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Effect of ethylene and temperature conditioning on sensory attributes and chemical composition of 'Bartlett' pears

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ABSTRACT

'Bartlett' pears are resistant to ripening after harvest. Ethylene and temperature conditioning have been successfully used to stimulate fruit ripening with improved eating quality over non-conditioned fruit. However, few studies have evaluated the effect of different conditioning treatments on the sensory attributes of the fruit. In this study, we compared a descriptive sensory evaluation with the chemical composition of 'Bartlett' pears after the fruit were exposed to the following conditioning treatments: 2 d 100 μl L^{-1} ethylene, 14 or 7 d at 0 °C, 7 or 3 d at 10 °C, or untreated control at 20 °C. Fruit were softened to 27, 18 and 9 N firmness before evaluation. At 9 N, fruit conditioned at 0 °C produced high levels of esters, and fruit conditioned at 0 °C for 14 d also were high in sweet taste and fruity flavor attributes. Fruit treated at 10 °C had lower concentrations of esters, but fruit treated at 10 °C for 3 d was high in sweet taste perception. Ethylene treated fruit produced low levels of esters and high levels of aldehydes and were associated with apple aroma, similar to the untreated control fruit. Water soluble pectin levels were highly and positively correlated with juiciness and sweetness and negatively correlated with firmness, crunchiness, and grittiness. Future studies should determine whether consumer liking of 'Bartlett' pear fruit is also influenced by conditioning treatment.

1. Introduction

Fruit of most European pear (*Pyrus communis*) cultivars resist ripening after harvest (Villalobos-Acuna and Mitcham, 2008). Although 'Bartlett' pear fruit can slowly ripen immediately after harvest when held at room temperature (20 °C), they fail to achieve good color and acceptable texture and flavor (Puig et al., 1996). Pear fruit ripened on the tree or immediately after harvest do not develop a buttery and juicy texture which are both considered important parameters of good eating quality (Murayama et al., 1998). The reason for poor eating quality is low ethylene production by the fruit (Murayama et al., 1998), which may not be sufficient to induce the expression of genes that are critical for aroma volatile production and cell wall breakdown. As a result, fruit develop low concentrations of aroma compounds and a coarse, dry, and mealy texture (Gerasopoulos and Richardson, 1997). To alleviate this issue, several methods have been developed to stimulate pear ripening after harvest, including temperature conditioning (exposure to temperatures of 0–10 °C) and ethylene conditioning (Wang et al., 1972; Agar et al., 2000a; Miro et al., 2001; Villalobos-Acuna and Mitcham, 2008).

Partially ripe 'Bartlett' pears are preferred over unripe pears by consumers (Turner et al., 2005; Kupferman et al., 2010). Therefore, it is important to promote ripening to achieve good quality after harvest. For 'Bartlett' pears harvested at 76–84 N, cold storage at −1 to 0 °C for 14–21 d allowed the fruit to soften completely within 7 d at 20 °C (Mitcham et al., 2006). The time for conditioning was reduced to 3 or 2 d when 93 N fruit were stored at 5 or 10 °C, respectively (Agar et al., 2000b). The shortest conditioning time required occurred when the fruit were conditioned with ethylene gas. One to two days of exposure to 100 μL L^{-1} ethylene at 20 °C was needed to stimulate ripening (Agar et al., 2000b). However, few studies have determined the influence of these various conditioning treatments on the sensory attributes, particularly taste and aroma, of pear fruit.

Texture, aroma and taste are important attributes related to the sensory quality of pears (Jaeger et al., 2003). With softening,

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pectin polyuronic acid materials become more water soluble, while the alcohol insoluble fractions and cell wall neutral sugars decrease (Ahmed and Labavitch, 1980; Murayama et al., 1998; Eccher Zerbini, 2002). Murayama et al. (1998) found that pear fruit that ripened to a dry and coarse texture had lower levels of water soluble polyuronides (WSP) than the fruit that ripened to a buttery and juicy texture. Puig et al. (1996) demonstrated that 'Bartlett' pears treated with 100 $\mu L\,L^{-1}$ ethylene or low temperatures (0 °C for 4 weeks) after harvest ripened to yield a buttery and juicy texture; these treatments also had a high WSP content.

In addition to texture, aroma is a key component of pear fruit flavor (Jennings et al., 1964; Heinz and Jennings, 1966). In pears, the most prominent volatile compounds are esters of short to medium chain alcohols, especially ethyl and methyl esters (Paillard, 1990; Suwanagul and Richardson, 1998). Among the esters in 'Bartlett' pears, ethyl trans-2, cis-4 decadienoate has been defined as a 'character impact compound' (Jennings et al., 1964; Heinz and Jennings, 1966; Suwanagul, 1996; Komes and Gani, 2010), while hexyl acetate is a 'contributory flavor compound' (Jennings and Sevenants, 1964; Komes and Gani, 2010).

Sensory descriptive analysis is a powerful method to evaluate the sensory quality of fruit. It provides quantitative descriptions of products based on the perceptions of a trained panel (Stone and Sidel, 1993). Puig et al. (1996) used a trained panel to determine that 'Bartlett' pears treated with 100 $\mu L\,L^{-1}$ ethylene after harvest or stored at 0 °C for 4 weeks could ripen in about 6 d with high sensory scores [buttery and juicy texture and flavor (acid/sugar balance and aroma)], while the fruit stored at 0 °C for 2 weeks or not treated with any cold storage or ethylene did not soften sufficiently in 7 d at 20 °C and had low sensory scores. Numerous studies have attempted to relate chemical composition to sensory attributes. Ideally, the instrumental measurements can then be used to predict related sensory properties effectively without performing sensory evaluation. Several studies have demonstrated good correlations between instrumental and sensory texture (Plocharski and Konopacka, 1999; Pitts et al., 2008; Chauvin et al., 2010); however, similar relationships between sensory attributes and volatile components have not been reported for pear.

The objectives of this study were to compare the effect of ethylene conditioning, or cold (0 °C) or intermediate (10 °C) temperature conditioning on the sensory attributes of 'Bartlett' pears, including aroma, texture, and taste, as evaluated by descriptive analysis. The relationship between sensory attributes and chemical composition, including volatile concentrations, cell wall polyuronide levels, SSC and TA, were also determined.

2. Materials and methods

2.1. Fruit source

Mature-green 'Bartlett' (*P. communis* L.) pears were harvested at the average firmness of 80 N from a commercial orchard in Sacramento, California early in the harvest season (July 19, 2010). The fruit were transported to the Postharvest Pilot Plant at the University of California, Davis on the same day, and visually sorted to eliminate defective fruit and to obtain fruit of uniform size (~200 g) and green color for use in the experiments. The fruit were stored at 20 °C and >90% relative humidity prior to the initiation of treatments on the following day.

2.2. Treatments

The pears were randomly divided into six treatment groups with 210 fruit per treatment. Five treatment groups were exposed to different storage temperatures and times; 0 °C (low temperature) for 7 or 14 d, 10 °C (intermediate temperature) for 3 or 7 d, and 20 °C (control) for more than 11 d (until reaching the required firmness stages) with >90% relative humidity. The remaining group was treated at 20 °C with 100 $\mu L\,L^{-1}$ ethylene gas in two 300 L stainless steel tanks for 48 h. Humidified air containing 100 $\mu L\,L^{-1}$ ethylene was passed through the tank at 4 L min^{-1} to maintain carbon dioxide concentrations <0.3 kPa. After the initial treatments, all treatment groups were transferred to 20 °C for ripening until they softened to 9 N. Four single fruit replicates were chosen from each treatment group when the average fruit firmness reached 27, 18, and 9 N, and the firmness of the four fruit selected for instrumental and sensory evaluation were as close to 27, 18 or 9 N as possible. Portions of each individual fruit were used for analysis of skin color, firmness, cell wall polyuronides, volatile composition, SSC, TA, and sensory evaluation by a trained panel.

2.3. Ethylene concentrations

Ethylene concentration was measured every day or every other day on a subset of fruit from each treatment after fruit transfer to 20 °C and until the fruit began to senesce. Six fruit were placed into a 3.8 L jar as one replicate with three replicates for each treatment. The jars were sealed for 10–30 min before a 1 mL headspace gas sample was collected and analyzed for ethylene concentration using a gas chromatograph (AGC Series 400; Hach-Carle CO., USA) with a flame ionization detector (FID) and alumina column (Villalobos-Acuna et al., 2010).

2.4. Flesh firmness

Fruit firmness was determined at harvest (30 random fruit) and was measured every day or every other day (15 random fruit per treatment) after transfer to 20 °C for ripening until the fruit softened to 9 N ± 2.00 N (eating ripe, Mitcham and Mitchell, 2007). For analysis, the skin was removed from an area ~20 mm in diameter on opposite sides of the equatorial region of each pear. Firmness was measured on each side of the pear using a Güss FTA Penetrometer (Güss, Strand, Western Cape, South Africa) fitted with an 8 mm probe (Villalobos-Acuna et al., 2010). The four fruit per replicate for each treatment and firmness stage were selected when the average firmness for each treatment reached 27, 18 or 9 N, and the firmness of the four fruit selected for instrumental and sensory evaluation were as close to 27, 18 or 9 N (±3.00 N) as possible.

2.5. Soluble solids content and titratable acidity

Two wedge-shaped slices were cut from stem to blossom end from opposite sides of each pear used for sensory evaluation and juiced for SSC and TA determination. A few drops of juice were used to measure SSC by refractometry (Reichert AR6 Series, Depew, NY) and 4 g of juice diluted in 20 mL deionized water were used for determination of TA (expressed as malic acid equivalents), using an automatic titrater (Radiometer TitraLab; Tim850 titration manager and SAC80 sample changer).

2.6. Sugar and acid contents

The same juice samples used for soluble solids and titratable acidity were also used to measure individual sugar and acid content. Fructose, sucrose, glucose, sorbitol, citric acid, and malic acid were quantified using an enzymatic procedure previously described for apple and tomato juices (Vermeir et al., 2007). Analysis was done using enzyme reagent kits (R-Biopharm, Marshall, MI), modified for use in 96-well microplates. The procedure followed kit instructions except that the volumes of water used to prepare the reagents were

modified from those indicated so that the final reagent concentrations were the same for the 200 μL volume used here as for the 3 mL procedure described in the kit instructions. Pear juice samples were clarified by centrifuging for 5 min at 16,100 × *g*, and then aliquots of the supernatants were diluted 100-fold with water for acid analysis, and 1000-fold with water for sugar analysis. For the analysis, 100 μL aliquots of the diluted supernatants were mixed with 100 μL of the modified kit reagents in the microplate wells. Absorbance at 340 nm was measured, then 4 μL of the appropriate enzyme suspension was added and the absorbance at 340 nm monitored until a stable new reading was obtained. Concentrations of sugars and acids were calculated from the absorbance differences at 340 nm and the extinction coefficient for NADPH of 6300 M^{-1} cm^{-1}. Standard solutions provided with the kits were used to verify the accuracy of the method. The details of the specific enzymatic reactions involved in the determination of each individual sugar and acid are described in Vermeir et al. (2007).

2.7. Volatile composition

Pear tissue samples for measurement of volatile composition were collected from each fruit used for sensory evaluation, cutting a wedge from the stem to the blossom end. Samples were frozen at −80 °C for 18–20 weeks prior to analysis. Frozen pear tissue flesh (8 g, without peel or core) was placed in a test tube and 10 mL concentrated $CaCl_2$ were added to prevent enzymatic reactions. The mixture was homogenized (Polytron PT 10/35; Brinkmann/Kinematica, Westbury, NY) at speed 4 for 1 min after warming to room temperature. A 7 mL aliquot of the puree was transferred to each of two 10 mL amber glass vials (Supelco Analytical, St. Louis, MO) as two technical replicates. An aliquot (7 μL of a 0.1 mM solution) of 2-methylbutyl isovalerate (Sigma–Aldrich Inc., St. Louis, MO) in methanol was added to each vial as an internal standard and vials were sealed with Magnetic Universal-Screw Caps with open tops and white silicone septums.

The volatiles were collected by headspace sorptive extraction (HSSE), then analyzed by GC–MS (Agilent7890A GC/5975CMSD; Santa Clara, CA) equipped with a Thermal Desorption Unit (TDU) and Cooled Injection System (CIS) (Gerstel, GmbH & Co. KG). The headspace was sampled using a 10 mm magnetic stir bar (also known as Twister™; Gerstel GmbH & Co. KG), coated with 24 μL of polydimethylsiloxane (PDMS). The bar, suspended above the sample in the vial, was exposed to the headspace for 1 h at room temperature, while the sample was stirred at 270 rpm, using a 15-position stir-plate (Gerstel, GmbH & Co. KG). After exposure, the bars were rinsed with dH_2O to remove any sample contamination, blotted dry with a Kimwipe, and placed onto the auto-sampler. The volatile compounds sorbed onto the PDMS coating were thermally desorbed into the TDU and then cryofocused prior to GC/MS analysis for separation and detection. For the thermal desorption, the following parameters were used: initial TDU temperature of 30 °C, then heated to 250 at 720 °C min^{-1}, held for 5 min; transfer line temperature at 280 °C. Simultaneously, the analytes were transferred into the PVT-injector where they were cryogenically focused at −80 °C, using liquid N_2. Initial injection temperature was programmed at −80 °C, and then heated to 280 °C at 12 °C min^{-1}. The inlet was operated in split mode (5:1). The GC was equipped with a DB-5MS capillary column (30 m × 0.25 mm; film thickness 0.25 μm) (Agilent Technologies, Santa Clara, CA), injector temperature 220 °C, helium carrier gas flow rate of 1.2 mL min^{-1}. The oven temperature started at 40 °C, increased to 80 °C at a rate of 3 °C min^{-1}, and then increased to 180 °C at a rate of 5 °C min^{-1}. MS parameters were: transfer-line temperature of 230 °C, source temperature of 230 °C, quadrupole temperature of 150 °C, continuous scan range from 30 to 300 amu. Spectral deconvolution was performed with AMDIS software (version 2.69; NIST, Gaithersburg, MD) and spectra were aligned and analyzed with Mass Profile Professional (version 2.0; Agilent Technologies, Santa Clara, CA). The identity of volatile compounds was confirmed by matching retention time and mass spectra with those of authentic standards whenever possible. When authentic standards were not available, identification was performed by comparing the calculated retention index with published values, and matching their spectra with those present in the NIST library (NIST 0.8). A series of C8 to C20 hydrocarbons were used to calculate the retention index. Volatile concentrations were calculated by comparing the integrated peak area of each compound with the internal standard (17.29 μg L^{-1} 2-methylbutyl isovalerate, final concentration) and are reported as μg kg^{-1} fruit fresh weight.

2.8. Cell wall polyuronides

Samples for cell wall polyuronide analyses were collected from each fruit used for sensory evaluation by cutting a wedge from stem to blossom end, and frozen at −80 °C for 14–16 weeks before analysis. About 10 g of frozen pear flesh tissue (without peel or core) were used for cell wall polyuronide determination. The percentage of water soluble polyuronides (water soluble polyuronides/total polyuronides × 100) was determined following the method of Ahmed and Labavitch (1978).

2.8.1. Cell wall extraction

Tissue samples (10 g) were boiled in 95% ethanol for 20 min followed by homogenizing for 1 min (Polytron PT 10/35; Brinkmann/Kinematica, Westbury, NY). The pellet was collected while the supernatant was decanted using centrifugation at 1000 × *g* for 10 min. The pellet was re-suspended in 80% ethanol and re-centrifuged at the same speed. This washing cycle was repeated twice to ensure that the pellet was colorless. The pellet was then washed with acetone and dried under a fume hood for 1 d. Next, the crude cell wall was suspended in dimethyl sulfoxide (DMSO):H_2O (9:1, v/v) and shaken at room temperature for 24 h to remove starch. The slurry was centrifuged (1000 × *g* for 10 min), the DMSO discarded, the pellet was washed twice in 95% ethanol to remove all trace of DMSO, and then washed twice in acetone. The solids were dried under a fume hood for 2–3 d. The alcohol-insoluble and starch-free cell wall material (CWM) was stored in a desiccator for subsequent analysis.

2.8.2. Total polyuronide preparation

Cell wall material was weighed (2–3 mg) into a test tube containing a magnetic stir bar. The sample was cooled in an ice water bath before adding 1 mL of chilled concentrated sulfuric acid. The mixture was stirred gently for 5 min before another 1 mL of chilled, concentrated sulfuric acid was added with an additional 5 min stirring. Distilled water (0.5 mL) was added dropwise into the mixture and stirred for 5 min followed by another 0.5 mL dH_2O and stirring continued until dissolution was complete (about 1 h). An additional 7 mL dH_2O was added to a total volume of 10 mL. This solution was used to assay for uronic acids to determine the total polyuronides.

2.8.3. Water soluble polyuronide (WSP) preparation

Cell wall material was weighed (30 mg) into a test tube containing a stir bar. Distilled water (10 mL) was added to dissolve WSP in the sample. The sample was stirred for 2 h, and then centrifuged at 11,840 × *g* for 25 min. The supernatant was collected for uronic acid assay to determine WSP content.

2.8.4. Uronic acid assay

An aliquot (400 μL) of the total polyuronide solution or the WSP supernatant was added to a test tube and cooled in an ice water bath. An aliquot (2.4 mL) of chilled uronic acid reagent (4.767 g

sodium tetraborate deca-hydrate/L concentrated sulfuric acid) was added and mixed. The mixture was heated in a 100 °C water bath for exactly 5 min. The sample was cooled immediately in an ice water bath. A 1.4 mL aliquot was transferred to another test tube. A 20 μL aliquot of meta phenyl phenol solution [0.15% (w/v) meta phenyl phenol in 0.5% (w/v) NaOH] was added to the test tube. A blank sample was included that contained only 20 μL of 0.5% sodium hydroxide (NaOH). The reaction was allowed to continue for about 1 h at room temperature to assure color stabilization. The color intensity of the sample was determined at 520 nm by spectrophotometry (UV-1601 UV-VIS; Shimadzu Co., Columbia, MD). A standard curve was generated using 0, 0.05, 0.10, 0.15 and 0.2 mg mL^{-1} uronic acid and used to calculate sample uronic acid content.

2.9. Descriptive sensory evaluation

The descriptive sensory analysis of fruit samples from each treatment at 21, 18, and 9 N firmness levels was performed by a trained panel. Panelists were recruited on the UC Davis campus and eleven were selected and trained during 6 training sessions of 1 h per day per session. Descriptive attributes for aroma, texture, and taste of pear and their definitions were developed during the first session. Reference standards for the attributes (Table 1) were placed in plastic cups with lids, the same as pear samples, except for aroma attributes which were placed in 1 ml glass vials with lids. Refinement of the attributes was discussed in two subsequent training sessions. In the following sessions, the panelists were exposed to pear samples of different ripening stages (firm and soft) to practice evaluating the attributes using an unstructured 10 cm line scale on a score sheet, and to achieve consensus for how to define and rate the attributes. During the last training session, panelists practiced evaluating pear samples in the actual sensory booths, using automated data collection (Compusense Five software, Ontario, Canada). The final attributes consisted of 4 aroma, 5 texture, 2 taste and 1 flavor-by-mouth attributes (Table 1).

Four individual fruit replicates of each firmness stage were selected from each treatment immediately after their firmness was measured. A slice from each of the four pear fruit, cut as a wedge from the stem to blossom end, and without peel or core, was presented to each panelist. Therefore, there were four replicates per judge and 44 samples (11 judges × 4 fruit reps) per treatment. Each slice was placed in a plastic cup with lid, and labeled with a random three-digit code, up to 30 min before tasting began. Pear slices were served with a cup of water and some unsalted saltine crackers as palate cleansers, and panelists were instructed to swallow the samples after tasting. With different ripening rates driven by each treatment, the panelists usually tasted four or eight samples each day using a randomized complete block design for assessing the samples. Evaluation was performed in individual sensory booths under red light at room temperature (20 °C). The physical reference standards for aromas and tastes were provided in each tasting booth; a summary of definitions for all attributes was also provided on a sheet of paper (Table 1). The panelists were asked to evaluate the pear attributes for aromas, textures, and tastes, respectively, on an unstructured 10 cm line scale using the software program Compusense Five (Compusense, Ontario, Canada).

Table 1
Pear attributes, definitions, and reference standards for sensory descriptive analysis of 'Bartlett' pears.

Attribute (general category)	Definition	Reference standards (intensity on 10 cm line scale)
Fruity (sweet) (aroma)	The aroma associated with a mixture of ripe and sweet fruit	Trans-2-hexenyl propionate Low: 0.1 mL L^{-1} water (2) High: 0.4 mL L^{-1} water (7)
Granny Smith Apple (aroma)	The aroma associated with fresh Granny Smith apple	'Granny Smith' apple fruit: 2 fruit in a glass jar closed with aluminum foil for 30 min before tasting (8)
Pear (Bartlett-like) (aroma)	The aroma note associated with fresh pears	Ethyl-2,4-decadienoate Low: 0.1 mL L^{-1} water (1.5) High: 0.4 mL L^{-1} water (7)
Aroma intensity (aroma)	The intensity of overall aroma in the sample	Mixture of 20% (v/v) trans-2-hexenyl propionate, (Z)-3-nonenyl acetate, ethyl-2,4-decadienoate, cis-3-hexen-1-ol, and methyl 3-nonenoate (high trans) Low: 0.1 mL L^{-1} water (2) High: 0.4 mL L^{-1} water (7)
Firmness (texture)	The force required to bite completely through the sample with the incisors (first bite/chew)	Firm: carrot (9.5) Medium: yellow peach (5) Soft: banana (1)
Crunchiness (texture)	The amount of noise generated when chewing with the back teeth	High: carrot (9.5), apple (8) Low: banana (0.5)
Juiciness (texture)	The amount of wetness or juiciness released from the sample during the first three chews	High: orange (8.5) Medium: apple (5) Low: banana (1)
Grittiness (texture)	The presence of small hard particles like sand in the flesh sample and detected when chewing	Medium: Asian pear (6) Low: banana (0.5)
Fibrousness (texture)	The presence of fibers which are continuous filaments or are in discrete elongated pieces in the sample	High: mango 'Tommy Atkins' (9) Low: banana (1)
Sweetness (taste)	The basic taste on the tongue stimulated by sugar and high potency sweeteners	High: 6% sucrose in water (7) Low: 2% sucrose in water (1)
Tartness (taste)	The sour taste with some sweetness	High: Lemon juice (8) Medium: "Lucerne" key lime flavor yogurt (6)
Fruity (flavor)	The taste and retronasal aroma of a mixture of non-specific fruit (both sweet and sour fruit) perceived when eating	"Dole" 100% juice of orange, strawberry, banana, pineapple, and apple mixed (8)

2.10. Statistical analysis

The data for each sensory attribute were analyzed across treatments at each firmness level (27, 18, and 9 N). Three-way analysis of variance (3-way ANOVA) was conducted to test the effects of treatment, panelists, replicates, and all two-way interactions for each sensory attribute using a pseudo-mixed model with the panelist by treatment interaction as denominator (SAS version 9.0, Cary, NC). The analysis of variance was also done across firmness level for each treatment using a pseudo-mixed model. The multiple least squares means comparisons were carried out using Tukey's test at $p = 0.05$.

The effect of treatments on volatile compound concentrations, SSC, TA, sugars and acids were analyzed by analysis of variance (1-way ANOVA) for each firmness level (27, 18, and 9 N) (SAS version

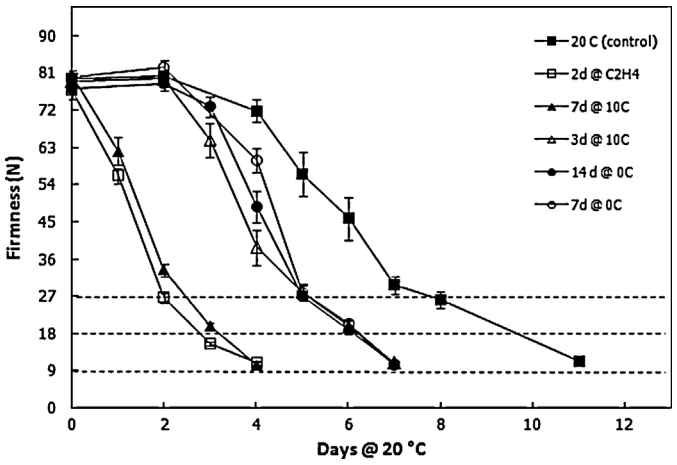

Fig. 1. Changes in firmness (N) of 'Bartlett' pears at 20 °C after conditioning for 2 d with C_2H_4 at 20 °C, or temperature conditioning for 7 or 14 d at 0 °C, and for 3 or 7 d at 10 °C, and untreated control at 20 °C. Vertical lines represent the standard error of the mean ($n = 15$).

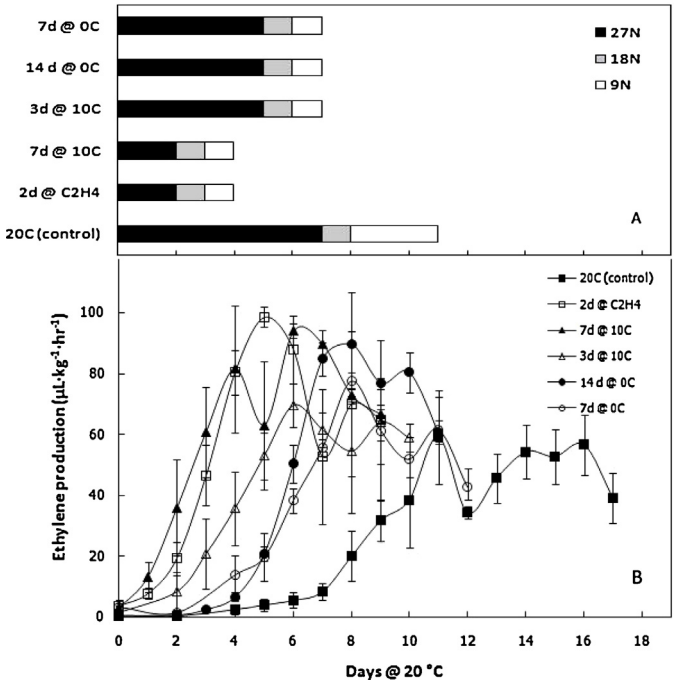

Fig. 2. Days required to soften to 27, 18, and 9 N firmness (A) and changes in ethylene (C_2H_4) production rate of 'Bartlett' pears at 20 °C after conditioning for 2 d with C_2H_4 at 20 °C, and temperature conditioning for 7 or 14 d at 0 °C, and for 3 or 7 d at 10 °C, and untreated control at 20 °C. Vertical lines represent the standard error of the mean ($n = 3$).

9.0, Cary, NC). Multiple least squares means comparisons were done using Tukey's test at $p = 0.05$.

Partial least squares (PLS) regression analysis was performed to evaluate the relationships between those sensory attributes (*Y*-variables) and instrumental data (*X*-variables) that were found to be statistically significant among treatments by ANOVA (Unscrambler version 9.2., CAMO A/S, Trondheim, Norway). Instrumental data included WSP, volatile compounds, SSC and TA.

3. Results

3.1. Physiochemical analysis

Throughout the experiment, the stage of ripeness of 'Bartlett' pears was monitored by changes in flesh firmness. Fruit held for 7 d at 10 °C or treated for 2 d with ethylene softened to a firmness of 9 N within 4 d at 20 °C after the end of the conditioning treatment (Figs. 1 and 2A). Fruit exposed to 10 °C for 3 d or 0 °C for 14 or 7 d softened to 9 N firmness within 7 d, while the untreated control fruit softened to 9 N within 11 d (Figs. 1 and 2A). Fruit treated for 2 d with ethylene, or held for 7 d at 10 °C, or 14 d at 0 °C produced the highest levels of ethylene, followed by fruit conditioned for 7 d at 0 °C or for 3 d at 10 °C. The untreated control fruit had the lowest ethylene production and the rapid increase in ethylene production was delayed by 3–7 d as compared to the other treatments (Fig. 2B).

At the 9 N firmness stage, fruit held for 3 d at 10 °C had higher SSC than control fruit, fruit held for 7 d at 0 °C, and fruit treated for 2 d with ethylene (Table 2). TA of ethylene treated fruit at 27 N firmness level was higher than that of the control fruit, while at the 9 N firmness stage, TA of the control fruit was higher than that of fruit treated with ethylene, and fruit conditioned at 0 °C (14 and 7 d) (Table 2). The SSC/TA ratio of the control fruit at 27 N firmness was higher than that of fruit conditioned for 3 d at 10 °C, or for 14 d at 0 °C, or treated with ethylene, while at 9 N firmness, control fruit had lower SSC/TA ratio than fruit held for 3 d at 10 °C or for 14 d at 0 °C (Table 2).

Enzymatic measurement of individual sugars showed that at 27 N, the sorbitol concentration of fruit held for 3 d at 10 °C was higher than that of fruit held for 7 d at 10 °C, but at 9 N firmness, the sorbitol concentration of fruit held for 7 d at 10 °C was higher than that of fruit held for 7 d at 0 °C. There were no differences in sorbitol content among the conditioning treatments for fruit softened to 18 N (Table 2). Sucrose concentration was very low and differed among treatments only at the 9 N firmness stage, where fruit conditioned for 14 d at 0 °C had higher sucrose content than fruit treated with ethylene. At 9 N firmness, the glucose concentration was highest in fruit held for 3 d at 10 °C, but was only higher than that of fruit conditioned for 14 or 7 d at 0 °C. At this firmness stage, there was approximately four times more fructose than glucose in the pears. At the 27 N firmness level, the fructose and total sugar concentrations in fruit held 3 d at 10 °C and the untreated control were higher than in fruit held for 7 d at 0 °C. For the other firmness stages, fructose and total sugar concentrations were similar across treatments (Table 2). There were a few variations in acid concentrations at the 27 N firmness stage. Fruit held for 7 d at 0 °C had the highest malic acid and lowest citric acid concentrations. The control fruit had the lowest malic acid and the highest citric acid concentrations (Table 2). Malic acid concentration was not different among treatments at 18 or 9 N firmness, but citric acid concentration of fruit held for 3 d at 10 °C or for 14 d at 0 °C was higher than that of fruit conditioned for 7 d at 0 °C at 18 N firmness (Table 2).

Water soluble polyuronide (WSP) levels were not different across treatments at any firmness level (data not shown). However, WSP levels increased from 23% to 29% to 34% as the fruit softened from 27 to 18 to 9 N, respectively.

Fifty-four volatile compounds were detected in 'Bartlett' pears. The most abundant compounds were esters followed by aldehydes and alcohols (Table 3). The different conditioning treatments had diverse effects on fruit volatile concentrations. At 27 N firmness, fruit held for 7 d at 10 °C were highest in levels of total esters (Table 4). At 18 N firmness, fruit held for 14 d at 0 °C were associated with higher levels of esters such as octyl acetate, pentyl acetate and 2-methylpropyl butanoate than the other treatments. At the same firmness stage, ethylene treated fruit had high concentrations of aldehydes. Once the fruit fully softened (9 N), treatments for 7 d at 0 °C and 10 °C resulted in fruit with the highest levels of esters, while the untreated control fruit had the lowest concentrations of esters. Conditioning with ethylene led to higher levels of aldehydes, hexanal and (E)-2-hexenal (Table 4).

Table 2
Mean sugar and acid concentrations by enzymatic assay (g/L), titratable acidity (%TA), soluble solids content (%SSC), and ratio of soluble solids to titratable acidity (SSC/TA) of fruit from each conditioning treatment at 27, 18, and 9 N firmness. Values with the same letters within a column of the same firmness level were not significantly different across treatments (Tukey: $p = 0.05$).

Firmness	Treatment	%SSC	%TA	SSC/TA	Sorbitol (g/L)	Sucrose (g/L)	Glucose (g/L)	Fructose (g/L)	Total sugar (g/L)	Malic acid (g/L)	Citric acid (g/L)
27 N	20 °C (control)	12.63	0.26b	47.96a	25.85ab	0.65	18.68	88.75a	133.90a	1.74c	2.84a
	2 d @ C_2H_4	12.98	0.32a	40.75c	24.37ab	0.05	16.73	85.38ab	126.48ab	2.68ab	2.38ab
	7 d @ 10 °C	13.18	0.28ab	46.92ab	22.03b	0.00	17.53	80.33ab	119.75b	2.37abc	1.71b
	3 d @ 10 °C	12.85	0.31ab	41.98bc	28.30a	0.60	17.10	89.00a	134.98a	1.97bc	2.42ab
	14 d @ 0 °C	12.85	0.31ab	42.25bc	25.80ab	0.03	19.33	82.58ab	127.75ab	2.44abc	2.34ab
	7 d @ 0 °C	12.65	0.28ab	46.86ab	23.35ab	0.00	18.40	78.60b	120.30b	2.97a	1.89b
18 N	20 °C (control)	13.55	0.29	46.57	24.60	0.80	18.23	89.30	132.93	1.84	2.50ab
	2 d @ C_2H_4	12.93	0.31	42.51	23.33	0.00	17.83	81.25	122.28	2.55	2.33ab
	7 d @ 10 °C	13.95	0.29	47.89	25.23	0.00	19.90	86.53	130.98	2.10	2.45ab
	3 d @ 10 °C	13.58	0.32	42.56	22.25	0.25	17.18	84.95	124.63	2.30	2.80a
	14 d @ 0 °C	13.88	0.29	47.75	22.63	0.08	17.65	80.00	120.40	2.79	2.67a
	7 d @ 0 °C	13.35	0.29	46.59	25.35	0.68	19.88	86.90	132.88	2.53	1.90b
9 N	20 °C (control)	12.48b	0.36a	34.99b	20.13ab	0.80ab	17.83ab	85.10	123.85	2.34	1.98
	2 d @ C_2H_4	11.98b	0.30b	40.58ab	20.28ab	0.20b	18.32ab	83.98	122.75	2.03	2.19
	7 d @ 10 °C	13.05ab	0.33ab	39.68ab	24.40a	0.53ab	17.63ab	90.13	132.78	1.91	2.23
	3 d @ 10 °C	13.75a	0.33ab	42.34a	22.80ab	0.58ab	20.11a	87.60	130.53	2.02	2.51
	14 d @ 0 °C	12.85ab	0.30b	42.6a	21.93ab	2.20a	16.53b	83.95	124.63	2.33	1.77
	7 d @ 0 °C	12.2b	0.30b	41.28ab	18.50b	0.58ab	16.50b	82.60	118.15	2.06	2.35

The number of volatiles detected as well as their concentrations increased as the fruit softened to 9 N (Table 4). In particular, the relative levels of butyl acetate and hexyl acetate increased when fruit softened to 9 N. The concentration of ethyl (E,Z)-2,4-decadienoate and methyl (E,Z)-2,4-decadienoate followed a similar trend. Many medium and long chains esters, such as heptyl acetate, methyl octanoate, ethyl octanoate, ethyl (E)-2-octenoate, methyl 4-decenoate, methyl decanoate, and ethyl (E)-4-decenoate were first detected when the fruit softened to 9 N. These changes in ester concentration were observed in all treatments, but were more pronounced in fruit held for 14 or 7 d at 0 °C and fruit held for 7 d at 10 °C (Table 4).

3.2. Descriptive sensory analysis

Analysis of variance with a pseudo mixed effect model showed that there were differences among the treatments at each firmness level. At the 27 N firmness stage, panelists found differences across treatments in several sensory attributes, including apple aroma, firmness, crunchiness, grittiness, fibrousness and tartness (Table 5). Fruit from the conditioning treatment with ethylene for 2 d were higher in many sensory attributes, including apple aroma, grittiness, fibrousness, and tartness. On the other hand, fruit held for 14 d at 0 °C were the lowest in apple aroma. Firmness and crunchiness sensory attributes were higher in fruit exposed for 7 d at 0 °C, and lowest in the untreated control fruit (Table 5).

At a firmness of 18 N, differences across treatments were perceived for apple aroma, firmness, juiciness, crunchiness, sweetness, tartness, and fruity flavor sensory attributes (Table 5). Sensory sweetness, firmness, and juiciness were predominant in fruit held for 14 d at 0 °C, while apple aroma, firmness, juiciness, tartness and fruity flavor were high in fruit treated with ethylene. Fruit treated for 7 d at both 0 °C and at 10 °C were high in sensory crunchiness, which was opposite to ethylene treated fruit (Table 5).

At the 9 N firmness stage, sensory fruity aroma, apple aroma, crunchiness, sweetness, and fruity flavor were different among treatments (Table 5). Ethylene treated fruit were predominant in apple aroma and fruity flavor. Fruity aroma and sweetness attributes were strong in fruit stored for 3 d at 10 °C and for 14 d at 0 °C. Sweetness perception was also high in ethylene treated fruit. Sensory crunchiness was highest in control fruit (Table 5).

3.3. Relationship between chemical and sensory analysis

Partial least squares (PLS) regression analysis was used to evaluate the relationships between chemical (x-variable) and sensory measurements (y-variable). Only x- and y-variables that were different among treatments at each firmness level were used for the analysis. At the 27 N firmness stage, the first two latent factors accounted for 77% and 48% of the variance for x- and y-variables, respectively (Fig. 3). Sensory firmness and crunchiness were correlated with the concentration of malic acid and total esters; conditioning for 7 d at 0 °C was positively correlated while the control fruit was negatively correlated with these variables. Conditioning for 3 d at 10 °C was associated with higher fructose, total sugar, sorbitol, and citric acid concentrations compared to the other

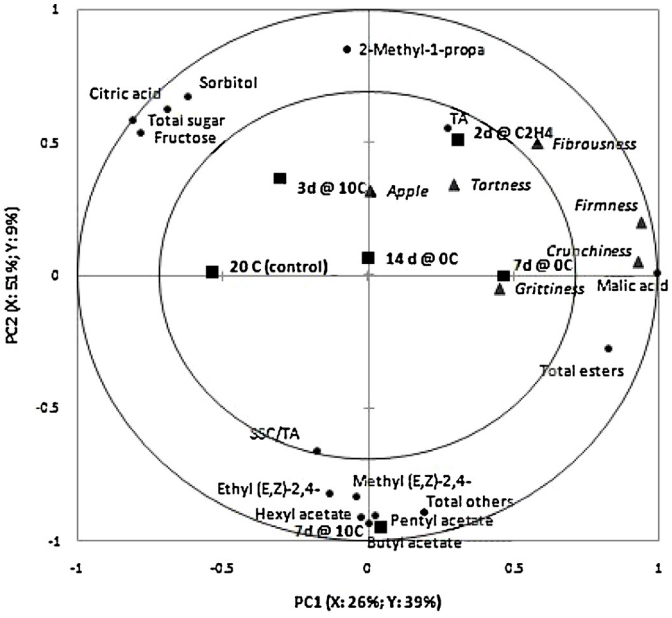

Fig. 3. Bi-plot on correlation loading scale of partial least squares (PLS) analysis of sensory attributes (Y variable) and instrumental measurements (X variable) of 'Bartlett' pears at 27 N. ▲, sensory attributes; ●, chemical compounds; ■, conditioning treatments. 2-Methyl-1-propa = 2-methyl-1-propanol, Methyl (E,Z)-2,4- = methyl (E,Z)-2,4-decadienoate, Ethyl (E,Z)-2,4- = ethyl (E,Z)-2,4-decadienoate.

Table 3
Volatiles found in 'Bartlett' pears as measured by headspace sorptive extraction and gas chromatography–mass spectrometry.

Class	Peak No.	Compound	RT[a] (min)	RI[b] (calc)	RI[c] (std)	RI[d] (lit)	MS[e]	Pear refs[f]
Aldehydes	7	Hexanal	4.26	800	800	801[g]	A, B	h, o, r, z
	11	(E)-2-Hexenal	5.53	848	848	850[g]	A, B	h, o, r, z
	15	Heptanal	6.96	902	901	90[g]	A, B	h, z
	19	Benzaldehyde	9.00	956	956	95[h]	A, B	h, z
	21	Octanal	10.74	1003	1006	100[h]	A, B	h, z
	26	(E)-2-Octenal	13.07	1057	1062	106[h]	A, B	h, z
	30	Nonanal	15.03	1104	1109	110[g]	A, B	h, o, z
	36	Decanal	18.71	1205	1208	120[g]	A, B	z
Alcohols	1	1-Propanol	1.96	590	588	558[n]	A, B	aa
	3	2-Methyl-1-Propanol	2.26	614	618	606[o]	A, B	h, o, aa
	4	1-Butanol	2.48	644	647	634[o]	A, B	o, aa
	12	1-Hexanol	6.03	867	867	865[g]	A, B	h, o, r, aa
	25	2-Ethyl-1-hexanol	11.87	1029	1030	1012[o]	A, B	o
	27	1-Octanol	13.71	1072	1075	1070[g]	A, B	h, o, r, aa
Esters	2	Ethyl Acetate	2.14	599	603	600[r]	A, B	h, o, r, z
	5	n-Propyl acetate	2.93	705	708	707[g]	A, B	o, r, aa
	6	2-Methylpropyl acetate	3.80	767	765	764[r]	A, B	r, aa
	8	Ethyl butanoate	4.30	802	805	804[h]	A, B	h, r, aa
	9	Butyl acetate	4.59	813	813	812[g]	A, B	h, o, r, aa
	10	Ethyl 2-methylbutanoate	5.46	846	846	842[r]	A, B	h, r, aa
	13	3-Methylbutyl acetate	6.28	877	877	876[g]	A, B	h, o, r, aa
	14	Propyl butanoate	6.88	900	902	897[g]	A, B	r, aa
	16	Pentyl acetate	7.42	914	914	912[t]	A, B	o, r, aa
	17	Methyl hexanoate	7.77	924	925	922[g]	A, B	r, aa
	18	2-Methylpropyl butanoate	8.90	954	954	953[g]	A, B	z
	20	Ethyl hexanoate	10.65	1000	1001	999[t]	A, B	h, o, r, aa
	22	(Z)-3-Hexenyl acetate	10.92	1007	1006	1004[t]	A, B	z, aa
	23	Hexyl acetate	11.24	1014	1015	1011[g]	A, B	h, o, r, aa
	28	Propyl hexanoate	14.71	1096	1097	1094[g]	A, B	z
	29	Ethyl heptanoate	14.86	1099	1100	1099[g]	A, B	r, aa
	31	Heptyl acetate	15.43	1115	1115	1111[g]	A, B	r, aa
	32	Methyl octanoate	15.87	1127	1127	1107[r]	A, B	r, aa
	35	Ethyl octanoate	18.48	1198	1198	1191[h]	A, B	h, r, aa
	37	Octyl acetate	18.95	1213	1215	1194[g]	A, B	h, r, aa
	38	Ethyl (E)-2-octenoate	20.06	1248	1249	1223[r]	A, B	r, aa
	39	Methyl 3-hydroxyoctanoate (Tent)	20.36	1258		1244[o]	B	o
	42	Ethyl nonanoate	21.57	1296	1296	1288[h]	A, B	h, r
	43	Methyl 4-decenoate (Tent)	21.94	1309		1293[o]	B	o, r
	44	Methyl decanoate	22.37	1325	1325	1307[r]	A, B	o, r, aa
	47	Ethyl (E)-4-decenoate	23.92	1381	1383	1378[v]	A, B	o, r, aa
	48	Methyl (E,Z)-2,4-decadienoate (Tent)	24.34	1396		138[h]	B	h, o, r, aa
	49	Ethyl (E,Z)-2,4-decadienoate	26.24	1470	1471	1457[h]	A, B	h, o, r, aa
	52	Ethyl dodecanoate	29.26	1596	1596	1598[h]	A, B	h, r, aa
Others	24	(D) Limonene	11.72	1026	1029	1029[g]	A, B	h, o
	33	Unknown 33: *m/z* 43 71 58 98	16.07	1132				
	34	Unknown 34: *m/z* 69 72 101 55 43	17.77	1178				
	40	Nonanoic acid (Tent)	20.90	1275		1280[k]	B	
	41	Unknown 41: *m/z* 97 125 168 81 123 95	20.95	1277				
	45	Unknown 45: *m/z* 117 71 43 88 89 55	22.55	1331				
	46	Unknown 46: *m/z* 87 153 110 74	23.67	1372				
	49	α-Farnesene	27.21	1509	1506	1496[r]	A, B	o, r, aa
	51	Unknown 51: *m/z* 100 69 41 55 136 101	28.20	1551				
	53	Unknown 53: *m/z* 114 86 69 55 41 68	29.90	1624				
	54	Unknown 54: *m/z* 67 79 80 81 164 93	32.86	1756				

[a]RT: retention time in minute on DB-5MS column. [b]RI (calc): retention indices calculated from C_8-C_{20} n-alkanes. [c]RI (std): retention indices calculated from authentic standards. [d]RI (lit): retention indices reported in literature. [e]MS: mass spectrometry ion comparisons where A = match with authentic standard; B = match with library (NIST08). [f]Pear refs: references of compounds reported in pears. [g]Beaulieu and Grimm, 2001 (DB-5). [h]Riu-Aumatell et al., 2005 (HP-5MS). [i]Hadaruga et al., 2006 (HP-5). [j]Adams, 1995 (DB-5). [k]Pino et al., 2005 (HP-5MS). [l]Hognadottir and Rouseff, 2003 (HP-5). [m]Tent: tentatively identified. [n] Leffingwell and Alford, 2005 (HP-5). [o]Shiota, 1990 (DB-1). [p]Isidorov et al., 2006 (HP-5). [q]Stashenko et al., 2003 (HP-5). [r]Takeoka et al., 1992 (DB-1). [s]Bicalho et al., 2000 (HP-5). [t]Beaulieu, 2005 (DB-5). [u]Ramsey and Flanagan, 1982 (OV-1). [v]Adams, 2000 (DB-5). [w]Korhonen and Lind, 1985 (OV-351). [x]Acree and Arn, 2004 (OV-101). [y]Peng, 2000 (DB-1). [z]Rapparini and Predieri, 2002. [aa]Suwanagul and Richardson, 1998.

treatments. Sensory tartness and apple aroma sensory attributes were positively associated with measured TA and 2-methyl-1-propanol concentration, but apple aroma, tartness, and TA were only 50% explained in this model (plotted in the inner circle). A large group of volatile compounds, including ethyl (E,Z)-2,4-decadienoate, methyl (E,Z)-2,4-decadienoate, hexyl acetate, pentyl acetate, butyl acetate, and total other compounds, was positively associated with conditioning for 7 d at 10 °C, while these variables were negatively associated with ethylene conditioning.

When fruit softened to 18 N firmness, the total variance explained along the first two PCs was 83% for *x*-variable and 72% for *y*-variable (Fig. 4). Sensory sweetness was positively correlated with octyl acetate, pentyl acetate, and 2-methylpropyl butanoate. This group of variables positively described fruit held for 14 d at 0 °C, while it was negatively associated with the control treatment. Sensory apple aroma, fruity flavor, tartness, and juiciness described fruit treated with ethylene, which contained high concentrations of the aldehydes (E)-2-hexenal and hexanal; these variables were

Table 4
Concentration ($\mu g\,kg^{-1}$ fresh weight fruit) of volatiles measured in 'Bartlett' pears after temperature or ethylene-conditioning and softening to 27, 18 or 9 N. Only volatiles that were significantly different across treatments, as determined by ANOVA, are reported.

No.	Compound class and firmness level	Compound	Treatment															
			20 °C (control)			2 d @ C_2H_4			7 d @ 10 °C			3 d @ 10 °C			14 d @ 0 °C			7 d @ 0 °C		
	Aldehydes																		
7	27	Hexanal	26.08			66.01			12.27			31.38			57.09			51.04		
	18		25.46	ab[a]		42.95	a		2.97	b		10.55	ab		13.51	ab		6.49	ab	
	9		14.47	a		8.66	ab		2.66	b		4.62	ab		3.52	ab		1.70	b	
11	27	(E)-2-Hexenal	21.94			36.69			6.44			17.85			44.00			26.95		
	18		20.35	ab		46.53	a		5.48	b		10.08	ab		8.25	ab		8.22	ab	
	9		9.22	a		5.41	b		2.06	c		5.39	b		2.63	bc		1.81	c	
	Alcohols																		
3	27	2-Methyl-1-Propanol	0.79	ab		1.25	a		0.47	b		1.15	ab		1.15	ab		0.65	ab	
	18		0.81			1.08			0.91			0.40			5.40			1.84		
	9		1.59			1.62			1.93			3.22			3.20			3.52		
4	27	1-Butanol	5.31			5.21			7.64		B	6.05		B	9.04			6.49		
	18		5.58	b		6.41	ab		22.06	ab	A	13.42	ab	AB	22.77	a		8.28	ab	
	9		11.03	b		15.27	ab		23.65	ab	A	27.03	a	A	20.28	ab		15.09	ab	
	Esters																		
8	27	Ethyl butanoate	0.06			0.36		B	0.22		B	0.10		A	0.07			0.79		
	18		nd			0.02		B	0.51		B	0.38		A	0.95			0.55		
	9		2.76			3.24		A	3.00		A	2.27		A	3.70			7.40		
9	27	Butyl acetate	40.89	ab	B	33.69	b	B	100.42	a	B	41.72	ab	B	56.98	ab	B	39.99	ab	B
	18		43.33		AB	87.34		AB	127.08		B	107.91		AB	167.22		B	69.02		AB
	9		192.47		A	215.51		A	278.48		A	211.66		A	260.80		A	240.41		A
10	27	Ethyl 2-methylbutanoate	1.89			2.19			3.65			1.30			0.51		B	8.49		
	18		0.06			1.68			0.25			0.18			7.26		AB	1.63		
	9		1.93			3.43			0.68			0.73			1.03		A	4.09		
14	27	Propyl butanoate	nd		B	0.03			nd			nd			nd		B	nd		
	18		nd		B	nd			0.02			nd			nd		B	nd		
	9		0.17		A	0.09			0.06			0.30			0.27		A	0.29		
16	27	Pentyl acetate	4.86	b		4.89	b	B	13.77	a	B	4.88	b	B	6.57	b	B	4.29	b	B
	18		6.14	b		10.72	ab	AB	11.73	ab	AB	7.24	ab	B	15.32	a	B	6.85	ab	B
	9		13.09			19.76		A	19.88		A	17.72		A	20.56		A	24.43		A
17	27	Methyl hexanoate	0.06		B	0.04		B	0.04		B	nd		B	nd		B	0.13		B
	18		nd		B	0.13		B	nd		B	nd		B	nd		B	nd		B
	9		1.32		A	1.38		A	1.27		A	0.67		A	1.94		A	2.92		A
18	27	2-Methylpropyl butanoate	0.14			0.31			6.21			0.70			nd			nd		
	18		nd	b		1.03	ab		1.25	ab		0.03	ab		3.93	a		nd	b	
	9		1.00			1.51			0.11			1.52			0.91			2.12		
20	27	Ethyl hexanoate	3.06			1.20			4.24			0.29			0.27		B	4.92		
	18		nd			0.78			3.40			0.19			0.17		B	3.73		
	9		4.29			6.54			6.48			2.81			6.64		A	11.18		
23	27	Hexyl acetate	23.11	b	B	19.34	b	B	85.06	a	B	15.15	b	B	28.69	b	B	11.56	b	B
	18		35.51		AB	56.79		B	91.03		B	47.57		B	105.93		B	42.66		B
	9		141.26	b	A	243.18	ab	A	332.57	a	A	264.09	ab	A	345.40	a	A	350.88	a	A
31	27	Heptyl acetate	nd			nd		B	0.01		B	nd		B	nd		B	nd		B
	18		nd			nd		B	0.01		B	nd		B	nd		B	nd		B
	9		0.11	b		0.65	ab	A	0.98	ab	A	0.64	ab	A	1.70	a	A	1.70	a	A

Table 4 (*Continued*)

No.	Compound class and firmness level	Compound	Treatment															
			20 °C (control)			2 d @ C_2H_4			7 d @ 10 °C			3 d @ 10 °C			14 d @ 0 °C			7 d @ 0 °C		
32	27	Methyl octanoate	nd			nd			nd		B	nd			nd		B	nd		B
	18		nd			nd			nd		B	nd			nd		B	nd		B
	9		0.02			0.06			0.28		A	0.13			0.49		A	0.75		A
35	27	Ethyl octanoate	nd		B	nd			0.42		B	nd		B	nd		B	0.03		B
	18		nd		B	0.33			0.12		B	nd		B	nd		B	0.17		B
	9		0.49	b	A	1.16	ab		2.18	ab	A	1.21	ab	A	2.77	ab	A	4.47		A
37	27	Octyl acetate	nd			nd			0.93			0.19			nd			nd		B
	18		nd	b		nd	b		nd	b		nd	b		1.81	a		nd	b	B
	9		0.08			0.43			nd			0.52			0.08			0.42		A
38	27	Ethyl (E)-2-octenoate	nd			nd		B	nd		B	nd		B	nd		B	nd		B
	18		nd			nd		B	nd		B	nd		B	nd		B	nd		B
	9		0.06	c		0.43	bc	A	0.88	abc	A	0.81	abc	A	1.53	ab	A	1.70	a	A
39	27	Methyl 3-hydroxyoctanoate	nd		B	nd		B	0.44		B	nd		B	0.18		B	0.19		B
	18	(Tent)	0.06		AB	0.39		B	1.49		AB	0.73		B	0.02		B	0.03		B
	9		1.55	b	A	3.94	ab	A	3.86	ab	A	3.97	ab	A	6.93	a	A	7.98	a	A
42	27	Ethyl nonanoate	nd			nd			nd			nd			nd		B	nd		B
	18		nd			nd			nd			nd			nd		B	nd		B
	9		nd			nd			0.04			0.02			0.07		A	0.14		A
43	27	Methyl 4-decenoate (Tent)	nd		B	nd		B	nd		B	nd		B	nd		B	nd		B
	18		nd		AB	0.08		B	0.22		B	nd		B	nd		B	nd		B
	9		0.69	b	A	1.79	ab	A	3.02	ab	A	1.89	ab	A	4.28	ab	A	4.86	a	A
44	27	Methyl decanoate	0.01		B	nd		B	nd		B	nd		B	nd		B	nd		B
	18		nd		B	nd		B	nd		B	nd		B	nd		B	nd		B
	9		0.17	b	A	0.32	ab	A	0.64	ab	A	0.25	ab	A	0.75	ab	A	1.32	a	A
45	27	Unknown 45: ui 117 71 43 5	nd		B	0.03		B	1.41		B	0.32		B	0.60		B	0.76		B
	18	88 89 5	0.15		AB	0.47		B	4.89		AB	3.32		AB	0.25		B	0.28		B
	9		4.33	b	A	8.45	ab	A	9.40	ab	A	11.87	ab	A	18.38	ab	A	19.61	a	A
46	27	Unknown 46: ui 87 153 110	nd			nd			nd		B	nd			nd		B	nd		B
	18	74	nd			nd			nd		B	nd			nd		B	nd		B
	9		nd	b		nd	b		0.24	ab	A	nd	b		0.20	ab	A	0.46	a	A
47	27	Ethyl (E)-4-decenoate	0.02		B	0.01		B	0.01		B	0.01		B	tr[c]		B	nd		B
	18		nd		AB	nd		B	0.04		B	0.01		B	nd		B	nd		B
	9		0.44	b	A	1.42	ab	A	3.81	ab	A	2.57	ab	A	5.26	a	A	5.69	a	A
48	27	Methyl (E,Z)-2,4-decadienoate	5.30	b	B	4.57	b	B	20.01	a	B	3.93	b	B	12.10	a	B	2.25	b	B
	18	(Tent)	5.34		B	15.54		B	23.56		B	6.70		B	12.74		B	5.78		B
	9		55.96	b	A	180.47	ab	A	225.80	a	A	119.58	ab	A	233.20	a	A	255.11	a	A
49	27	Ethyl (E,Z)-2,4-decadienoate	6.28	ab	B	5.47	b	B	17.37	a	B	5.66	b	B	10.23	ab	B	2.53	b	B
	18		5.18		B	7.56		B	15.66		B	5.14		B	11.84		B	6.70	a	B
	9		34.08	b	A	118.46	ab	A	201.79	a	A	139.13	ab	A	255.77	a	A	266.85	a	A
	Others																			
34	27	Unknown 34: *m/z* 69 72 101	nd[b]			nd			nd		B	nd		B	nd		B	nd		B
	18	55 43	nd			nd			nd		B	nd		B	nd		B	nd		B
	9		nd	b		0.18	ab		0.58	ab	A	0.43	ab	A	0.65	a	A	0.52	ab	A

41	27	Unknown 41: *m/z* 97 125 168	nd		B	nd		B	nd		B	nd		B	nd		B	nd		B
	18	81 123 95	0.17		AB	0.14		B	0.46		B	0.13		B	0.51		B	0.41		B
	9		1.47	b	A	3.33	ab	A	3.72	ab	A	5.91	a	A	5.78	a	A	5.78	a	A
45	27	Unknown 45: *m/z* 117 71 43 5	nd		B	0.03		B	1.41		B	0.32		B	0.60		B	0.76		B
	18	88 89 5	0.15		AB	0.47		B	4.89		AB	3.32		AB	0.25		B	0.28		B
	9		4.33	b	A	8.45	ab	A	9.40	ab	A	11.87	ab	A	18.38	ab	A	19.61	a	A
46	27	Unknown 46: *m/z* 87 153 110	nd			nd			nd		B	nd			nd		B	nd		B
	18	74	nd			nd			nd		B	nd			nd		B	nd		B
	9		nd	b		nd	b		0.24	ab	A	nd	b		0.20	ab	A	0.46	a	A
51	27	Unknown 51: *m/z* 100 69 41	nd			nd			nd		B	nd			nd		B	nd		B
	18	55 136 101	nd			nd			nd		B	nd			nd		B	nd		B
	9		nd	b		0.11	ab		0.31	ab	A	0.13	ab		0.51	a	A	0.55	a	A
53	27	Unknown 53: *m/z* 114 86 69	nd			nd		B	nd		B	nd		B	nd		B	nd		B
	18	55 41 68	nd			nd		B	nd		B	nd		B	nd		B	nd		B
	9		nd	b		0.27	ab	A	0.64	ab	A	0.48	ab	A	1.45	a	A	1.48	a	A
54	27	Unknown 54: *m/z* 67 79 80	nd		B	nd		B	nd		B	nd		B	nd		B	nd		B
	18	81 164 93	nd		AB	nd		B	nd		B	nd		B	nd		B	nd		B
	9		0.18	b	A	0.61	ab	A	1.64	ab	A	1.09	ab	A	3.70	ab	A	4.30	a	A
	27	**Total aldehydes**	69.34			120.74			33.95			89.61			134.12			100.24		
	18		55.74			96.89			15.31			25.91			27.93			27.96		
	9		40.89	a		31.21	ab		20.77	ab		35.62	ab		23.05	ab		16.70	b	
	27	**Total alcohols**	21.73			22.84			34.39			28.74			28.95			22.41		
	18		9.06			17.34			33.95			20.91			61.45			23.29		
	9		17.50			34.76			34.54			44.22			36.63			25.01		
	27	**Total esters**	111.65	b	B	108.42	b	B	267.42	a	B	91.36	b	B	129.42	b	B	99.93	b	B
	18		101.07		AB	189.15		B	293.18		B	191.53		B	349.18		B	159.94		B
	9		467.08	b	A	824.25	ab	A	1105.92	a	A	796.23	ab	A	1184.68	a	A	1230.32	a	A
	27	**Total others**	0.32	b		0.53	ab		2.56	a		0.54	ab		0.35	b	B	0.76	ab	B
	18		1.13			1.38			0.48			3.87			2.34		AB	1.88		AB
	9		0.72	b		1.17	ab		4.63	ab		2.61	ab		6.41	a	A	6.41	a	A
	27	**Total volatiles**	203.04		B	339.47		B	338.78		B	246.06		B	292.85		B	300.62		B
	18		167.20		AB	318.92		B	352.36		B	353.17		B	483.63		B	217.12		B
	9		526.19	b	A	979.44	ab	A	1208.58	a	A	962.00	ab	A	1250.85	a	A	1278.56	a	A

[a] Within each row, values with the same lower case letter are not significantly different across treatments (Tukey: $p = 0.05$). Within each column, values with the same capital letter are not significantly different across firmness levels within each compound (Tukey: $p = 0.05$).

[b] nd: not detected.

[c] tr: less than 0.005.

Table 5
Mean sensory score for each attribute in 'Bartlett' pears during softening after temperature or ethylene-conditioning.

Attribute	Firmness	Treatment																	
	(N)	20 °C			2 d @ C_2H_4			7 d @ 10 °C			3 d @ 10 °C			14 d @ 0 °C			7 d @ 0 °C		
Fruity (sweet) aroma	27	5.19			5.19		B	5.69			4.82		C	5.02		C	5.16		A
	18	5.01			5.51		B	5.35			5.31		B	5.46		B	5.61		A
	9	5.63	b[a]		6.00	ab	A	5.73	b		6.39	a	A	6.33	a	A	5.56	b	A
Apple aroma	27	3.23	b		3.74	a		3.04	bc		3.07	b		2.52	c		2.83	bc	
	18	2.98	b		3.54	a		2.72	bc		3.04	b		2.38	c		2.65	bc	
	9	3.10	b		3.91	a		3.02	b		2.96	bc		2.74	bc		2.57	c	
Pear (Bartlett-like)	27	5.16			5.49		B	5.32		B	4.67		C	4.70		C	4.83		C
aroma	18	4.70			5.56		B	5.19		B	5.20		B	5.30		B	5.43		B
	9	5.45			6.25		A	6.07		A	6.23		A	6.16		A	6.29		A
Aroma intensity	27	5.16			5.31		B	5.84		B	4.92		C	5.04		C	5.16		C
	18	5.31			5.72		B	5.54		B	5.42		B	5.98		B	6.03		B
	9	6.15			6.26		A	6.30		A	6.67		A	6.61		A	6.34		A
Firmness	27	3.94	c	A[b]	4.87	ab	A	4.36	bc	A	4.32	bc	A	4.35	bc	A	5.26	a	A
	18	2.62	b	B	3.53	a	B	3.15	ab	B	2.82	b	B	3.57	a	B	3.04	ab	B
	9	1.88		C	1.31		C	1.50		C	1.24		C	1.43		C	1.46		C
Juiciness	27	2.17		C	2.84		C	2.19		C	2.66		C	2.21		C	2.59		C
	18	3.70	cb	B	4.35	a	B	2.87	d	B	3.15	cd	B	4.60	a	B	4.14	ab	B
	9	5.54		A	5.72		A	5.19		A	6.12		A	5.69		A	5.29		A
Crunchiness	27	3.10	c	A	3.96	ab	A	3.55	bc	A	3.21	c	A	3.33	bc	A	4.48	a	A
	18	1.81	cd	B	1.66	d	B	2.33	ab	B	1.89	bcd	B	2.38	a	B	2.14	ab	B
	9	1.41	a	B	1.03	b	C	1.20	ab	C	1.11	b	C	0.99	b	C	1.00	b	C
Grittiness	27	3.79	bc		4.59	a	A	4.11	ab		3.39	c		3.67	bc		3.72	bc	
	18	3.10			3.44		B	3.59			2.92			2.76			3.23		
	9	3.24			3.14		B	3.21			3.00			2.76			2.96		
Fibrousness	27	2.15	b		3.24	a	A	2.22	b		2.23	b		2.27	b		2.41	b	
	18	2.09			2.27		B	2.54			1.97			2.11			2.62		
	9	2.06			2.21		B	2.17			2.10			1.57			2.07		
Sweetness	27	3.93		B	3.68		C	4.04		C	4.00		C	3.76		B	3.79		C
	18	4.23	c	B	5.02	b	B	4.35	c	B	4.89	b	B	5.62	a	A	4.66	bc	B
	9	5.14	c	A	5.90	a	A	5.45	bc	A	5.99	a	A	5.80	ab	A	5.28	c	A
Tartness	27	3.46	b	B	4.43	a		3.44	b		3.39	b	B	2.84	b	C	3.38	b	
	18	3.28	c	B	4.38	a		3.58	bc		3.71	bc	B	3.97	ab	B	3.71	cb	
	9	4.16		A	4.61			4.13			4.64		A	4.42		A	4.06		
Fruity (flavor)	27	3.99			4.26		B	3.80		B	3.84		C	3.41		C	3.55		C
	18	4.58	bc		5.33	a	A	4.10	cd	B	4.33	bcd	B	4.76	b	B	4.00	d	B
	9	4.48	d		5.65	a	A	5.00	bc	A	5.12	b	A	5.31	ab	A	4.59	cd	A

[a] Within each row, values with the same lower case letter are not significantly different across treatments (Tukey: $p = 0.05$).
[b] Within each column, values with the same capital letter are not significantly different across firmness levels within each compound (Tukey: $p = 0.05$).

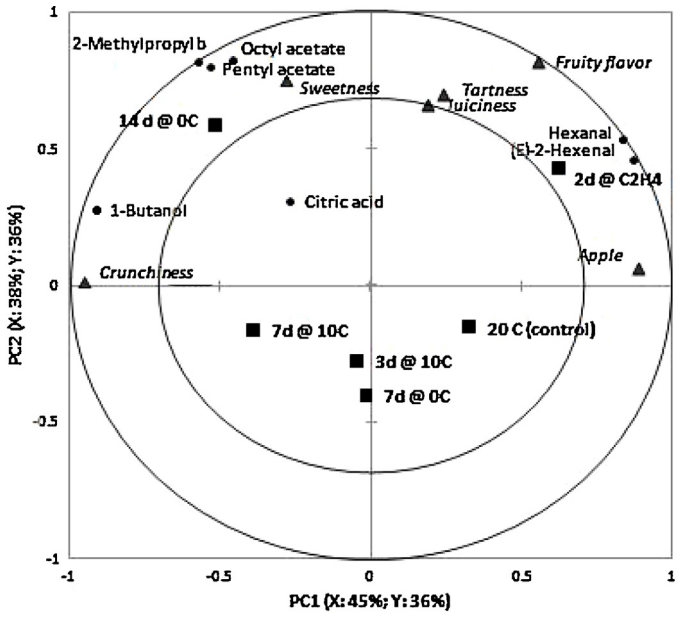

Fig. 4. Bi-plot on correlation loading scale of partial least squares (PLS) analysis of sensory attributes (*Y* variable) and instrumental measurements (*X* variable) of 'Bartlett' pears at 18 N. ▲, sensory attributes; ●, chemical compounds; ■, conditioning treatments. 2-Methylpropyl b = 2-methylpropyl butanoate.

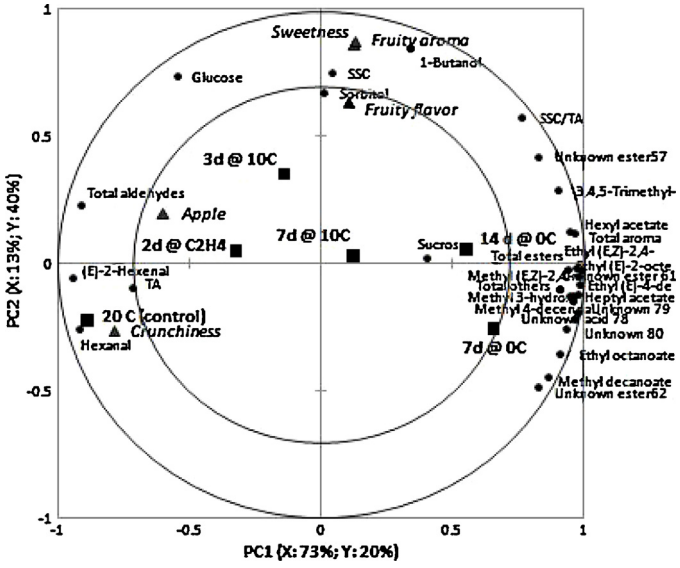

Fig. 5. Bi-plot on correlation loading scale of partial least squares (PLS) analysis of sensory attributes (*Y* variable) and instrumental measurements (*X* variable) of 'Bartlett' pears at 9 N. ▲, sensory attributes; ●, chemical compounds; ■, conditioning treatments. 3,4,5-Trimehyl- = 3,4,5-trimehyl-4-heptanol, Ethyl (E,Z)-2,4- = ethyl (E,Z)-2,4-decadienoate, Methyl (E,Z)-2,4- = methyl (E,Z)-2,4-decadienoate, Methyl 3-hydroxy = methyl 3-hydroxyoctanoate, Methyl 4-decenoa = methyl 4-decenoate, Ethyl (E)-2-octe = ethyl (E)-2-octenoat,. Ethyl (E)-4-de = ethyl (E)-4-decenoate.

negatively associated with fruit conditioned for 7 d at 10 °C. In addition, fruit held for 7 d at 0 °C, for 3 d at 10 °C and the control fruit were negatively correlated with sensory sweetness, tartness, and juiciness (Fig. 4).

When fruit reached an average of 9 N firmness, total variance explained along the first two PCs was 86% in *x*-variable and 60% in *y*-variable (Fig. 5). Control fruit and ethylene conditioned fruit were associated with high sensory scores for crunchiness and high concentrations of hexanal, (E)-2-hexenal, and total aldehydes, and TA. Sensory fruity aroma, sweetness, and fruity flavor were positively correlated with 1-butanol, SSC, sorbitol, glucose, and SSC/TA. These attributes were weakly associated with fruit treated for 3 d at 10 °C (Fig. 5). The 0 °C conditioning treatments resulted in fruit with high concentrations of many volatile compounds, especially esters, while no sensory attribute was positively associated with this treatment (Fig. 5).

Pearson correlation coefficients were calculated for all sensory attributes and all instrumental measurements across all the treatments and firmness levels. The correlations are highlighted in Table 6. Many esters were positively correlated with fruity aroma, pear (Bartlett-like) aroma, aroma intensity, juiciness, sweetness, tartness, and fruity flavor, and were negatively correlated with firmness, crunchiness, and fibrousness. Most aldehydes, including hexanal and (E)-2-hexenal, had the opposite correlations to that of esters. Some alcohols such as 2-methyl-1-propanol and 1-butanol, were correlated with sensory attributes with the same trend as esters, while 1-octanol had similar correlations as the aldehydes. The three highest positive correlations with fruity aroma were unknown 41, butyl acetate, and hexyl acetate. For pear aroma, the three highest positive correlations were with hexyl acetate, total aromas, and total esters, while butyl acetate, pentyl acetate, and hexyl acetate were most positively correlated with the aroma intensity attribute.

WSP had the highest positive correlation with juiciness and sweetness, and the highest negative correlation with firmness, crunchiness, and grittiness (Table 6). SSC was not correlated with sweetness. TA and malic acid were not correlated with tartness, but SSC/TA was negatively correlated with tartness. The correlations of sucrose to the sensory attributes were similar to esters, but only the negative correlations with textures were statistically significant (negative correlation with firmness, crunchiness, grittiness, and fibrousness), whereas those of sorbitol were similar to aldehydes (negative correlation with most aroma and taste attributes and positive correlation with firmness and crunchiness).

The odor description and estimated odor units (i.e. measured concentration/published odor threshold) for volatiles showing differences among treatments are shown in Table 7. Most esters had higher odor units than alcohols and aldehydes; hexyl acetate had the highest estimated odor unit (Table 7). This may suggest that esters, hexyl acetate in particular, had more influence on odor perception than the other classes of volatiles in 'Bartlett' pear.

4. Discussion

The different conditioning treatments had diverse effects on the ripening of 'Bartlett' pear fruit. The ripening rate, as monitored by fruit softening, of fruit treated for 2 d with ethylene agrees with Agar et al. (2000b), and the ripening rate of fruit held for 7 d at 10 °C or for 14 d at 0 °C is in agreement with previous work in our laboratory (Mitcham et al., 2006; unpublished data).

Ethylene biosynthesis is an important factor involved in ripening of fruit. Sfakiotakis and Dilley (1974) found that high ethylene biosynthesis resulted in faster and more uniform ripening of pear fruit. In our study, the different conditioning treatments had differing effects on ethylene biosynthesis, in a manner consistent with the results of Sfakiotakis and Dilley (1974). Fruit conditioned for 7 d at 10 °C and for 2 d with ethylene had among the highest ethylene production rates and softened fastest, whereas the unconditioned control fruit produced the least ethylene and softened slowest.

Numerous studies have reported that esters are the most abundant volatile compounds in pear (Nursten, 1970; Suwanagul and Richardson, 1998; Lopez et al., 2001). Fully ripe pears (9 N) had a higher total ester concentration than firmer stages regardless of the conditioning treatment. However, each conditioning method

Table 6
Pearson correlation coefficients between sensory attributes and instrumental values for 'Bartlett' pears across all treatments and firmness levels.

Variables	Fruity (sweet)[a]	Apple[a]	Pear[a]	Intensity[a]	Firm	Crunchy	Gritty	Fibrous	Juicy	Sweet	Tart	Fruity (flavor)
Hexanal	**−0.614**	0.282	**−0.554**	**−0.712**	**0.765**	**0.723**	**0.664**	**0.546**	**−0.574**	**−0.690**	−0.302	−0.436
(E)-2-Hexenal	**−0.561**	0.274	**−0.516**	**−0.659**	**0.658**	**0.538**	**0.540**	0.427	**−0.508**	**−0.589**	−0.283	−0.308
Heptanal	−0.406	0.151	−0.354	**−0.554**	**0.553**	**0.661**	**0.483**	0.314	**−0.479**	**−0.535**	−0.347	**−0.504**
Benzaldehyde	**−0.601**	−0.113	**−0.601**	**−0.679**	**0.690**	**0.734**	0.409	0.342	**−0.562**	**−0.614**	**−0.498**	**−0.632**
Octanal	**−0.532**	−0.132	**−0.599**	**−0.571**	0.436	0.427	0.213	0.268	−0.433	**−0.502**	**−0.501**	**−0.556**
(E)-2-Octenal	**−0.555**	−0.062	**−0.535**	**−0.597**	0.439	0.434	0.158	0.010	−0.455	−0.455	**−0.496**	**−0.481**
1-Propanol	**0.578**	−0.112	**0.527**	**0.611**	**−0.582**	**−0.487**	−0.329	−0.285	**0.627**	**0.518**	**0.474**	0.316
2-Methyl-1-propanol	**0.471**	−0.437	**0.510**	**0.628**	−0.435	−0.445	**−0.584**	−0.302	**0.639**	**0.676**	0.456	0.457
1-Butanol	**0.662**	−0.329	**0.605**	**0.702**	**−0.654**	**−0.597**	**−0.575**	−0.364	**0.632**	**0.760**	**0.471**	**0.520**
1-Octanol	**−0.480**	−0.021	**−0.476**	**−0.530**	0.386	0.372	0.100	0.098	−0.418	−0.383	−0.382	−0.454
Ethyl Acetate	**0.647**	−0.219	**0.798**	**0.776**	**−0.773**	**−0.683**	**−0.505**	**−0.472**	**0.726**	**0.676**	**0.520**	**0.493**
n-Propyl acetate	0.436	−0.246	**0.513**	**0.598**	**−0.683**	**−0.630**	**−0.567**	**−0.500**	**0.669**	**0.614**	0.415	0.371
2-Methylpropyl acetate	**0.682**	0.244	**0.739**	**0.658**	**−0.558**	**−0.469**	−0.279	−0.273	**0.709**	**0.678**	**0.713**	**0.593**
Ethyl butanoate	**0.536**	−0.130	**0.773**	**0.709**	**−0.717**	**−0.632**	**−0.468**	−0.378	**0.710**	**0.625**	**0.505**	**0.472**
Butyl acetate	**0.783**	−0.118	**0.842**	**0.887**	**−0.855**	**−0.793**	**−0.609**	**−0.529**	**0.842**	**0.873**	**0.639**	**0.695**
3-Methylbutyl acetate	**−0.484**	0.144	−0.403	**−0.548**	**0.752**	**0.813**	**0.728**	**0.730**	**−0.612**	**−0.675**	−0.255	**−0.577**
Propyl butanoate	**0.715**	−0.122	**0.757**	**0.763**	**−0.731**	**−0.633**	−0.447	−0.427	**0.751**	**0.650**	**0.601**	**0.500**
Pentyl acetate	**0.768**	−0.106	**0.863**	**0.879**	**−0.790**	**−0.744**	**−0.529**	**−0.480**	**0.786**	**0.823**	**0.615**	**0.685**
Methyl hexanoate	**0.551**	−0.050	**0.766**	**0.697**	**−0.731**	**−0.656**	−0.447	−0.443	**0.710**	**0.610**	**0.513**	**0.512**
Ethyl hexanoate	**0.514**	−0.063	**0.699**	**0.613**	**−0.529**	−0.402	−0.196	−0.230	**0.480**	0.401	0.355	0.276
(Z)-3-Hexenyl acetate	−0.452	0.313	−0.291	**−0.542**	**0.627**	**0.693**	**0.777**	**0.693**	**−0.529**	**−0.626**	−0.121	−0.435
Hexyl acetate	**0.772**	−0.093	**0.881**	**0.863**	**−0.842**	**−0.757**	**−0.538**	**−0.495**	**0.808**	**0.795**	**0.620**	**0.670**
Propyl hexanoate	0.352	−0.224	**0.533**	**0.489**	**−0.483**	−0.420	−0.301	−0.185	**0.477**	0.389	0.325	0.205
Ethyl heptanoate	0.301	−0.314	**0.552**	0.466	−0.466	−0.437	−0.365	−0.376	0.410	0.350	0.242	0.254
Heptyl acetate	**0.626**	−0.147	**0.786**	**0.711**	**−0.710**	**−0.634**	**−0.480**	**−0.487**	**0.664**	**0.623**	**0.496**	**0.538**
Methyl octanoate	0.436	−0.276	**0.667**	**0.586**	**−0.585**	**−0.533**	−0.419	−0.418	**0.530**	**0.471**	0.349	0.365
Ethyl octanoate	**0.540**	−0.170	**0.770**	**0.684**	**−0.674**	**−0.612**	−0.425	−0.417	**0.624**	**0.565**	0.446	0.464
Ethyl (E)-2-octenoate	**0.623**	−0.197	**0.779**	**0.711**	**−0.700**	**−0.623**	**−0.480**	**−0.475**	**0.658**	**0.613**	**0.486**	**0.507**
Methyl 3-hydroxyoctanoate[b]	**0.675**	−0.111	**0.826**	**0.752**	**−0.773**	**−0.691**	**−0.497**	**−0.480**	**0.708**	**0.674**	**0.543**	**0.568**
Ethyl nonanoate	0.371	−0.312	**0.621**	**0.536**	**−0.534**	**−0.489**	−0.391	−0.380	**0.478**	0.415	0.298	0.301
Methyl 4-decenoate[b]	**0.621**	−0.143	**0.801**	**0.726**	**−0.738**	**−0.659**	**−0.481**	**−0.471**	**0.689**	**0.636**	**0.508**	**0.542**
Methyl decanoate	**0.473**	−0.178	**0.734**	**0.638**	**−0.667**	**−0.599**	−0.432	−0.407	**0.609**	**0.539**	0.414	0.436
Ethyl (E)-4-decenoate	**0.614**	−0.190	**0.779**	**0.714**	**−0.709**	**−0.630**	**−0.473**	**−0.473**	**0.662**	**0.614**	**0.483**	**0.511**
Methyl (E,Z)-2,4-decadienoate[b]	**0.670**	−0.018	**0.848**	**0.762**	**−0.787**	**−0.698**	**−0.471**	−0.450	**0.734**	**0.698**	**0.562**	**0.624**
Ethyl (E,Z)-2,4-decadienoate	**0.666**	−0.129	**0.822**	**0.753**	**−0.751**	**−0.665**	**−0.481**	**−0.475**	**0.703**	**0.665**	**0.527**	**0.567**
Ethyl dodecanoate	0.304	−0.311	**0.577**	**0.483**	**−0.489**	−0.453	−0.363	−0.347	0.431	0.366	0.255	0.256
Limonene	**−0.481**	0.253	**−0.472**	**−0.608**	**0.775**	**0.841**	**0.783**	0.442	**−0.714**	**−0.747**	−0.378	**−0.608**
α-Farnesene	**0.554**	0.036	**0.521**	**0.568**	**−0.497**	−0.416	−0.180	−0.282	**0.474**	0.463	0.381	0.411
Unknown 33: *m/z* 43 71 58 98	**−0.516**	−0.005	**−0.568**	**−0.674**	**0.735**	**0.810**	**0.591**	0.172	**−0.745**	**−0.731**	**−0.622**	**−0.719**
Unknown 41: *m/z* 97 125 168 81 123 95	**0.787**	−0.098	**0.862**	**0.835**	**−0.821**	**−0.723**	**−0.540**	**−0.472**	**0.809**	**0.766**	**0.633**	**0.634**
Unknown 45: *m/z* 117 71 43 88 89 55	**0.693**	−0.161	**0.808**	**0.756**	**−0.774**	**−0.686**	**−0.514**	**−0.499**	**0.698**	**0.675**	**0.531**	**0.541**
Unknown 46: *m/z* 87 153 110 74	0.275	−0.285	**0.581**	**0.479**	**−0.502**	−0.461	−0.343	−0.323	0.427	0.365	0.241	0.269
Unknown 51: *m/z* 100 69 41 55 136 101	**0.534**	−0.218	**0.720**	**0.643**	**−0.639**	**−0.577**	−0.450	−0.466	**0.585**	**0.543**	0.414	0.458
Unknown 53: *m/z* 114 86 69 55 41 68	**0.567**	−0.234	**0.721**	**0.656**	**−0.638**	**−0.576**	−0.463	**−0.484**	**0.594**	**0.553**	0.429	0.459
Unknown 54: *m/z* 67 79 80	**0.524**	−0.250	**0.703**	**0.635**	**−0.624**	**−0.566**	−0.453	**−0.470**	**0.579**	**0.527**	0.405	0.427

81 164 93													
Total aldehydes	**−0.587**	0.260	**−0.545**	**−0.701**	**0.716**	**0.675**	**0.619**	0.464	**−0.551**	**−0.666**	−0.331	−0.440
Total alcohols	0.445	−0.332	0.332	0.430	−0.158	−0.121	−0.288	−0.178	0.288	**0.489**	0.268	0.246
Total esters	**0.740**	−0.095	**0.873**	**0.837**	**−0.819**	**−0.734**	**−0.527**	**−0.488**	**0.786**	**0.769**	**0.603**	**0.646**
Total others	**0.553**	−0.322	**0.654**	**0.662**	**−0.599**	**−0.578**	**−0.554**	**−0.550**	**0.530**	**0.591**	0.369	0.432
Total aroma	**0.735**	−0.044	**0.880**	**0.813**	**−0.784**	**−0.692**	**−0.496**	−0.445	**0.780**	**0.767**	**0.638**	**0.655**
SSC[c]	−0.032	−0.404	−0.268	−0.051	0.105	0.047	−0.124	0.082	−0.150	−0.010	−0.161	−0.100
TA[d]	0.237	0.160	0.278	0.328	−0.431	−0.427	−0.201	−0.061	**0.489**	0.375	0.444	0.321
SSC/TA	−0.249	−0.359	−0.418	−0.332	0.453	0.423	0.123	0.101	**−0.516**	−0.356	**−0.492**	−0.364
Malic acid	−0.079	−0.156	−0.187	−0.105	**0.509**	0.456	0.222	0.347	−0.155	−0.159	0.011	−0.228
Sorbitol	**−0.570**	−0.063	**−0.650**	**−0.663**	**0.552**	**0.514**	0.353	0.352	**−0.613**	**−0.599**	**−0.540**	**−0.497**
Sucrose	0.438	−0.182	0.332	0.440	**−0.533**	**−0.489**	**−0.491**	**−0.584**	0.466	0.383	0.242	0.340
WSP[e]	**0.644**	−0.223	**0.707**	**0.831**	**−0.903**	**−0.898**	**−0.709**	**−0.545**	**0.859**	**0.800**	**0.516**	**0.680**

Values in bold are significant with $p = 0.05$.

[a] Aroma attributes.

[b] Tentatively identified.

[c] SSC = soluble solids content.

[d] TA = titratable acidity.

[e] WSP = water soluble polyuronides.

also brought about qualitative and quantitative differences in ester concentrations.

In the aroma biosynthesis pathway, the important enzymes involved in ester biosynthesis are alcohol dehydrogenase (ADH), converting aldehydes to alcohols (Speirs et al., 1998), and alcohol acyltransferase (AAT) converting alcohols to esters (Fellman et al., 2000). Ethylene biosynthesis plays a key role in aroma volatile production (Romani et al., 1983; Dandekar et al., 2004; Defilippi et al., 2004). However, ADH and ATT enzyme activities have been found to be both ethylene-dependent and ethylene independent in different fruit (Chen and Chase, 1993; Perez et al., 1993; Sarno-Manchado et al., 1997; Golding et al., 1999; Flores et al., 2002; Defilippi et al., 2005). In this study, fruit conditioned with ethylene produced as much ethylene as fruit conditioned for 14 d at 0 °C and for 7 d at 10 °C and ethylene conditioned fruit also had high concentrations of aldehydes in ripe fruit. Fruit conditioned at 0 °C and 7 d at 10 °C were higher in esters. Untreated control fruit had the lowest ethylene concentrations and the lowest ester concentrations, but aldehyde levels in ripe control fruit were highest. This suggests that different types of conditioning treatments may have diverse influences on ADH and AAT gene expression and enzyme activity during ripening. Further work is needed to determine this relationship and to investigate if these genes are under ethylene regulation in 'Bartlett' pears.

By using the headspace sorptive extraction (HSSE) technique, we found most of the volatile compounds previously reported in pear (Shiota, 1990; Takeoka et al., 1992; Suwanagul and Richardson, 1998; Rapparini and Predieri, 2002) using other extraction techniques (i.e. solid phase microextraction (SPME), dynamic headspace concentration on carbon traps, simultaneous distillation and extraction), and several compounds that have not previously been reported in pears. The HSSE technique has much higher sensitivity than the SPME technique (Tienpont et al., 2000; Pfanncoch et al., 2002; David et al., 2003) for esters, chlorinated hydrocarbons, linear hydrocarbons, and aromatic hydrocarbons (Tienpont et al., 2000). For all treatments, the mean scores for firmness and crunchiness decreased and the score for juiciness increased as the fruit softened from 27 to 18 to 9 N. Moreover, the correlation analysis showed that WSP had the highest negative correlation with firmness, crunchiness, and grittiness, and positive correlation with juiciness. This is consistent with previous studies which found that WSP increased when pear fruit ripened, concurrent with increases in sensory perception of juiciness and butteriness (Ahmed and Labavitch, 1980; Murayama et al., 1998; Eccher Zerbini, 2002).

However, WSP was not different among the conditioning treatments for a given firmness level, suggesting that all treatments resulted in similar changes in cell wall pectin composition as the fruit softened. However, there were differences in sensory perception of firmness and crunchiness among conditioning treatments that had the same instrumentally measured firmness level (i.e. measured with the penetrometer). Most texture attributes related to unripe pear fruit were different among treatments at 27 N. Grittiness and fibrousness characterized fruit treated with ethylene, and firmness and crunchiness were predominant in fruit held for 7 d at 0 °C. When the fruit softened to 18 N, crunchiness and juiciness were higher in all fruit conditioned at 0 °C. When the fruit softened to a firmness of 9 N, juiciness was similar in all treatments, while crunchiness was high in control fruit. This may indicate that conditioning treatments did not have different effects on the texture of the fruit once they softened to 9 N, although the conditioned fruit were different from the untreated/control fruit. In addition, people may be more sensitive to the differences in texture than the instruments. The instrument measures only one aspect of firmness, resistance to penetration, while sensory perceptions are more integrated responses to many variable inputs.

Table 7
Odor description, published odor thresholds, relative concentration, and odor units of significant volatile compounds in 'Bartlett' pear.

Class	Compounds	Odor description	Published odor threshold μg/kg water	Relative conc. μg/kg	Odor units U_0[a]
Esters	Butyl acetate	Vanilla, sweet, fruity, pear[q,r]	66[b,c]	228.20[d]	3.46[d]
	Hexyl acetate	Apple, pear, floral, banana [n,q,r]	2[c,e], 101[f], 115[b]	302.23[d]	2.63–151.12[d]
	Pentyl acetate	Floral, fruity, banana[s]	5[c], 38[f], 43[b]	17.99[d]	0.42–3.60[d]
	Ethyl (E,Z)-2,4-decadienoate	Pear, apple, fruity, tropical[t]	100[g]	223.80[d]	2.24[d]
Alcohols	1-Butanol	Fermented, fruity, medicinal, cheesy[u]	500[c]	23.66[h]	0.05[h]
Aldehydes	Hexanal	Green, sour[n]	4.5[i], 5[c,j], 5.8[k], 9.2[l], 10.5[m], 50[n], 479[o]	12.66[p]	0.03–2.81[p]
	(E)-2-Hexenal	Green grass, almond, sweet, fruity, apple, plum, vegetable[n,s]	17[c,j], 123[o]	8.06[p]	0.07–0.47[p]

[a] U_0 = compound concentration divided by its odor threshold.
[b] Takeoka et al., 1996.
[c] Flath et al., 1967.
[d] Relative concentration at 9 N of fruit treated at 0 °C for 14 d.
[e] Buttery et al., 1982.
[f] Belitz et al., 2009.
[g] Takeoka et al., 1992.
[h] Relative concentration at 9 N of fruit treated at 10 °C for 3 d.
[i] Guadagni et al., 1963.
[j] Buttery et al., 1987.
[k] Rychlik et al., 1998.
[l] Ahmed et al., 1978.
[m] Grosch et al., 1993.
[n] Larsen and Poll, 1992.
[o] Tandon et al., 2000.
[p] Relative concentration at 9 N of fruit treated at 20 °C (control).
[q] Rapparini et al., 2008.
[r] Chen et al., 2006.
[s] Beaulieu, 2005.
[t] Good Scents Company.
[u] El-Sayed, 2011.

Sweetness perception was higher for some treatments (14 d at 0 °C, 3 d at 10 °C and 2 d with C_2H_4) at full ripeness (9 N), while it was low in others (untreated control and 7 d at 10 °C or 0 °C). Sweetness perception in fruit at 9 N firmness was positively associated with SSC, SSC/TA, sorbitol content, and glucose content. However, at 18 N firmness, the sensory panelists detected differences in sweetness among different conditioning treatments, but there were no differences in the concentrations of chemical components typically associated with sweet taste. Akhavan and Wrolstad (1980) and Drake and Eisele (1999) reported that SSC measurements did not accurately detect changes in sugar concentration in pears. In our study, we measured sorbitol, sucrose, glucose and fructose, in addition to SSC. In pears ripened to 18 N, sensory sweetness was not associated with SSC or individual sugars; however, in 9 N pears, glucose, sorbitol and SSC were correlated with sensory sweetness. In apple, Harker et al. (2002) found that SSC was a better method to indicate sensory sweetness than individual sugar concentrations.

Fruit conditioned with ethylene were high in sensory perception of tartness at 27 N and 18 N. The perception of tartness at the 27 N firmness stage was correlated with TA and malic acid content, but not with citric acid content. These compounds were high in ethylene-conditioned fruit. Moreover, tartness was correlated with SSC/TA, which was lowest in ethylene-conditioned fruit as well. At 18 N, panelists found differences in tartness intensity across the treatments; however, there was no difference in chemical measurements associated with tartness (i.e. TA, SSC/TA, or malic acid content). At 9 N the panelists could not perceive any differences in tartness for the various conditioning treatments, while analytical measurements of TA and SSC/TA were different among samples. It appears that human perception of tartness in 'Bartlett' pears was not well correlated with instrumental measurements.

Sweetness was positively related to esters, sorbitol and WSP in fruit from all three firmness levels. However, in soft pears, sweetness and fruity flavor were positively correlated with SSC, SSC/TA, sorbitol and glucose concentrations, and negatively correlated with TA. It remains to be shown whether there is a causal relationship of these volatiles and WSP with sweetness perception or merely a correlative relationship.

The relationships between sensory and chemical evaluations were elucidated by PLS and correlation analysis. For aroma, PLS showed a negative correlation between apple aroma and concentrations of the most prevalent esters (i.e. butyl acetate, pentyl acetate, hexyl acetate, ethyl (E,Z)-2,4-decadienoate, and methyl (E,Z)-2,4-decadienoate) at the 27 N firmness stage. Apple aroma was also negatively correlated with concentrations of 1-butanol, octyl acetate, and 2-methylpropyl butanoate, and positively correlated with concentrations of hexanal and (E)-2-hexenal when the fruit softened to 18 N firmness. When the fruit were softest (9 N), apple aroma was negatively correlated with the concentrations of a large group of esters, total esters, and total aroma, and was positively associated with the total aldehyde concentration.

A predominance in apple aroma (referenced as the aroma of 'Granny Smith' apples) suggests that such fruit may contain higher concentrations of aldehydes compared to esters. This has been shown with 'Granny Smith' apple, which was considered to be a low ester producing cultivar (Lopez et al., 1998; Holland et al., 2005; Zhu et al., 2008). Zhu et al. (2008) showed that aldehydes were predominant compounds in 'Granny Smith' apples and hexanal was the most abundant volatile in this cultivar at harvest and during 2–6 weeks at 20 °C after harvest. In our study, hexanal and (E)-2-hexenal, which have a green odor, characterized the control and ethylene treated fruit. These compounds tended to decrease, although not in all treatments as the fruit softened. The published

odor thresholds of hexanal and (E)-2-hexenal are variable (Table 7), resulting in variable estimated odor units for the control fruit at 9 N firmness. Hexanal, which has a range of odor units >1.0, may contribute to the apple aroma in pear fruit.

The perception of fruity aroma was different across treatments only at 9 N firmness, and was most closely associated with fruit treated 3 d at 10 °C, although not strongly. However, fruity aroma was not associated with concentrations of esters (which are typically thought to have fruity odors), but was associated with levels of 1-butanol, SSC, sorbitol, glucose, and SSC/TA, similar to sensory sweetness and fruity flavor. The odor unit of 1-butanol, which was also associated with fruit of 9 N firmness previously conditioned for 3 d at 10 °C, was very low (0.05) which suggests that 1-butanol has a minor contribution to aroma perception.

It may be that sweetness perception has an interaction with fruity aroma perception whether it is orthonasal or retronasal. This hypothesis is supported by Delwiche (2004), who reported that the sensations of taste and smell interact. Odor ratings increase with the increase in taste compound concentration and taste ratings increase with the increase in odor compound concentration (i.e. interaction between strawberry odor and sweetness) (Frank et al., 1989; Bonnans and Noble, 1993). As a result, panelists perceived fruity aroma as much from ripe fruit conditioned for 3 d at 10 °C and with ethylene as from fruit treated for 14 d at 0 °C. Although fruit treated for 3 d at 10 °C and with ethylene had fewer types and lower concentrations of esters, they had high scores in sweetness and fruity flavor while fruit treated for 7 d at 0 °C or 10 °C had lower sweetness and fruity flavor scores. These treatments were perceived to be lower in fruity aroma even though they had higher concentrations of esters which typically have fruity, sweet, and pear notes.

Across all treatments and firmness levels, most esters had a positive correlation with fruity aroma, especially the most abundant esters, butyl acetate and hexyl acetate. The positive correlation between butyl acetate and hexyl acetate with fruity aroma, fruity flavor and sweet taste have been previously reported in apple (Karlsen et al., 1999) Moreover, although the perception of pear aroma was not different among treatments, many esters had strong positive correlation with pear aroma (Table 4). Hexyl acetate, which has pear notes and a very high odor unit (Table 7), had the highest correlation ($r = 0.881$) with sensory pear aroma (Table 6), supporting the role of hexyl acetate as an important contributory compound to pear aroma in 'Bartlett', as was reported previously (Jennings and Sevenants, 1964; Suwanagul and Richardson, 1998; Komes and Gani, 2010). Moreover, ethyl (E,Z)-2,4-decadienoate, considered to be the character impact compound of 'Bartlett' pear (Jennings et al., 1964; Heinz and Jennings, 1966; Suwanagul, 1996; Komes and Gani, 2010) was also highly correlated with pear aroma ($r = 0.822$), but has a lower odor unit than hexyl acetate. Each of these odor unit calculations are based on the relative concentrations of volatile compounds to the internal standard, and these hypotheses require further investigation by aroma extract dilution analysis, and aroma recombination and omission experiments to determine the precise contribution of each compound to pear aroma following each conditioning treatment.

While there were no differences in WSP related to texture among treatments at each firmness level, different conditioning treatments resulted in statistically significant variations in sensory attributes related to fruit texture. This indicates that other unknown changes in pear fruit biochemistry influence the perception of texture among conditioning treatments. However, these texture-related sensory attributes were correlated with other chemical components. For example, at 27 N, crunchiness, firmness, grittiness, and fibrousness were positively correlated with TA and malic acid, and negatively correlated with SSC/TA. Also, at 9 N, crunchiness had a positive relationship with TA, hexanal, and (E)-2-hexenal, and a negative relationship with SSC/TA and many esters.

A similar study was recently conducted with 'Comice' pears yielding similar results in some aspects, but also a few differences (Makkumrai et al., 2014). A larger number of different ester compounds and fewer different alcohols and aldehydes were detected in 'Bartlett' pears compared with 'Comice'. 'Bartlett' pears were high in ethyl (E,Z)-2,4-decadienoate, but this ester was not detected in 'Comice'. 'Comice' pears were high in ethyl 2-methylbutanoate. In both cultivars, WSP was highly correlated with sensory attributes associated with ripe pears, including juiciness and sweetness. Ethylene-conditioned fruit of both cultivars were associated with sensory sweetness and green aroma. 'Bartlett' pears conditioned with ethylene were high in aldehydes, but this was not observed in 'Comice' 'Comice' pears conditioned at 0 °C were high in alcohols. For both cultivars, conditioning fruit at 10 °C resulted in fruity aroma and moderate to high levels of esters.

5. Conclusion

Sensory properties and chemical composition of 'Bartlett' pears changed as pears softened from 27 to 9 N, and were influenced by different conditioning methods. When softened to 9 N, cold temperature (0 °C) conditioning for either 7 or 14 d resulted in fruit with high concentrations of esters, described as having fruity, sweet, and pear note aromas. Fruit treated for 14 d at 0 °C also scored high in sweetness and fruity flavor attributes. Intermediate temperature (10 °C) conditioning resulted in fruit with lower quantities of esters, but fruit conditioned for 3 d at 10 °C were still described as having sweet taste and fruity flavor. Ethylene treated fruit had even lower concentrations of esters, but high concentrations of aldehydes compared to fruit conditioned by low and intermediate temperatures. Ethylene treatment was positively associated with apple aroma, similar to untreated fruit; however, fruit conditioned with ethylene had higher fruity flavor scores than the untreated fruit. Our results indicate that the 'Bartlett' pear industry should emphasize conditioning pears at 0 °C over conditioning with ethylene to deliver the best eating quality to consumers. However, additional studies should determine whether the differences in sensory quality of ripe fruit resulting from different conditioning treatments can be perceived by consumers and will influence consumer liking.

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