Kinetics of aseptic concentrated orange juice quality changes during commercial processing and storage

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Summary

Aseptically concentrated orange juice (COJ) was processed commercially at three holding temperatures (84, 87 and 90°C, 72 s) and stored for up to 7 weeks at 32°C and 15 weeks at 22°C. No differences were found in nonenzymic browning (NEB), vitamin C, sucrose, fructose and glucose, furfural, HMF (5-hydroxymethyl fufural), and DMHF (2,5-dimethyl-4-hydroxy-3(2H)-furanone) concentrations due to the different thermal treatment. The dominating factors affecting vitamin C retention and NEB were time and storage temperature. A lag-time was observed in NEB formation and its length depended on storage temperature. Furfural concentration was below 1 ppm. HMF reached c. 11 ppm after 7 weeks at 32°C. DMHF concentration decreased throughout the storage period. Sensory evaluation showed a nonsignificant preference for COJ processed at the lower temperature.

Keywords

Aseptic citrus juice, DMHF, furfural, nonenzymic browning, vitamin C.

Introduction

Aseptic packaging of citrus products provides products with improved quality, where nutritional and sensory attributes play a significant role (Kaana\-\-ne et al., 1988). Process and storage conditions are the main factors affecting quality factors such as vitamin C retention and nonenzymic browning (NEB) formation (Kaana\-\-ne et al., 1988; Kennedy et al., 1992; Lee & Nagy, 1988a; Marcy et al., 1989; Marshall et al., 1986; Nagy et al., 1990; Saguy et al., 1978a, b; Trammell et al., 1986). Vitamin C degradation leads to NEB, and the reduction of citrus product’s commercial value (Kaana\-\-ne et al., 1988; Kacem et al., 1987; Kennedy et al., 1990; Lee & Nagy, 1988a; Ostermann & Lorenz, 1988).

Other quality factors include sucrose loss due to hydrolysis (Lee & Nagy, 1988a, b; Kaana\-\-ne et al., 1988), furfural, 5-hydroxymethyl fufural (HMF), 2,5-dimethyl-4-hydroxy-3(2H)-furanone (DMHF), flavour loss and others (Kaana\-\-ne et al., 1988; Kanner et al., 1982; Lee & Nagy, 1988b; Marcy et al., 1989; Mannheim & Hawkin, 1981). Furfural and HMF are the end products of vitamin C decomposition (Nagy, 1980), or carbohydrate breakdown (Lee & Nagy, 1988b). The taste threshold concentration of these two components is too high to cause taste changes of stored citrus juices (Fors, 1983; Lee & Nagy, 1988b; Kanner et al., 1981, 1982); they are precursors to brown pigment formation. DMHF is a highly potent, off-flavour compound even
at 0.05 ppm, and imparts the strong caramel, and pineapple-like odour of aged orange juice (Lee & Nagy, 1988a).

The deterioration kinetics of vitamin C in citrus products is commonly described as a first-order reaction (Saguy et al., 1978a). However, it could also follow a pseudo-zero, first or second order reaction (Kennedy et al., 1992). The mode of decomposition could change at storage temperatures above 30°C (Lee & Nagy, 1988a). Nonenzymic browning and the formation of brown pigments in citrus products take place after a lag time in which uncoloured compounds are formed (Lee & Nagy, 1988a). The browning process is referred to as a zero-order reaction (Berk & Mannheim, 1986). Sucrose hydrolysis and furfural formation were described as a zero-order reaction (Kaanane et al., 1988), and HMF buildup as a first-order reaction (Lee & Nagy, 1988b). The objective of this research was to investigate the effect of thermal processing and storage conditions on the quality of commercial aseptic COJ.

Materials and methods

Concentrated orange juice (COJ)

Israeli orange juices were concentrated commercially on a 7-effect falling film evaporator (Cook Machinery, Tampa, FL) to 59.5°Brix, thermally processed in a triple holding tube aseptic unit (Olympic 8000, Rossi Cattelli, Parma, Italy) for 72 s at 84, 87 or 90°C, cooled immediately to about 25 ± 2°C and aseptically filled (PKL Verpackungsysteme, Linnich, Germany) in 1 litre cartons (consisting of five layers: PE, aluminium, PE, cardboard and PE) and stored at 22 ± 0.5 and 32 ± 1°C. Samples (two different cartons were opened per treatment) were taken initially and withdrawn periodically (1, 4, 7, 9, 12 and 15 weeks at 22°C, and 1, 2, 4, 5, 6 and 7 weeks at 32°C), and reconstituted to 11.2°Brix before duplicate analysis. Chemicals used were AR and HPLC grades. The samples were analysed immediately, or frozen and kept as concentrate at −18°C until testing.

Nonenzymic Browning (NEB)

Absorbance was measured at 420 nm (Meydav et al., 1977).

Vitamin C

A computerized HPLC method (Lee & Coats, 1987) was used in a system (Waters, Milford, MA) equipped with a Model 510 pump; automatic injector (Wisp 710B), a C-18 5-μm column (Licrospher, 250 × 4 mm, Merck, Darmstadt, Germany) with a C-18 guard column (Waters); and a spectrophotometer detector (Model 441, Waters) measuring absorbance at 254 nm. Data was expressed as g vitamin C 1−1 reconstituted single strength juice (11.2°Brix for orange juice). Meta-phosphoric acid was added to the sample before analysis to prevent ascorbic acid loss during the analysis.

Carbohydrates content

Reconstituted juice samples were centrifuged at 12 500 g for 10 mins. The supernatant (1 ml) and an internal standard (1 ml) of glycerol (30 g l−1) were transferred to a 100-ml flask and made up to volume with distilled water. The standard solution contained 0.3 mg l−1 of glucose (Merck), fructose (Panreac, Barcelona, Spain), sucrose (Sigma Chemicals, St. Louis, MO) and glycerol (Merck). The HPLC system was used with a Sugar-Pak column, in a 90°C oven (Waters) and a refractive index detector (Waters, 440 RI). Carbohydrates were eluted with 10−4 M Ca-EDTA (Aldrich Chemicals, Milwaukee, WI) at a flow rate of 0.5 ml min−1 (Anon. 1984).

Furfural, HMF and DMHF

To 10 ml juice, 0.5 ml of Carrez solution #1 (15% of K₄[Fe(CN)₆]·3H₂O; Merck, Darmstadt, Germany)
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Germany) and 0.5 ml of Carrez solution #2 (30% of ZnSO$_4$·7H$_2$O; Sigma) were added, mixed gently and left for 5 min before centrifuging at 2270 g for 10 min. One millilitre of the supernatant was passed through a C-18 Sep-Pak cartridge (preconditioned with 2 ml methanol, followed by 5 ml of water), and washed with 0.5 ml of hexane (Frutarom, Haifa, Israel). Furfural HMF and DMHF were eluted with 3 × 3 ml dry ethyl-acetate (Frutarom), and evaporated with N$_2$ to 1 ml in a water bath (35°C). The HPLC analyses were calibrated against 0.1% w/v freshly prepared standards in 10% methanol in water and diluted with ethyl-acetate to 1–5 ppm of the three compounds. A C-18 5-μm column (Licrospher, 250 × 4 mm; Merck) with a C-18 guard column (Waters) was used with a mobile phase at 1 ml min$^{-1}$ of 10% acetonitrile (Merck, Darmstadt, Germany), 0.5% glacial acetic acid (Merck) and 89.5% water. Absorbance was measured at 280 nm and the injection volume was 25 μl (Lee et al., 1986; Lee & Nagy, 1987; Lee & Nagy, 1988a).

Sensory evaluation

Samples processed at 84, 87 and 90°C were stored for 15 weeks at 22°C. The juice was reconstituted (1.2°Brix) before tasting by 25 panelists (13 people well-trained, 12 not). The main reason for utilizing both an expert and untrained panel was to verify whether quality changes detected by an expert panel could be also picked up by an ‘average’ consumer. The samples were scored on 0 to 99 scales for quality of appearance, colour, odour, overall taste, off-flavour, acidity, sweetness and bitterness. Off-flavour was scored as 0 (no off-flavour) to 99 (maximum off-flavour). Each assessor tasted all the three different juices in randomized order. An approximately 15-min rest between sampling was applied, and an unsalted cracker was eaten.

Results and discussion

Concentrated commercial orange juice pasteurized at various holding temperatures (84, 87 or 90°C for 72 s) showed no significant differences due to the different thermal processes in its quality attributes immediately after processing and during storage as depicted in Figs. 1 and 2 for NEB and vitamin C retention in COJ stored at 22 and 32°C, respectively. Hence, the data derived from the different holding temperatures were combined. This unexpected finding highlights the fact that the deterioration indexes utilized to monitor quality deterioration are not sensitive enough to exhibit the differences in quality of the processed citrus products.

A lag-time for NEB (Mannheim & Passy, 1979; Lee & Nagy, 1990), of approximately 4 and 1 weeks at 22 and 32°C, respectively was observed (Fig. 1). NEB formation followed a zero-order reaction ($P < 0.001$) with a rate constant of 0.003 and 0.034 OD week$^{-1}$ at 22 and 32°C, respectively. These values are only partially in agreement with data on COJ (0.006 and 0.014 OD week$^{-1}$ for 25 and 35°C, respectively; Berk & Mannheim, 1986). The discrepancy which is mainly due to the accumulative effect of the commercial process highlights the possibility that data collected on juice prepared under controlled conditions may underestimate the actual quality changes during realistic commercial conditions. Utilizing the kinetic data, $Q_{10}$ (defined as the ratio between the rate constant at $T + 10^°K$ over the rate constant at $T^°K$) for NEB yielded a very high value of c. 10. This extremely high value of $Q_{10}$ compared to the literature (Saguy et al., 1978 a, b), with an expected value of two to four suggests that commercially processed COJ is extremely susceptible at high storage temperatures above 22°C.

The loss of vitamin C (Fig. 2) could be fitted to either a pseudo-zero or a pseudo-first order reaction with derived rate constants of 5 and 29 mg l$^{-1}$ week$^{-1}$ or 0.018 and 0.138 week$^{-1}$ for a pseudo-zero or a pseudo-first order reaction at 22 and 32°C, respectively. These values showed that both time and storage temperature were the main factors influencing vitamin C deterioration.
during storage. Although the order of the reaction agrees with those reported previously (Kennedy et al., 1992; Marcy et al., 1989), the rate constants derived for COJ under our commercial processing conditions show much faster losses than those expected in SSOJ. Hence, commercial COJ should be stored at the lowest possible temperature.

Storage of COJ at 32°C shows a decrease in sucrose and a simultaneous increase in both fructose and glucose concentration (Fig. 3) due to breakdown of glucosidic bonds in an acidic environment (Whistler & Daniel, 1985). This inversion process is enhanced at pH < 4, and at higher storage temperatures (Kennedy et al., 1990). After 7 weeks of storage at 32°C, sucrose
loss was 69 mM with an increase of 59 and 66 mM in glucose and fructose, respectively. The small discrepancy between sucrose lost and glucose and fructose accumulated may arise due to side reactions of reducing sugars, such as caramelization (Whistler & Daniel, 1985) and formation of oligosaccharides (Rassis et al., 1994) and NEB (Lee & Nagy, 1988a).

Sugar kinetics can also be described as pseudo-zero or pseudo-first order reaction, with apparent rate constants of 3.4 g l⁻¹ week⁻¹ or 0.13 week⁻¹, 1.5 g l⁻¹ week⁻¹ or 0.05 week⁻¹ and 1.7 g l⁻¹ week⁻¹ or 0.05 week⁻¹, for sucrose, glucose and fructose, respectively. These kinetic data highlight the importance of inversion of sugar during COJ storage, which has a significant effect on oligosaccharide formation (Rassis et al., 1994), and other quality deterioration reactions.

Furfural is a highly reactive chemical compound which shows little accumulation during COJ storage (Kanner et al., 1982). Our data (Fig. 4) show minimal (below 1 ppm) and variable furfural accumulation during storage for 7 weeks at 32°C. Furfural produced during storage may react with aldehydes, ketones and amino acids. These reactions are accelerated in COJ compared to single strength orange juice (Kanner et al., 1981; 1982). Furfural kinetics could be described both as a pseudo-zero or pseudo-first order reaction, with an apparent reaction rate constant of 0.17 ppm week⁻¹ or 0.16 week⁻¹. These kinetic data indicate a much faster increase than values reported in the literature (Kaanane et al., 1988), probably due to the higher solid concentration which could accelerate the reaction (Saguy et al., 1978b). Accumulation (below 1 ppm) was also reported in grapefruit juice stored for 15 weeks at 10 to 30°C (Lee & Nagy, 1988a). Hence furfural is not a suitable quality index to predict shelf-life of aseptic COJ. This finding contradicts previously reported information where 40 mg l⁻¹ furfural was utilized to determine SSOJ end-of-shelf-life attributed mainly with off-flavours (Kaanane et al., 1988).

The concentration of HMF in aseptic COJ stored at 32°C showed an apparent lag-time of c. 2 weeks (Fig. 4) before increasing steadily to 11 ppm. A lag-time has not been reported in citrus juice, but was found in apple juice (Toribio & Lozano, 1987). HMF and furfural are precursors of brown pigments of NEB. Due to its low chemical reactivity, HMF accumulates during storage (Lee & Nagy, 1988a). As the lag-time for NEB at 32°C was shorter (c. 1 week), it may suggest that other NEB precursors have a higher chemical reactivity. HMF accumulation
during storage could be described as a pseudo-zero or pseudo-first order reaction with an apparent rate constant of 1.7 ppm week$^{-1}$ or 0.54 week$^{-1}$, respectively.

In aseptic COJ, DMHF is formed mainly during the thermal processing (Fig. 4) and diminishes gradually during storage following a pseudo-zero or first-order reaction with an apparent rate constant of 0.60 ppm week$^{-1}$ or 0.27 week$^{-1}$, respectively. This contrasts with canned commercial grapefruit juice where DMHF concentration increased with time and temperature (Lee & Nagy, 1987). Hence, DMHF data clearly indicate that its utilization as a quality index for flavour changes in aseptic COJ is not justified. The decomposition of DMHF may be caused by reactions with other juice compounds, which may ultimately lead to the formation of off-flavours (Lee & Nagy, 1987).

The effect of the various thermal processing conditions (84, 87 and 90°C, for 72 s) after 15 weeks storage at 22°C was also evaluated sensorially. As no difference was observed between the trained and untrained panel, the data was combined. None of the differences (Table 1) were significant ($t$-test analysis; $P < 0.05$). However, COJ processed at 90°C was perceived brownish, it scored lower on overall taste, and had a higher bitterness and stronger off-flavour notes. Although the differences observed were not significant, the data suggest that decreasing the processing temperature might be preferable. It is worth emphasizing that even a small decrease in processing temperature (e.g. from 90 or 87 to 84°C) could improve the perceived product quality and acceptance. It is also worth noting that from a marketing point of view, even minor improvements in sensory attributes could be important to some consumers.

In conclusion, this work presents data collected from an actual commercial aseptic COJ plant. No significant differences were found in the quality attributes measured (i.e. NEB, vitamin C concentration, carbohydrates content, HMF, furfural and DMHF) between the different thermal treatments (84, 87 and 90°C for 72 s). The dominate factors affecting vitamin C retention and NEB were time and storage temperature. A lag-time was observed for NEB and HMF formation. Organoleptic attributes of aseptically COJ suggests that reducing processing temperature might be beneficial.
Table 1. Effect of processing temperature on average sensory attributes (0–99 scale; 25 panellists) after 15 weeks storage at 22°C

<table>
<thead>
<tr>
<th>Attribute</th>
<th>84</th>
<th>87</th>
<th>90</th>
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<tr>
<td>Colour</td>
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<td>65</td>
<td>59</td>
</tr>
<tr>
<td>Browning</td>
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<td>38</td>
<td>46</td>
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<tr>
<td>Odour</td>
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<td>47</td>
<td>54</td>
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<tr>
<td>Overall taste</td>
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<tr>
<td>Sweetness</td>
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<td>50</td>
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<td>Bitterness</td>
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<tr>
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<td>30</td>
<td>37</td>
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</tbody>
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References


