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Volatile compound emissions and sensory attributes of 'Big Top' nectarine and 'Early Rich' peach fruit in response to a pre-storage treatment before cold storage and subsequent shelf-life

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ABSTRACT

Pre-storage at 20 °C before cold storage was used to improve volatile compound emissions of 'Big Top' nectarine and 'Early Rich' peach fruit without negatively affecting quality measures and sensory attributes. Commercially harvested fruit were subjected to pre-storage at 20 °C for 0, 10, 24, or 36 h and then stored at −0.5 °C for 10, 20, or 40 d. After cold storage, the fruit were kept at 20 °C for up to three days. 'Big Top' nectarines given 10 h pre-storage followed by 10 and 20 d cold storage were perceived as more flavourful, juicy, and sweet, had higher soluble solid contents, and contained more butyl propanoate, 2-methybutyl-2-methylpropanoate, and 2-methyl-1-butanol than control fruit. 'Early Rich' peaches given 36 h pre-storage followed by 20 d cold storage were perceived as sweeter and had more propyl acetate, pentyl acetate, and 2-methyl-1-butanol than control fruit.

1. Introduction

Spain's increasing peach and nectarine production requires that an increasingly larger portion of the harvest must be stored to regulate commercial availability. Harvesting at a slightly unripe stage makes fruit more tolerant of postharvest handling, but such fruit often fail to develop desirable sensory attributes, decreasing consumer acceptance. Stone fruit can be given a pre-storage treatment by holding them at 20 °C for up to 48 h after harvest and before cold storage (Zhou et al., 2000; Crisosto et al., 2004). While this can produce weight loss and fruit softening, it does not usually harm the quality of nectarine and peach fruit (Lurie and Crisosto, 2005). Furthermore, pre-stored peaches maintain their sensory characteristics longer during cold storage than control fruit (Infante et al., 2009). Nevertheless, if pre-stored fruit are not monitored properly, fruit quality diminishes and excessive flesh softening may occur (Girardi et al., 2005). Not surprisingly, the efficacy of this treatment depends on fruit variety and length of exposure. Thus, for 'Flavortop' nectarines, two days of pre-storage prior to storage at 0 °C for 42 d prevented chilling injury (Zhou et al., 2000).

Chilling injury results in fruit that are dry and have a mealy or woolly texture (mealiness or woolliness), hard-textured fruit with no juice (leatheriness), fruit with flesh or pit cavity browning (internal browning), or fruit with flesh bleeding (internal reddening). The onset of chilling injury symptoms determines postharvest storage potential because this injury reduces consumer acceptance (Lurie and Crisosto, 2005). Aromatic volatile compounds were significantly reduced when chilling injury was found in cold-stored 'Hujingmilu' peaches (Zhang et al., 2011). Although storage temperatures between −0.5 and +0.5 °C can help control damage associated with cold (Robertson et al., 1990; Ceretta et al., 2000), it is very important to carefully control such treatment to optimize fruit quality for fresh consumption and thereby satisfy consumers.

Any positive effects on storage potential or quality attributes derived from a given postharvest procedure must therefore be globally evaluated. Flavour is particularly important, as consumer acceptance of peach fruit is strongly associated with perception of its characteristic flavour (Ortiz et al., 2009). Flavour, in turn, is partly determined by concentrations of γ and δ-lactones, compounds responsible for characteristic fruity flavours in peach and nectarine fruit (Spencer et al., 1978; Engel et al., 1988). The composition and concentration of lactones is largely determined by genetic background (Wang et al., 2009). The favourable effects of maturation and ripening on γ-and δ-lactones have been reported often (Robertson et al., 1990; Chapman et al., 1991; Visai and Vanoli, 1997; Lavilla et al., 2002; Aubert et al., 2003; Rizzolo et al., 2006;

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Zhang et al., 2010). Cold storage alters flavour volatiles and partially inhibits ester synthesis, largely due to substrate deficiencies caused by suppressed oxidation in the peach fruit during storage (Robertson et al., 1990; Raffo et al., 2008; Ortiz et al., 2009). Even so, shelf-life at 20 °C after cold storage at 0 °C increased the total lactone concentration of 'Hujingmilu' peaches (Zhang et al., 2011). A combination of instrumental and sensory analyses can help define the roles of particular volatile compounds and/or maturity measures in the perception of flavour by consumers. Our group established that peach consumer acceptance was influenced by γ-hexalactone and (Z)-3-hexen-1-ol in four yellow-fleshed cultivars cold-stored at −0.5 °C (Cano-Salazar et al., 2012). Despite the importance of aroma to nectarine and peach quality (Aubert et al., 2003; Infante et al., 2008), to the best of our knowledge, no previous studies have examined the relationships between volatile compounds and sensory evaluation in pre-stored peaches and nectarines. The present work assessed the influence of different pre-storage treatments at 20 °C on volatile compound emissions, quality measures, and sensory attributes in 'Big Top' nectarines and 'Early Rich' peaches cold-stored at −0.5 °C followed by shelf-life at 20 °C. 'Big Top' was chosen for this study because it is the most widely grown nectarine variety in Europe and 'Early Rich' peach was chosen because of its unusually high yield.

2. Materials and methods

2.1. Plant materials and storage treatments

Peach (*Prunus persica* L. Batsch, cv 'Early Rich') and nectarine (*P. persica* L. Batsch, cv 'Big Top') fruit were hand-picked on June 30, 2009, which was 115 and 125 d, respectively, after full bloom. At this time, most fruit had turned from green to yellow but flesh firmness was ≥42 N. The two cultivars were grown in commercial orchards at Alcarràs, Lleida, Catalonia, in northeast Spain. Immediately after harvest, four lots of 50 kg (≈250 fruit) of each variety were pre-stored at 20 °C for 0, 10, 24, or 36 h (0, 10, 24, and 36 h, respectively). These lots were then placed in a 22 m^3 cold-storage chamber (21 kPa O_2/0.03 kPa CO_2) at −0.5 °C and 92–93% RH for 10, 20, or 40 d (S10, S20, and S40, respectively). Samples were transferred to 20 °C and analyses were carried out after 0 or 3 d (SL0 or SL3).

2.2. Chemicals

All standards for volatile compounds were analytical grade or the highest quality available. Ethyl acetate (ea), 2,3-butanodione (23bone), eucalyptol (eOH), butyl acetate (ba), pentyl acetate (pa), acetophenone (aone), and γ-hexalactone (hlac) were obtained from Fluka (Buchs, Switzerland). 2-Methylpropyl acetate (2mpra) was obtained from Avocado Research Chemicals, Ltd. (Madrid, Spain). 2-Ethyl-1-hexenal (2e1hal), Z-3-hexenyl acetate (Z3hea), methyl octanoate (mo), and decanoic acid (deac) were obtained from SAFC Supply Solutions (St. Louis, MO, USA). All other compounds were supplied by Sigma–Aldrich (Steinheim, Germany): propyl acetate (pra), hexyl acetate (ha), butyl propanoate (bpr), propyl hexanoate (prh), pentyl hexanoate (ph), butyl hexanoate (bh), hexyl hexanoate (hh), hexyl propanoate (hp), ethyl octanoate (eo), butyl octanoate (bo), 2-methylbutyl acetate (2mba), 2-methylbutyl-2-methylbutanoate (2mb2mb), ethyl 2-methylbutanoate (e2mb), butyl 2-methylbutanoate (b2mb), 2-methylbutyl-2-methylpropanoate (2mb2mpr), hexyl 2-methylbutanoate (h2mb), 2-methylpropyl hexanoate (2mprh), γ-octalactone (olac), δ-decalactone (dlac), γ-dodecalactone (dolac), hexanal (hal), benzaldehyde (byde), linalool (liOH), acetic acid (aac), benzoic acid (bac), 1-pentanol (pOH), 1-hexanol (hOH), 2-methyl-1-butanol (2mbOH), Z-3-hexen-1-ol (Z3OH), 2-ethyl-1-hexanol (2ehOH) and benzyl alcohol (bOH).

2.3. Quality measures

Twenty fruit at harvest and for each combination of factors (four pre-storage times × three cold-storage times × two shelf-life times) were individually assessed for flesh firmness, soluble solids content (SSC), titratable acidity (TA), and skin colour. Flesh firmness was measured on opposite sides of each fruit with a digital penetrometer (Model. 53205; TR, Forlí, Italy) equipped with an 8 mm diameter plunger tip. Two measurements were made on opposite sides of each fruit after the removal of a 1 mm thick slice of skin. The results were expressed in Newtons (N). SSC and TA were measured in juice pressed from whole fruit. SSC was determined with a Palette-10 hand refractometer (Atago PR-32, Tokyo, Japan) and the results were expressed as % sucrose equivalents. TA was determined by titrating 10 mL juice with 0.1 M NaOH to pH 8.1 and the results were given as g L^{-1} malic acid. Fruit epidermis colour was determined with a portable tristimulus colorimeter (chrome metre CR-400, Konica Minolta Sensing, Inc., Osaka, Japan) using CIE illuminant D_{65} and an 8-mm measuring aperture diameter. The skin colour was measured at two points on the equator of each fruit that were 180° apart, one on the side exposed to sunlight (ES) and the other on the shaded side (SS). Hue angle was determined on both sides and the resulting values were used as measurements of superficial and background colour, respectively.

2.4. Analysis of volatile compounds

Volatile compounds were measured as described (Cano-Salazar et al., 2012). Six kilograms fruit (2 kg per replicate × 3) per pre-storage time, cold-storage time, and cultivar were selected for analysis of volatile compounds, both at harvest and after removal from storage. Intact fruits (≈10 fruit per replicate) were placed in an 8 L Pyrex container through which an air stream (150 mL min^{-1}) was passed for 60 min. The resulting effluent was passed through an adsorption tube filled with 350 mg Tenax TA/Carbograph 1TD. The volatile compounds were desorbed into an Agilent 7890A gas chromatograph (Agilent Technologies, Inc., Barcelona, Spain) at 275 °C for 15 min, using an automated UNITY Markes thermal desorption system (Markes International Ltd., Llantrisant, United Kingdom). Identification and quantification of volatile compounds were achieved on an Agilent 7890A gas chromatograph (Hewlett-Packard Co., Barcelona, Spain) equipped with a flame ionization detector and a cross-linked free fatty acid phase (FFAP; 50 m × 0.2 mm × 0.33 μm) capillary column. Compounds were identified by comparing their respective retention index with those of standards and by enriching peach extract with authentic standards. Quantification was performed using individual calibration curves for each identified compound. Standard concentrations were prepared by dilution in diethyl ether (ACS > 99.8%, Fluka, Barcelona, Spain), and ranged between 0.01 and 100 μg kg^{-1}. They were freshly prepared at calibration. The concentrations were expressed as ng kg^{-1}. Compound confirmation was performed in an Agilent 6890 N gas chromatograph/mass spectrometer (Agilent Technologies, Inc.), using the same capillary column as for GC analyses. Spectrometric data were recorded (Hewlett-Packard 3398 GC Chemstation) and compared with those from the original NIST HP59943C library mass spectra.

2.5. Sensory analyses

For sensory evaluation, fruit samples from each pre-storage and cold-storage time were kept in a room at 20 °C for three days. Prior to sensory evaluation, colour and flesh firmness were measured on both sides of each fruit. Two longitudinal wedges were used to determine quality measures as described above. The rest of the fruit was used for sensory evaluation. Four pieces of fruit per cultivar (one from each pre-storage time) were placed on white plates and immediately presented to a tasting panel. Nine panellists (trained according to ISO, 1993) evaluated the intensity of the following properties: crispness (Cr), ease of breakdown (Eb), flavour (Fv), fibrousness (Fi), hardness (hs), juiciness (Ju), sourness (So), and sweetness (Sw). Crispness was defined as the amount and pitch of sound generated when a sample is first bitten with the front teeth, ease of breakdown as the amount of chewing required to break down the flesh so that it can be swallowed, fibrousness as the presence of wet and soft fibrous structures detected in the mouth during chewing, and hardness as the force required to compress the sample between the back teeth (López et al., 2011). The intensity of each attribute was recorded on a 150 mm unstructured linear scale, anchored at 0 = absent and 150 = extreme, with the exception of firmness, which was anchored at 10 = low and 140 = high. All evaluations were conducted in individual booths under white-light illumination and at room temperature.

2.6. Statistical analyses

A multifactorial statistical design was used to analyse the results. The factors considered were cultivar and the lengths of pre-storage, cold storage, and shelf-life. All data were tested using analysis of variance (GLM-ANOVA procedure) with the SAS program package (SAS, 2004). Means were separated by the least significant difference (LSD) test at $p \leq 0.05$. Unscrambler software version 9.1.2 (Camo, 2004) was used to develop a principal component analysis (PCA). This PCA provided a global overview of volatile compound emissions, quality measures, and sensory evaluation data for each cultivar. As a pre-treatment, data were centred and weighted using the inverse of the standard deviation of each variable to compensate for the different scales used (Martens and Naes, 1989). Variables and samples analysed are labelled as specified in parentheses inside Sections 2.2–2.5.

3. Results

3.1. Fruit quality at harvest and after storage

Significant changes in some quality measures were found in response to different postharvest procedures (Table 1 and Supplementary Table 1a). Firmness loss after 3 d shelf-life at 20 °C was significantly greater in pre-stored than in immediately cold-stored fruit, regardless of pre-storage time; this effect was most intense in 'Early Rich' peaches. The firmness of 'Big Top' nectarines remained stable during 20 and 40 d cold storage when the fruit were not subjected to shelf-life. In 'Early Rich' peaches, 10 h pre-storage maintained flesh firmness during cold storage without shelf-life. The combination of 36 h pre-storage plus 3 d shelf-life increased SSC and SSC/TA ratio above controls in 'Early Rich' fruit regardless of cold storage time. In general, in 'Big Top' nectarines pre-stored for 10 or 24 h, SSC increased beyond controls after 40 d plus 3 d at 20 °C.

3.2. Volatile compound emission changes in response to pre-storage before cold storage

The effects of pre-storage on volatile compounds depended on cultivar, length of cold storage, and shelf life (Tables 2–5 and Supplementary Tables 2a–5a). 'Early Rich' peaches and 'Big Top' nectarines subjected to 36 h pre-storage followed by 20 d cold storage (36 h + S20 + SL0) had the most total volatiles at 16,766.5 and 8633.7 ng/kg, respectively; these contrasted with 9398.1 and 2193.6 ng/kg in control fruit (0 h + S20 + SL0). This increase in total volatile emissions was mainly due to increased total esters, which predominated in the volatile profiles of both varieties at harvest and after cold storage. Acids were the predominant volatile class (48% of the total) only in control 'Big Top' fruit after 40 d cold storage (0 h + S40 + SL0). In these nectarines, 24 h pre-storage decreased the total acid compounds by up to 10%.

In 'Big Top' nectarines, the combination 36 h + S20 + SL0 increased the concentrations of propyl, pentyl, and hexyl acetates, butyl propanoate, butyl hexanoate, 2-methylpropyl acetate, 2-methybutyl-2-methypropanoate, butyl 2-methylbutanoate, and 2-methybutyl-2-methybutanoate (Tables 3 and 4 and Supplementary Tables 3a and 4a). These nine esters comprised over 41% of the total volatile compounds in this nectarine variety. After 3 d at 20 °C, there was an increase in ethyl octanoate. In 'Early Rich' peaches at 36 h + S20 + SL0, significant increases in the concentrations of ethyl, propyl, butyl, pentyl, and hexyl acetate, butyl hexanoate, ethyl octanoate, and 2-methylpropyl and 2-methylbutyl acetate were also observed; these constituted >79% of total volatile compounds. Shelf-life increased propyl acetate, ethyl octanoate, and 2-methylpropyl acetate.

There were significantly more total alcohols and aldehydes in 'Big Top' nectarines after 36 h + S20 + SL0 than in controls (Supplementary Table 2a). These conditions produced the most 1-hexanol, 2-methyl-1-butanol, and 2-ethyl-1-hexanol (Table 5) and the concentrations of hexanal, 2-ethyl-1-hexenal and benzaldehyde were also higher. After 3 d shelf-life, there was a decrease in amounts of these compounds.

In control peaches and nectarines, the total esters decreased after 40 d cold storage, but no significant differences were observed when 'Early Rich' peaches were pre-stored 10 h (Table 2). When pre-storage was extended to 24 h, there was a significant increase in total esters, alcohols, aldehydes, and lactones in 'Big Top' nectarines (Supplementary Table 2a). In many types of fruit, esters are important flavour compounds and are subdivided into straight-chain and branched-chain esters. The combination 24 h + S40 + SL0 increased straight-chain esters by 57% and branched-chain esters by 56% in 'Big Top', while increases of 21% for straight-chain esters and 33% for branched-chain esters were observed in 'Early Rich' (Supplementary Tables 3a and 4a). In both varieties, significant increases were observed in the concentrations of propyl acetate, butyl acetate, 2-methylpropyl acetate, butyl 2-methybutanoate, and 2-methylpropyl hexanoate. When the fruit were ripened at 20 °C after cold storage, there was an increase in pentyl acetate and ethyl octanoate (Tables 3–5).

Four lactones accounted for 0.3–5.4% of total volatiles at harvest and during cold storage (Supplementary Tables 2a and 4a). There was a significant increase in total lactones after 3 d shelf life after 10 d cold storage. Individual lactones did not contribute to changes in response to pre-storage before cold storage in the same way. Pre-storage increased concentrations of γ-hexalactone and γ-octalactone in both varieties (Table 4). γ-Hexalactone was most abundant and stable during cold storage, but while it took 10 h at 20 °C to increase its concentration in 'Early Rich', in 'Big Top' 24 h were needed to obtain the same result. Production of γ-octalactone was significantly inhibited by 0 h + S40 + SL0, with a significant increase after fruit were pre-stored 10 h or 24 h (Table 4). The combination 36 h + SL3 increased δ-decalactone in 'Big Top' nectarines after cold storage and the same result was obtained in 'Early Rich' peaches after 20 d or 40 d cold storage. Concentrations of γ-dodecalactone were almost below the threshold of detection in cold-stored fruit, but increased after three days shelf life in pre-stored 'Early Rich' (Supplementary Table 4a).

After 10 d cold storage without shelf-life, pre-storage for 36 h increased the total terpenes in 'Big Top' nectarines and 'Early Rich' peaches (Supplementary Table 2a). During cold storage, the

Table 1
Fruit quality at harvest and after pre-storage at 20 °C followed by cold storage at −0.5 °C and 0 or 3 d at 20 °C.

	Hours at 20 °C	Big Top nectarine												
		Harvest	Days −0.5 °C + days at 20 °C											
			10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Firmness (N)	0	43.1	37.6	Aab	26.2	Ba	43.0	Aa	29.4	Ba	42.2	Aa	29.2	Ba
	10		42.0	Aa	29.5	Ba	44.2	Aa	26.1	Bab	41.1	Aa	27.7	Ba
	24		33.6	BCb	28.6	cDa	43.2	Aa	27.4	CDab	40.2	ABa	23.9	Da
	36		37.4	Bab	23.3	Ca	44.4	Aa	23.8	Cb	38.9	ABa	25.7	Ca
SSC (%)	0	11.3	11.6	ABa	11.1	ABab	11.4	ABa	12.2	Aa	11.5	ABa	10.6	Bb
	10		11.6	BCa	11.7	Bab	10.6	Ca	12.8	Aa	12.5	ABa	12.3	ABa
	24		11.9	Aa	12.1	Aa	10.6	Ba	11.7	ABab	12.4	Aa	12.1	Aa
	36		11.6	ABa	10.8	ABb	10.8	ABa	10.7	ABb	12.1	Aa	10.3	Bb
TA (g malic acid/L)	0	6.9	6.0	Abc	5.9	ABb	5.1	Cb	4.9	Db	5.2	Ca	5.8	Ba
	10		6.3	Ba	6.5	Aa	5.0	Db	4.5	Ec	5.3	Ca	5.3	Cb
	24		5.9	Bc	6.4	Aa	5.1	Cb	4.7	Db	4.6	Db	5.8	Ba
	36		6.1	Ab	5.7	Bc	5.3	Da	5.5	Ca	3.8	Fc	4.4	Ec
SSC/TA	0	16.3	19.4	BCa	18.6	BCa	22.1	ABa	24.9	Aa	22.3	ABc	18.2	Cb
	10		18.4	Ca	18.0	Ca	21.3	BCa	28.4	Aa	23.8	Bbc	23.3	Ba
	24		20.0	Ca	18.7	Ca	20.8	Ca	24.7	ABa	26.8	Ab	20.9	BCab
	36		19.2	Ca	18.9	Ca	20.3	BCa	19.3	Cb	32.0	Aa	23.5	Ba

	Hours at 20 °C	Early Rich peach												
		Harvest	Days −0.5 °C + days at 20 °C											
			10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Firmness (N)	0	41.8	35.4	Aa	7.2	Ba	38.2	Aa	15.4	Ba	39.9	Aa	14.9	Ba
	10		35.4	Aa	6.5	Ba	31.1	Aa	9.0	Ba	32.9	Aa	12.1	Bab
	24		25.6	Ab	6.0	Ba	28.9	Aa	8.5	Ba	25.0	Ab	6.0	Bab
	36		18.9	Ab	5.8	Ba	12.1	ABb	9.8	ABa	12.2	ABc	4.5	Bb
SSC (%)	0	10.4	10.9	Ab	10.9	Ab	11.1	Ab	11.1	Ab	10.9	Ab	10.7	Ac
	10		11.7	Aa	11.5	Aab	11.3	Ab	11.7	Aa	11.4	Ab	11.1	Abc
	24		11.3	Bab	11.3	Bb	12.5	Aa	11.8	Ba	11.6	Bab	11.4	Bb
	36		11.1	Bab	11.7	ABa	11.6	ABb	11.7	ABa	12.1	Aa	12.2	Aa
TA (g malic acid/L)	0	9.8	8.3	Cc	9.0	Ba	9.2	Aa	7.3	Ea	8.2	Cb	7.6	Da
	10		8.9	Aa	7.8	Cb	7.9	Cc	5.7	Eb	8.5	Ba	7.0	Db
	24		8.6	Bb	5.9	Dc	8.8	Ab	4.9	Fc	7.2	Cd	5.3	Ed
	36		6.6	Bd	5.6	Cd	6.6	Bd	4.8	Dc	8.0	Ac	5.5	Cc
SSC/TA	0	10.9	13.2	ABb	12.1	Bc	12.0	Bb	15.2	Ac	13.2	ABb	14.1	Ab
	10		13.1	Db	14.7	BCb	14.2	BCDb	20.4	Ab	13.4	CDb	15.8	Bb
	24		13.1	Eb	18.6	Ca	14.2	DEb	24.0	Aa	16.0	Da	21.4	Ba
	36		16.8	CDa	21.0	Ba	17.6	Ca	24.6	Aa	15.1	Dab	22.1	Ba

Means within the same hours at 20 °C followed by the same capital letter and means within the same days −0.5 °C + days at 20 °C followed the same small letter are not significantly different at $p \leq 0.05$ (LSD test).

relative proportion of total terpenes decreased from 7.7 to 0.4% in ‘Big Top’ nectarines. Terpenes were not detected in ‘Early Rich’ samples stored for 20 d or 40 d without shelf-life. Linalool was the major terpene compound found and it increased after 36 h pre-storage.

Two ketones detected in the two cultivars accounted for 8–27% of total volatiles at harvest and during cold storage (Supplementary Table 2a). Acetophenone and 2,3-butanodione concentrations were stable during cold storage in ‘Big Top’ nectarines, but decreased in control ‘Early Rich’ peaches. The combination of pre-storage plus shelf-life increased ketone concentrations, especially in ‘Early Rich’ peaches. The highest concentrations of the two ketones were obtained in ‘Big Top’ at 10 h + S10 + SL3 (Supplementary Table 5a).

3.3. *Relationships between sensory and measured attributes after cold storage following ripening at 20 °C*

Because of the large number of measurements obtained, principal component analysis (PCA) was used to interpret the data. A full-data PCA model, focusing on samples held three days at 20 °C after harvest and cold storage, was separately developed for each cultivar. Volatile emissions, quality measures, and sensory attributes were used to characterize each sample. For both cultivars, samples held three days at 20 °C after harvest grouped separately from those subjected to cold storage (data not shown); cold storage was the main factor that accounted for sample differentiation. Since one objective of this work was to evaluate whether pre-storage at 20 °C could improve and/or preserve overall fruit quality during cold storage, we omitted the harvest fruit from the set of samples and focused on differentiating among different combinations of pre-storage at 20 °C or/and cold storage periods.

A combination of principal components 1 (PC1) and 2 (PC2) explained 49% of total variability among ‘Big Top’ samples pre-stored at 20 °C for 0, 10, 24 or 36 h and then kept in cold storage for 10, 20 or 40 d plus 3 d at 20 °C (Fig. 1). Although this percentage is not very high, the degree of variance encountered was sufficient for the qualitative purpose of this plot. Variances explained by emissions of different volatile compounds tend to overlap because of the repeated information that they provide to the PCA model. The analysis separated four well-distinguished groups. Three groups (to the right of the plot) correspond to samples pre-stored for 0, 10, or 24 h at 20 °C before cold storage for 10 or 20 d. Another group, located to the left of the plot, corresponds to samples pre-stored for 36 h at 20 °C and samples cold-stored for 40 d, regardless of pre-treatment time at 20 °C. Pre-storage had a clear influence on ‘Big Top’

Table 2
Esters, acids, and total volatile compounds emitted (ng kg^{-1}) by two fruit varieties at harvest and after pre-storage at 20 °C followed by cold storage at −0.5 °C plus 0 or 3 days at 20 °C.

	Big Top nectarine													
	Harvest	Hours at 20 °C	Days at −0.5 °C + days at 20 °C											
			10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Esters	867.9	0	2550.0	Aa	2678.7	Aa	1086.4	Bb	3144.4	Aa	431.4	Bb	1094.9	Ba
		10	1152.7	Ab	1283.7	Ab	1252.4	Ab	1184.8	Ab	1377.2	Ab	594.6	Aa
		24	1001.8	Bb	924.2	Bb	591.4	Bb	1047.3	Bb	3048.0	Aa	919.5	Ba
		36	3157.2	Aa	1345.8	Bb	3994.6	Aa	1667.1	Bb	1071.9	Bb	1340.9	Ba
Acids	244.2	0	117.7	Ba	259.1	Bb	138.6	Ba	492.3	Ba	1243.4	Aa	1602.4	Aa
		10	115.6	Ba	1315.4	Aa	86.6	Ba	240.7	Ba	769.2	ABa	428.8	Bb
		24	127.4	Ba	1387.0	Aa	128.4	Ba	201.5	Ba	657.5	Ba	715.7	ABb
		36	180.4	Ba	163.6	Bb	223.7	Ba	205.0	Ba	1269.5	Aa	1251.9	Aa
Total	2985.3	0	4257.1	ABab	5360.1	Aab	2193.6	Bb	5747.5	Aa	2573.7	Bb	4171.7	ABa
		10	2608.7	BCbc	5824.2	Aa	2463.7	Bb	2657.5	BCb	3312.3	Bb	1724.5	BCb
		24	2189.9	Cc	3791.4	Cbc	1299.3	Cb	2393.7	Cb	6250.7	Ba	3490.0	Cab
		36	5922.8	Ba	3146.6	Cc	8633.7	Aa	3749.1	Cab	3278.4	Cb	3523.8	Cab
	Early Rich peach													
	Harvest	Hours at 20 °C	Days at −0.5 °C + days at 20 °C											
			10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Esters	1749.0	0	3385.2	ABa	4490.9	ABa	6235.1	Abc	2119.4	Bb	620.5	Ba	2281.8	Ba
		10	2578.6	Aa	3365.4	Aa	3202.0	Ac	1407.3	Ab	868.5	Aa	2356.2	Aa
		24	2539.8	BCa	5677.1	ABa	6991.5	Ab	2021.4	Cb	1027.8	Ca	1290.6	Ca
		36	4658.5	BCa	3532.6	CDa	14,086.5	Aa	7217.0	Ba	609.9	Da	1792.6	CDa
Acids	863.3	0	102.9	Ca	354.5	BCa	1130.3	ABCa	1927.8	Aab	1260.2	ABc	1798.1	Aa
		10	145.6	Da	243.0	CDa	1233.9	BCa	1572.2	Bb	2889.3	Aa	1592.7	Ba
		24	nd		655.4	Ba	1644.3	ABa	2649.9	Aa	2300.2	Aab	1237.1	Ba
		36	392.7	Ca	216.8	Ca	763.7	BCa	2243.6	Aab	1698.3	ABbc	1531.6	ABa
Total	4848.6	0	7845.9	Aab	9206.7	Aab	9398.1	Ab	6352.0	ABb	3772.0	Ba	6545.2	ABa
		10	5412.8	Ab	6429.7	Ab	7028.2	Ab	4658.9	Ab	6181.0	Aa	5557.0	Aa
		24	4170.1	Bb	10,270.5	Aa	10,216.4	Ab	6201.9	Bb	6021.3	Ba	4347.5	Ba
		36	10,756.0	BCa	7417.2	CDb	16,766.5	Aa	12,279.6	Ba	4319.7	Da	5446.2	Da

Means within the same hours at 20 °C followed by the same capital letter and means within the same days −0.5 °C + days at 20 °C followed the same small letter are not significantly different at $p \leq 0.05$ (LSD test).

nectarines kept in cold storage for 10 or 20 d. For short or medium cold storage periods, the length of pre-storage at 20 °C had the greatest influence on the differences among samples. For samples kept in cold storage for 40 d, this separation was less clear; even so, there was separation among these samples by pre-storage time along the PC2 axis.

'Big Top' fruit kept in cold storage for 10 or 20 d after pre-storage for 10 h at 20 °C correlated primarily with volatile compounds 2-methylbutyl 2-methylpropanoate (2mb2mpr), 2-methyl-1-butanol (2mbOH), and butyl propanoate (bpr), the sensory attributes sweetness and peach/nectarine flavour, and SSC. 'Big Top' fruit pre-stored for 24 h at 20 °C and then cold stored 10 or 20 d correlated mainly with volatile compounds 2-methylbutyl-2-methylpropanoate (2mb2mpr), 2-methyl-1-butanol (2mbOH), and decanoic acid (deac) and the sensory attributes juiciness, peach/nectarine flavour, and ease of breakdown.

Perception of sweetness correlated positively with the emission of volatile compounds such as acetophenone (aone), butyl propanoate (bpr), 2,3-butanodione (23bone) and SSC. In addition, a significant correlation was found between peach/nectarine flavour, SSC, and the volatile compounds 2-methylbutanol (2mOH), 2-methylbutyl-2-methylpropanoate (2mb2mpr), and butyl propanoate (bpr). Most volatiles emitted by 'Big Top' nectarines, including γ-hexalactone (hlac), γ-octalactone (olac), δ-decalactone (dlac), ethyl 2-methylbutanoate (e2mb), and propyl hexanoate (prh), did not influence flavour perception.

Principal components 1 (PC1) and 2 (PC2) together explained 60% of total variability in 'Early Rich' samples pre-stored at 20 °C for 0, 10, 24, or 36 h and then cold-stored for 10, 20, or 40 d plus three days at 20 °C (Fig. 2). There were two well-separated groups: samples with 10 d cold storage and no pre-storage are clustered on the left, while samples cold-stored for 20 or 40 d were located to the right. These results show a clear effect of cold storage time on 'Early Rich' peach segregation. Within the group of samples located on the right, the sample pre-treated at 20 °C for 36 h and then kept in cold storage for 20 d clearly separated from the rest of the samples. For this cultivar, perception of sweetness was not in perfect agreement with the measured SSC values: neither measure appeared close to the biplot. Fruit kept in cold storage for 20 d after 36 h at 20 °C had the highest total volatile emissions (Table 2), although their SSCs were similar to those of the rest of the samples (Table 1). However, most volatile compounds identified were associated with fruit stored for 10 d. These samples were also perceived as being more flavourful and acidic. Increasing the cold storage time decreased emissions of most volatile compounds (Supplementary Tables 3a–5a).

4. Discussion

'Big Top' nectarines maintained a similar flesh firmness to fruit at harvest after 40 d cold storage without shelf life. This firmness retention extends marketing possibilities because a rapid loss of firmness is the main factor limiting the commercial life of stone fruit (Murray et al., 2007). The combination 36 h at 20 °C plus 3 d shelf life increased SSC and SSC/TA ratio in 'Early Rich' peaches. In contrast, pre-storage at 20 °C for 24–48 h did not affect SSC in another yellow-flesh peach variety cold-stored at 0 °C for up to 40 d plus shelf life at 20 °C (Infante et al., 2009). High consumer

Table 3
Selected straight-chain esters (ng kg^{-1}) in 'Big Top' nectarine and 'Early Rich' peach, PCA analysis codes in brackets, and retention index (RI) at harvest and after pre-storage at 20 °C followed by cold storage at −0.5 °C plus 0 or 3 d at 20 °C.

	Hours at 20 °C	RI	Big Top												
			Harvest	Days −0.5 °C + days at 20 °C											
				10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Propyl acetate (pra)	0	995	<10	488.2	ABa	516.1	Aa	171.9	Bb	601.9	Aa	nd		nd	
	10			459.1	Aa	507.6	Aa	63.3	Bb	462.1	Aab	96.4	Ba	33.0	Ba
	24			260.3	Aa	240.4	Aab	62.2	Ab	268.3	Abc	109.6	Aa	71.3	Aa
	36			230.2	Ba	30.3	Bb	564.4	Aa	35.4	Bc	137.3	Ba	93.1	Ba
Butyl acetate (ba)	0	1183	42.1	97.7	ABa	103.9	Aab	30.6	Ca	120.4	Aa	nd		36.1	BCa
	10			114.9	Aa	126.9	Aa	17.0	Ca	115.9	Aa	98.4	ABa	41.6	BCa
	24			44.5	Ba	41.0	Bbc	21.4	Ba	45.7	Bb	129.4	Aa	45.5	Ba
	36			63.4	Aa	21.1	Ac	72.0	Aa	25.4	Ab	67.9	Aa	55.5	Aa
Pentyl acetate (pa)	0	1307	10.0	<10		<10		<10		<10		<10		12.1	Ac
	10			<10		<10		<10		<10		63.1	Ab	25.9	Ba
	24			<10		<10		<10		<10		146.7	Aa	13.1	Bc
	36			10.3	Ca	<10		46.4	Aa	11.5	Ca	nd		17.2	Bb
Hexyl acetate (ha)	0	1393	45.1	73.2	ABb	79.5	Aa	37.3	Cb	90.2	Aa	43.6	BCc	95.5	Aa
	10			32.2	Bc	35.5	Bbc	39.8	Bb	32.7	Bb	115.3	Ab	57.9	Bb
	24			21.1	Bc	19.5	Bc	28.3	Bb	21.7	Bb	213.3	Aa	nd	
	36			115.4	Ba	69.9	CDa	557.7	Aa	85.1	BCa	44.4	Dc	69.1	CDab
Butyl propanoate (bpr)	0	1257	113.1	17.9	Aa	19.3	Aa	28.2	Ab	22.0	Aab	nd		nd	
	10			28.9	Aa	31.9	Aa	23.4	Ab	29.1	Aa	nd		nd	
	24			26.7	Aa	24.6	Aa	13.0	Ab	27.3	Aab	nd		nd	
	36			34.3	Ba	<10		222.8	Aa	10.2	Bb	nd		nd	
Ethyl octanoate (eo)	0	1555	229.0	81.1	ABa	84.3	ABa	329.0	Aa	100.1	ABa	26.8	Bb	86.5	ABb
	10			69.0	Aa	76.4	Aa	73.0	Aa	69.1	Aa	139.2	Aab	87.2	Ab
	24			278.2	Aa	258.5	Aa	166.2	Aa	292.4	Aa	165.4	Aab	123.0	Ab
	36			235.6	Ba	159.0	Ba	nd		186.2	Ba	302.4	Ba	758.4	Aa

	Hours at 20 °C	RI	Early Rich												
			Harvest	Days −0.5 °C + days at 20 °C											
				10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Propyl acetate (pra)	0	995	18.9	1098.0	Aa	231.1	Bab	66.7	Bb	103.1	Bc	nd		nd	
	10			662.6	Ab	150.4	BCab	44.5	Cb	93.5	Cc	122.9	BCa	367.7	Ba
	24			1130.7	Aa	391.3	Ba	259.9	BCb	360.2	Bb	48.0	Ca	138.4	Bca
	36			938.7	Ba	80.8	Db	649.6	Ca	1265.3	Aa	47.5	Da	147.9	Da
Butyl acetate (ba)	0	1183	51.6	34.9	BCc	66.6	ABa	24.2	Cc	56.7	ABCb	nd		75.5	Aa
	10			198.3	Aa	49.9	BCa	23.7	Cc	40.2	Cb	25.0	Ca	79.3	Ba
	24			120.6	Ab	80.9	Ba	62.7	BCb	70.8	Bb	34.8	Ca	55.4	BCa
	36			144.3	Ab	56.6	Ca	110.1	Ba	135.6	ABa	31.3	Ca	62.3	Ca
Pentyl acetate (pa)	0	1307	15.9	19.8	Ba	52.1	Aa	11.2	Bc	26.1	Abc	<10		19.1	Ba
	10			10.0	Ba	33.9	Ba	92.9	Aab	82.7	Ab	nd		31.5	Ba
	24			11.0	Ba	56.3	Aa	76.0	Ab	76.1	Ab	nd		nd	
	36			31.6	Ba	34.5	Ba	120.5	Aa	114.4	Aa	nd		26.4	Bca
Hexyl acetate (ha)	0	1393	127.9	128.1	Bb	336.5	Ab	64.2	Cb	149.1	Bab	49.1	Ca	119.4	Ba
	10			77.0	Bc	270.4	Ac	62.7	Bb	103.5	Bb	nd		nd	
	24			78.6	Cbc	397.4	Aa	110.7	Cab	176.7	Ba	nd		94.2	Ca
	36			211.9	ABa	247.0	Ac	151.7	CDa	194.2	BCa	nd		105.8	Da
Butyl propanoate (bpr)	0	1257	37.1	20.1	Ab	11.2	Aa	nd		nd		nd		nd	
	10			27.2	Ab	<10		12.5	Ba	nd		nd		nd	
	24			19.6	Ab	<10		16.9	Aa	nd		nd		nd	
	36			52.3	Aa	<10		nd		nd		nd		nd	
Ethyl octanoate (eo)	0	1555	376.7	172.1	Ba	643.3	ABa	230.6	Bc	305.6	Bb	60.3	Ba	1148.2	Aa
	10			139.0	Ba	449.1	Ba	82.7	Bc	445.1	Bb	nd		1098.5	Aa
	24			368.5	ABa	428.3	ABa	937.0	Ab	nd		nd		385.0	ABb
	36			538.4	Ca	453.6	Ca	1597.8	Ba	3936.3	Aa	nd		500.7	Cb

Means within the same hours at 20° C followed by the same capital letter and means within the same days −0.5 °C + days at 20 °C followed the same small letter are not significantly different at $p \le 0.05$ (LSD test). RI: Kovats retention index in column cross-linked FFAP.

acceptance of nectarines with high SSC/TA ratios has been reported and this ratio increased during ripening (Aubert et al., 2003), as also observed in peaches (Crisosto and Crisosto, 2005). The decrease in TA throughout cold storage was no more evident in pre-stored fruits than previously reported in other peach and nectarine varieties (Crisosto and Crisosto, 2005; Infante et al., 2009).

The effects of storage temperature, storage atmosphere, and shelf-life on peach and nectarine aroma have been reported previously (Robertson et al., 1990; Aubert et al., 2003; Raffo et al., 2008; Infante et al., 2009; Ortiz et al., 2009, 2010; Yang et al., 2009; Zhang et al., 2010, 2011). However, no data on relationships between peach/nectarine volatiles and pre-storage before cold storage are

Table 4
Selected branched-chain esters (ng kg^{-1}) in 'Big Top' nectarine and 'Early Rich' peach, PCA analysis codes in brackets, and retention index (RI) at harvest and after pre-storage at 20 °C followed by cold storage at −0.5 °C plus 0 or 3 d at 20 °C.

	Hours at 20 °C	RI	Big Top													
			Harvest	Days −0.5 °C + days at 20 °C												
				10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3		
2-Methylpropyl acetate (2mpra)	0	1052	21.5	40.7	Ba	42.7	Ba	55.0	ABb	50.2	ABa	nd		116.1	Aa	
	10			46.1	Aa	50.9	Aa	25.7	Ab	46.6	Aa	68.3	Aa	46.0	Ab	
	24			41.0	Ba	37.9	Ba	29.9	Bb	42.3	ABa	110.5	Aa	91.5	ABab	
	36			57.7	Ba	33.5	Ba	374.2	Aa	40.1	Ba	66.6	Ba	71.0	Bab	
2-Methylbutyl-2-methylpropanoate (2mb2mpr)	0	1310	153.9	51.8	Ab	53.7	Aab	36.0	Ab	63.9	Aa	32.4	Ac	50.3	Aa	
	10			77.1	Aab	85.1	Aa	24.6	Bb	78.3	Aa	87.5	Ab	nd		
	24			81.5	Bab	75.2	Bab	19.3	Cb	83.7	Ba	139.3	Aa	nd		
	36			101.4	Ba	43.6	Cb	318.4	Aa	52.9	Ca	54.1	Cbc	nd		
γ-Hexalactone (hlac)	0	1880	26.5	30.7	ABCb	34.1	ABab	28.7	BCa	37.8	ABb	12.7	Cd	49.7	Aa	
	10			32.6	BCb	36.0	BCab	23.3	Ca	32.9	BCb	96.0	Ab	42.5	Ba	
	24			29.6	Cb	27.4	Cb	21.7	Ca	30.5	Cb	196.8	Aa	55.5	Ba	
	36			55.9	Aa	49.0	Aa	21.6	Ba	58.9	Aa	52.4	Ac	56.5	Aa	
γ-Octalactone (olac)	0	2111	9.0	12.8	Aa	14.1	Aa	13.2	Aa	15.7	Aab	nd		nd		
	10			16.2	Ca	17.9	Ca	10.2	Ca	16.4	Cab	49.1	Aa	31.3	Ba	
	24			12.1	Ba	11.2	Ba	<10		12.4	Bb	51.4	Aa	nd		
	36			15.1	Aa	19.5	Aa	nd		23.1	Aa	nd		nd		
δ-Decalactone (dlac)	0	2417	2.4	16.8	Aa	20.6	Ab	51.9	Aa	20.6	Ab	nd		12.8	Aa	
	10			17.6	Aa	19.5	Ab	20.4	Aa	17.5	Ab	nd		12.6	Aa	
	24			<10		<10		19.0	Aa	8.5	Ab	nd		11.0	Aa	
	36			16.5	Ba	100.4	Aa	nd		118.7	Aa	nd		15.7	Ba	

	Hours at 20 °C	RI	Early Rich													
			Harvest	Days −0.5 °C + days at 20 °C												
				10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3		
2-Methylpropyl acetate (2mpra)	0	1052	25.7	87.6	Cab	504.7	Aa	47.8	Cb	314.0	Bbc	nd		327.7	Bab	
	10			75.1	Cb	380.2	Ab	61.7	Cb	269.4	Bc	88.9	Ca	394.1	Aa	
	24			80.6	Cb	683.1	Ab	115.1	Cab	370.0	Bb	89.5	Ca	297.8	Bb	
	36			158.8	CDa	343.7	Bb	184.9	Ca	528.3	Aa	87.9	Da	299.6	Bb	
2-Methylbutyl-2-methylpropanoate (2mb2mpr)	0	1310	42.40	71.0	Ab	71.1	Aab	27.7	Bb	36.3	Bab	11.4	Ca	18.0	Ca	
	10			39.5	Ac	31.5	ABc	nd		20.2	BCb	nd		12.4	Ca	
	24			27.4	Bc	54.9	Ab	nd		22.9	Bb	nd		nd		
	36			120.5	Aa	76.8	Ba	49.5	Ca	48.8	Ca	nd		nd		
γ-Hexalactone (hlac)	0	1880	99.0	108.39	Bb	155.07	Ab	100.73	BCa	95.12	BCa	74.92	Cb	73.28	Ca	
	10			142.69	Aa	158.35	Ab	30.34	Cb	61.27	BCb	132.75	Aa	78.77	Ba	
	24			74.31	BCc	192.78	Aa	94.64	Ba	95.05	Ba	60.26	Cb	89.58	BCa	
	36			169.81	Aa	110.83	BCc	77.08	Da	68.37	Dab	130.51	Ba	93.05	CDa	
γ-Octalactone (olac)	0	2111	42.4	26.90	Bb	42.61	Ab	47.81	Aa	35.05	ABa	nd		22.16	Ba	
	10			57.88	Aa	65.65	Aa	nd		15.06	Bb	nd		27.58	Ba	
	24			35.49	Bb	65.81	Aa	20.93	BCb	25.72	BCab	13.89	Cb	35.20	Ba	
	36			67.68	Aa	49.72	Bb	nd		15.53	Cb	42.29	Ba	23.62	Ca	
δ-Decalactone (dlac)	0	2417	10.4	38.03	Bb	174.03	Ab	80.65	Ba	73.75	Ba	nd		nd		
	10			27.63	Bb	232.75	Aa	nd		63.66	Ba	nd		nd		
	24			30.16	Bb	265.97	Aa	16.16	Bb	56.39	Ba	nd		nd		
	36			273.40	Aa	274.66	Aa	nd		22.49	Ba	nd		26.13	Ba	

Means within the same hours at 20 °C followed by the same capital letter and means within the same days −0.5 °C + days at 20 °C followed the same small letter are not significantly different at $p \le 0.05$ (LSD test). RI: Kovats retention index in column cross-linked FFAP.

available in the literature. Here, we show that there are changes in impact volatiles of peach and nectarine fruit in response to different pre-storage, cold storage, and shelf-life times. Generally, in control fruit the concentration of total volatiles decreased with longer cold storage, consistent with previous studies (Robertson et al., 1990; Infante et al., 2009; Zhang et al., 2011). 'Big Top' nectarines subjected to 36 h pre-storage followed by 20 d cold storage without shelf-life had increased emissions of esters, C6 alcohols and C6 aldehydes, but after 3 d at 20 °C there was a decrease in these volatile compounds. The C6 aldehydes and alcohols are generated using linoleic and linolenic acids as precursors through the lipoxygenase (LOX) pathway (Schwab et al., 2008). LOX and hydroperoxide lyase (HPL) convert linoleic acids to hexanal. The aldehydes can then be reduced to the corresponding C6 alcohols by alcohol dehydrogenase (ADH). The aromatic esters are produced when alcohol acyltransferase (AAT) catalyses the final

Table 5
Selected aldehydes, terpenes, and alcohols (ng kg^{-1}) in 'Big Top' nectarine and 'Early Rich' peach, codes in brackets, and retention index (RI) at harvest and after pre-storage at 20 °C followed by cold storage at −0.5 °C plus 0 or 3 d at 20 °C.

	Hours at 20 °C	RI	Big Top												
			Harvest	Days −0.5 °C + days at 20 °C											
				10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Hexanal (hal)	0	1082	223.3	240.5	Aab	230.4	ABb	101.5	Cb	170.9	ABCa	129.8	Ca	137.2	BCb
	10			170.4	Bb	822.3	Aa	129.2	BCb	166.5	Ba	80.3	BCa	46.8	Cb
	24			157.0	BCb	282.3	Ab	63.9	Cb	118.5	Ca	156.0	BCa	253.2	ABa
	36			299.6	Aa	306.0	Ab	399.6	Aa	123.2	Ba	95.9	Ba	104.2	Bb
2-Ethyl-l-hexenal (2elhal)	0	1293	133.7	115.2	ABa	127.7	Aa	77.2	Bbc	141.8	Aa	82.1	Bc	116.2	ABa
	10			71.1	Bb	78.6	Bb	86.6	Bb	71.7	Bb	167.8	Ab	55.6	Bb
	24			52.3	Cb	48.2	Cb	43.7	Cc	53.7	Cb	305.1	Aa	126.5	Ba
	36			149.5	Ba	70.9	Cb	514.5	Aa	87.1	Cb	nd		58.6	Cb
Benzaldehyde (byde)	0	1521	112.0	26.2	Ba	18.4	Bb	51.3	ABb	63.7	ABa	34.4	ABa	71.8	Aab
	10			24.3	Ba	119.3	Aa	25.0	Bb	70.9	Ba	42.3	Ba	32.6	Bb
	24			21.6	CDa	135.7	Aa	17.4	Db	nd		65.5	BCa	89.0	ABa
	36			nd		48.1	Bb	180.3	Aa	77.4	Ba	58.9	Ba	54.4	Bab
Linalool (HOH)	0	1679	574.9	49.3	Ab	54.5	Ab	40.5	ABa	60.7	Ab	10.2	Cd	22.1	BCa
	10			52.4	Bb	57.8	Bb	15.5	Cb	53.1	Bb	120.4	Ab	37.0	BCa
	24			69.8	Bb	64.5	Bb	35.6	Cab	72.2	Bb	176.7	Aa	14.9	Ca
	36			112.9	Aa	94.5	Aa	31.0	Bab	111.5	Aa	37.8	Bc	13.1	Ba
1-Hexanol (hOH)	0	1480	37.1	29.9	ABb	31.9	ABa	11.7	Cb	36.9	Aa	nd	BCb	26.1	ABCb
	10			19.2	Bbc	21.2	Bab	15.5	Bb	19.5	Bb	nd		46.9	Aa
	24			12.1	Cc	11.2	Cb	10.2	Cb	12.4	Cb	271.7	Aa	40.4	Bab
	36			50.6	Ba	nd		571.1	Aa	nd		16.7	Cb	nd	
2-Methyl-l-butanol (2mbOH)	0	1329	24.8	34.7	Aa	37.3	Aa	nd		42.7	Aa	19.2	Ab	16.4	Aa
	10			51.0	Aa	56.4	Aa	nd		51.2	Aa	nd		nd	
	24			nd		nd		nd		nd		103.6	Aa	nd	
	36			nd		nd		149.1	Aa	nd		nd		nd	
2-Ethyl-l-hexanol (2ehOH)	0	1619	134.2	526.6	Ab	638.4	Aa	97.4	Ab	646.7	Aa	134.1	Aa	361.1	Aa
	10			163.5	Ab	180.5	Aa	465.5	Ab	165.9	Aa	292.3	Aa	119.5	Aa
	24			125.7	Ab	115.9	Aa	82.2	Ab	129.1	Aa	508.4	Aa	417.7	Aa
	36			1308.3	Aa	460.2	Ba	1453.9	Aa	572.3	Ba	126.4	Ba	99.8	Ba
	Hours at 20 °C	RI	Early Rich												
			Harvest	Days −0.5 °C + days at 20 °C											
				10 + 0		10 + 3		20 + 0		20 + 3		40 + 0		40 + 3	
Hexanal (hal)	0	1082	672.1	1255.1	Aa	752.4	Ba	367.1	Cbc	529.9	BCa	363.3	Cab	385.1	Ca
	10			571.2	ABb	360.2	Abc	680.4	Aa	357.9	ABab	554.8	ABat	138.6	Ca
	24			357.0	ABb	433.8	ABbc	223.9	Bc	190.6	Bb	595.0	Aa	309.7	Ba
	36			1446.4	Aa	637.7	Bab	451.4	BCab	314.6	Cab	328.3	Cb	302.4	Ca
2-Ethyl-l-hexenal (2elhal)	0	1293	240.7	332.3	Aab	273.0	ABa	194.0	BCa	205.3	BCa	149.5	Ca	171.8	Ca
	10			263.8	Ab	185.5	ABb	100.5	CDb	24.8	Db	199.8	ABa	138.0	BCa
	24			131.3	Cc	227.3	ABab	19.0	Dbc	44.6	Db	231.1	Aa	148.3	BCa
	36			382.9	Aa	223.9	Bab	nd		76.8	CDb	169.7	Ba	157.0	BCa
Benzaldehyde (byde)	0	1521	92.0	73.8	Bb	98.1	ABbc	71.2	Ba	81.8	ABa	106.3	Aa	97.5	ABab
	10			93.1	Ab	69.4	ABc	93.5	Aa	67.8	ABa	77.1	ABa	61.7	Bc
	24			33.8	Cc	152.1	Aa	nd		36.5	Cb	95.3	Ba	73.3	Bbc
	36			130.5	Aa	125.3	Aab	66.6	Ca	76.0	BCa	80.5	BCa	105.2	Aba
Linalool (HOH)	0	1679	38.3	nd		10.2	Aa	<10		nd		nd		nd	
	10			<10		13.4	Aa	nd		nd		nd		nd	
	24			nd		<10		nd		nd		nd		nd	
	36			89.1	Aa	<10		nd		13.2		nd		nd	
1-Hexanol (hOH)	0	1480	64.0	112.2	Ab	127.6	Aa	26.5	Bb	52.9	Ba	33.1	Ba	47.6	Ba
	10			81.7	Ab	89.8	Ab	41.6	Bb	40.0	Ba	nd		38.7	Ba
	24			35.1	Cc	117.9	Aab	29.3	Cb	46.3	BCa	nd		70.5	Ba
	36			198.9	Aa	101.3	Bab	78.7	Ba	71.9	BCa	nd		40.9	Ca
2-Methyl-l-butanol (2mbOH)	0	1329	nd	13.8	Aa	12.2	Aa	23.5	Ac	nd		25.5	Aa	26.5	Aa
	10			nd		nd		134.1	Aa	13.7	Bb	nd		nd	
	24			nd		nd		67.2	Ab	47.3	Ab	nd		nd	
	36			nd		nd		80.1	Bb	158.5	Aa	nd		nd	
2-Ethyl-l-hexanol (2ehOH)	0	1619	583.9	1361.6	Ab	769.4	Ba	nd	Bab	583.3	Ba	508.7	Ba	532.4	Ba
	10			1032.0	Ac	616.2	BCa	804.7	ABa	457.8	Ca	467.8	Ca	399.6	Ca
	24			448.5	BCd	633.9	ABa	378.4	BCb	323.8	Ca	736.4	Aa	423.3	BCa
	36			1721.6	Aa	654.0	Ba	576.9	Bab	527.5	Ba	511.1	Ba	508.8	Ba

Means within the same hours at 20 °C followed by the same capital letter and means within the same days −0.5 °C + days at 20 °C followed the same small letter are not significantly different at $p \leq 0.05$ (LSD test). RI: Kovats retention index in column cross-linked FFAP.

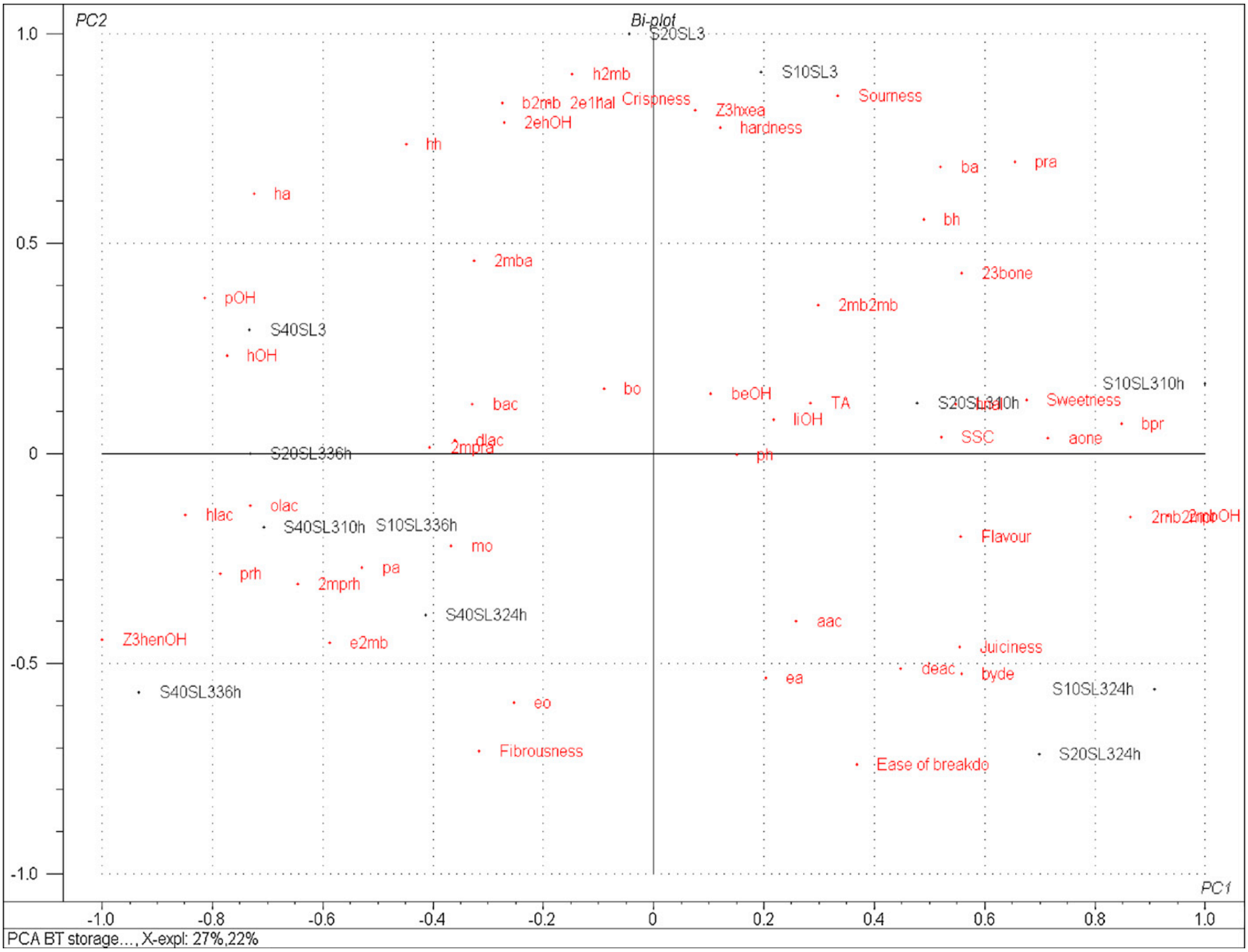

Fig. 1. PCA plot of emission of volatile compounds, quality measures, and sensory attributes of 'Big Top' nectarine fruit after pre-storage followed by cold storage plus 0 or 3 d at 20 °C. Codes for volatile compounds, quality measures, and sensory attributes are defined in Section 2. S refers to the cold-storage period, the first number represent days of cold storage at −0.5 °C (10, 20, or 40), SL is shelf life, the second number means days during shelf life (0 or 3), the last number represents hours of pre-storage at 20 °C before cold storage (0, 10, 24, or 36).

linkage between acyl moiety and alcohol. Zhang et al. (2010) examined volatile production and gene expression in peach (cv. 'Yulu') and found a rapid decline in hexanal during the first day of ripening at 20 °C. In previous studies carried out on another yellow peach ('Spring Lady'), higher concentrations of hexanal and 2-ethyl-1-hexenal were obtained after 14 d cold storage at 1 °C plus 1 d at 22 °C than after 7 d (Raffo et al., 2008).

In the present study, pre-storage increased concentrations of the four lactones detected. Several previous studies reported decreases of γ- and δ-lactone concentrations after cold storage without pre-storage (Raffo et al., 2008; Yang et al., 2009; Zhang et al., 2011) and increases during maturation and ripening at 20 °C (Lavilla et al., 2002; Aubert et al., 2003; Rizzolo et al., 2006). In two varieties, 10 h pre-storage increased their concentration after 40 d cold storage. In previous studies, there was an association between consumer acceptance of 'Early Rich' peach after cold storage and the concentrations of γ-hexalactone, γ-octalactone and γ-dodecalactone (Cano-Salazar et al., 2012). Here, 'Early Rich' peaches pre-stored for 36 h before 10 d cold storage plus 3 d shelf-life correlated with increased γ-hexalactone, γ-octalactone, and γ-octalactone emissions. This same pre-storage time before 20 d cold storage plus 3d shelf-life was also associated with perceptions of greater sweetness and higher propyl acetate, ethyl octanoate, linalool, and 2-methyl-1-butanol concentrations than control fruit. Linalool concentrations in 'Cresthaven' and 'Rich Lady' peaches decreased throughout storage at 0 °C (Robertson et al., 1990; Ortiz et al., 2009).

'Big Top' samples given 10 h pre-storage followed by 10 or 20 d cold storage were associated with perceptions of greater flavour, juiciness, and sweetness; higher SSC and butyl propanoate, 2-methylbutyl-2-methylpropanoate, 2,3-butanodione, and 2-methyl-1-butanol concentrations than control fruit.

As reported by others such as Baldwin et al. (1998), the perception of sweetness was affected by certain volatile compounds. We found a strong association between perceived sweetness and the emission of two ketones and butyl propanoate in 'Big Top' nectarines, while in Early Rich peaches, perceived sweetness was associated with higher concentrations of 2-methylbutyl acetate and two ketones.

Pre-storage for 10 h or 36 h before cold storage for 20 h and 3 d shelf-life increased the perceived flavour and sweetness of 'Big Top' or 'Early Rich' fruit, respectively. These pre-storage times also augmented the emissions of 2-methyl-1-butanol in both cultivars and other specific volatile compounds in each cultivar.

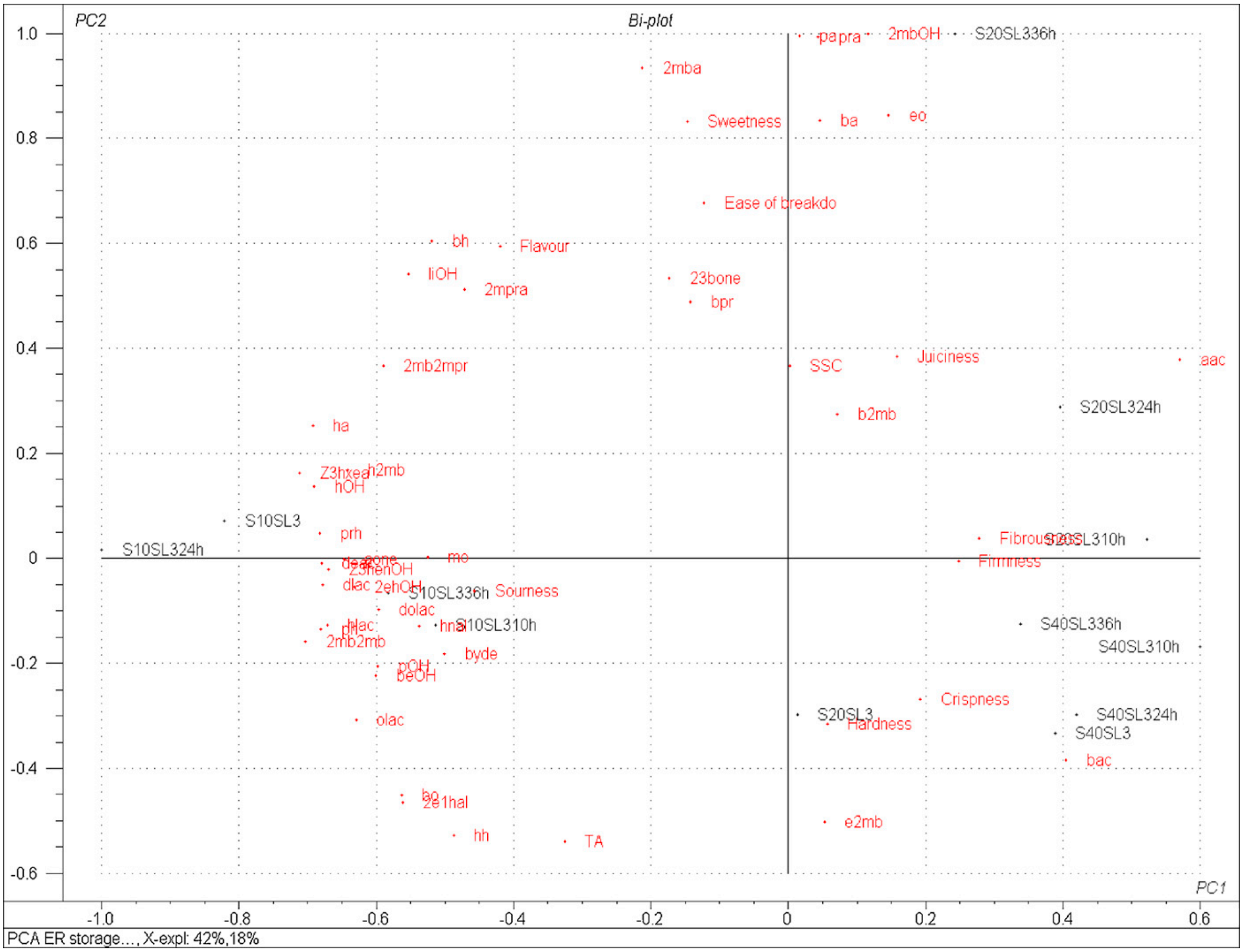

Fig. 2. PCA plot of emission of volatile compounds, quality measures, and sensory attributes of 'Early Rich' peach fruit after pre-storage followed by cold storage plus 0 or 3 d at 20 °C. Codes for volatile compounds, quality measures, and sensory attributes are defined in Section 2. S refers to the cold-storage period, the first number represent days of cold storage at −0.5 °C (10, 20, or 40), SL is shelf life, the second number means days during shelf life (0 or 3), the last number represents hours of pre-storage at 20 °C before cold storage (0, 10, 24, or 36).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.postharvbio.2012.10.001.

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