Effect of Coatings and Prolonged Storage Conditions on Fresh Orange Flavor Volatiles, Degrees Brix, and Ascorbic Acid Levels

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Valencia oranges were treated with a commercial polysaccharide-based coating or a commercial shellac-based water wax or were left uncoated. The fruit were then stored at 16 or 21 $^\circ C$ with 95% relative humidity for up to 56 days. Samples were periodically analyzed for internal gases, flavor volatiles, water loss, "Brix, and ascorbic acid. Coated fruit had lower internal O_2 and higher CO_2 and ethylene concentrations than uncoated. Shellac-coated fruit had the lowest and highest amounts of O2 and CO2, respectively, at 21 °C. Generally, coated fruit showed higher concentrations of many volatile compounds as time in storage increased, most notably ethanol, ethyl butanoate, ethyl acetate, and α -pinene. This was especially true for shellac-coated fruit, for coated fruit at the higher storage temperature, and after the second month of storage. In contrast, levels of valencene, α -terpineol, and hexanol were generally lower in shellac-coated fruit and all coated fruit at the higher storage temperature. Several hydrocarbon and minor alcohol volatiles increased then decreased during the storage period. Some exceptions were α -pinene, sabinene, and isobutanol which generally increased in coated fruit by the end of the storage period. Shellac-coated fruit had significantly less weight loss than fruit subjected to all other treatments, whereas polysaccharide-treated fruit did not retard water loss compared to uncoated fruit. No significant differences were found for °Brix or ascorbic acid concentrations.

Keywords: Cellulose; ethylene; internal gas; modified atmosphere; shellac

The flavor volatile profile of citrus fruit juice has been reported to change in response to storage conditions such as temperature (Nisperos-Carriedo and Shaw, 1990a) and controlled atmosphere (low O_2) (Bruemmer and Roe, 1969; Ke and Kader, 1990; Shaw et al., 1990). Use of low O_2 storage atmospheres resulted in increased ethanol and acetaldehyde concentrations in citrus fruit (Davis et al., 1973; Pesis and Avissar, 1989; Shaw et al., 1990), suggesting a shift to anaerobic respiration. Waxing (coating) of fruit can result in the creation of a modified internal atmosphere within the fruit consisting of relatively low O₂ and high CO₂ compared to unwaxed fruit (Ben-Yehoshua, 1969; Davis and Hofmann, 1973; Ben-Yehoshua et al., 1985; Nisperos-Carriedo et al., 1990; Hagenmaier and Baker, 1993a). It also induces an increase in the amount of some flavor volatiles such as ethanol and acetaldehyde (Davis, 1970; Davis and Hofmann, 1973; Davis et al., 1973; Burns and Echeverria, 1988; Nisperos-Carriedo et al., 1990). In grapefruit, the increase in ethanol correlated to a decrease in °Brix and acid, but such a correlation was not found for oranges (Bruemmer and Roe, 1970; Davis et al., 1973).

It has been reported that waxing of citrus fruit can adversely affect the fruit flavor (Davis and Hofmann, 1973; Cohen et al., 1990; Hagenmaier and Baker, 1993b), perhaps due to overproduction of volatiles associated with anaerobic conditions, such as ethanol, methanol, and acetaldehyde. Harvested tangerine fruits, especially those that are waxed, are particularly susceptible to off-flavor development (Cohen et al., 1990). Another report claimed no adverse flavor effects when Shamouti or Valencia oranges were coated with various waxes, although the waxing treatments caused changes in internal O_2 and CO_2 concentrations (Ben-Yehoshua, 1969).

Commercial "waxes" (coatings) for citrus fruit are often composed of shellac and other ingredients. Often they do not contain an actual wax component. Their purpose is to retard water loss, add shine, and carry fungicides. With shellac-based coatings, however, there may be a trade-off between shine/water loss control and creation of anaerobic conditions in the fruit which may lead to off-flavor development (Davis and Hofmann, 1973; Hagenmaier and Baker, 1993a,b). Shellac-type coatings have been shown to have low permeability to gases compared to other types of coatings and are, therefore, more likely to affect the fruit internal atmosphere (Davis and Hofmann, 1973; Hagenmaier and Shaw, 1991, 1992).

Temperature and humidity levels can affect coating permeability (Kester and Fennema, 1988). The permeability of shellac-type coatings to O_2 and CO_2 was shown to increase at high humidity levels, such as are used for commercial storage of citrus (Hagenmaier and Shaw, 1992). Polysaccharide-type coatings, on the other hand, are generally poor barriers to moisture but are more permeable to gases than shellac (Kester and Fennema, 1988).

Storage temperature can affect fruit respiration. The oxygen requirement of fruit increases significantly with increased storage temperature (Beaudry et al., 1992). Therefore, the temperature and humidity levels at which fruit are held affect both fruit respiratory demand and coating permeability to gases. These combined factors contribute to alteration of the fruit internal

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atmosphere and thus may affect flavor. Previous studies on citrus fruit involving coatings, internal fruit atmosphere, flavor, and/or flavor volatiles were conducted using storage conditions and/or coatings that do not reflect those used by the industry (Nisperos-Carriedo et al., 1990; Hagenmaier and Baker, 1993a). In this study, fruit were coated by a standard industry waxer with a popular commercial "water wax" shellac coating or a more gas-permeable polysaccharide coating. The main objective of this research was to determine the effects of commercially available coatings on the flavor and aroma volatiles, among other factors, in stored citrus fruit.

MATERIALS AND METHODS

Valencia orange fruit, commercially harvested from a grove in Lake Placid, FL, were obtained the next day at a local packinghouse in Winter Haven, FL. The fruit were transported to the University of Florida Citrus Experiment Station, sorted, and either washed and waxed, washed only (washedunwaxed), or left untreated (field-run). Fruit were washed with a commercial detergent (395 FMC detergent; 1:20, detergent to water), delivered to the fruit with a foam applicator at an exposure of 30 s prior to rinsing. The fruit were then coated using a commercial-type waxer (16 brush bed conveying line) equipped with drip emitters (2 rows \times 21 nozzles/row, 53 cm spray width) at a rate of 54 mL of coating material to 23 kg of fruit (flow rate = 110 mL/min). Care was taken to ensure adequate tumbling action of the fruit so that uniform coverage could be achieved. After coating, the fruit were conveyed to a dryer, where drying occurred at 58 °C for a duration of 2 min (simulating commercial packinghouse conditions). Waxer brushes were thoroughly washed and allowed to dry between coating treatments. The coating treatments included a commercial water wax (shellac-type coating) and a commercial polysaccharide-type coating (cellulose-based), both with 2000 ppm of thiabendazole. Half of the fruit were stored at 21 $^{\circ}$ C and the other half at 16 $^{\circ}$ C (to simulate marketing and storage temperatures). Relative humidity in both storage rooms was maintained at approximately 95%. The fruit were periodically sampled and analyzed for internal gases, flavor volatiles, weight loss, °Brix, and ascorbic acid levels.

Internal O_2 , CO_2 , and ethylene were measured on five fruit per treatment as described previously (Nisperos-Carriedo et al., 1990). Samples were analyzed using a Hewlett-Packard Model 5890 GC equipped with Porapak Q and molecular sieve columns (Supelco, Bellefonte, PA) and a thermal conductivity detector for O_2 and CO_2 measurements (0.5 mL sample injection) and a Perkin-Elmer 8500 GC with an activated alumina column and FID detector for ethylene (0.5 mL sample injection).

Flavor volatiles, °Brix, and ascorbic acid were measured on hand-extracted juice samples. For flavor volatiles, three replicates, each consisting of a composite juice sample from 10 fruit, were analyzed per treatment. Two milliliters of the composite juice sample was transferred to 6 mL vials with crimp-top caps and TFE/silicone septa seals. Volatile flavor components were analyzed using a Perkin-Elmer 8500 GC with an HS-6 headspace sampler, a flame ionization detector, and a 0.53 mm \times 30 m polar Stabilwax column (1.0 μ m film thickness) (Restek Corp., Bellefonte, PA) under conditions described previously (Nisperos-Carriedo et al., 1990). Juice samples were equilibrated in the headspace sampler for 15 min at 80 °C prior to injection. Injection parameters for the headspace sampler were 0.5 min of vial pressurization time followed by 0.02 min of injection time. Column oven temperature programming was 40 °C for 6 min and then raised at 6 °C/min to 180 °C. The different volatile components were identified by comparison of retention times with standards and by enrichment of the juice with authentic samples. Concentrations of the individual volatile compounds were calculated by using regression equations (five concentrations per standard) to obtain a peak height calibration curve as described previously (Nisperos-Carriedo et al., 1990). Fresh weight was measured individually on 10 fruit per treatment. °Brix was measured using a refractometer: three readings were averaged per fruit on three fruit per treatment.

Ascorbic acid content was measured in the hand-extracted juice by a high-performance liquid chromatography method developed for separation of ascorbic acid from other organic acids in fruits (Nisperos-Carriedo et al., 1992). The chromatographic equipment consisted of a solvent delivery system (Perkin-Elmer isocratic LC pump 250) and a sample injector. Detection of ascorbic acid was performed at 215 and 260 nm using a diode array detector (Perkin-Elmer LC 235) interfaced with two portable integrators (Hewlett-Packard 3396A).

Data for the flavor volatile components were analyzed by analysis of variance using the General Linear Model (GLM) procedure of the Statistical Analysis System (SAS Institute Inc., Cary, NC). Data were analyzed in a completely randomized design (CRD) with a split-plot treatment arrangement. Specific differences were determined by least significant difference (lsd) and least-squares means. All comparisons were made at a 5% level of significance.

RESULTS AND DISCUSSION

Valencia oranges that received coating treatments exhibited lower concentrations of internal O_2 (Figure 1) and higher concentrations of internal CO_2 (Figure 2), resulting in a modified atmosphere compared to uncoated fruit at both storage temperatures. The differences between the two types of coatings were evident in fruit stored at 21 °C (Figures 1B and 2B), with the shellac-coated fruit having the lower and higher O_2 and CO_2 , respectively, but were minimized in fruit stored at 16 °C (Figures 1A and 2A). This is probably due to the difference in oxygen demand for fruit held at these two temperatures and the differences in permeability of the two types of coatings to these gases. The fruit would have an increased O2 demand at the higher storage temperature and, therefore, the fruit internal atmosphere would be more affected by the gas permeability characteristics of the coating. The high levels of CO₂ in coated fruit fluctuated but generally declined over time, especially for those treated with the polysaccharide coating. This may have been due to the effects of time and handling of the fruit (which were inspected once a week to discard infected oranges) that possibly altered coating continuity. There were no differences between field-run fruit (which have the natural waxy coating intact) and washed-unwaxed fruit for internal O_2 or CO_2 . Natural and synthetic waxes have been shown to be quite permeable to gases (Hagenmaier and Shaw, 1992). The concentration for internal CO_2 in shellac-coated fruit reached a maximum of approximately 9% after 1-2 weeks of storage (Figure 2), which is considerably lower than that reported by Hagenmaier and Baker (1993b) for shellac- and resin-coated Valencia oranges stored for up to 1 week at 21 °C. They observed amounts as high as 16-18%; however, the storage relative humidity reported for that study was 50% compared to 95% used in this study and commonly by the citrus industry. As mentioned above, shellac coatings increase in permeability under conditions of high humidity (Hagenmaier and Shaw, 1992).

Internal ethylene levels were monitored in fruit stored at 16 °C (Figure 3) for the first month of storage. Washing and coating of fruit increased internal concentrations of ethylene compared to field-run fruit on the day of treatment. Coated fruit showed higher internal ethylene amounts over the storage period compared to washed-unwaxed fruit until the fourth week of storage, when ethylene concentrations declined. Perhaps the decline of internal ethylene, as with the internal CO_2 , signified coating breakdown over time due to handling.



Figure 1. Internal oxygen concentration ($\%O_2$) of orange fruits: field run (FIELD), washed-unwaxed (WU), coated with a commercial polysaccharide-based coating (PS), or coated with a shellac-based commercial "water-wax" (SH) and stored at (A) 16 or (B) 21 °C. Values represent means of five fruit.

There were no obvious differences between the coating treatments for internal ethylene concentrations. The increase in internal ethylene amounts may have been a "wound" response to the presence of coating on the fruit surface and/or due to the partial permeability of the coatings to this gas (Hagenmaier and Shaw, 1992) which would result in ethylene accumulation.

Volatiles, which have been reported to be important to citrus flavor (desirable or undesirable) (Nisperos and Shaw, 1990b), were analyzed in the juice of coated and uncoated (washed-unwaxed) oranges that were stored at the two different temperatures (Figures 4-7). Orange volatiles analyzed in this study include the major alcohols (ethanol and methanol) (Figure 4), esters (ethyl butanoate and ethyl acetate) (Figure 4), hydrocarbons (valencene, α -pinene, Γ -terpinene, and sabinene) (Figure 5), aldehydes (acetaldehyde, hexanal, and decanal, and octanal) (Figure 6), and minor alcohols (α -terpineol, linalool, cis-3-hexenol, hexanol, and isobutanol) (Figure 7). All flavor volatile levels were influenced by coating and/or storage temperatures. Of the 17 volatiles quantified, 12 showed significantly increased concentrations due to one or both coating treatments at one or both storage temperatures after 56 days of storage: ethanol, methanol, ethyl butanoate, ethyl acetate (Figure 4), α -pinene, Γ -terpinene, sabinene (Figure 5), acetaldehyde, decanal, octanal (Figure 6), linalool, and isobutanol (Figure 7). Conversely, there were significant decreases in valencene (Figure 5) and α -terpineol (Figure 7) in one or both coating treatments at 21 °C. With storage of up to 2 months, fruit coated with shellac exhibited generally higher volatile amounts than those coated with the polysaccharide. Ethanol, methanol (21 °C only) (Figure 4), and linalool (Figure 7) increased roughly 2-fold at both storage temperatures in shellaccoated fruit, the esters 4–8-fold (Figure 4), α -pinene and sabinene over 2-fold (Figure 5), and octanal and isobutanol 2-5-fold (Figures 6 and 7, respectively), compared to uncoated controls by the end of the storage period. These results are similar to those of earlier studies from this laboratory which showed that storage of oranges under lowered O2 conditions afforded the greatest increases to occur in the more water soluble volatile components, especially ethanol, methanol, isobutanol, ethyl butanoate, and other esters (Shaw et al., 1990). Conversely, α -terpineol showed significantly decreased amounts in shellac-coated fruits compared to polysaccharide-coated or uncoated fruits at both storage temperatures at the end of the storage period (Figure 7). Valencene and hexanol (21 °C) also showed significantly decreased concentrations in coated fruit at different times during the storage period (Figures 5 and 7B, respectively). This instrumental evidence of altered flavor volatile profiles in coated fruit would seem to support previous studies in which coated fruit were determined to have off-flavors compared to uncoated (Davis and Hofmann, 1973; Cohen et al., 1990; Hagenmaier and Baker, 1993b).



Figure 2. Internal carbon dioxide concentration ($%CO_2$) of orange fruits: field run (FIELD), washed-unwaxed (WU), coated with a commercial polysaccharide-based coating (PS), or coated with a shellac-based commercial "water-wax" (SH) and stored at (A) 16 or (B) 21 °C. Values represent means of five fruit.



Figure 3. Internal ethylene concentration (ppm of C_2H_4) of orange fruits: washed-unwaxed (WU), coated with a commercial polysaccharide-based coating (PS), coated with a shellac-based commercial "water-wax" (SH) and stored at 16 °C. Values represent means of five fruit.

Significant changes occurred in volatile concentrations within the first 2 weeks of storage. All flavor volatiles but sabinene increased or decreased in shellaccoated fruit at one or both temperatures after 2 weeks of storage compared to uncoated fruit, resulting in an altered volatile profile (Figures 4-7). These changes were significant for all except ethyl acetate, α -pinene, hexanal, decanal, octanal, and linalool. For polysaccharide-coated fruit, a similar pattern was observed, with the exception of methanol (Figure 4), for which the concentration generally remained similar to that of uncoated fruit, and for sabinene (Figure 5) and linalool



Figure 4. Concentration (ppm) of volatile ethanol (ETOH), methanol (MEOH), ethyl butanoate (ETH-BUTE), and ethyl acetate (ETH-ACET) flavor components of fresh hand expressed orange juice. Values represent means of three replicate samples, each a composite of 10 washed-unwaxed (WU), polysaccharide- (PS) or shellac- (SH) coated fruit stored at (A) 16 or (B) 21 °C.

(Figure 7), for which significant changes were observed. Volatile concentrations in harvested fruit continued to change during storage. Volatile compounds that increased significantly at some point over time for control





Figure 5. Concentration (ppm) of volatile valencene (VAL), α -pinene (PIN), Γ -terpinene (TERP), and sabinene (SAB) flavor components of fresh hand-expressed orange juice. Values represent means of three replicate samples, each a composite of 10 washed-unwaxed (WU), polysaccharide- (PS) or shellac- (SH) coated fruit stored at (A) 16 or (B) 21 °C.

fruit included ethanol, methanol (Figure 4), valencene, α -pinene (Figure 5), acetaldehyde, hexanal (Figure 6),

 α -terpineol, linalool, *cis*-3-hexenol, hexanol, and isobutanol (Figure 7) at one or both temperatures. Ethyl





Figure 6. Concentration (ppm) of volatile acetaldehyde (ACET), hexanal (HEX), decanal (DEC), and octanal (OCT) flavor components of fresh hand-expressed orange juice. Values represent means of three replicate samples, each a composite of 10 washed-unwaxed (WU), polysaccharide- (PS) or shellac- (SH) coated fruit stored at (A) 16 or (B) 21 °C.

butanoate showed a significant decrease in control fruit stored at 16 °C (Figure 4A). Coated fruit showed opposite trends for ethyl butanoate (Figure 4), which significantly increased at one or both storage temper-



Figure 7. Concentration (ppm) of volatile α -terpineol (TERPIN), linalool (LIN), *cis*-3-hexenol (C3HEX), hexanol (HEX), and isobutanol (ISO) flavor components of fresh hand-expressed orange juice. Values represent means of three replicate samples, each a composite of 10 washed–unwaxed (WU), polysaccharide- (PS) or shellac- (SH) coated fruit stored at (A) 16 or (B) 21 °C.

atures, and valencene (Figure 5), which decreased. Otherwise, coated fruit showed similar trends to uncoated fruit with the addition of significant increases in decanal and octanal (Figure 6) for shellac-coated fruit and in ethyl acetate (Figure 4) and Γ -terpinene (Figure 5) for both coating treatments for at least one storage temperature.

For some volatiles, the greatest change took place during the second month of storage, which resulted in substantial increases in ethanol and methanol concentrations (Figure 4) and significant decreases in α -terpineol (Figure 7) in fruit coated with shellac, the changes being more evident at 21 °C. For polysaccharide-coated fruit, methanol concentrations remained similar to that of uncoated fruit. Although ethanol concentrations in polysaccharide-coated fruit increased significantly during the 2 month storage period, they were still lower than that of shellac-coated fruit.

Some volatile compounds peaked at some point during the storage period and then declined. For control fruit, these included the hydrocarbons (Figure 5) and minor alcohols (Figure 7). The changes in volatile concentrations were significant for all but α -pinene and Γ -terpinene. For coated fruit, a similar pattern occurred for valencene, Γ -terpinene, α -terpineol, linalool, *cis*-3-hexenol, and hexanol, especially at 16 °C. The other volatiles (α -pinene, sabinene, and linalool) showed significant increases for at least one storage temperature for one or both coating treatments by the end of the storage period.

The storage temperature had surprisingly little effect on the accumulation of volatile compounds. When volatile amounts for the two storage periods were compared (additive for all time periods and treatments), only ethanol and ethyl butanoate (Figure 4) showed significantly higher concentrations in fruit stored at 21 °C compared to 16 °C. Methanol, ethyl acetate (Figure 4), α -pinene (Figure 5), and isobutanol (Figure 7) also showed a similar trend, mostly due to amounts in coated fruit after the second month of storage. Conversely, the additive values for *cis*-3-hexenol, hexanol, and sabinene were significantly higher in fruit stored at 16 °C.

Orange flavor is the most delicate and complex of the citrus flavors in terms of the number of volatile compounds identified. Apparently there are not one or two flavor-impact compounds responsible for orange flavor, as is the case for grapefruit, lemon, and lime, but rather a combination of volatile components in specific proportions (Shaw, 1991). The flavor of orange juice is known to be relatively unstable and easily changed by processing and storage conditions (Shaw, 1986). Compositional changes in the volatile profile, resulting from processing or storage conditions, cause alteration in flavor and aroma (Nisperos-Carriedo and Shaw, 1990b; Shaw et al., 1990). Earlier studies reported that correct proportions of the different volatile components are critical to orange flavor. Typical orange aroma is attributed to acids, alcohols, aldehydes, esters, hydrocarbons, and other components (Alberola and Izquierdo, 1978). Esters and aldehydes are thought to be the primary contributors to fresh orange flavor, but other components could also be important (Shaw, 1977). Of the volatile compounds analyzed in this study, ethyl butanoate, ethyl acetate, α -pinene, acetaldehyde, decanal, octanal, and *cis*-3-hexenol are considered to have a positive contribution to citrus flavor. High amounts of decanal (0.72 ppm), however, have been reported to have a negative contribution to orange flavor (Ahmed et al., 1978). Hexanal, although not considered to be very important, possibly contributes a green flavor note (Arctander, 1969). The esters quantified in this study, ethyl acetate and ethyl butanoate, are known to contribute to the "top note" of fruit flavors, including oranges (Arctander, 1969; Ahmed et al., 1978; NisperosCarriedo and Shaw, 1990a). cis-3-Hexenol contributes a green leafy top note in fresh orange and other fruit flavors (Arctander, 1969). Sabinene and Γ -terpinene, components of orange peel oil, give a spicy and citruslike aroma and flavor, respectively (Arctander, 1969). Their contribution and importance to overall orange flavor, however, have not vet been determined (Nisperos-Carriedo and Shaw, 1990a). Ethanol and methanol are generally thought to be associated with off-flavor in fruits; however, in synthetic flavorings and perfumes ethanol functions as a solvent that accentuates other aromas (Arctander, 1969) and probably performs a similar function in orange juice at appropriate concentrations (Nisperos-Carriedo and Shaw, 1990a). Methanol levels in fresh orange juice may be due to the presence of active pectin methylesterase enzymes which demethylate pectin in the fresh-squeezed juice, liberating methanol in the process. A similar phenomenon was observed in tomato fruit (Baldwin et al., 1991). The compound, α -terpineol, is associated with off-flavor in citrus, but at amounts higher than found here (Tatum et al., 1975), while valencene contributes a weak citruslike aroma. The flavor threshold level of valencene, however, has not been determined (Tatum et al., 1975; Nisperos-Carriedo and Shaw, 1990a). Isobutanol and linalool are minor alcohols; the former is present in fresh juice in trace amounts, and the latter is a component of peel oil (Nisperos-Carriedo and Shaw, 1990b). Linalool, although not considered to be an important contributor to orange flavor, was shown to make a positive contribution at a level of 0.84 ppm in combination with several other orange volatiles (Ahmed et al., 1978).

Shellac coatings, which are less permeable to O₂, CO₂, and ethylene than are polysaccharide-type coatings (Hagenmaier and Shaw, 1992), may present more resistance to the diffusion of these volatiles out of the fruit compared to the polysaccharide coating or fruit peel alone. Restriction of gas exchange and the resulting creation of a modified internal atmosphere by coatings may also alter fruit metabolism and affect volatile synthesis. However, volatile changes in shellac-coated fruit stored at 16 °C were generally greater than for polysaccharide-coated fruit stored at the same temperature, yet the difference in the internal atmospheres $(O_2$ and CO_2) of fruits from these treatment/storage temperature combinations was negligible (Figures 1A and 2A, respectively). Nevertheless, both of the above situations could have occurred simultaneously with the additive result of altered volatile levels in the juice. Certainly, low oxygen atmospheres have been shown to result in increased production of ethanol, methanol, and acetaldehyde in citrus fruit (Davis et al., 1973; Pesis and Avisser, 1989; Shaw et al., 1990).

Weight loss was measured weekly for the first month of storage and again at the end of the 2 month storage period. Field-run, washed-unwaxed, and polysaccharide-coated fruit exhibited a weight loss of 7.7 ± 0.8 to $8.9\pm0.3\%$, whereas shellac-coated fruit lost only 5.5 \pm 0.2% of their total weight after 2 months of storage. Substantial weight loss occurred in the first 2 weeks of storage (1.4-2.2%) of total weight). Weight loss was then fairly consistent over the second to fourth weeks, the fruit losing 0.6-1.1% per week. Finally, the fruit lost 2.4-3.7% of their total weight over the second month of storage. A previous study reported shrinkage rate (determined as weight loss over a specified period) to be greater in washed-unwaxed than "nonwashednonwaxed" (field-run) fruit after 1 week at 22 °C and 50% relative humidity. The increased shrinkage rate was believed to be due to alteration of the natural waxy

coating by the action of detergent and wash brushes (Hagenmaier and Baker, 1993a). The weight loss for field-run fruit observed in this study, however, was almost identical to that of washed-unwaxed fruit for the first 4 weeks of storage (for example, 4.2 ± 0.4 vs $4.3 \pm 0.2\%$, after 4 weeks). Apparently, appropriate storage conditions (with 95% relative humidity) and/or detergent can help to minimize the damaging effects of washing the fruit.

No significant differences or even discernable trends in °Brix were detected for the different storage temperatures or over the storage period. Uncoated fruit appeared to have slightly higher °Brix than coated fruit, but in most cases this was not significant (all measurements fell between 10.8 and 12.1 °Brix). Levels for ascorbic acid were measured in fruit stored at 16 °C after 2 days and again after 1 month of storage. Although not statistically significant, the amount of ascorbic acid in the juice showed a decreasing trend after 1 month of storage (from initial values of 41.4– 42.7 to 33.6-34.7 mg/100 mL juice after 4 weeks of storage). There was no apparent effect due to coating treatment, however.

In conclusion, long-term storage of oranges resulted in changes in the flavor volatile profile of the handextracted juice. Coating of the orange fruit altered the internal gas composition $(O_2, CO_2, and ethylene)$ during the storage period, which may have directly or indirectly caused the observed changes in the flavor volatile composition in the fruit juice. The presence of the coating barrier may also have caused a buildup of some volatiles. This may be especially true for amounts of ethanol and in fruit coated with shellac compared to those treated with the more permeable polysaccharidetype of coating. Some of the flavor volatiles that increased are reported to be desirable contributors to citrus flavor (ethyl butanoate, ethyl acetate, and acetaldehyde are examples). Others such as ethanol and methanol are generally associated with off-flavor. Nevertheless, deviation from the normal volatile flavor profile of freshly harvested uncoated (washed-unwaxed) fruit supports previous studies in which coated fruit exhibited altered flavor (Davis and Hofmann, 1973; Cohen et al., 1990; Hagenmaier and Baker, 1993b). Flavor of fruit stored for extended periods may be somewhat altered as well, even without coatings, but this is most likely to occur with shellac-coated fruit. Altered flavor profiles may be enhanced in fruit stored at marketing temperatures, even within the first 1-2weeks. The shellac coating, however, gave the fruit more shine and exhibited better weight loss control compared to the other treatments, and both of these attributes are important to the citrus industry. The polysaccharide coating was not effective in retarding water loss, and although it imparts an attractive sheen to the fruit, it does not give the high gloss effect of shellac coatings. For this reason, unless water barrier and "gloss" characteristics are improved, polysaccharidetype coatings are not likely to be used by the citrus industry at this time for most types of citrus fruits. Mandarin fruit, however, are more susceptible to anaerobic conditions (Cohen et al., 1990) and could possibly benefit from a polysaccharide-type of coating if improvements could be made in weight loss control. There were no significant effects of coating treatments or storage time on levels of soluble solids or ascorbic acid or of storage temperature for levels of soluble solids.

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LITERATURE CITED

- Ahmed, E. M.; Dennison, R. A.; Dougherty, R. H.; Shaw, P. E. Effect of nonvolatile components on flavor quality of pumpout orange juice. J. Agric. Food Chem. 1978, 26, 368-372.
- Alberola, J.; Izquierdo, L. J. The volatile fraction of orange juice. Methods for extraction and study of composition. In *Flavor of Foods and Beverages, Chemistry and Technology*; Charalambous, G., Inglett, G. E., Eds.; Academic Press: New York, 1978; pp 283-304.
- Arctander, S. Perfume and Flavor Chemicals; Arctander: Montclair, NJ, 1969; Vol. I and II.
- Baldwin, E. A.; Nisperos, M. O.; Scott, J. Quantitative analysis of flavor parameters in six Florida tomato varieties (*Lycopersicon esculentum Mill*). J. Agric. Food Chem. **1991**, 39, 1135-1140.
- Beaudry, R. M.; Cameron, A. C.; Shirazi, A.; Dostal-Lange, D. L. Modified atmosphere packaging of blueberry fruit: effect of temperature on package O₂ and CO₂. J. Am. Soc. Hortic. Sci. **1992**, 117, 436-441.
- Ben-Yehoshua, A. Gas exchange, transpiration, and the commercial deterioration in storage of orange fruit. J. Am. Soc. Hortic. Sci. 1969, 94, 524-528.
- Ben-Yehoshua, S.; Burg, S. P.; Young, R. Resistance of citrus fruit to mass transport of water vapor and other gases. *Plant Physiol.* **1985**, 79, 1048-1053.
- Bruemmer, J. H.; Roe, B. Postharvest treatment of citrus fruit to increase Brix/acid ratio. Proc. Fla. State Hortic. Soc. 1969, 82, 212-215.
- Bruemmer, J. H.; Roe, B. Biochemical changes in grapefruit during anaerobic metabolism. Proc. Fla. State Hortic. Soc. 1970, 83, 290-294.
- Burns, J. K.; Echeverria, E. Assessment of quality loss during commercial harvesting and postharvest handling of Hamlin oranges. Proc. Fla. State Hortic. Soc. 1988, 101, 76-78.
- Cohen, E.; Shalom, Y.; Rosenberger, I. Postharvest ethanol buildup and off-flavor in Murcott tangerine fruits. J. Am. Soc. Hortic. Sci. 1990, 115, 775-778.
- Davis, P. L. Relation of ethanol content of citrus fruits to maturity and to storage conditions. Proc. Fla. State Hortic. Soc. 1970, 83, 294-298.
- Davis, P. L.; Hofmann, R. C. Effects of coatings on weight loss and ethanol buildup in juice of oranges. J. Agric. Food Chem. 1973, 21, 455-458.
- Davis, P. L.; Roe, B.; Bruemmer, J. H. Biochemical changes in citrus fruits during controlled-atmosphere storage. J. Food Sci. 1973, 38, 225-229.
- Hagenmaier, R. D.; Baker, R. A. Cleaning method affects shrinkage rate of citrus fruit. *HortScience* 1993a, 28, 824-825.
- Hagenmaier, R. D.; Baker, R. A. Reduction in gas exchange of citrus fruit by wax coatings. J. Agric. Food Chem. 1993b, 41, 283-287.
- Hagenmaier, R. D.; Shaw, P. E. Permeability of shellac coatings to gases and water vapor. J. Agric. Food Chem. 1991, 39, 825-829.
- Hagenmaier, R. D.; Shaw, P. E. Gas permeability of fruit coating waxes. J. Am. Soc. Hortic. Sci. 1992, 117, 105-109.
- Ke, D.; Kader, A. A. Tolerance of Valencia oranges to controlled atmospheres as determined by physiological responses and quality attributes. J. Am. Soc. Hortic. Sci. **1990**, 115, 779– 783.
- Kester, J. J.; Fennema, O. R. Edible coatings: a review. Food Technol. 1988, 42, 47-59.
- Nisperos-Carriedo, M. O.; Shaw, P. E. Comparison of volatile flavor components in fresh and processed orange juices. J. Agric. Food Chem. **1990a**, 38, 1048-1052.
- Nisperos-Carriedo, M. O.; Shaw, P. E. Volatile flavor components of fresh and processed orange juices. Food Technol. 1990b, 44, 134-139.
- Nisperos-Carriedo, M. O.; Shaw, P. E.; Baldwin E. A. Changes in volatile flavor components of Pineapple orange juice as influenced by the application of lipid and composite films. J. Agric. Food Chem. 1990, 38, 1382-1387.
- Nisperos-Carriedo, M. O.; Buslig, B. S.; Shaw, P. E. Simultaneous detection of dehydroascorbic, ascorbic, and some

organic acids in fruits and vegetables by HPLC. J. Agric. Food Chem. 1992, 40, 1127-1130.

- Pesis, E.; Avisser, I. The postharvest quality of orange fruits as affected by pre-storage treatments with acetaldehyde vapor or anaerobic conditions. J. Hortic. Sci. **1989**, 64, 107-113.
- Shaw, P. E. Essential oils. In Citrus Science and Technology; Nagy, S., Shaw, P. E., Veldhuis, M. K., Eds.; AVI: Westport, CT, 1977; Vol. 1, pp 463-478.
- Shaw, P. E. The flavour of non-alcoholic fruit beverages. In Food Flavours. Part B. The Flavour of Beverages; Morton, E. D., Macleod, A. J., Eds.; Elsevier: Amsterdam, 1986; pp 337-368.
- Shaw, P. E. Fruits. In Volatile Compounds in Foods and Beverages; Maarse, H., Ed.; Dekker: New York, 1991; pp 305-327.
- Shaw, P. E.; Carter, R. D.; Moshonas, M. G.; Sadler, G. Controlled atmosphere storage or oranges to enhance aqueous essence and essence oil. J. Food Sci. 1990, 55, 1617– 1619.

Tatum, J. H.; Nagy, S.; Berry, R. E. Degradation products formed in canned single-strength orange juice during storage. J. Food Sci. 1975, 40, 707-709.

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