Food Chemistry 115 (2009) 1291–1298

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Quality of nectarine and peach nectars as affected by lye-peeling and storage

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ARTICLE INFO

Article history:
Received 1 September 2008
Received in revised form 26 November 2008
Accepted 20 January 2009

Keywords:
Prunus persica
Colour
Puree and nectar processing
Phenolics
Carotenoids
Ascorbic acid
Antioxidant activity

ABSTRACT

This study was focused on nectarine and peach nectars, with the aim to evaluate different quality indices at the time of production and to devise a predictive model for quality variation during storage at 23 and 37 °C. Nectars were produced from the Elegant Lady and Redhaven peach varieties and from the Stark Red Gold nectarine variety, from both peeled and unpeeled fruits. The effects of processing on antioxidant contents, antioxidant activity and colour were evaluated. At the time of production, β-carotene ranged from 0.52 to 0.79 mg/kg, hydroxycinnamic acids (chlorogenic and neochlorogenic) from 34 to 73 mg/kg, catechin from 0 to 24 mg/kg, quercetin 3-*O*-glycosides from 3.9 to 12.7 mg/kg, and cyanidin 3-*O*-glucoside from 0 to 9.4 mg/kg. Within the same variety, carotenoid and phenolic contents were lower in the nectars obtained from peeled fruits than in those obtained from unpeeled fruits. However, as ascorbic acid was adjusted to a level of 300 mg/kg during blending, which is far higher than the observed levels of phenolics and carotenoids, it mainly accounted for nectar radical-scavenging activity towards the 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazyl radical, which on average was 1.8 mmoles Trolox equivalents/kg. The colour of nectars was improved by processing lye-peeled fruits at room temperature, whatever the variety used; i.e., this process decreased the redness index, a^*, and increased the lightness index, L^*, and yellowness index, b^*, with respect to the traditional process.

During storage, ascorbic acid degraded by following pseudo-first order kinetics, with the same rate constant for all nectars. The colorimetric parameters a^*, L^*, and b^* varied following pseudo-zero order kinetics, with the same rate constant in all the nectars. Therefore, the better the colour after processing, the better it remained during storage. These results were validated by an independent process carried out with the Springebelle peach variety. From the kinetic models defined, which can be applied to the nectars whatever the variety and process used, it was demonstrated that an increase in storage temperature from 23 to 37 °C caused a 3.5-fold increase in the rate constant for ascorbic acid degradation and a 4-fold increase in the rate constants for a^* and L^* variations.

1. Introduction

The standard technology for producing puree from peaches and nectarines (*Prunus persica*) is comprised of processing the unpeeled fruit, and includes two steps during which the epicarp (peel) and mesocarp (pulp) come into close contact. These are: pitting, carried out by machines that cause fruit crushing, and sieving, carried out by pulpers and finishers. During these steps some peel components can solubilise from the peel to the pulp, and, consequently, transfer to the puree.

Fruit skin, like other outer cell layers of plant organs, contains several defencive molecules designed to cope with abiotic and biotic stresses. Among defencive molecules, lipid transfer proteins (LTPs) have been found to act against pathogenic bacteria and fungi, and are present as homologous forms in many vegetables of different botanical families (Cruesta-Herraz et al., 1988). These molecules are responsible for Ig-E-mediated allergy in sensitised subjects (Ahrazem et al., 2007). In different peach and nectarine varieties the LTPs Pru p 1 and Pru p 3 have been identified, and found to be far more concentrated in the peel than in the pulp (Ahrazem et al., 2007). LTPs occur in these fruits even at the early stage of ripening (Brenna, Pastorello, Farioli, Pravettoni, & Pompei, 2004). Hence, it is not feasible to reduce the level of peach allergens by means of breeding and agronomical operations. During the standard puree processing procedure, LTPs, having an isoelectric point 9.0 (Pastorello et al., 1999) are solubilised by the acid medium present in the pulp. Indeed these proteins have been found in peach-based products (Brenna et al., 2000).

Low molecular weight plant antioxidants also act as part of the plant defencive system. In fact, these compounds can act against pathogenic microorganisms, UV radiation, and reactive oxygen species (ROS) which are produced during photosynthetic and respiratory processes (Diplock et al., 1998). Peaches and nectarines

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doi:10.1016/j.foodchem.2009.01.047

contain relevant amounts of antioxidants, including hydroxycinnamic acids, flavan-3-ols, flavonols, anthocyanins, procyanidins, and carotenoids, which are mainly located in the skin (Tomás-Barberán et al., 2001; Gil, Tomás-Barberán, Hess-Pierce, & Kader, 2002), where abiotic and biotic stresses mainly occur. It has been hypothesised that an increased consumption of fruit and vegetable antioxidants could reduce oxidative stress and prevent diseases. In fact, a number of human diseases are thought to be the result, in part, of oxidative stress, which can lead to damage (Diplock et al., 1998). Besides their potential health properties, some of these compounds are responsible for the attractive colour of the fruit.

Lye-peeling of peach proved to be an effective technology to produce hypoallergenic peach-based products (Brenna et al., 2000). Lye-peeling probably leads to a decrease in the antioxidant content of peach-based products and could also affect colour and stability during storage. This technology cannot be generally promoted for all fruit products but it deserves particular attention if the strictest requirements of particular consumers are to be satisfied. In fact, there is a growing concern for food allergy as a result of its increased incidence in the population (Ortolani & Pastorello, 1997).

In the present study nectars were produced from lye-peeled and unpeeled peaches and nectarines. The effects of lye-peeling on nectar antioxidant activity and colour were studied at the time of production and during storage at room temperature and at 37 °C, in order to define a predictive model for variations in quality indices.

2. Materials and methods

2.1. Fruits

Peaches of the Redhaven, Elegant Lady and Springbelle varieties, and nectarines of the Stark Red Gold variety, were collected on different days at the fully-ripe stage, and processed separately on the same day of harvesting.

2.2. Puree and nectar production at the pilot plant

Batches of the Redhaven, Elegant Lady and Springbelle peaches and of Stark Red Gold nectarines were processed separately in the laboratory. Each fruit batch was divided into two groups of the same size. One group was peeled before processing, whereas the other group was processed with the peel. Lye-peeling of peaches and nectarines is carried out to produce fruit syrups by using 5–11% NaOH at 99 °C for 30–60 s, followed by washing with 1% citric acid. The conditions depend on fruit maturity and variety (Lopez, 1981; Luh & El-Tinai, 1993; Pompei, 2005). In this study, based on preliminary trials, the temperature of the peeling step was lowered, achieving good peel removal.

In fact, half of the fruit batch was peeled by dipping the fruits in a 7% NaOH solution at 80 °C for 30 s. These were left to drip, washed twice in a cold 1% citric acid solution, after which the peel was removed by gentle rubbing. For puree production, peeled fruits were manually pitted, transferred to a Malavasi Qbo 150 RoboQuo (Bologna, Italy), with the addition of 0.5 g/kg fruit of ascorbic acid, and pulped by rotating the cutter at 1000 rpm. The pulp was then transferred from the Malavasi Qbo 150 RoboQuo to a 0.5 mm screen pulper/finisher (Bertuzzi, Brugherio, Italy). The pulping/finishing step was repeated three times (the whole time being around 7 min). Afterwards, the puree was transferred again into the Malavasi Qbo 150 RoboQuo, degassed under vacuum for 9 min at 60 °C, and heated to 90 °C (about 7 min was required). The puree was hot-filled into glass bottles (125 ml). These were closed and heat treated in a water bath at 100 °C for 5 min. The remaining half of the unpeeled fruit batch was washed in cold water, rinsed, and processed to puree using the same conditions as described above, except that after cutting in the Malavasi Qbo 150 RoboQuo, the pulp was heated to reach 90 °C (about 10 min were required) and transferred hot to the pulper/finisher for peel removal.

Four batches of purees obtained from peeled fruits and four batches obtained from unpeeled fruits were processed to nectars immediately after production. Purees were blended with water (50% w/w), ascorbic acid (300 mg/kg final), and sucrose (14–15 °Brix final). Citric acid was added to adjust the pH in the range 3.5–3.7. The mixture was homogenised using an APV homogeniser (Milano, Italy) operating at 100 bar, heated to 90 °C and filled into glass bottles (125 ml). These bottles were closed and heat treated in a water bath at 100 °C for 5 min.

Two sets of experiments were carried out. The first set, carried out on the nectars obtained from the Redhaven and Elegant Lady peaches and from the Stark Red Gold nectarines, was used to study the effects of the process on different quality indices and to evaluate their variation kinetics during storage. The second set, carried out on the nectars obtained from the Springbelle variety was used for validation.

2.3. Storage study

Nectars were stored in the dark, in 125 ml glass bottles for 15 months at room temperature (23 °C) and 12 months at 37 °C. Analyses were carried out at scheduled times.

2.4. Soluble solids, pH and acidity, and Bostwick consistency

Soluble solids were measured at 20 °C using a RFM 340 refractometer (Bellingham & Stanley Ltd., Tunbridge Wells, UK), and expressed as °Brix (grams of sucrose per 100 g of fresh product).

The pH was determined with a PB-20 pH meter (Sartorius, Ravenna, Italy). Purees were diluted with water (1:10 v/v) and the mixture was titrated in the presence of phenolphthalein with 0.1 M NaOH. Results were expressed as grams of citric acid per 100 g of product.

Puree consistency was determined by measuring the distance (in centimetres) over which the product flowed in a Bostwick consistometer (LS 100, Labo Scientifica, Parma, Italy) at 20 °C for 30 s. With this technique, the higher the values were, the lower the thickness of the sample.

2.5. Colour

Colour was measured with a SL-2000 Chromameter (Labo Scientifica) and expressed as the Hunter L^*, a^*, and b^* coordinates, representing: lightness and darkness (L^*), redness ($+a^*$), greenness ($-a^*$), yellowness ($+b^*$), and blueness ($-b^*$). The chromameter was calibrated with a red standard (No. 482, Bureau Communitaire de Reference: $L^* = 25.6$, $a^* = 33.5$, $b^* = 14.7$).

2.6. Extraction and analysis of ascorbic acid

Purees and nectars (5 g) were diluted with water to 200 ml, and 5 ml of 30% metaphosphoric acid in glacial acetic acid were added. The mixture was titrated with 2,6-dichlorophenolindophenol (AOAC, 1997). Ascorbic acid was quantified from a calibration curve prepared with a pure standard (Sigma, Milano, Italy), and expressed as milligrams per kilogram of fresh product.

2.7. Extraction and analysis of phenolics and 5-hydroxymethyl furfural

Puree and nectar extracts were obtained by adding 5 g to 10 ml of 5% formic acid in water:methanol (80:20). The mixture was stirred for 1 min and centrifuged at 16,000*g* for 10 min at 15 °C.

The phenolic and 5-hydroxymethyl furfural (HMF) contents of the extracts were analysed using a model 600 HPLC pump coupled with a Model 2996 photodiode array detector, operated by Empower software (Waters, Vimodrone, Italy). A reverse-phase Symmetry C-18 column (250 × 4.6 mm i.d.; particle size 5 μm) (Waters) equipped with a Symmetry C-18 precolumn was used. Chromatographic separation was carried out according to the method of Tomás-Barberán et al. (2001). Briefly, formic acid (5%) was added to both methanol and water before preparing the following mobile phases: 95% water + 5% methanol (A); 88% water + 12% methanol (B); 20% water + 80% methanol (C); and methanol (D). The gradient elution was: 0–5 min, 100% A; 5-10 min linear gradient to reach 100% B; 10–13 min 100% B; 13–35 min linear gradient to reach 75% B and 25% C; 35–50 min linear gradient to reach 50% B and 50% C; 50–52 min linear gradient to reach 100% C; 52–57 min 100% C; 57–60 min 100% D. The injection volume was 50 μl and the flow rate was 1 ml/min.

Phenolic compounds were identified by their UV–vis spectra and retention times, and were quantified by calibration curves built with external standards, namely catechin at 280 nm, cyanidin 3-*O*-glucoside at 510 nm, chlorogenic acid at 330 nm for the hydroxycinnamic acids, and rutin at 350 nm for the flavonols (all these standards were by Extrasynthese, Lyon, France). HMF was identified by an external standard at 282 nm. Concentrations were expressed as milligrams per kilogram of fresh product.

2.8. Extraction, saponification, and analysis of carotenoids

The extraction was based on that of Wright and Kader (1997). Puree or nectar (50 g) was added to 100 ml of cooled ethanol. The mixture was homogenised with a model T25 Ultra-Turrax (JK GmBH, Staufen Germany) at 8000 rpm for 2 min, before adding 80 ml of hexane. The mixture was centrifuged for 5 min at 16,000*g* and the carotenoid-bearing hexane layer was transferred into a volumetric flask. To the residue, 50 ml of saturated sodium chloride solution was added. Hexane was added again (80 ml), and the mixture was centrifuged as described previously. The second hexane extract was combined with the first one and the volume was brought up to 200 ml with hexane.

Saponification was carried out, as described by Kimura, Rodriguez-Amaya, and Godoy (1990). In brief, 15 ml of hexane extract was transferred into a Pyrex bottle and added to 15 ml of 10% methanolic potassium hydroxide, flushed with nitrogen, sealed, and wrapped in aluminium foil to exclude light. The reaction was carried out at room temperature for 16 h, with gentle shaking. The mixture was then transferred to a separatory funnel and washed to remove the potassium hydroxide, first with 50 ml of 10% NaCl and then with deionised water until the rinse liquid had a neutral pH. The water phase was extracted with 10 ml of hexane; the combined hexane extracts were evaporated under nitrogen to dryness and then redissolved in the mobile phase.

Carotenoid content was analysed by HPLC as described previously (Riso & Porrini, 1997). Briefly, a Vydac 201TP54 C-18 column (250 mm × 4.6 mm), equipped with a C-18 precolumn, was used. Chromatographic separation was performed with 95:5 methanol:tetrahydrofuran stabilised by the addition of 0.1% butylated hydroxytoluene (2,6-di-tert-butyl-*p*-cresol) as eluent under isocratic conditions, 1.0 ml/min flow rate, at room temperature. The UV–vis detector was set at 454 nm. β-Carotene was quantified from a calibration curve built with pure β-carotene standard (Extrasynthese) and expressed as milligrams per kilogram of fresh product.

2.9. Antioxidant activity

This assay was performed as described previously (Lavelli, 2002). Briefly, 1 ml of different dilutions of the nectar extracts in water:methanol (80:20) containing 5% formic acid was added to 2 ml of a 25 mg/l methanolic solution of 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazyl (DPPH, Sigma). The decrease in absorbance was determined at 515 nm after 30 min (when a constant value was reached) by a Jasco UVDEC-610 spectrophotometer (Jasco Europe, Cremella, LC, Italy).

The percentage decrease of DPPH concentration was calculated with respect to the initial value after 30 min of reaction. A dose–response curve was constructed, and the amount of product required to lower the initial DPPH concentration by 50%, IC_{50}, was interpolated. 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox, Sigma) was used as a reference antioxidant and the antioxidant activity was expressed as Trolox equivalents (TE). Trolox equivalents are the ratio of the IC_{50} of Trolox (nanomoles) to the IC_{50} of the sample (milligrams, fresh weight).

2.10. Statistical analysis

Data represent the mean of three determinations. Two-dimensional regression of data and analysis of variance were conducted using Statgraphics 5.1 software (STCC Inc., Rockville, MD); Fisher's least significant difference (LSD) procedure ($p < 0.05$) was used to discriminate the means.

3. Results and discussion

3.1. Effect of processing on the quality of peach and nectarine nectars

The effects of processing on different quality indices of puree and nectar were studied by comparing the proposed technology, which involves a lye-peeling step followed by pulping/finishing at room temperature, with the traditional technology, which involves hot pulping/finishing of unpeeled fruits.

As shown in Table 1, for the Elegant Lady and Redhaven peach varieties, the soluble solids contents of the purees obtained from lye-peeled fruits were lower than those obtained from unpeeled fruits. Puree consistency, which is inversely correlated to the flow rate (i.e., distance in cm run in 30 s), was lower when lye-peeling was applied. The lower consistency of the purees obtained from peeled fruits could be due to residual pectinase activity after lye-peeling, which was thermally inactivated after the degassing step, whereas, in the purees obtained from unpeeled fruits, enzymatic inactivation was carried out at an earlier step (before pulping/finishing). The purees obtained from the Stark Red Gold nectarines were not significantly different in soluble solids content and consistency with respect to the process applied. A possible reason for the different behaviour of the Stark Red Gold nectarine could be due to the pectinase activity of the Stark Red Gold nectarine being lower than those of the other varieties under study. Therefore in this variety, any process applied would not affect the soluble solids content and consistency. However, the pectinase activities of all these varieties were not investigated in this study, since the differences in soluble solids content between the purees obtained from peeled and unpeeled fruits were negligible and could be levelled out by sucrose addition during nectar production.

As typical for fully-ripe fruits of peaches and nectarines, the pH and titratable acidity of the purees considered in these study were in the range of 3.5–3.7 and 0.65–1%, respectively (Gil et al., 2002; Tomás-Barberán et al., 2001).

During fruit processing to puree, 500 mg/kg of ascorbic acid was added. The ascorbic acid decrease depended on the process applied. In fact, the average final ascorbic acid contents of the three processed varieties were 308 ± 46 and 108 ± 39 mg/kg in the traditional purees and in the purees obtained by pulping/finishing the lye-peeled fruits at room temperature, respectively. Both the

Table 1
Soluble solids content, Bostwick consistency, pH and titratable acidity of peach and nectarine purees and nectars, obtained from peeled and unpeeled fruits.

Quality index	Peach/nectarine	Process applied			
		Puree		Nectar	
		Traditional	Lye-peeling	Traditional	Lye-peeling
Soluble solids (°Brix)	RH p.	11.5[b]	10.7[a]	14.3[a]	14.7[a]
	EL p.	13.5[b]	12.8[a]	15.0[a]	14.5[a]
	SRG n.	12.4[a]	12.0[a]	14.9[a]	15.0[a]
Consistency (cm in 30 s)	RH p.	12.8[a]	14.0[b]		
	EL p.	12.0[a]	13.0[b]		
	SRG n.	12.5[a]	12.3[a]		
pH	RH p.	3.70[a]	3.74[b]	3.73[b]	3.66[a]
	EL p.	3.68[a]	3.68[a]	3.69[a]	3.66[a]
	SRG n.	3.64[b]	3.54[a]	3.61[b]	3.52[a]
Acidity (% citric acid)	RH p.	0.72[b]	0.65[a]	0.35[a]	0.39[a]
	EL p.	0.81[a]	0.82[a]	0.40[a]	0.40[a]
	SRG n.	1.02[a]	0.99[a]	0.51[a]	0.53[a]

Different letters within the same row indicate significant differences between the purees obtained from unpeeled or peeled fruits, or between the nectars obtained from unpeeled or peeled fruits (LSD; $p < 0.05$). RH p.: Redhaven peach; EL p.: Elegant Lady peach; SRG n.: Stark Red Gold nectarine.

delayed thermal inactivation of ascorbic acid oxidase, and the higher air incorporation due to the lower temperature applied, could account for the greater ascorbic acid oxidation in the purees obtained from the lye-peeled fruits. Ascorbic acid content of commercial citrus fruit juices ranges from 24 to 430 mg/l (Kabasakalis, Siopodou, & Moshatou, 2000). According to guidelines for high quality orange juice production, the content of ascorbic acid should be 350 mg/l, whereas an amount of 200 mg/l of ascorbic acid is considered as the minimum acceptable (Fry, Martin, & Lees, 1995). Fruit juices other than those obtained from citrus fruits may contain added ascorbic acid, however optimal or minimal ascorbic acid contents in these juices have not been established (Southgate, Johnson, & Fenwick, 1995). In this study, during nectar manufacturing, ascorbic acid was adjusted to a final value of 300 mg/kg, which is the same addition as that used under industrial practice according to Italian producers (Lavelli, Pompei, & Casadei, 2008).

Processing fruits into purees caused a decrease in phenolic and carotenoid contents (Lavelli et al., 2008), whereas no further degradation of these antioxidants occurred during the processing of purees into nectars. In fact, carotenoid and phenolic contents of the nectars, which are shown in Table 2, were half of the concentration in their corresponding purees (data not shown), due to the 50:50 (w/w) dilution during nectar manufacturing. At the time

Table 2
Phenolic, carotenoid and HMF contents and antioxidant activity of peach and nectarine nectars, obtained from peeled and unpeeled fruits, at the time of production and after storage for 3 months at 37 °C.

Quality index	Peach/Nectarine	Process applied					
		Traditional Storage time (months)			Lye-peeling Storage time (months)		
		0	1.5	3	0	1.5	3
Neochlorogenic acid (mg/kg)	RH p.	25[c]	23[b](8)	22[a](12)	20[b]	19[ab]	18[a](10)
	EL p.	22[b]	21[b]	19[a](14)	20[b]	19[ab]	17[a](17)
	SRG n.	28[b]	27[b]	23[a](18)	18[b]	19[b]	15[a](15)
Chlorogenic acid (mg/kg)	RH p.	36[b]	34[b]	33[a](8)	20[a]	20[a]	19[a]
	EL p.	51[b]	49[b]	47[a](8)	35[a]	33[a]	33[a]
	SRG n.	37[b]	38[b]	34[a](8)	16[a]	16[a]	15[a]
Catechin (mg/kg)	RH p.	24[c]	22[b](8)	19[a](20)	15[a]	16[a]	n.d.
	EL p.	20[c]	16[b](20)	15[a](25)	13	n.d.	n.d.
	SRG n.	13[b]	13[b]	10[a](23)	n.d.	n.d.	n.d.
Quercetin 3-*O*-glycosides (mg rutin equivalents/kg)	RH p.	7.1[b]	4.2[a](41)	3.6[a](49)	3.9[b]	1.8[a](54)	1.4[a](64)
	EL p.	10.6[c]	8.1[b](24)	6.1[a](42)	8.1[c]	4.1[b](49)	2.8[a](65)
	SRG n.	12.7[c]	10.1[b](20)	7.5[a](40)	5.4[c]	2.6[b](52)	1.6[a](70)
Cyanidin 3-*O*-glucoside (mg/kg)	RH p.	2.1	n.d.	n.d.	n.d.	n.d.	n.d.
	EL p.	9.4[b]	0.7[a](93)	n.d.	1.0	n.d.	n.d.
	SRG n.	6.1	n.d.	n.d.	1.2	n.d.	n.d.
β-Carotene (mg/kg)	RH p.	0.63[a]	0.61[a]	0.60[a]	0.52[a]	0.53[a]	0.50[a]
	EL p.	0.79[a]	0.77[a]	0.77[a]	0.61[a]	0.61[a]	0.59[a]
	SRG n.	0.63[a]	0.63[a]	0.64[a]	0.60[a]	0.60[a]	0.59[a]
Antioxidant activity (mmol TE/kg)	RH p.	1.7[c]	1.2[b](29)	1.0[a](41)	1.6[c]	1.2[b](25)	0.9[a](44)
	EL p.	1.9[c]	1.5[b](21)	1.5[a](21)	2.0[c]	1.6[b](20)	1.4[a](30)
	SRG n.	1.9[c]	1.5[b]	1.4[b]	1.6[c]	1.2[b]	1.1[b]
HMF (mg/kg)	RH p.	0.13[a]	0.96[b]	3.6[c]	n.d.	0.49[a]	3.3[b]
	EL p.	0.32[a]	1.47[b]	4.98[c]	n.d.	0.81[a]	3.8[b]
	SRG n.	0.26[a]	1.75[b]	7.67[c]	n.d.	1.69[a]	7.0[b]

Different letters within the same row and the same technology indicate significant differences (LSD; $p < 0.05$). Values in parentheses are the percent of losses calculated with respect to the value at the time of production. RH p.: Redhaven peach; EL p.: Elegant Lady peach; SRG n.: Stark Red Gold nectarine.

of production, β-carotene ranged from 0.52 to 0.79 mg/kg, hydroxycinnamic acids (chlorogenic and neochlorogenic) from 34 to 73 mg/kg, catechin from 0 to 24 mg/kg, quercetin 3-*O*-glycosides from 3.9 to 12.7 mg/kg, and cyanidin 3-*O*-glucoside from 0 to 9.4 mg/kg. Within the same variety, carotenoid and phenolic contents were lower in the nectars obtained from peeled fruits than in those obtained from unpeeled fruits (Table 2). Accordingly, phenolics and carotenoids are more concentrated in the peel than in the pulp (Gil et al., 2002; Tomás-Barberán et al., 2001). As discussed for ascorbic acid, this difference could also be ascribed to delayed polyphenol oxidase and peroxidase thermal inactivation, and to a greater air incorporation during the pulping/finishing step of the peeled fruits at room temperature.

The antioxidant activity, evaluated as DPPH radical-scavenging activity relative to Trolox, was the same in all the nectars, irrespective of the process applied. The average antioxidant activity was 1.8 ± 0.2 mmol TE/kg. As will be discussed in the following paragraph, this value depended mostly on the ascorbic acid content, which was adjusted to 300 mg/kg in all nectars, and was far higher than the phenolic and carotenoid contents (Table 2).

HMF can be formed by hexose degradation and by the Maillard reaction from reducing sugars and the free amino groups of amino acids (Hoseney, 1984). HMF was not detectable in any of the nectars obtained by the process operating the pulping/finishing step of peeled fruits at room temperature. In the nectars obtained by the traditional process HMF ranged from 0.13 to 0.32 mg/kg (Table 2).

The colour of peach and nectarine products is considered to be one the main criteria affecting consumer preference (Carabasa, Ibarz, Garza, & Barbosa-Canovas, 1998; Guerrero-Beltrán, Barbosa-Canovás, & Swanson, 2004; Lopez-Nicolas, Perez-Lopez, Carbonell-Barrachina, & Garcia-Carmona, 2007; Talcott, Howard, & Brenes, 2000). Both the genotypic factors and the process applied greatly affected this quality parameter. According to an internal industrial standard, the purees obtained from the Redhaven peach have optimal colorimetric parameters, i.e., lowest a^* value, and highest b^* and L^* values (Table 3). Processing the lye-peeled fruits caused a decrease in the a^* values and an increase in the L^* and b^* values in all purees, as compared to the traditional processing of the unpeeled fruits. The improvement was particularly evident in the a^* values, which decreased as a result of anthocyanin loss, due to peel removal (Table 3). In fact, the presence in the puree of the prevalent anthocyanin, namely cyanidin 3-*O*-glucoside, accounts for an unstable and undesirable red hue of the products, even when its concentration is very low. The colour improvement observed in the purees obtained from peeled fruits could also be partially due to the lower temperature applied during processing (Lavelli et al., 2008), which also caused lower HMF formation (Table 2).

3.2. Effect of storage on the quality of peach and nectarine nectars

During 3 months of storage at 37 °C, antioxidant degradation observed was similar, irrespective of the process used in puree production (Table 2). Cyanidin 3-*O*-glucoside, catechin, and quercetin glycosides were the least stable phenolics, whereas chlorogenic acid and neochlorogenic acid degraded at a lower rate. β-Carotene content did not show any variation during storage. As expected, HMF increased during storage at 37 °C.

As shown in Fig. 1, the antioxidant activity was linearly correlated to ascorbic acid content ($r = 0.92$, $p < 0.01$). This correlation is consistent with the prevalence of ascorbic acid in the nectars, compared to other antioxidants. Previous studies demonstrated that the antioxidant activity of different peach and nectarine fruits, evaluated as both the ability to scavenge the DPPH radical and the ferric reducing capacity, is correlated to total phenolic content, whereas no correlation exists with the ascorbic acid and carotenoid contents (Gil et al., 2002). In this study, ascorbic acid was mainly responsible for the antioxidant activity of peach and nectarine juices. This is due to the quite different antioxidant composition of peach and nectarine nectars, with respect to that of the corresponding fruits, as the result of antioxidant loss during puree processing (Lavelli et al., 2008), water dilution and ascorbic acid addition during nectar manufacturing. Similarly, ascorbic acid accounts for 65–100% of the antioxidant activity of beverages derived from citrus fruits, due to this high content of this compound, with respect to phenolic and carotenoid contents (Gardner, White, McPhail, & Duthie, 2000; Miller & Rice-Evans, 1997).

The slope of the relationship between ascorbic acid content and DPPH radical-scavenging activity indicated that a decrease of 1 mmol of ascorbic acid (176 mg) in the nectar corresponded to a decrease of DPPH radical-scavenging activity of 1 mmol TE. This result is consistent with the DPPH radical-scavenging activities of pure ascorbic acid and Trolox, which are the same (Spranger, Sun, Mateus, de Freitas, & Ricardo-da-Silva, 2008). Hence, ascorbic acid can be considered as one of the major quality indices for peach and nectarine juices, and the variation of the antioxidant activity *in vitro* can be easily predicted by evaluating the variation of this compound.

Ascorbic acid degradation was studied during storage at 23 and 37 °C for 15 and 12 months, respectively. It is known that ascorbic acid takes part in the Maillard reaction. In fact, under anaerobic conditions, ascorbic acid undergoes a spontaneous decarboxylation and dehydration to form 3-deoxypentosulose, and furfural, by way of the α,β-unsaturated dicarbonyl intermediate, 3,4-dideoxypentosulos-3-ene. These products are the same as the intermediates in the Maillard browning of pentoses. In addition, non-decarboxylated ascorbic acid molecules can also be directly incorporated into

Table 3
Hunter a^*, b^*, and L^* colorimetric parameters, at the time of production, of peach and nectarine purees and nectars, obtained from peeled and unpeeled fruits.

Colour index	Peach/nectarine	Process applied			
		Puree		Nectar	
		Traditional	Lye-peeling	Traditional	Lye-peeling
a^*	RH p.	0.80[b]	−5.97[a]	−1.98[b]	−7.35[a]
	EL p.	13.62[b]	−2.90[a]	5.65[b]	−5.31[a]
	SRG n.	9.62[b]	−2.56[a]	2.61[b]	−4.26[a]
b^*	RH p.	24.42[a]	25.81[b]	19.08[a]	20.69[b]
	EL p.	16.69[a]	24.35[b]	15.08[a]	19.67[b]
	SRG n.	19.52[a]	23.77[b]	17.58[a]	19.27[b]
L^*	RH p.	46.96[a]	53.62[b]	41.41[a]	42.38[b]
	EL p.	38.90[a]	50.18[b]	36.35[a]	44.12[b]
	SRG n.	39.90[a]	44.91[b]	36.51[a]	38.18[b]

Different letters within the same row indicate significant differences between the purees obtained from unpeeled or peeled fruits or between the nectars obtained from unpeeled or peeled fruits (LSD; $p < 0.05$). RH p.: Redhaven peach; EL p.: Elegant Lady peach; SRG n.: Stark Red Gold nectarine.

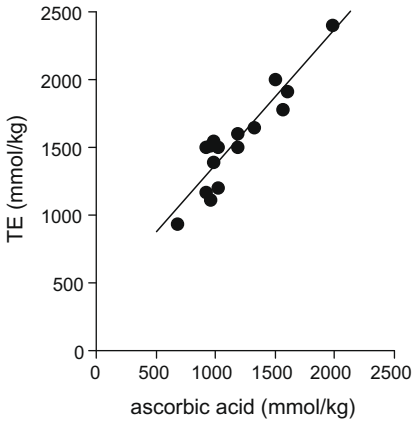

Fig. 1. Relationship between ascorbic acid content and DPPH radical-scavenging activity of nectars.

the melanoidin to a large extent, as demonstrated by means of specifically labelled $^{14}C_1$-ascorbic acid (Davies & Wedzicha, 1994).

Regarding the kinetics of ascorbic acid degradation, as a first step, a regression analysis of ascorbic acid decrease *versus* time was carried out for each nectar, to find the best fit kinetic model. Ascorbic acid was found to decrease, following pseudo-first order kinetics in all the nectars. The pseudo-first order rate constants for ascorbic acid degradation did not show significant differences among nectars produced with the same technology from three different fruit varieties (data not shown). Therefore in the second step, the average values were calculated. As shown in Table 4, the ascorbic acid degradation was also unaffected by the technology applied; the same rate constants were found for both the nectars obtained by operating the pulping/finishing step of lye-peeled fruits at room temperature, and those obtained by the traditional process. After 12 months of storage at 23 °C the average loss of ascorbic acid was 35%. An increase in temperature to 37 °C accelerated the degradation rate constant by 3.5-fold, resulting in an average decrease of this compound of about 73% over the same storage period.

There are no previous data available on ascorbic acid degradation in peach and nectarine nectars. In orange juices, ascorbic acid degradation was found to be about 28.9% after 4 months of storage at room temperature (Kabasakalis et al., 2000). This value is close to the percentages of ascorbic acid degradation found in this study, which were 11% and 34% at 23 and 37 °C, respectively, over the same storage time. However, it is worth noting that the kinetic parameters for ascorbic acid degradation in a specific fruit juice cannot accurately predict the rate of degradation of this compound in a different fruit juice. In fact, ascorbic acid degradation could also be affected by the presence of phenolics. As a matter of fact, ascorbic acid and anthocyanins can be mutually destructive (De Rosso & Mercadante, 2007; Garcia-Viguera & Bridle, 1999; Kirca, Özkan, & Cemeroğlu, 2006), while it has also been found that some phenolic compounds protect ascorbic acid degradation (Miller & Rice-Evans, 1997).

At the beginning of storage a positive variation in the colorimetric parameters of the nectars occurred: the redness index a^* decreased, whereas the yellowness index b^* and the lightness index L^* increased. These changes are related to the degradation of anthocyanins, which are very unstable in peach nectars (Kirca et al., 2006; Lavelli et al., 2008). After 3 months of storage, the values of the colorimetric parameters were still dependent on the variety used and on the process applied, as they were at the time of production. However, their evolution kinetics over time were similar. As an example in Fig. 2, colour variations of the nectars obtained from the Elegant Lady variety with both processes and that of the nectar obtained from the Redhaven variety with the traditional process are shown. After storage times longer than 3 months, undesirable changes in the colours of the nectars were observed, which were consistent with the typical trends of non-enzymatic browning (Avila & Silva, 1999; Garza, Ibarz, Pagan, & Giner, 1999): a^* increased markedly, whereas b^* and L^* decreased. Non-enzymatic browning reactions are considered to consist of two stages. A first stage following a zero order kinetic pathway, during which coloured polymeric compounds are formed, and a second stage following a combined kinetic model, which supposes zero order kinetics for coloured polymers formation and first order kinetics for pigment destruction (Garza et al., 1999). Previous studies carried out on peach puree submitted to severe heat treatments reported kinetic models for browning. In peach purees heated at temperatures in the range 80–98 °C for 8 h, the L^* decrease fits a pseudo-first order model; accordingly, HMF content in these purees is higher than 87 mg/kg, indicating an advanced stage of the Maillard reaction (Garza et al., 1999). Thermal treatments of peach puree in the temperature range 110–135 °C for 0.5–2 h causes intense colour variations; L^* and b^* decreases followed a pseudo-first order kinetic pathway, while the a^* increase follows a combined kinetic model (Avila & Silva, 1999).

In this study, a regression analysis was carried out on the colorimetric parameters for each nectar *versus* storage times longer than

Table 4
Rate constants for ascorbic acid degradation and colour variation in the peach and nectarine nectars stored at 23 and 37 °C.

Quality index	T (°C)	Process applied			
		Traditional		Lye-peeling	
		Rate constant		Rate constant	
		1st order (month^{-1})	zero-order (colour unit $*$ month^{-1})	1st order (month^{-1})	zero-order (colour unit $*$ month^{-1})
Ascorbic acid	23	−0.029 ± 0.003		−0.030 ± 0.004	
	37	−0.109 ± 0.004		−0.101 ± 0.008	
$a^*_{normalized}$	23		0.09 ± 0.04		0.13 ± 0.02
	37		0.43 ± 0.02		0.47 ± 0.02
$b^*_{normalized}$	23		−0.14 ± 0.02		−0.16 ± 0.02
	37		−0.44 ± 0.02		−0.43 ± 0.02
$L^*_{normalized}$	23		−0.18 ± 0.02		−0.15 ± 0.03
	37		−0.74 ± 0.02		−0.71 ± 0.03

Values are the average ± SD rate constants of three nectars (obtained from the Redhaven and Elegant Lady peach varieties and the Stark Red Gold nectarine variety). Ascorbic acid degradation was fitted to pseudo-first-order kinetics: $\ln(C/C_0) = k * t$ (correlation coefficients were >0.91). Changes in the normalised colorimetric parameters (values at a given time–values at 3 months of storage) were fitted to pseudo-zero-order kinetics: $C - C_{3\ months} = k * t$ (correlation coefficients were >0.82 and >0.97 for the kinetics variations at 23 and 37 °C, respectively).

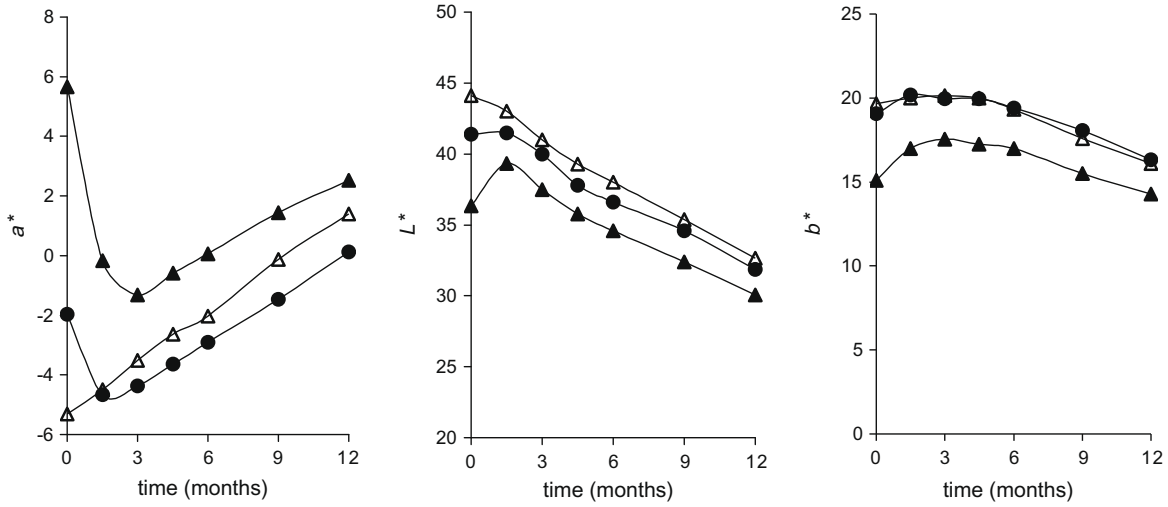

Fig. 2. Time course of the variations of the colorimetric parameters a^*, b^*, and L^*, in the nectars during storage at 37 °C. (●) Nectar processed by the traditional technology using the Redhaven peach variety, which has optimal colour; (▲) nectar processed by the traditional technology using the Elegant Lady variety; and (△) nectar processed by pulping/finishing at room temperature of peeled fruits of the Elegant Lady variety.

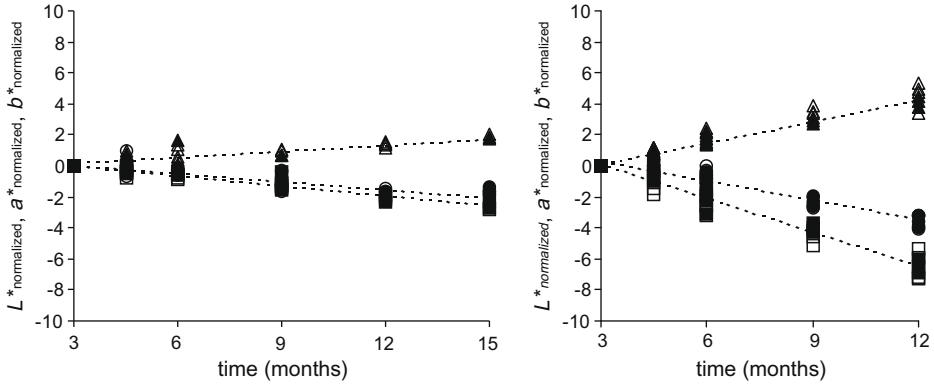

Fig. 3. Time course of the variations of the normalised colorimetric parameters (values at a given time–values at 3 months of storage) of the nectars obtained from the Redhaven and Elegant Lady peaches and the Stark Red Gold nectarines during storage at 23 (left) and 37 °C (right) (▲,△) a^*; (■,□) L^*; (●,○) b^*. Full symbols: nectar processed by the traditional technology and open symbols: nectar processed by pulping/finishing at room temperature of peeled fruits.

3 months, in order to find the best fit kinetic model. The colorimetric parameter variations followed a pseudo-zero order kinetic. Indeed, the low HMF contents of the nectars during storage (8 mg/kg) is consistent with the initial stage of the Maillard reaction. The same pseudo-zero order rate constants were observed for nectars produced with the same technology from three different fruit varieties (data not shown). Therefore in the second step, the average values were calculated. To this aim, the colorimetric parameters of the nectars after 3 months of storage were taken as a reference, to level out the effects of cyanidin-3-*O*-glucoside degradation (Lavelli et al., 2008). In fact, the colorimetric parameters of the nectars obtained from the three fruit varieties were normalised by subtracting the corresponding value observed after 3 months of storage (Fig. 3). The normalised values were then fitted to pseudo-zero order kinetics. As shown in Table 4, the rate constants for the variations in the colorimetric parameters were not significantly different with respect to the process applied. An increase in storage temperature from 23 to 37 °C caused a 4-fold increase in the rate of L^* and a^* variations. To validate the kinetic models for colour variation, nectars were produced from the Springbelle peach variety and stored for 12 months at 23 and 37 °C. The observed and predicted values for the colorimetric parameters were compared. In general, as shown in Table 5, the experimental data for the colorimetric parameters could be reliably predicted by the equations developed, except that the increase in a^* and the decrease in L^* during storage of the nectar obtained by the lye-peeling process at 37 °C were just outside the 95% prediction limits.

4. Conclusions

The lye-peeling process, which has previously been found to be effective for the manufacture of hypoallergenic nectars, was also effective in improving the nectar colour, both at the time of production and during storage. In addition, although phenolic and carotenoid contents were slightly lower in the nectars obtained from peeled fruits with respect to those obtained from unpeeled fruits, the nectars had the same antioxidant activity whatever the process applied. This was due to the addition of high concentrations of ascorbic acid during blending in both processes, which mainly accounted for the antioxidant activity of the nectars.

Kinetic models for the main quality changes of nectars during storage at 23 and 37 °C were elaborated. By using these models, which can be applied to the nectars whatever the variety and process used, it was demonstrated that an increase in storage temperature from 23 to 37 °C caused a 3.5-fold increase in the rate

Table 5
Observed and predicted values for colour variation in the nectars obtained from the Springbelle peach after storage at 23 and 37 °C.

Colour index	T (°C)	Storage time								
		3 months	9 months				12 months			
		Observed mean ± SD	Observed mean ± SD	Predicted mean 95% prediction limits			Observed mean ± SD	Predicted mean 95% prediction limits		
Traditional process										
a^*	23	−2.86 ± 0.03	−2.69 ± 0.01	−2.36	−3.36	−1.36	−2.08 ± 0.07	−2.09	−3.09	−1.09
	37	−1.77 ± 0.02	0.41 ± 0.01	0.78	−0.02	1.58	1.95 ± 0.04	2.07	1.27	2.87
b^*	23	16.9 ± 0.1	16.8 ± 0.01	16.1	15.1	17.1	16.1 ± 0.1	15.6	14.6	16.6
	37	16.0 ± 0.1	15.0 ± 0.01	13.4	12.7	14.1	13.8 ± 0.1	12.0	11.3	12.7
L^*	23	39.8 ± 0.1	38.7 ± 0.01	38.7	37.9	39.5	37.7 ± 0.1	38.2	37.4	39.0
	37	37.5 ± 0.1	33.1 ± 0.01	33.1	32.1	34.1	30.9 ± 0.1	31.0	30.0	32.0
Lye-peeling process										
a^*	23	−5.96 ± 0.03	−5.35 ± 0.01	−5.18	−5.88	−4.88	−4.18 ± 0.06	−4.79	−5.49	−4.09
	37	−4.58 ± 0.02	−0.68 ± 0.01	−1.76	−2.76	−0.76	1.30 ± 0.1	−0.35	−1.35	0.75
b^*	23	19.0 ± 0.1	19.0 ± 0.01	17.8	17.1	18.5	18.0 ± 0.1	17.5	16.7	18.2
	37	18.3 ± 0.1	16.6 ± 0.01	15.7	14.7	16.7	14.9 ± 0.1	14.4	13.4	15.4
L^*	23	43.3 ± 0.1	42.8 ± 0.01	42.4	41.5	43.3	41.3 ± 0.1	42	40.7	43.3
	37	41.3 ± 0.1	35.8 ± 0.01	37.0	35.5	38.5	32.7 ± 0.1	34.9	33.4	36.4

Observed values are average ± SD. Predicted values were calculated by using the kinetic equations reported in Table 4.

constant for ascorbic acid degradation, and a 4-fold increase in the rate constants for a^* and L^* variations.

Acknowledgements

We thank Rita Mezzini and Ludovico Martignoni for their collaboration in the experimental work.

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