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# Influence of 1-Methylcyclopropene and Storage Atmosphere on Changes in Volatile Compounds and Fruit Quality of Conference Pears

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Conference pears (*Pyrus communis* L.) were treated with 25 and 50 nL L<sup>-1</sup> 1-methylcyclopropene (1-MCP) at -0.5 °C for 24 h, then stored for up to 22 weeks in air (NA) and controlled atmosphere (CA). After 7 and 14 weeks of storage, fruits were retreated with 1-MCP. After 7, 14, and 22 weeks of storage, fruits were kept for up to 7 days at 20 °C in air for poststorage ripening. The effects of 1-MCP treatment declined with duration of storage in both storage atmospheres, indicating that retreatments had little additional effects on subsequent ripening. Ethylene production was lower and firmness was higher in 50 nL L<sup>-1</sup> fruits, while the 25 nL L<sup>-1</sup> dose was not very different from the control. Development of superficial scald was not prevented by 1-MCP treatments, but the severity of the symptoms was influenced. The 1-MCP effects were perceivable on texture (juiciness) and flavor. Control fruit and 25 nL L<sup>-1</sup> fruit reached their best sensory quality after 14 weeks of storage, while 50 nL L<sup>-1</sup> fruit reached the same sensory quality later, keeping a fresh flavor when the quality of control fruit declined and became watery or grainy. The fresh flavor in 50 nL L<sup>-1</sup> fruit was probably due to the presence below the odor detection threshold concentrations of the volatile compounds responsible for the "ripe pear" aroma, mainly of butanol and ethyl butanoate. CA prolonged or enhanced the effects of 1-MCP; 1-MCP cannot substitute for CA but can reinforce the CA effects.

KEYWORDS: Conference pears, 1-MCP, CA storage, ethylene, volatile compounds, sensory quality.

## INTRODUCTION

Conference pears are usually stored in controlled atmosphere (CA) to prolong their market period. However, the low  $O_2$  or high CO<sub>2</sub> concentrations, or both used during CA storage often result in high incidence of disorders such as brown heart, core browning, and cavities. The incidence varies among countries with pears grown in the northwestern part of Europe showing these disorders more often and more severely than pears grown in the southern part of Europe. Conference pears in Italy are often subject to superficial scald in cold storage; this postharvest disorder is related to the products of oxidation, consisting mainly of conjugated trienes, primarily  $\alpha$ -farnesene, acting on epidermal cells. Scald is prevented by using CA (1), CO<sub>2</sub> preventing the oxidation of  $\alpha$ -farnesene (2). Generally, scald is higher in immature fruits for Packham's Triumph and d'Anjou pears but not for Bartlett fruits, which show a different trend in scald susceptibility and cuticle composition with harvest maturity (3). Lo Scalzo et al. (4) found for Conference pears that the appearance of scald was related to a decrease of  $\alpha$ -farnesene

and of esters of long chain fatty acids and to a relative increase of conjugated trienols.

1-Methylcyclopropene (1-MCP) is a synthetic cyclic olefin capable of inhibiting ethylene action. It acts as a competitor of ethylene, blocking its access to the ethylene-binding receptors (5). 1-MCP, a gaseous nontoxic product, delays softening and improves poststorage quality of various climacteric fruits (6, 7) and is being studied as a tool to extend postharvest life.

In pears, as in other fruit, 1-MCP treatment inhibits ethylenedependent processes, including softening. Bartlett pears exposed to 2  $\mu$ L L<sup>-1</sup> 1-MCP for 16 h ripened and softened over a 10day period (8), while after a 0.4  $\mu$ L L<sup>-1</sup> 1-MCP treatment, there was a temporary inhibition of ethylene production, a delayed climacteric, and a concomitant postponement of fruit softening and degreenning (9). The duration of 1-MCP-induced responses was dependent on 1-MCP treatment concentration in d'Anjou pears, and when 1-MCP-treated fruits began to ripen, these was a softening and a production of volatile compounds similar to that of untreated fruits (10). The effect of 1-MCP on Bartlett (9) and Conference (11) pear ripening was not totally uniform, because a percentage of the 1-MCP-treated pears reached their climacteric peak, lost the green color, and softened prematurely.

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Treatments at harvest between 10 and 100 nL L<sup>-1</sup> were effective in retarding ripening of Abbé Fétel and Conference pears (12), the same dose of 1-MCP being more effective on Conference than on Abbé Fétel fruits. A 1  $\mu$ L L<sup>-1</sup> 1-MCP dose effectively prevented scald on Bartlett pears, but these fruits failed to soften with ripening at 20 °C (13). Retreatment with 1-MCP on Bartlett pears after 4 weeks of cold storage further delayed the onset of climacteric, its effectiveness being noticeably lower (9), and it had a greater effect on color development and softening after storage than did the initial 1-MCP application (13).

Because the effects of 1-MCP treatments at harvest at doses below 50 nL L<sup>-1</sup> decline rapidly during the cold storage period of pear fruit (*12*), the objective of this research was to evaluate the effect of the repetition of the treatment at harvest with 1-MCP at low doses (25 and 50 nL L<sup>-1</sup>) during storage in normal and controlled atmospheres. Different ripening and quality indices (ethylene production, firmness, color, percent juice) and volatile compounds in Conference pears were evaluated, as well as the effect of 1-MCP on conjugated trienes and  $\alpha$ -farnesene contents in fruit peel and appearance of scald.

#### MATERIALS AND METHODS

**Plant Material.** Conference pears were harvested from a commercial orchard in the Modena province at commercial maturity on 21st August, 2002. On the day of harvest, fruits were randomized in 24 boxes (50 fruits per box), transported to IVTPA, and put in a cold room in normal atmosphere (NA) at -0.5 °C.

**Chemicals.** Ethanol and butanol were supplied by VWR International GmbH (Dermstadt, Germany); butyl propanoate was purchased from TCI (Tokyo, Japan); acetaldehyde, propanol, 2-methyl-propanol, pentanol, hexanol, hexanal, (*E*)-2-hexenal, acetone, methylethyl ketone, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, pentyl acetate, hexyl acetate, ethyl butanoate, and butyl butanoate were obtained from Fluka Chemie (Buchs, SG, Switzerland).

**Experimental Plan.** 1-MCP treatments were carried out with 25 and 50 nL L<sup>-1</sup> doses (eight boxes per dose) at -0.5 °C for 24 h 1 day after harvest and after 7 and 14 weeks of storage after having taken fruits for assessments. Eight boxes of nontreated fruits (0 1-MCP dose) were used as control sample. After 1-MCP treatments at harvest, fruits were stored at -0.5 °C in NA. Five days after harvest, four boxes per dose (0, 25, and 50 nL L<sup>-1</sup> of 1-MCP) were moved to CA (2% O<sub>2</sub> + 0.7% CO<sub>2</sub>) containers at -0.5 °C. The storage period in NA and CA lasted for 22 weeks. So, fruits stored for 14 and 22 weeks had been treated two and three times, respectively; and after every 1-MCP treatment, fruit had been stored for seven weeks. Hereafter fruit treated at harvest ( $25 \times 1$ ;  $50 \times 1$ ) are referred to as 7 weeks samples,  $25 \times 2$  and  $50 \times 2$  fruits as 14 weeks samples, and  $25 \times 3$  and  $50 \times 3$  ones as 22 weeks samples.

At harvest, a sample of 20 fruits was analyzed for mass, skin color, firmness, starch hydrolysis, soluble solids, and titratable acidity. After 7, 14, and 22 weeks of storage, 18 fruits per dose per atmosphere were removed from cold storage and analyzed for firmness, color, and ethylene production rate during a shelf life period at 20 °C. The shelf life lasted 7, 6, and 5 days after 7, 14, and 22 weeks of storage, respectively, and the last day of shelf life is hereafter referred to as "day 7" for all the treatments. At the end of shelf life, percent juice, headspace volatiles,  $\alpha$ -farnesene, and conjugated trienes (CT) were analyzed, and an informal taste test was carried out by two volunteers. At the end of storage disorders were examined on 100 fruits per dose per atmosphere for control and 25×3 and 50×3 1-MCP doses.

**1-MCP Treatments.** The 1-MCP treatments were carried out at -0.5 °C for 24 h by placing each group of fruit in a 1.64 m<sup>3</sup> gastight container; 1-MCP was weighed into a 50 mL beaker (668 or 1336 mg of Smartfresh powder for 25 and 50 nL L<sup>-1</sup> dose, respectively); the beaker was placed in the container with fruits, and just before sealing it, 1.4 or 2.5 mL of 40 °C water for 25 and 50 nL L<sup>-1</sup> dose, respectively, was added and mixed to develop the gas.

Quality Indices. Skin color was measured in reflectance as  $L^*$ ,  $a^*$ , and  $b^*$  (CIE, 1976) on the greener side of the fruit using a Minolta chromameter (CR-200 chromameter, Minolta Co, Japan), and hue was computed from  $a^*$  and  $b^*$  values (14). Firmness of each fruit was measured on two opposite peeled areas in the equatorial region of the pear using an 8 mm diameter plunger mounted on an Instron Universal Testing Machine (model 4301, Instron Ltd, Great Britain) with the crosshead speed at 200 mm min<sup>-1</sup>. The stage of starch hydrolysis was determined by dipping half-cut pears into a Lugol solution and scoring the fruit according to the EUROFRU scale (1-10; 1 = minimum, 10)= maximum starch hydrolysis) (15). Soluble solids content (SS) and titratable acidity (TA) were determined using freshly prepared juice from each individual fruit; SS were measured using an automatic refractometer (RFM81, Bellingham-Stanley Ltd, England), and TA was by titrating 5 g of juice plus 50 mL of distilled water with 0.1 N NaOH to pH = 8. Percent juice was determined on pulp cylinders (diameter = 15 mm, height = 10 mm) taken from radial positions from fruit, and compressed between two plates with the Instron Universal Testing Machine (model 4301, Instron Ltd, Great Britain) at deformation rate of 50 mm min<sup>-1</sup> by a compression of 50% of the original height of the cylinder (16). This method correlated with sensory analysis, and only the juice that can be easily and quickly released by the pulp cylinder is measured (16).

**Storage Disorders.** Superficial scald was visually assessed using six degrees of severity of symptoms: 1, light scald, brown; 2, medium scald, brown; 3, severe scald, brown; 4, light scald, dark; 5, medium scald, dark; 6, severe scald, dark. Core browning was visually assessed as sound (0) or affected (1).

α-Farnesene and Conjugated Trienes. α-Farnesene and conjugated trienes were measured according to Zoffoli et al. (3), sampling eight skin disks of 0.8 cm<sup>2</sup> area from two sides of four pears (three replications) and extracting overnight at 2 °C with 6 mL of HPLC-grade hexane with 1 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>. The absorbance of the extracts at 232, 258, 269, 281, and 290 nm was measured by using a Unicam (model UV4) spectrophotometer. α-Farnesene was quantified from the absorbance at 232 nm using the extinction coefficient E = 27700 (*17*). As suggested by Du and Bramlage (*18*), for conjugated trienes (CT), three values were reported: CT258, OD<sub>258-290 nm</sub>; CT269, OD<sub>269-290 nm</sub>; CT281, OD<sub>281-290 nm</sub>. To quantify all CTs, the average extinction coefficient E = 25000 (*19*) was used. Data were expressed as nmol cm<sup>-2</sup>.

**Ethylene Production Rate.** The ethylene production rate (EP) was measured on fruit put in 1.7 L gastight glass jars (three replications, one fruit per jar) for 1 h at 20 °C; then, 1 mL of the headspace gas was sampled and analyzed for the ethylene content following the conditions reported by Rizzolo and Visai (20) using a deactivated aluminum oxide F1 (80–100 mesh) column (1/8 in. × 200 cm), column temperature 100 °C, injection temperature 100 °C, FID temperature 225 °C. Quantitative data were obtained by relating ethylene peak area to that of a 10  $\mu$ L L<sup>-1</sup> standard and were expressed as pmol kg<sup>-1</sup> s<sup>-1</sup>; GC data were corrected for fruit mass, empty volume of the jar, and time of production.

Volatile Compounds. Analysis of volatile compounds was carried out using static headspace sampling (21) on two replicate samples of three pears, which were sliced, pooled, and homogenized. Ten grams of homogenized pulp (two replications) was taken and put into 25 mL vials tightly closed with an aluminum cap with a silicone-Teflon rubber septum; then samples were immediately frozen and kept at -30 °C until the headspace GC analysis. After a 30 min thawing at room temperature, each vial was heated at 60 °C for 1 h, and 0.5 mL of the headspace gas was sampled and injected using the automatic headspace sampler HSS 58.90 DANI fitted to a gas chromatograph DANI 8400, equipped with a PTV injector port operating in splitless mode, and a DB-WAX column (60 m  $\times$  0.53 mm i.d., 1  $\mu$ m film thickness). The following GC conditions were used: helium carrier gas flow rate 1.6 mL min <sup>-1</sup>; hydrogen flow rate 66 mL min<sup>-1</sup>; air flow rate 146 mL min<sup>-1</sup>; oven temperature program 10 min at 50 °C, 3 °C min<sup>-1</sup> to 180 °C; injector port and detector temperatures 200 and 250 °C, respectively. Volatile compounds were identified by comparison with GC-MS data of pear extracts (22), Kovats index, and standard compounds and quantified by relating the peak area of each one to that of external



**Figure 1.** Ethylene production rate (pmol kg<sup>-1</sup> s<sup>-1</sup>) at 1, 3, and 7 days of poststorage ripening at 20 °C of 1-MCP-treated fruits stored in NA and CA compared to control. Doses: 7 weeks, 25×1, 50×1; 14 weeks, 25×2, 50×2; 22 weeks, 25×3, 50×3. Bars refer to pooled standard error.



**Figure 2.** Ethylene production rate (pmol kg<sup>-1</sup> s<sup>-1</sup>) of 1-MCP-treated Conference pears after 7, 14, and 22 weeks of storage compared to control in controlled (CA) and normal (NA) atmospheres. Bars refer to standard error of the mean.

standards, which were prepared in 25 mL vials by adding known amounts of standard compounds to 10 mL of water, sealing, and analyzing them in the same way as fruit samples. Data were expressed as  $\mu$ g kg<sup>-1</sup> fresh weight (FW) of pulp. The tentatively identified volatile compounds were quantified by relating their peak area to that of the hexyl acetate external standard.

**Statistical Analysis.** Data were subjected to ANOVA using SAS (SAS Institute, Raleigh, NC), and means were compared with Tukey's test at p < 0.05. Data of percent incidence of storage disorders were analyzed after angular transformation.

# RESULTS

At harvest, fruit mass was  $176 \pm 9.6$  g (standard error), firmness  $59 \pm 1.1$  N, stage of starch hydrolysis  $6.6 \pm 0.5$ , soluble solids  $12 \pm 0.2$  °Brix, and titratable acidity  $2.08 \pm 0.07$  mequiv (100 g)<sup>-1</sup> of juice.

**Ethylene Production.** On average, ethylene production rate (EP) (**Figure 1**) significantly increased with storage time, being  $39.6 \pm 7.65$ ,  $115.8 \pm 9.47$ , and  $192.5 \pm 9.19$  pmol kg<sup>-1</sup> s<sup>-1</sup> after 7, 14, and 22 weeks of storage, respectively, and it was lower in CA (CA 97.8  $\pm$  7.97; NA 133.8  $\pm$  9.63 pmol kg<sup>-1</sup> s<sup>-1</sup>). EP was significantly affected by 1-MCP dose at each storage time: the higher the 1-MCP dose, the lower the average EP, independent from storage atmosphere (**Figure 2**). During the shelf life at 20 °C (**Figure 1**) after the first (7 weeks) and the second (14 weeks) treatments, there was a rise in EP at the end of shelf life only for control and 25 nL L<sup>-1</sup> samples, the EP of the 25 nL L<sup>-1</sup> dose being on average lower than that of control fruit. EP of 50 nL L<sup>-1</sup> fruits did not significantly change with shelf life, and it was always lower than those of control

and 25 nL L<sup>-1</sup> dose fruits. After the third treatment (22 weeks), generally there was no rise in EP with shelf life, except for the higher 1-MCP dose stored in NA. Storage atmosphere significantly affected EP of 1-MCP treated pears (**Figure 2**): after 7 weeks of storage in NA, both 25 and 50 nL L<sup>-1</sup> fruits showed lower EP than the corresponding fruits that had been stored in CA. There was a lowering of EP rates in CA in both 1-MCP doses, which did not occur in NA; this effect of CA on 1-MCP treated fruits was more evident after three treatments with the 50 nL L<sup>-1</sup> dose (22 weeks). At the end of storage, 1-MCP treated fruits that had been stored in NA, even after the repetition of the treatment, were no more able to inhibit ethylene production (**Figure 2**).

Firmness. Both 1-MCP treatments delayed softening (Table 1). The delay of fruit softening induced by 1-MCP depended on 1-MCP dose at harvest, repetition of the treatment during storage, type of storage atmosphere, and poststorage ripening at 20 °C. In both atmospheres, plus 7 days at 20 °C, firmness of 50 nL L<sup>-1</sup> 1-MCP-treated fruit was higher than that of control and 25 nL  $L^{-1}$  ones after the treatment at harvest (7 weeks), whereas after the second (14 weeks) and third (22 weeks) treatments, firmness was higher in 50 nL L<sup>-1</sup> fruit stored in CA, plus 7 days of ripening. The 25 nL  $L^{-1}$  1-MCP-treated fruits were firmer than control ones after 7 weeks of storage in NA, plus 7 days at 20 °C. The largest differences in firmness between control and 1-MCP-treated fruit were detected for the 50 nL  $L^{-1}$  dose after 7 weeks in both atmospheres and after 14 weeks (50 nL  $L^{-1} \times 2$ ) in CA, plus 7 days at 20 °C. In addition, in control fruits plus 1 day at 20 °C, firmness decreased with storage time, more in NA than in CA; in 25 nL  $L^{-1}$  1-MCPtreated fruit stored in CA and in 50 nL L<sup>-1</sup> 1-MCP-treated fruit stored in both atmospheres, plus 1 day at 20 °C, the repetitions of treatment were effective in keeping firmness throughout the storage period. Only 50  $\times$  1 nL L<sup>-1</sup> 1-MCP-treated fruit stored in both atmospheres and 50  $\times$  2 nL L<sup>-1</sup> stored in CA did not become soft after 7 days at 20 °C.

**Color.** After storage in NA and CA, plus 1 day at 20 °C, there were no differences in color between control and both 1-MCP doses, whatever the storage atmosphere (**Table 1**). With ripening at 20 °C, generally fruit got yellower (lower hue), and the later the storage time, the yellower the pears. After 22 weeks storage in NA, control and 1- MCP treated fruits, notwithstanding the repetition of the treatment, were quite yellow already after 1 day at 20 °C; only 50 nL L<sup>-1</sup> 1-MCP-treated pears after 7 and 14 weeks storage in NA did not become yellower with poststorage ripening at 20 °C. After 7 and 14 weeks of storage,

Table 1. Firmness, Hue, and Percent Juice of Conference Pears Treated with 25 and 50 nL L<sup>-1</sup> 1-MCP at Harvest and during Storage in Normal (NA) and Controlled (CA) Atmosphere Compared to Control at Day 1 and Day 7 of Poststorage Ripening at 20 °C<sup>a</sup>

			day	/ 1			day 7									
	firmness (N)				hue (rad)			firmness (N)			hue (rad)			% juice		
weeks	7	14	22	7	14	22	7	14	22	7	14	22	7	14	22	
	СА															
control	58.03 (2.288)	59.44 (1.885)	51.35 (1.128)	1.97 (0.007)	1.97 (0.011)	1.93 (0.019)	5.32 (0.373)	5.44 (0.193)	7.24 (0.204)	1.83 (0.021)	1.82 (0.015)	1.83 (0.024)	41.95 (1.967)	47.90 (1.382)	39.97 (1.652)	
25	57.53 (1.160)	55.99 (2.878)	56.65 (1.685)	`1.95 (0.019)	1.96 (0.015)	1.92 (0.017)	11.31 (2.201)	6.90 (0.523)	7.75 (0.321)	1.85 (0.033)	1.87 (0.015)	1.85 (0.024)	33.75 (4.367)	40.29 (1.720)	39.34 (2.584)	
50	55.33 (1.190)	45.04 (7.973)	52.19 (2.529)	2.00 (0.008)	`1.98 (0.010)	1.93 (0.017)	46.90 (4.639)	31.51 (6.180)	19.10 (3.331)	`1.95 (0.015)	`1.92 (0.010)	`1.85 (0.023)	27.35 (2.227)	31.80 (3.051)	42.31 (1.351)	
							NA	Ą								
control	58.61 (2.319)	51.94 (1.481)	44.05 (2.461)	1.97 (0.017)	1.91 (0.021)	1.79 (0.020)	7.48 (0.697)	4.66 (0.247)	7.60 (0.319)	1.86 (0.025)	1.75 (0.024)	1.67 (0.025)	29.26 (4.150)	41.76 (2.987)	42.51 (2.318)	
25	56.36 (1.634)	58.32 (2.385)	43.02 (3.717)	`1.99 ´ (0.013)	1.89 (0.022)	1.76 (0.038)	13.98 (2.294)	`5.01 ´ (0.385)	7.53 (0.401)	`1.87 <sup>′</sup> (0.013)	1.77 (0.021)	`1.71 (0.035)	30.02 (1.649)	40.28 (3.486)	43.71 (1.036)	
50	56.10 (2.492)	52.04 (2.485)	53.22 (0.743)	`1.96 (0.019)	1.94 (0.010)	1.79 (0.023)	56.23 (2.121)	12.55 (2.616)	12.75 (3.018)	1.95 (0.010)	1.94 (0.014)	1.73 (0.024)	26.82 (1.274)	38.83 (3.505)	45.37 (1.042)	

	day 1			day 7		
	firmness	hue	firmness	hue	% juice	
		Main Effects <sup>b</sup>				
storage time (A)	***	***	***	***	***	
storage atmosphere (B)	ns	***	ns	***	ns	
1-MCP treatment (C)	ns	ns	***	***	**	
		Interactions				
$A \times B$	ns (0.054)	***	***	***	**	
$A \times C$	*	ns	***	ns	**	
$B \times C$	*	ns	ns (0.06)	ns	*	
$A \times B \times C$	ns	ns	**	ns	ns	

<sup>a</sup> Doses: 7 weeks,  $25 \times 1$ ,  $50 \times 1$ ; 14 weeks,  $25 \times 2$ ,  $50 \times 2$ ; 22 weeks,  $25 \times 3$ ,  $50 \times 3$ . The results are the average (n = 10); in parentheses is the standard error of the mean. <sup>b</sup> *P*-value of *F* ratio: ns = not significantly different; \* denotes P < 0.05; \*\* denotes P < 0.01; \*\*\* denotes P < 0.001.

plus 7 days of ripening at 20 °C, 50 nL  $L^{-1}$  treated pears were greener than control and 25 nL  $L^{-1}$  treated ones, independent of the storage atmosphere.

**Percent Juice.** 1-MCP treatment had little influence on percent juice at the end of ripening at 20 °C (**Table 1**). The 7 and 14 weeks samples of 50 nL L<sup>-1</sup> treated fruits stored in CA were less juicy than control fruits, while there were no differences between control and 25 × 3 and 50 × 3 1-MCPtreated fruits at the end of storage in CA and in NA. All samples stored in NA became more juicy from 14 weeks of storage upward. In CA, control fruit had lower percent juice at the end of storage, 25 nL L<sup>-1</sup> treated fruit did not show any significant variation, while 50 nL L<sup>-1</sup> fruits became more juicy after 22 weeks of storage.

**Storage Disorders.** After 22 weeks of storage, there was little or no decay or core browning, and 1-MCP treatments did not influence the percentage of fruit affected by superficial scald (**Table 2**). Superficial scald incidence was lower in fruits stored in CA, and the distribution of the classes of severity of symptoms in both atmospheres was 1-MCP-concentration dependent (**Figure 3**). The 50 nL L<sup>-1</sup> dose in CA, compared to control and the 25 nL L<sup>-1</sup> dose, caused a reduction of total brown scald (degrees 1 to 3), coupled with a majority of fruits affected by degree 4 slight dark scald. After NA storage, there was a higher incidence of fruits affected by degree 6 severe dark scald, whatever the 1-MCP dose.

 $\alpha$ -Farnesene and Conjugated Trienes. Lower amounts of  $\alpha$ -farnesene, CT258, CT269, and CT281 were detected in 50 nL L<sup>-1</sup> treated fruits regardless of repetition of the treatment and storage atmosphere (**Table 3**), except for CT258 and CT269, whose amounts after 7 weeks of storage in NA were higher

Table 2. Physiological Disorders and Decay of Control and 25×3 and 50×3 nL L<sup>-1</sup> 1-MCP-treated Conference Pears after Storage in Normal (NA) and Controlled (CA) Atmospheres<sup>a</sup>

	decay (%)	superf	icial scald (%)	core browning (%)								
		C	A									
control	1.32 b		25.10 a	0.44 a								
25	0.36 a		23.34 a	0.31 a								
50	1.40 b		23.15 a	0.12 a								
avg CA	1.02		23.86 A	0.29 B								
		Ν	A									
control	0 a		64.91 a	0 a								
25	2.36 b		58.97 a	0 a								
50	1.78 b		60.01 a	0 a								
avg NA	1.38		61.61 B	0 A								
		decay	superficial sca	ld core browning								
	Main Effects <sup>b</sup>											
storage atm	osphere (A)	ns	***	ns (0.054)								
1-MCP dose		*	ns	ns								
		Inter	action									
$A \times B$		***	ns	ns								

<sup>a</sup> Means in a column followed by different letters are statistically different for *p* < 0.05 (Tukey's test); small letters indicate 1-MCP dose within the same storage atmosphere, capital letters indicate between storage atmospheres. <sup>b</sup> *P*-value of *F*-ratio. ns = not significantly different; \* denotes *P* < 0.05; \*\* denotes *P* < 0.01; \*\*\*denotes *P* < 0.001.

than those of control pears. Generally, 25 nL  $L^{-1}$  treated fruits had similar amounts of  $\alpha$ -farnesene, CT258, CT269, and CT281 as control fruit with few exceptions. Regardless of the 1-MCP dose and the storage atmosphere,  $\alpha$ -farnesene and CT281 increased with storage time, despite the repeated treatments,

**Table 3.** Concentration of  $\alpha$ -Farnesene (nmol cm<sup>-2</sup>), Conjugated Trienes CT281, CT269, and CT258 (nmol cm<sup>-2</sup>), and Conjugated Trienes Ratios CT258/CT281 and CT269/CT281 in the Peel of Conference Pears Treated with 25 and 50 nL L<sup>-1</sup> 1-MCP at Harvest and during Storage in Normal (NA) and Controlled (CA) Atmospheres Compared to Control<sup>a</sup>

	$\alpha$ -farnesene		CT 281			CT 269			CT 258			CT258/CT281			CT269/CT281			
weeks	7	14	22	7	14	22	7	14	22	7	14	22	7	14	22	7	14	22
									CA									
control	26.82	22.49	31.35	2.47	2.72	5.92	11.67	8.63	12.20	14.40	9.15	10.75	5.82	3.37	1.82	4.72	3.18	2.06
	(0.769)	(1.362)	(0.288)	(0.117)	(0.073)	(0.117)	(0.858)	(0.160)	(0.176)	(1.074)	(0.181)	(0.077)	(0.163)	(0.056)	(0.023)	(0.129)	(0.035)	(0.011)
25	20.53	24.77	28.09	1.97	2.72	5.17	10.20	8.90	10.03	12.10	9.45	8.53	6.16	3.48	1.65	5.19	3.27	1.94
	(0.224)	(0.585)	(1.051)	(0.093)	(0.089)	(0.270)	(0.456)	(0.377)	(0.511)	(0.479)	(0.379)	(0.481)	(0.050)	((0.038)	(0.029)	(0.016)	(0.049)	(0.014)
50	7.69	19.33	24.80	0.88	1.85	2.95	4.10	8.82	6.83	4.82	10.12	5.75	5.50	5.47	1.96	4.68	4.77	2.32
	(0.394)	(0.544)	(0.801)	(0.060)	(0.029)	(0.105)	(0.050)	(0.270)	(0.417)	(0.060)	(0.326)	(0.307)	(0.327)	(0.239)	(0.152)	(0.267)	(0.202)	(0.137)
									NA									
control	24.58	27.33	30.55	2.00	4.25	8.13	7.05	11.43	14.18	8.48	10.78	10.75	4.24	2.54	1.32	3.53	2.69	1.75
	(0.432)	(0.833)	(0.363)	(0.018)	(0.058)	(0.394)	(0.133)	(0.307)	(0.386)	(0.193)	(0.407)	(0.306)	(0.073)	(0.087)	(0.039)	(0.058)	(0.099)	(0.0439
25	20.62	25.86	29.74	1.97	4.02	6.52	10.10	11.48	10.72	12.23	11.12	7.85	6.22	2.77	1.21	5.13	2.86	1.65
	(0.250)	(1.500)	(0.686)	(0.073)	(0.102)	(0.321)	(0.485)	(0.274)	(0.346)	(0.440)	(0.360)	(0.190)	(0.011)	(0.099)	(0.056)	(0.055)	(0.055)	(0.035)
50	10.42	21.22	29.33	1,50	2.38	6.43	9.47	9.38	10.05	11.58	9.50	6.98	7.72	3.99	1.09	6.31	3.94	1.56
	(0.340)	(0.497)	(0.686)	(0.029)	(0.067)	(0.369)	(0.218)	(0.131)	(0.461)	(0.333)	(0.219)	(0.247)	(0.202)	(0.066)	(0.035)	(0.132)	(0.068)	(0.024)

	$\alpha$ -farnesene	CT 281	CT 269	CT 258	CT258/CT281	CT269/CT281
			Main Effects <sup>b</sup>			
storage time (A)	***	***	***	***	***	***
storage atmosphere (B)	***	***	***	*	***	***
1-MCP treatment (C)	***	***	***	***	***	***
			Interactions			
$A \times B$	*	***	***	ns	***	***
$A \times C$	***	***	***	***	***	***
$B \times C$	*	**	***	***	***	***
$A \times B \times C$	**	***	***	***	***	***

<sup>a</sup> Doses: 7 weeks,  $25 \times 1$ ,  $50 \times 1$ ; 14 weeks,  $25 \times 2$ ,  $50 \times 2$ ; 22 weeks,  $25 \times 3$ ,  $50 \times 3$ . The results are the average (n = 3). In parentheses is the standard error of the mean. <sup>b</sup> *P*-value of *F* ratio: ns=not significantly different; \* denotes *P* < 0.05; \* \*denotes *P* < 0.01. \*\*\* denotes *P* < 0.001.



Figure 3. Superficial scald after 22 weeks of storage and 2 days of shelf life at 20 °C presented as percent distribution of the classes of severity of symptoms in control and 1-MCP-treated Conference pears stored in controlled (CA) and normal (NA) atmospheres. Degrees of severity of symptoms: 1, light scald, brown; 2, medium scald, brown; 3, severe scald, brown; 4, light scald, dark; 5, medium scald, dark; 6, severe scald, dark.

while the trends of CT258 and CT269 with storage differed according to both 1-MCP dose and storage atmosphere (**Table 3**). Storage atmosphere influenced the amounts of  $\alpha$ -farnesene and CT258, CT269, and CT281, especially in control and 50 nL L<sup>-1</sup> treated fruits. In control fruits, CT258, CT269, and CT281 were higher in CA after 7 weeks of storage and in NA after 14 and 22 weeks of storage, while  $\alpha$ -farnesene amount was higher in NA only after 14 weeks of storage. On the other hand, in 25 nL L<sup>-1</sup> treated fruits, generally there were no differences between atmospheres, with the exceptions of CT258,

CT269, and CT281, which were higher in NA after 14 weeks of storage (25 × 2). In 50 nL L<sup>-1</sup> treated pears,  $\alpha$ -farnesene, CT258, CT269, and CT281 were always higher in NA, independent of the repetition of treatment. The ratios CT258/CT281 and CT269/CT281 decreased in both atmospheres and with all 1-MCP doses. Generally the values were higher the higher the 1-MCP dose, except for 50 nL L<sup>-1</sup> treated fruit after 7 weeks in CA, where the ratios were lower than control.

Volatile Compounds. The headspace volatile compounds from Conference pears included alcohols, aldehydes, ketones, and esters (Table 4), the major volatile compounds being 2-methylpropyl acetate, methyl acetate, butyl acetate, and 3-methylbutyl 2-methylbutanoate among esters and ethanol, butanol, acetaldehyde, hexanal, and methylethyl ketone among the other volatiles. Volatile compounds were dependent on storage time and 1-MCP dose. Esters, particularly acetate esters and 3-methylbutyl 2-methylbutanoate, increased over the storage period. Ethanol increased with storage time, as did the straight chain C<sub>3</sub>-C<sub>6</sub> alcohols; only 2-methylpropanol had a decreasing trend with storage time. Hexanal, acetone, and methylethyl ketone peaked after 14 weeks of storage, and acetaldehyde increased at the end of storage. Fruits stored in NA developed more propanol, 2-methylpropyl acetate, and butyl propanoate and less 2-methylpropanol and acetone than pears stored in CA. The 50 nL  $L^{-1}$  1-MCP-treated fruit, compared to control, developed less acetate esters (methyl, 2-methylpropyl, propyl, butyl), ethyl butanoate, ethanol, propanol, butanol, acetaldehyde, and propanal and more 3-methylbutyl 2-methylbutanoate. The 25 nL L<sup>-1</sup> 1-MCP-treated pears produced on average lower amounts of all the volatile compounds detected than control fruits but higher quantities than 50 nL  $L^{-1}$  1-MCP treated ones. Only 3-methylbutyl 2-methylbutanoate was present in a similar

Table 4. Volatile Compounds (µg kg<sup>-1</sup>) at the End of Poststorage Shelf Life at 20 °C of Conference Pears<sup>a</sup>

				weeks of stor	age		storage	e atmosphe	res	1- MCP dose			
	RI on DB-WAX	ID <sup>b</sup>	7	14	22	Pc	CA	NA	Pc	control	25 nL L <sup>-1</sup>	50 nL L <sup>-1</sup>	Pc
acetaldehyde	690	а	2506 a	2300 a	4252 b	***	2940	3057	ns	3698 b	3364 ab	1963 a	**
propanal	784	а	9.5 a	43 a	33 a	ns	23	34	ns	61 b	21 ab	3.5 a	*
acetone	810	а	49 a	422 b	75 a	***	296	68	***	179 a	236 a	131 a	ns
methyl acetate	813	а	44 a	92 a	158 b	***	96	99	ns	129 b	99 ab	65 a	*
2-methylpropanol	871	а	176 b	276 b	62 a	***	212	131	*	159 a	183 a	173 a	ns
ethyl acetate	872	а	2.4 a	28 ab	35 b	*	24	20	ns	36 a	24 a	6.0 a	ns (0.06)
ethanol	900	а	6602 a	16610 ab	24260 b	***	13974	17619	ns	22196 b	17283 ab	7369 a	***
methylethyl ketone	945	а	126 a	211 b	120 a	**	144	161	ns	121 a	148 a	189 a	ns (0.06)
propyl acetate	962	а	0.9 a	3.5 b	3.7 b	*	2.7	2.8	ns	4.8 b	2.6 ab	0.9 a	***
2-methylpropyl acetate	1000	а	283 a	558 b	608 b	***	385	581	***	791 c	499 b	189 a	***
propanol	1002	а	22 a	49 b	65 b	***	38	52	*	58 b	46 ab	32 a	**
ethyl butanoate	1025	а	0.4 a	1.4 ab	2.3 b	**	1.2	1.6	ns	2.0 b	1.6 ab	0.6 a	*
butyl acetate	1059	а	14 a	45 a	89 b	***	48	51	ns	79 b	48 ab	21 a	**
hexanal	1084	а	154 ab	222 b	126 a	*	176	159	ns	178 a	196 a	128 a	ns
butanol	1113	а	120 a	284 a	812 b	***	357	454	ns	579 b	385 ab	252 a	*
butyl propanoate	1130	а	0.03 a	0.2 b	0.2 b	**	0.1	0.2	**	0.2 a	0.1 a	0.1 a	ns (0.06)
pentyl acetate	1161	а	0.5 a	1.8 a	5.1 b	**	1.9	3.0	ns	3.2 a	3.4 a	0.8 a	ns
(E)-2-hexenal	1204	а	2.4 a	3.5 a	3.1 a	ns	3.0	3.1	ns	3.1 a	3.4 a	2.6 a	ns
butyl butanoate	1207	а	2.4 a	3.5 a	3.1 a	ns	3.0	3.1	ns	3.1 a	3.4 a	2.6 a	ns
pentanol	1213	а	8.3 a	45b	31 b	***	26	30	ns	25 a	26 a	33 a	ns
3-methylbutyl 2-methylbutanoate	1273	b	2.7 a	52 b	38 b	***	34	28	ns	28 ab	23 a	42 b	*
hexyl acetate	1307	а	2.0 a	7.3 ab	17 b	*	8.7	9.1	ns	13 a	10 a	3.2 a	ns
hexanol	1316	а	17 a	18 a	33 b	*	21	24	ns	29 a	25 a	13 a	ns (0.06)
total C3–C6 alcohols			343 a	672 ab	1003 b	**	654	691	ns	850 b	665 ab	503 a	**
total C3–C6 aldehydes			166 ab	269 b	162 a	*	202	196	ns	242 a	220 a	354 a	ns
total ketones			175 a	633 b	195 a	***	505	229	***	300 a	384 a	320 a	ns
total esters			352 a	793 ab	959 b	***	605	799	ns	1089 b	715 ab	326 a	**

<sup>*a*</sup> Main effects: storage time, storage atmosphere (NA, normal atmosphere; CA, controlled atmosphere), and 1-MCP dose (average of the treatments). <sup>*b*</sup> Identification remarks: (a) identification based on comparison of retention data with those of authentic reference compounds and of GC/MS analysis on pear extracts (22); (b) tentatively identified on the basis of Kovats index and of retention data of GC/MS analysis on pear extracts (22). <sup>*c*</sup> Weeks of storage and 1-MCP dose: means followed by different letters are statistically different for  $p \le 0.05$ ; \*\* denotes P < 0.05; \*\* denotes P < 0.01; \*\*\* denotes P < 0.001.

amount as in control fruits and in a lower quantity than in 50  $nL L^{-1}$  treated Conference pears.

To evaluate whether the difference in volatile compound compositions among treatments affects the overall odor, concentrations were converted into odor units (Uo) (23). Uo were calculated from concentrations using the odor thresholds reported in the literature (24) (**Table 5**), according to Uo = C/OT, where C is the concentration in the sample and OT is the odor detection threshold concentration. Only compounds with Uo equal to or greater than 1 actually contribute to aroma because they are above their odor threshold concentration.

In consideration of the average Uo at every storage time (**Table 5**), only nine volatiles out of 23 actually contributed to the odor pattern of Conference pears: the two aldehydes (acetaldehyde and hexanal), the alcohol butanol, some acetate esters (2-methylpropyl, ethyl, hexyl, butyl), ethyl butanoate, and 3-methylbutyl 2-methylbutanoate. All the other compounds were present in too low quantities to contribute to odor, even though some of them have a relatively low odor threshold concentration, such as propanol, (E)-2-hexenal, and butyl propanoate. Ethanol, the main volatile compound present in the headspace from Conference pears, although making up from 65% to 81% of the total volatile production depending on the sample, did not contribute to the fruit odor pattern, owing to its very high odor threshold concentration.

The major odor contributors changed from 7 to 22 weeks of storage (**Table 5**). After 7 weeks of storage, more than 80% of the total Uo was made up of aldehydes (mainly acetaldehyde and hexanal), while at the end of storage more than 40% of the total Uo was made up by esters (**Figure 4A**,**B**). These changes

**Table 5.** Volatile Compounds of Headspace Conference Pears, Odor Detection Thresholds (OT) from Literature (*24*), and Average Odor Units (Avg Uo) of All the Samples (Total) and Samples after 7, 14, and 22 Weeks of Storage

			avg	l No	
	OT ( <i>24</i> ),	total	7	14	22
	μyky	lolai	1	14	22
nexanal	5	33.6	30.7	43.9	25.3
acetaldehyde	198	15.2	12.6	11.6	21.5
2-methylpropyl acetate	3.9	12.7	7.25	15.0	15.6
ethyl acetate	5	4.60	0.49	6.09	7.08
nexyl acetate	2	4.45	1.01	3.74	8.65
3-methylbutyl	8.6	3.61	0.31	5.86	4.46
2-methylbutanoate					
ethyl butanoate	1	1.41	0.40	1.46	2.35
outanol	500	0.80	0.24	0.56	1.62
outyl acetate	66	0.76	0.21	0.72	1.36
oropanal	9.5	0.33	0.099	0.52	0.35
(E)–2-hexenal	17	0.17	0.14	0.20	0.19
outyl butanoate	100	0.030	0.024	0.035	0.032
methyl acetate	4600	0.021	0.0095	0.019	0.034
ethanol	1000000	0.016	0.0066	0.017	0.024
nexanol	2500	0.0089	0.0068	0.0071	0.013
outyl propanoate	25	0.0064	0.0012	0.0090	0.0087
propyl acetate	670	0.0043	0.0014	0.0058	0.0055
pentyl acetate	670	0.0037	0.00069	0.0034	0.010
2-methylpropanol	7000	0.0025	0.0025	0.0039	0.00089
pentanol	4000	0.00072	0.00008	0.0012	0.00084
oropanol	9000	0.00051	0.00025	0.00055	0.00072
acetone	500000	0.00036	0.00009	0.00073	0.00015
methylethyl ketone	50000	0.00031	0.00025	0.00042	0.00024



**Figure 4.** Odor active compounds (Uo) of control (white bar) and 25 nL L<sup>-1</sup> (grey bar) and 50 nL L<sup>-1</sup> (black bar) 1-MCP treated Conference pears after 7, 14, and 22 weeks of storage in controlled (A) and normal (B) atmospheres. No bar drawn on the *x* axis means that the compound is absent. Compound abbreviations and description of odors: AcALE = acetaldehyde (pungent, fruity), HexALE = hexanal (herbaceous), 2MpropAc = 2-methylpropyl acetate (sharp), EtAc = ethyl acetate (sweet); HexAc = hexyl acetate (fruity); EtBut = ethyl butanoate (fruity, ripe); ButOH = butanol (fruity); ButAc = butyl acetate (fruity); MButMBut = 3-methylbutyl 2-methylbutanoate (sweet, ethereal).

of the odor-active compounds were detected in CA and, anyway, to a greater extent for 50 nL L<sup>-1</sup> dose fruit. With storage, ethyl acetate, 3-methylbutyl 2-methylbutanoate, and ethyl butanoate became detectable in the odor after 14 weeks of storage, while butanol and butyl acetate only after 22 weeks of storage. All the odor contributors were detectable after 22 weeks of storage in NA, independent of the 1-MCP dose (**Figure 4A**), while after 22 weeks of storage in CA in 50 nL L<sup>-1</sup> treated fruits, ethyl acetate, hexyl acetate, ethyl butanoate, butanol, and butyl acetate were present under their odor threshold concentration (**Figure 4B**).

At the informal taste test,  $25 \text{ nL L}^{-1}$  and control Conference pears were juicy, firm, and aromatic and kept their best organoleptic characteristics until 14 weeks of storage, while 50 nL L<sup>-1</sup> treated fruits were still unripe and without flavor. After 22 weeks of storage, 50 nL L<sup>-1</sup> 1-MCP-treated pears ripened with fresh flavor and juicy texture, while control and 25 nL L<sup>-1</sup> treated fruits had poor flavor and texture, being grainy and watery.

## DISCUSSION

The physiological phenomena associated with ripening of European pears, such as Conference cultivar, are softening, change in the peel color from green to yellow, and development of characteristic taste and aroma related to changes in sugars, organic acid contents, and volatile production (25-27). Low

 $O_2$  and high  $CO_2$  atmosphere storage reduces the rates of respiration and ethylene production, as well as delays the onset of climacteric (28, 29).  $CO_2$  concentration has to be below 1 KPa to prevent physiological disorders such as brown heart of Conference pears (1), as well as to avoid the development of off-flavors (29).

The effects of 1-MCP treatments on Conference pears declined with duration of storage, indicating that retreating pears with 1-MCP after 7 and 14 weeks of storage had little additional effect on subsequent ripening.

Ethylene production rate increased with storage time and was 1-MCP dose dependent, being lower in higher 1-MCP dose. These fruits, when stored in CA, kept the effect of 1-MCP treatment longer than the 25 nL L<sup>-1</sup> treated ones. Also the duration of the delay of fruit softening depended on both 1-MCP dose and storage atmosphere. The effect of treatments on fruit texture lasted longer in CA than in NA. The 50 nL L<sup>-1</sup> fruits retained firmness and did not soften to a juicy texture with poststorage ripening if stored in CA for 7 and 14 weeks; afterward, the 50 nL L<sup>-1</sup> fruits softened with a juicy texture as assessed by both percent juice analysis and the informal taste test. These findings confirm our previous results on the interactions between 1-MCP dose and storage atmosphere (*12*). Furthermore it was confirmed that the 50 nL L<sup>-1</sup> dose was effective in keeping Conference pears greener, while the 25 nL  $L^{-1}$  dose, different from previous year results (12), did not prevent fruit from yellowing, being as yellow as the control fruit.

1-MCP treatments did not reduce the development of superficial scald, which was reduced by CA, even if they had an influence on the severity of symptoms, the 50 nL L<sup>-1</sup> dose fruits mainly affected by slight dark scald. Also in our previous researches on this cultivar (*12*), 1-MCP treatments, even at higher doses than those used in this experiment, did not prevent the formation of superficial scald in Conference pears both in CA and NA, independent of the storage time. The higher proportion of fruits affected by slight dark scald found in 50 nL L<sup>-1</sup> treated fruits could be related to the lower amounts of  $\alpha$ -farnesene and conjugated trienes detected and to the higher ratio CT258/CT281. It has been reported that  $\alpha$ -farnesene increases with storage time and decreases when superficial scald appears (*3*, *4*), and in apples, there is greater resistance to scald when there is a high CT258/CT281 ratio (*18*).

The profile of volatile compounds produced by Conference pears after ripening found in the present study was similar to that previously reported (30). The most abundant volatiles found in the headspace were ethanol and acetaldehyde, markers of fermentative paths if produced in high amounts (31). These volatiles were detected in similar amounts in Conference pears at harvest and after storage in CA (2%  $O_2 + 0.7\% CO_2$ ) in previous research (32).

Esters and  $C_3-C_6$  alcohols increased with storage time, while aldehydes and ketones peaked at 14 weeks of storage; the few differences relating to storage atmospheres were mainly linked to acetone (higher in CA) and 2-methylpropyl acetate (higher in NA). Treatments with the 50 nL L<sup>-1</sup> 1-MCP dose greatly influenced the volatile pattern, lowering the productions of acetaldehyde, ethanol,  $C_3-C_6$  alcohols, and esters, while the 25 nL L<sup>-1</sup> dose did not significantly affect volatiles.

The increase in alcohols over the storage period has been detected in pears after storage both in NA and CA (32, 33), and the availability of alcohols may be one of the factors necessary for ester production in climacteric fruits, such as apples and pears (34).

As in other pear cultivars (35, 36), acetate esters are the predominant esters produced by Conference pears, the main one being 2-methylpropyl acetate. Decadienoate esters, the character impact compounds in pear cultivars with Bartlett-like aroma (37, 38), are produced by Conference pears (30) but were not detected in this study, and this may have been due to the use of static headspace without trapping volatiles on a suitable sorbent material.

The impact of 1-MCP treatments on sensory aroma quality of Conference pears differed according to the dose and the storage atmosphere, as was seen by computing the odor units of all the samples. Even though the odor units is an approximation of the sensory impact of single components on the total aroma, because it is based on odor detection threshold concentrations from the literature, it is a valuable tool to understand the impact of a treatment on fruit odor pattern. Regardless of the 1-MCP dose and storage atmosphere, after 7 weeks of storage the predominant odor notes were "herbaceous" of hexanal, "pungent/fruity" of acetaldehyde, and "sharp" of 2-methylpropyl acetate. Afterward, there were different odor patterns, depending on both 1-MCP dose and storage atmosphere. After 14 weeks of storage in NA, for control and 25 nL  $L^{-1}$  fruits, the odor was made up, besides the "herbaceous", "pungent/fruity" and "sharp" of the three main odor-active compounds, of the "sweet" note of ethyl acetate, the "fruity"

note of butyl and hexyl acetate, and the "sweet/ethereal" note of 3-methylbutyl 2-methylbutanoate, along with the "fruity/ripe" note of ethyl butanoate. Only at the end of storage, was there also the "fruity" contribution of butanol. In 50 nL L<sup>-1</sup> 1-MCPtreated pears stored in NA, the contribution of the compounds with "fruity", "sweet", "fruity/ripe" odor notes was either nearly absent in 14 weeks samples (50×2 dose) or very low in  $50\times3$ dose (22 weeks) fruits. The 25×2 and 50×2 nL L<sup>-1</sup> pears stored in CA, compared to control ones, had a prevalence of "herbaceous, "pungent/fruity", and "sweet/ethereal" notes on the "fruity" and "fruity/ripe" ones, which made up almost half of the odor units of control fruits. At the end of storage in CA, in  $25 \times 3$  nL L<sup>-1</sup> and control pears there was a great contribution of the "fruity" and "fruity/ripe" notes, which were not present in 50 nL  $L^{-1}$  fruits. This difference in the odor pattern between 50 nL  $L^{-1}$  fruits and the others could explain the fresh flavor kept by 50 nL L<sup>-1</sup> fruits at the end of CA storage as assessed by the informal taste testing.

In conclusion, the effects of 1-MCP treatment at harvest declined with duration of storage in both atmospheres, indicating that the repetition of the treatment during storage was not effective. As regards firmness and ethylene production, the 25 nL  $L^{-1}$  1-MCP dose was not very different from control; however, the effects of 1-MCP were perceivable on texture (juiciness) and flavor. Control fruit and 25 nL  $L^{-1}$  fruit reached their best sensory quality after 14 weeks of storage; 50 nL  $L^{-1}$ fruit reached the same sensory quality later, keeping a fresh flavor while the quality of control fruit declined, becoming watery or grainy. The fresh flavor in 50 nL  $L^{-1}$  fruit was probably due to a lower amount of volatile compounds responsible for the "ripe pear" aroma. CA prolonged or enhanced the effects of 1-MCP; 1-MCP treatment was not effective in reducing superficial scald but influenced the severity of the symptoms; the low  $\alpha$ -farnesene and the high conjugated trienes contents could indicate a greater oxidation of the cuticle components. 1-MCP cannot substitute for CA but can reinforce the CA effect.

#### LITERATURE CITED

- Bertolini, P.; Bottardi, S.; Dalla Rosa, M.; Folchi, A. Effect of controlled atmosphere storage on the physiological disorders and quality of 'Conference' pears. *Ital. J. Food Sci.* **1997**, *4*, 303– 312.
- (2) Drake, S. G. Elevated carbon dioxide storage of 'Anjou' pears using purge-controlled atmosphere. *HortScience* **1994**, *29*, 299– 301.
- (3) Zoffoli, J. P.; Richardson, D.; Chen, P.; Sugar, D. Spectrophotometric characterization of superficial and senescent scald in pear fruits relative to different stages of maturity. *Acta Hortic.* **1998**, 475, 543–558.
- (4) Lo Scalzo, R.; Eccher Zerbini, P.; Grassi, M. Composition of hexane extracts from 'Conference' pear peel. *Acta Hortic.* 2002, 596, 867–870.
- (5) Sisler, E. C.; Serek, M. Inhibition of ethylene responses in plant at the receptor level: recent developments. *Physiol. Plant.* 1997, 100, 577–582.
- (6) Blankenship, S. M.; Dole, J. M. 1-Methylcyclopropene: a review. Postharvest Biol. Technol. 2003, 28, 1–25.
- (7) Watkins, C. B.; Miller, W. B. A summary of physiological processes or disorders in fruits, vegetables and ornamental products that are delayed or decreased, increased, or unaffected by application of 1-methylcyclopropene (1-MCP). http://www.hort.cornell.edu/department/faculty/watkins/ ethylene/index.htm, 2003.

- (8) Baritelle, A. L.; Hyre, G. M.; Fellman, J. K.; Varith, J. Using 1-MCP to inhibit the influence of ripening on impact properties of pear and apple tissue. *Postharvest Biol. Technol.* 2001, 23, 153–160.
- (9) Trinchero, G. D.; Sozzi, G. O.; Covata, F.; Fraschina, A. A. Inhibition of ethylene action by 1-methylcyclopropene extends postharvest life of 'Bartlett' pears. *Postharvest Biol. Technol.* 2004, *32*, 193–207.
- (10) Argenta, L. C.; Fan, X.; Mattheis, J. P. Influence of 1-methylcyclopropene on ripening, storage life, and volatile production by d'Anjou cv. pear fruit. J. Agric. Food Chem. 2003, 51, 3858– 3864.
- (11) Cambiaghi, P.; Eccher Zerbini, P.; Grassi, M.; Rizzolo, A. Problematiche nel dosaggio di 1-MCP nelle pere. *Atti VII Giornate Scientifiche SOI*, Società Octicola Italiana: Firenze, 2004.
- (12) Eccher Zerbini, P.; Cambiaghi, P.; Grassi, M.; Rizzolo, A. Effect of 1-MCP on the quality of pears during storage. In *Biology* and *Biotechnology of the Plant Hormone Ethylene III*; Vendrell, M., Klee, H., Pech, J. C., Romojaro, F., Eds.; IOS Press: Amsterdam, 2003, pp 402–407.
- (13) Ekman, J. H.; Clayton, M.; Biasi, W. V.; Mitcham, E. J. Interactions between 1-MCP concentration, treatment interval and storage time for 'Bartlett' pears. *Postharvest Biol. Technol.* 2004, *31*, 127–136.
- (14) Hunter, F. E.; Harold, R. W. *The measurement of appearance*; John Wiley and Sons: New York, 1987; p 411.
- (15) Planton, G. Le test amidon des pommes. *Le Point* n.6; CTIFL: Paris, august 1995.
- (16) Eccher Zerbini, P.; Grassi, M.; Grazianetti, S. Operating parameters for instrumental measurement of juiciness in fruits. In Agri-Food Quality II: Quality Management of Fruits and Vegetables; Hägg, M., Ahvenainen, R., Evers, A. M., Tiilikkala, K., Eds.; Special Publication no. 229; The Royal Society of Chemistry: London, 1999, pp 290–293.
- (17) Huelin, F. E.; Coggiola, I. M. Superficial scald, a functional disorder of stored apples: V. Oxidation of α-farnesene and its inhibition by diphenylamine. J. Sci. Food Agric. **1970**, 21, 44– 48.
- (18) Du, Z.; Bramlage, W. J. A modified hypothesis in the role of conjugated trienes in superficial scald development on stored apples. J. Am. Soc. Hortic. Sci. 1993, 118, 807–813.
- (19) Anet, E. F. Superficial scald: a functional disorders of stored apples. IX. Effect of maturity and ventilation. J. Sci. Food Agric. 1972, 23, 763–769.
- (20) Rizzolo, A.; Visai, C. Metodo per il dosaggio del 2,5-norbornadiene e dell'etilene in atmosfere a volumi costanti. Ann. I. V. T. P. A. 1985, 16, 17–24.
- (21) Rizzolo, A.; Polesello, A.; Polesello, S. Use of headspace capillary GC to study the development of volatile compounds in fresh fruits. *High Resolut. Chromatogr.* **1992**, *15*, 472–477.
- (22) Rizzolo, A.; Cocucci, M.; Tagliabue, S.; Polesello, S. Gas chromatographic characterization of a pear aroma with parallel sniffing/FID, sniffing/PID and MS detection. Nineteenth International Symposium on Capillary Chromatography and

Electrophoresis, Wintergreen, Virginia, 19–23 May, 1997. Annali dell'Istituto Sperimentale per la Valorizzazione Tecnologie dei Prodotti Agricoli **1998**, 25, 93.

- (23) Guadagni, D. G.; Buttery, R. G.; Harris, J. Odour intensities of hop oil components. J. Sci. Food Agric. 1966, 17, 142–144.
- (24) Leffingwell, J. C. Flavor-base 98. www.leffingwell.com, 2000.
- (25) Eccher Zerbini, P. The quality of pear fruit. *Acta Hortic.* **2002**, *596*, 805–810.
- (26) Sugar, D. Postharvest physiology and pathology of pears. *Acta Hortic.* **2002**, *596*, 833–838.
- (27) Elgar, F. A.; Watkins, C. B.; Murray, S. H.; Gunson, F. A. Quality of "Beurré Bosc" and "Doyenne du Comice" pears in relation to harvest date and storage period. *Posthavest Biol. Technol.* **1997**, *10*, 29–37.
- (28) Richardson, D. G.; Kupferman, E. Controlled atmosphere storage of pears. In *Proceeding of the Seventh International Controlled Atmosphere Research Conference*; Mitchum, E. J., Ed.; Univeristy of California: Davis, CA, 1997; Vol. 2, pp 31–36.
- (29) Kader, A. A. Mode of action of oxygen and carbon dioxide on postharvest physiology of "Bartlett" pears. *Acta Hortic.* 1989, 258, 161–166.
- (30) Eccher Zerbini, P.; Balzarotti, R.; Rizzolo, A.; Spada, G. L. Effect of picking date on quality and sensory characteristics of pears after storage and ripening. *Acta Hortic.* **1993**, *326*, 291–298.
- (31) Perata, P.; Alpi, A. Plant responses to anaerobiosis. *Plant Sci.* 1993, 93, 1–17.
- (32) Eccher Zerbini, P.; Grassi, M.; Pianezzola, A.; Rizzolo, A.; De Colellis, G.; Brambilla, A. Metabolismo fermentativo e imbrunimento interno di pere Conference conservate in atmosfera controllata. *Atti V Giornate Scientufuche SOI*; Società Octicola Italiana: Firenze, 2000; Vol. 2, pp 503–504.
- (33) Chervin, C.; Truett, J. K., Speirs, J. Alcohol dehydrogenase expression and alcohol production during pear ripening. J. Am. Soc. Hortic. Sci. 1999, 124, 71–75.
- (34) Paillard, N. M. M. The flavour of apples, pears and quinces. In Food Flavour. Part C. The flavour of fruits; Morton, I. D., MacLoad, A. J., Eds.; Elsevier Science Publishing B. V.: The Netherlands, 1990; pp 1–41.
- (35) Shiota, H. Change in the volatile composition of La France pear during maturation. J. Sci. Food Agric. 1990, 52, 421–429.
- (36) Suwanagul, A.; Richardson, D. G. Identification of headspace volatile compounds from different pear (*Pyrus communis* L.) varieties. *Acta Hortic.* **1998**, 475, 605–623.
- (37) Russell, L. F.; Quamme, H. A.; Gray, J. I. Qualitative aspects of pear flavor. J. Food Sci. 1981, 46, 1152–1158.
- (38) Quamme, H. A. Decadienoate ester concentrations in pear cultivars and seedlings with Bartlett-like aroma. *HortScience* **1984**, *19*, 822–824.

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