) through a 0.250-in. screen at high speed (1150 to 3000 rpm). The ground material was slurried with one to two parts of water at about 27°C with stirring, for 2 hr. The slurry was then passed through a screw-type finisher (Chisholm-Ryder Co., Niagara Falls, N.Y.) using a 0.033-in. screen and 17 psig air pressure. The resultant aqueous extract was then pumped into a Turba-film evaporator (Votator Division, Chemtron Corp., Louisville, Ky.) of 1-ft<sup>2</sup> evaporation surface, with the rotor operating at 1290 rpm. Steam at 31 psig was supplied to the jacket to provide about 20% vaporization. The vapors were passed into a glass distillation column through a glass tee. Two columns each 30-in. × 3-in. were connected above and below the tee. The columns were filled with 5/8-in. stainless steel "Pall" rings. The bottom half served as the stripping and reboiler section, and the upper half served as a fractionating column. A stainless steel reflux condenser of 22.5 ft<sup>2</sup> was mounted atop the fractionating column. Tap water was used in the cooling side of this condenser to remove most of the water vapor, and to provide reflux. Some of the water vapor along with the volatile flavoring materials passed through and was condensed by a 4.5 ft<sup>2</sup> condenser, cooled with 55°F water. The condensate was collected in a glass oil trap, where the oil and aqueous layers were separated. The aqueous layer was used for extraction and subsequent analysis. Single strength orange juice and centrifuge effluent were simply passed directly into the Turba-film evaporator without prior grinding and slurry steps.

Using the aqueous condensate from the oil trap, anhydrous aroma solution was obtained by the solvent extraction method of Wolford *et al.* (1962). A 1400-ml sample of aqueous aroma solution was saturated with sodium sulfate, extracted with three 400-ml portions of distilled methylene chloride, and concentrated by distillation through a Vigreux column to give a sample of anhydrous aroma concentrate, substantially free of ethanol and residual solvent.

The anhydrous aroma concentrate samples were analyzed by gas-liquid chromatography on a 20-ft × 0.25-in. i.d. aluminum column packed with 20% Carbowax 20M on 60/80 Gas Chrom P, with the column programmed from 80°C to 220°C at 1°C/min and a helium flow rate of 60 ml/min. The

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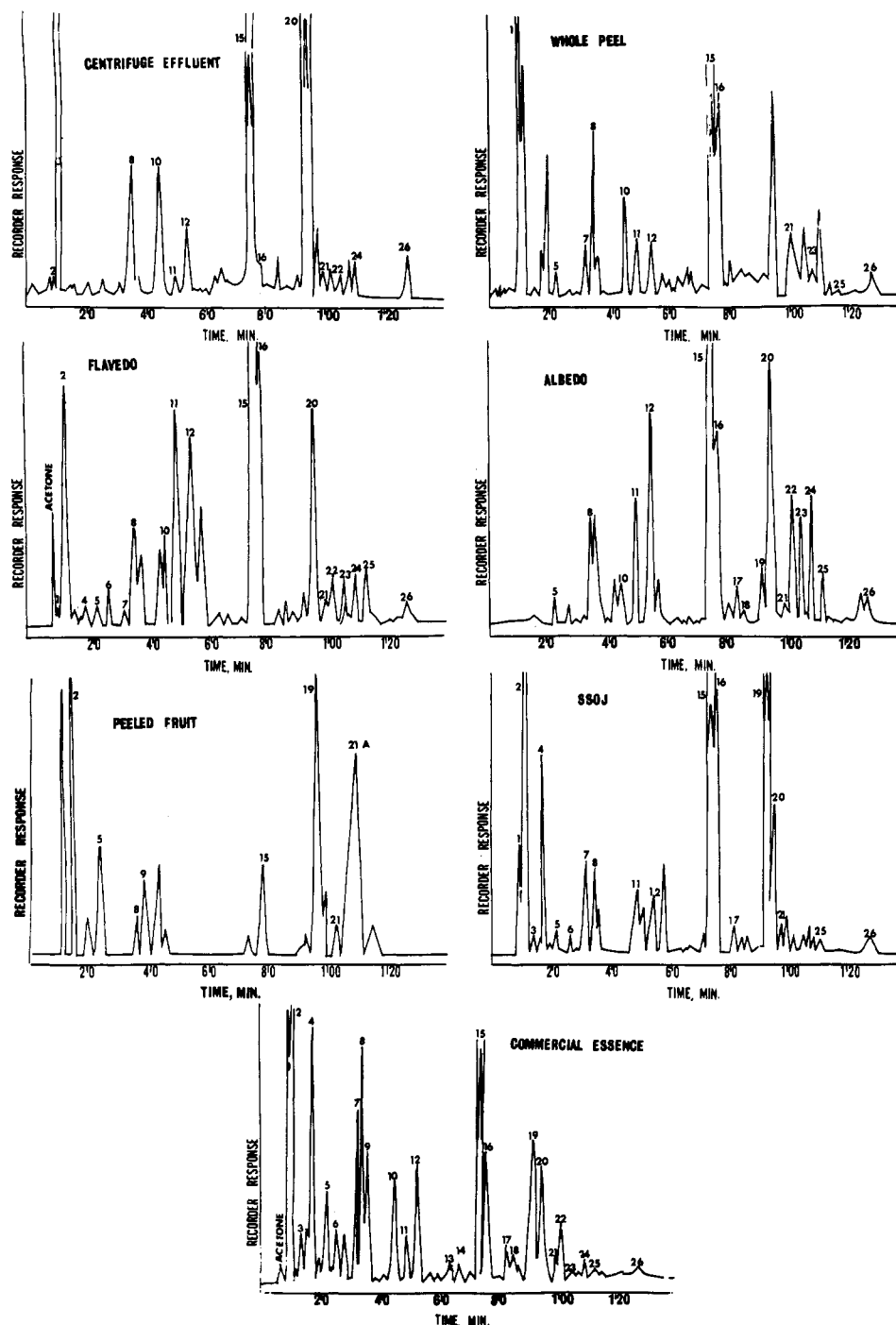


Figure 1. Glc chromatograms of nonaqueous aroma solutions from various parts of Valencia orange

injector port temperature was 250°C and the thermal conductivity detector temperature was 280°C. Injection volume was 20  $\mu$ l.

The peaks were collected and identified by mass spectrometry and infrared spectroscopy. Mass spectra were obtained with a Bendix Model 3012 TOF mass spectrometer and infrared on a Perkin-Elmer Infracord Model 137A.

#### RESULTS AND DISCUSSION

According to the results, tabulated in Figure 1 and Table I, the principal volatile aroma constituents of the Valencia orange varied considerably in different parts of the fruit. Reference to the glc trace for the commercial juice essence sample in Figure 1 revealed that ethyl butyrate (4), *d*-limonene

(8), and linalool (15) were the major constituents of the essence. The glc trace for "SSOJ" was similar to juice essence, which was to be expected, since the method of preparing this aroma sample was similar to that used with commercial essence. Both were derived by extraction of the distillate from orange juice.

The aroma solution from peeled fruit was quite different from the juice essence, as shown in Figure 1. In the peeled fruit aroma solution ethyl 3-hydroxyhexanoate (19) and valencene (21A) were found to be the major constituents. Linalool (15) was a relatively minor component in the solution from the peeled fruit. The linalool found in the juice essence must, therefore, be derived almost entirely from the peel. The traces for albedo, flavedo, and whole peel aroma solutions

Table I. Volatile Compounds in Orange

Compound	Peeled fruit	SSOJ	Flavedo	Commercial essence	Centrifuge effluent	Albedo	Whole peel
Acetone			X	X			
1. acetal	X	X	X	X	X		X
2. methylene chloride <sup>a</sup>		X	X	X	X		
3. methyl butyrate <sup>a</sup>		X		X			
4. ethyl butyrate	X	X	X	X			
5. <i>n</i> -hexanal		X	X	X		X	X
6. unidentified, MW84		X	X	X			
7. isoamyl alcohol	X	X	X	X			X
8. <i>d</i> -limonene	X	X	X	X	X	X	X
9. 2-hexenal				X			
10. <i>n</i> -octanal		X	X	X	X	X	X
11. <i>n</i> -hexanol		X	X	X	X	X	X
12. <i>cis</i> -3-hexene-1-ol		X	X	X	X	X	X
13. <i>trans</i> -linalool oxide				X			
14. <i>cis</i> -linalool oxide				X			
15. linalool	X	X	X	X	X	X	X
16. <i>n</i> -octanol			X	X	X	X	X
17. terpinene-4-ol		X		X		X	
18. <i>trans</i> -2,8- <i>p</i> -menthadiene-1-ol <sup>b</sup>				X		X	
19. ethyl 3-hydroxyhexanoate	X	X		X		X	
20. $\alpha$ -terpineol, neral		X	X	X	X <sup>c</sup>	X	X
21. geraniol	X	X	X	X	X	X	X
21A. valencene	X						
22. citronellol, carvone			X	X	X	X	
23. nerol			X	X	X	X	
24. <i>trans</i> -carveol, geraniol			X	X <sup>d</sup>	X	X <sup>d</sup>	
25. <i>cis</i> -carveol			X	X	X	X	
26. 1,8- <i>p</i> -menthadiene-9-ol <sup>b</sup>			X	X	X	X	X
27. <i>p</i> -menthane-1,2-diol <sup>b</sup>				X			

<sup>a</sup> Identified by mass spectrum only. <sup>b</sup> Identified as a component of orange essence for the first time. <sup>c</sup>  $\alpha$ -Terpineol. <sup>d</sup> Geraniol.

verify this, linalool being the major component of aroma solutions from both albedo and flavedo. Ethyl 3-hydroxyhexanoate and valencene appeared to be the volatile organic compounds characteristic of the aqueous aroma from the interior of the fruit, while linalool was characteristic of aroma solution from the peel (Swift, 1961; Wolford *et al.*, 1963).

The presence of a large amount of ethyl 3-hydroxyhexanoate in an earlier study of orange essence (Schultz *et al.*, 1964) was not verified in a later study (Schultz *et al.*, 1967). Results of this current study may help explain that discrepancy. Carefully peeled oranges free of peel oil were used for the earlier study, while peel oil was not excluded from the oranges used in the later study. Components characteristic of the interior of the fruit, such as ethyl 3-hydroxyhexanoate, predominate in the earlier analysis as reported, while peel oil components dominate the later one.

Other glc peaks also pointed up differences in the aroma solutions from different sources. The alcohols hexanol (11) and *cis*-3-hexene-1-ol (12) represent prominent components of both albedo and flavedo aroma solution. *Cis*-3-hexene-1-ol was more highly concentrated in the albedo and hexanol in the flavedo. In the centrifuge effluent aroma solution  $\alpha$ -terpineol (peak 20, Figure 1) was the major constituent and was much larger, relatively, than this peak in any of the other samples. This high percentage of  $\alpha$ -terpineol in centrifuge effluent aroma solution probably is due to the conversion of limonene into  $\alpha$ -terpineol by hydration (Murdock and Hunter, 1968).

Thus, it has been shown that although the quantity of constituents of aroma solutions derived from different fruit parts varies considerably, all of them contain certain constituents which may be useful for specific applications. Aroma solutions from all the different sources studied had components which would be expected to influence flavor of products. A predominance of specific components such as *cis*-3-hexene-1-ol, hexanol, and  $\alpha$ -terpineol was also shown to be characteristic of aroma solutions derived from specific sources. It was also noted that a great number of the same components were found in all samples regardless of source.

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