

## Relationship of Soluble Solids, Acidity and Aroma Volatiles to Flavor in Late-Season Navel Oranges

D. Obenland  
Crop Protection and Quality  
San Joaquin Valley Agricultural Science  
Sciences Center  
U.S. Department of Agriculture  
Parlier, California  
USA

S. Collin, J. Sievert, K. Fjeld and M.L. Arpaia  
Kearney Agricultural Center  
University of California  
Parlier, California  
USA

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### Abstract

Late-season navel oranges in California sometimes have poor flavor even though they have high soluble solids content (SSC) and are very sweet. The reasons for this low flavor quality were investigated by evaluating individual late-season navel oranges for sensory attributes and then measuring SSC, titratable acidity (TA) and aroma volatiles from juice taken from the same oranges. A wide range in hedonic scores from below a rating of 4 (dislike slightly) to above 8 (like very much) was obtained for the 95 fruit evaluated, although 78% of the fruit were above a rating of 6 (like slightly). Correlation coefficients calculated between the sensory and chemical (SSC, TA and flavor volatiles) attributes were mostly non-significant and, in every case, very low, indicating that there were no clearly identifiable reasons for the flavor differences observed among the individual fruit. Partial least squares analysis using the combined chemical data as a dependent variable came to a similar conclusion and was able to account for only 25% of the variation in the sensory data by using the chemical data. It is possible that components other than those that were evaluated were responsible for the flavor differences or that the fruit were too similar in taste for our sensory panel to accurately categorize on an individual fruit basis.

### INTRODUCTION

Navel orange flavor is determined by a variety of factors that change during the development of the fruit and are influenced by the time of the season at which the harvest occurs. Fruit in the earliest part of the season typically have low SSC and high TA levels which are the primary factors that determine acceptability in this part of the season. As fruit develops the TA declines and SSC increases, leading to better flavor. Associated with this development is an alteration in the quantities of aroma-active constituents present in the fruit that are important to the overall flavor (Obenland et al., 2009). Less well-known and understood is what happens to and influences flavor in the later part of the season. Typically what is seen during the season is that flavor quality reaches a plateau and even begins to decline toward the end of the season. Although this has been associated with a loss of flavor balance due to the SSC/TA ratio that is present in these fruit, the reasons for the loss of flavor quality in late-season navel oranges are poorly understood.

Individual oranges, even those harvested off of the same tree, can differ greatly in quality parameters that can affect flavor. Position within the canopy strongly influences the level of SSC and TA in oranges (Sites and Reitz, 1949; Sites and Reitz, 1950) and was reported to influence flavor volatiles present in apples (Miller et al., 1996). Although fruit-to-fruit variability is a recognized problem in trying to associate sensory and instrumental data (Gunnness et al., 2009), generally flavor component analysis is conducted on pooled fruit samples due to the difficulty in performing the measurements on individual fruit. While this is useful in providing a picture of the overall differences in fruit composition between fruit types and treatments, the opportunity to link these

measurements to the individual tasted fruit is lost, potentially reducing the ability to detect important differences that may influence flavor.

In this study we characterized the differences in sensory characteristics among a group of individual late-season navel oranges and attempted to determine associations between these characteristics and the quality (chemical) attributes present in each fruit. The goal was to utilize these differences in individual fruit to try to better understand the basis of the reduced flavor quality sometimes observed in California late-season navel oranges.

## **MATERIALS AND METHODS**

### **Fruit**

Fruit were harvested on a single day in May 2008 from the University of California Lindcove Research and Extension Center near Exeter, CA. The time of year was considered very late in the California navel orange season. The three navel orange stains ('Chislett', 'Rohde' and 'Powell') used for the experiment were thought to have different SSC/TA ratios based upon previous work. The purpose of this was to examine the effect on flavor of differences in odor-active volatile composition in fruit with differing SSC/TA. After harvest the fruit were transported to the Kearney Agricultural Center, Parlier, CA and stored at 10°C until they were evaluated.

### **Sample Preparation**

The fruit for each day of tasting were removed from storage, washed and dried. The fruit were then cut to remove the top and bottom third, leaving a 2.5-cm section from the center of the fruit. Half of this remaining section was peeled and cut into six bite-sized wedges for presentation to the sensory panelists. The other half was peeled and juiced by hand using a Hamilton-Beach table-top juicer. This juice was filtered through a screen and a portion placed into 15-ml centrifuge tubes for determination of SSC and TA. The samples were kept cold or were frozen prior to analysis. A further sample of the juice was placed into 23×75.5 mm (20 ml) glass vials, sealed with a Teflon-coated septum, and frozen for later determination of odor-active volatiles. All samples were labeled to maintain the identity of each individual fruit throughout the test.

### **Quality and Sensory Analysis**

Soluble solids concentration for each fruit was determined from the juice by using a temperature-compensated refractometer (AO Scientific, Model 10423, Buffalo, NY, USA) and TA by titration with 0.1 mol L<sup>-1</sup> to an endpoint of pH 8.2 using a Radiometer TitraLab 80 Titration System (Lyon, France). Titratable acidity was calculated using the volume of titrant and expressed on a percent citric acid basis. BrimA was determined from SSC and TA by using the following formula:  $BrimA = SSC - 4(TA)$ . Sensory panelists used for these tests were employees of the Kearney Agricultural Center and can be considered as being semi-expert due to their previous experience in tasting navel oranges in prior sensory experiments. Prior to testing they had been instructed on how to evaluate for the sensory attributes of interest. Generally there were 12-20 panelists present for each tasting. Panelists, seated separately in three-sided booths, were presented individual fruit wedges in 30-ml soufflé cups that had been marked with a unique identification number. Each panelist tasted eight fruit samples per day over a three-day period, with each individual fruit being tasted three times by different panelists. A total of 189 fruit were tasted over the course of the experiment. Panelists rated each fruit sample for likeability (hedonic score) by giving each sample a rating from 1 (dislike) to 9 (dislike extremely). In addition, samples were rated for richness, sweetness, tartness and the degree of old flavor present by placing a mark on a 150-mm line scale. A larger number indicated more richness, more sweetness, less tartness and less old flavor.

## Volatile Analysis

Based upon results from the sensory data, 10 juice samples from individual fruit were identified for gas chromatography/olfactometry analysis by selecting five samples that came from fruit of very poor flavor and five from fruit with excellent flavor. Each headspace sampling vial contained 6 ml of juice with no added salt. Prior to analysis the frozen juice samples were thawed for 15 min in a 40°C water bath. Trapping of the volatiles in the vial headspace was conducted with slow stirring at the same temperature for 30 min, using a 75- $\mu$ m carboxen/polydimethylsiloxane solid phase microextraction (SPME) fiber in a manual holder. Following trapping the SPME fiber was desorbed in the heated inlet of a 6890 gas chromatograph (Agilent, Palo Alto, CA, USA). Analytical parameters for the chromatography were as previously given (Obenland et al., 2008). After exiting the column the effluent was equally split between a flame ionization detector and an SGE ODO II olfactory port (Austin, TX, USA). Sniffing from the olfactory port was accomplished by two panelists that had been extensively trained on the evaluation of aromas from navel orange juice. Odors detected by panelists during the run were noted by moving a lever on a self-made potentiometer that would register a mark on the FID chromatogram that would indicate odor-active peaks. The size of the olfactory peak registered by the potentiometer also was some indication of the intensity of the odor. Each aroma had to be detected by both panelists for it to be declared a valid aroma-active compound. As a result of the gas chromatography/olfactometry work a list of aroma-active compounds present in fruit of both poor and good flavor with their associated retention indices was generated and used to designate what compounds to quantify in the late navel samples.

Volatile identification and quantification was conducted by gas chromatography/mass spectrometry. 95 randomly-chosen samples, 50% of the total number tasted, were analyzed. Just before analysis the vials were thawed and placed into a refrigerated vial holder in a MPS2 automated sampler (Gerstel, Linthicum, MD, USA). All further measurement steps were conducted by the MPS2 sampler. Each sample was heated for 15 min at 40°C prior to trapping of volatiles in the headspace using a 75- $\mu$ m carboxen/polydimethylsiloxane SPME fiber. The temperature of the vial was maintained at 40°C with stirring for the duration of the 30-min trapping period. The SPME fiber was then removed from the vial and desorbed into an Agilent 7890 gas chromatograph coupled to an Agilent 5975 mass spectrometer. Analytical conditions were as outlined in Obenland et al. (2008). Identification and matching of peaks with those in the gas chromatography/olfactory chromatogram was conducted by the use of retention indices, standard compounds and comparison to Wiley/NBS library spectra.

## Statistics

Each fruit was tasted by at least four panelists, with the analysis being conducted on the mean sensory values for each fruit across panelist. Analysis of the sensory data using a one-way analysis of variance with navel strain as the dependent variable indicated that there were no significant differences ( $P \leq 0.05$ ) in hedonic score, and ratings of oldness, richness, sweetness or tartness among the three navel orange strains utilized for this study (data not shown). As a result, the data from the three strains (95 total fruit) were pooled for the subsequent analyses. Pearson's correlation coefficients were calculated between the sensory, quality and aroma volatile data for each of the 95 fruit to identify relationships between these variables. A partial least squares procedure (SAS, Cary, NC, USA) was used to determine the overall amount of variability in the sensory parameters that could be explained by the quality and aroma volatile data.

## RESULTS AND DISCUSSION

Sensory analysis of the individual fruit indicated that in general the panelists liked eating these particular lots of late-season fruit as the majority of the individual fruit (78%) had average hedonic scores that exceeded 6, a rating that indicates slight liking (Fig. 1). This is not surprising given that SSC/TA is generally very high at this point in the season

and is an important factor in determining consumer acceptance (Ivans and Feree, 1987; Obenland et al., 2009). Nonetheless, there was a wide range in hedonic scores for the 95 individual fruit, with 22% given a rating less than 6 and 5% less than 5 (neither like nor dislike). This fruit-to-fruit variability in flavor provided an opportunity to determine potential causes for the poor flavor that is sometimes observed in late-season navel oranges.

Fruit with higher hedonic scores were generally perceived as having a less old and a sweeter, richer flavor than fruit with lower scores, while tartness was unrelated to hedonic score ratings (data not shown). Sweetness, richness and oldness were also closely related to each other.

Measurements of the SSC and TA of each fruit indicated that a range of values existed for these two quality parameters, as well as for the combination values of SSC/TA and BrimA, among the fruit (Table 1). Correlations ( $r$ ) between these quality measurements and the sensory parameters indicated that there were no significant relationships with hedonic score, oldness or tartness. Sweetness and richness were significantly correlated with SSC and TA, but the correlation values were low (less than 0.25), indicating a weak association. It is possible that the SSC values were simply too high and the TA values too low for any differences in these two measurements to be much of a factor in influencing the flavor characteristics of the fruit. We previously observed, however, that hedonic score increased in a fairly linear manner over the same range of BrimA values that were observed in this study (Obenland et al., 2009). That there was no relationship between BrimA and hedonic score in this study may indicate that other factors, such as flavor volatiles or other unknown components in the fruit are playing some important role.

Twenty aroma-active compounds were detected by means of gas chromatography/olfactometry in the juice from the late navels in this study of which 15 could be identified (Table 2). Many of these compounds have been reported to likely have impact in determining orange flavor (Ahmed et al., 1978; Buettner and Schieberle, 2001). As the data are presented in a relative basis it is not possible to identify which of these odor-active compound are above the aroma threshold and more likely to be contributing to flavor, but it is possible to study potential associations with flavor. Many of the same compounds had been previously found in navel oranges harvested earlier in the season (Obenland et al., 2008), although the late-season oranges used in this study possessed a greater number of identifiable compounds. As can be seen by comparing the maximum and minimum values on the basis of percent peak area, individual fruit varied greatly in the content of odor-active volatiles present. Hexanal, for example, was twenty times greater on a percentage basis, in the fruit with the highest content as compared to the lowest. Although a great deal of variability in volatile content was present it did not appear to translate obviously into differences in flavor. Correlations between the sensory parameters and measured volatiles were all very low, most being less than 0.1 (Table 2).

In looking at the data in a more combined manner, analysis using partial least squares indicated that at a maximum only 24% of the variability in the sensory data, including hedonic score, can be explained by all of the chemical data taken together. This result is consistent with the previous correlation data and it is clear that the chemical attributes that we have assessed were not very predictive of the flavor. As has been previously discussed, the lack of a relationship between SSC, TA and flavor is not surprising given that all of the fruit at this point in the season were very sweet with low acid. The inability of any flavor volatile or combination of volatiles to account for the sensory difference is more difficult to explain. It may be that we did not measure the compounds that were really important in determining the differences. Also, it cannot be ruled out that factors such as texture and juiciness are playing a role. Another possibility is that even though three people tasted each fruit, our sensory evaluations were not accurate enough to adequately differentiate between individual fruit, especially given that the majority of the fruit had good flavor and exceeded a hedonic score of 6. Further research will be necessary to determine the answer to these questions.

## ACKNOWLEDGEMENTS

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## Tables

Table 1. Minimum and maximum values of soluble solids (SSC), titratable acidity (TA), SSC/TA ratio and BrimA (SSC - 4\*TA) among 95 individual late season navel oranges and Pearson's correlation coefficients between these measures and sensory parameters evaluated for the same fruit.

Quality measurement	Min.	Max.	Correlation (r) with sensory parameters <sup>z</sup>				
			Hedonic	Oldness	Richness	Sweetness	Tartness
SSC	10.1	15.2	0.184	0.193	0.244*	0.237*	0.085
TA	0.35	0.74	0.172	0.144	0.255*	0.229*	-0.077
SSC/TA	17.2	32.0	-0.098	-0.048	-0.154	-0.115	0.161
BrimA	8.4	12.5	0.152	0.172	0.191	0.192	0.126

An asterisk indicates statistical significance at  $P \leq 0.05$

<sup>z</sup> For hedonic (score), richness, and sweetness a higher rating indicated more of each parameter, while for oldness and tartness the opposite was true.

Table 2. Aroma-active volatile compounds present among 95 individual late-season navel oranges as determined by gas chromatography/olfactometry and associations of the volatiles with sensory parameters determined using the same fruit.

Compound <sup>x</sup>	Aroma	RI <sup>y</sup>	% of total peak area		Correlation (r) with sensory parameters <sup>z</sup>				
			Min.	Max.	Hedonic	Oldness	Richness	Sweetness	Tartness
acetaldehyde	sweet		0	0.21	0.191	-0.025	0.255*	0.144	-0.137
1-penten-3-one	metallic	691							
hexanal	grassy	803	0.58	5.93	0.088	0.146	0.122	0.050	-0.033
ethyl butanoate	fruity	806	0.14	2.85	-0.012	-0.042	0.014	-0.018	0.168
unknown 1	cereal	872							
heptanal	fatty	902	0.12	1.00	0.108	0.166	0.157	0.080	-0.023
unknown 2	mushroom	983							
unknown 3	fatty, lemon	990							
β-myrcene	musty	997	6.67	15.32	-0.121	-0.121	-0.104	-0.078	0.103
ethyl hexanoate	sweet	1005	0	0.51	0.019	-0.012	0.037	0.059	0.215*
octanal	fatty	1009	0.57	3.79	-0.109	-0.094	-0.082	0.026	0.106
limonene	minty	1047	76.48	84.84	-0.127	-0.119	-0.153	-0.115	0.042
α-terpinolene	fresh	1101	0.26	3.25	-0.010	0.036	0.013	0.089	-0.019
linalool	citrus	1109	0	0.93	0.116	0.208	0.165	0.190	-0.056
unknown 4	cereal	1153							
unknown 5	cucumber	1165							
(E)-2-nonenal	plastic	1169	0.01	0.07	0.115	0.197	0.202*	0.120	0.081
decanal	fatty, lemon	1215	0.05	2.34	-0.030	-0.013	0.023	0.096	0.072
n-octyl acetate	fruity	1219	0.03	0.53	-0.048	-0.077	0.023	0.066	0.164
carvone	mint	1262	0.05	0.35	0.083	0.184	0.123	0.079	0.076
total					-0.119	-0.111	-0.131	-0.097	0.057

An asterisk indicates statistical significance at  $P \leq 0.05$ .

<sup>z</sup> For hedonic (score), richness, and sweetness a higher rating indicated more of each parameter, while for oldness and tartness the opposite was true.

<sup>y</sup> Retention index values calculated using a series of n-alkane standards run under the same chromatographic conditions.

**Figures**

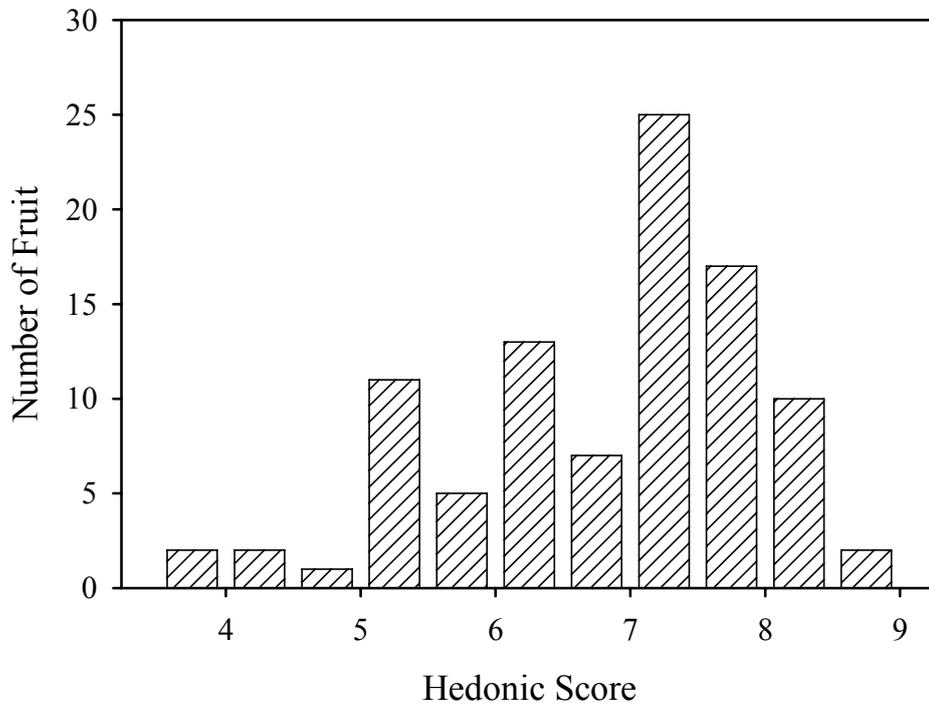


Fig. 1. Number of fruit within different hedonic score classifications. A rating of 4=dislike slightly, 5=neither like nor dislike, 6= like slightly, 7= like moderately, 8= like very much, 9=like extremely.

