AGRICULTURAL AND FOOD CHEMISTRY

Influence of 1-methylcyclopropene on Ripening, Storage Life, and Volatile Production by d'Anjou cv. Pear Fruit

LUIZ C. ARGENTA,[†] XUETONG FAN,[‡] AND JAMES P. MATTHEIS*

USDA, ARS Tree Fruit Research Laboratory, 1104 N. Western Avenue, Wenatchee, Washington 98801

d'Anjou cv. pear fruit (*Pyrus communis* L.) exposed at harvest to 0, 0.42, 4.2, or 42 μ mol m⁻³ 1-methylcyclopropene (1-MCP) for 12 h at 20 °C were stored at 1 °C for up to 8 months. After storage, half of the fruit was continuously exposed to ethylene (0.45 or 4–18 mmol m⁻³) for 7 days at 20 °C. All fruit treated with 1-MCP had lower respiration and ethylene production compared to untreated controls. Fruit quality changes were delayed following 1-MCP treatment, as was development of superficial scald and peel yellowing. The duration of 1-MCP-induced responses was dependent on 1-MCP treatment concentration. When 1-MCP-treated fruit began to ripen, softening and production of volatile compounds proceeded similar to that of untreated fruit. Post-storage ethylene exposure did not consistently stimulate ripening of fruit previously treated with 1-MCP. Efficacy of ethylene treatment depended on 1-MCP concentration and storage duration.

INTRODUCTION

A threshold level of internal ethylene controls initiation of ripening-related physiological process of climacteric fruits, including European pears, *Pyrus communis* L. (1). A postharvest cold treatment is required to induce endogenous ethylene production and subsequent ripening of green pears (2, 3). d'Anjou cv.fruit harvested at optimum maturity require 60 days of postharvest chilling to trigger ethylene production and uniform ripening (4). Alternatively, autocatalytic ethylene production and full ripening of under-chilled d'Anjou pears can be promoted by exposure to exogenous ethylene (5).

Inhibition of ethylene synthesis slows down the ripening process and enhances storage life of pear fruit (6). Inhibition of ethylene action in pear fruit with 1-methylcyclopropene reduces ethylene production (7, 8) and the chilling-induced accumulation of ACC synthase and ACC oxidase mRNAs (9). Inhibition of ethylene action with 1-MCP can also delay or prevent development of physiological disorders such as superficial scald and core flush, as well as delay ripening in other climacteric fruit (10-14).

d'Anjou pears stored in a controlled atmosphere (CA) have reduced rates of ripening and development of physiological disorders (15). CA storage slows fruit ripening in part by inhibiting ethylene production (16, 17). Operation of CA storage requires precise control of room gas composition to prevent CO_2/O_2 injury and preserve optimum quality (18, 19), but even under optimum CA conditions, d'Anjou pears can develop physiological disorders such as superficial scald and brown core (20, 21).

The ethylene action inhibitor 1-methylcyclopropene (1-MCP) (22, 23) inhibits ethylene-dependent ripening processes in pear fruit including softening (7, 24) and production of volatiles that contribute to aroma of climacteric fruit including banana (25), apple (26) and apricot (27). Whether or not 1-MCP-treated fruit recover the capacity to produce a volatile profile typical of normal ripening when fruit ethylene production resumes has not been established.

Because 1-MCP binding to ethylene receptors is irreversible (23), it is unclear whether ripening of 1-MCP-treated pear fruit is promoted by exogenous ethylene exposure. 1-MCP-treated banana fruit continuously exposed to propylene initiate ethylene production and ripening earlier than 1-MCP-treated fruit exposed to propylene-free air (25). After storage over a range of temperatures and atmospheres, 1-MCP-treated apple fruit recover the ability to ripen (13, 28, 29), which could be related to formation of new ethylene receptors (30).

The objective of this study was to determine if 1-MCP treatment induces responses in d'Anjou pears similar to other climacteric fruit, including eventual recovery of typical ripening after storage. The impact of 1-MCP on aroma volatile profile and the efficacy of reversing 1-MCP effects by post-storage ethylene exposure were also evaluated.

MATERIALS AND METHODS

^{*} Corresponding author. Tel.: 509-664-2280. Fax: 509-664-2287. E-mail address: mattheis@tfrl.ars.usda.gov.

[†] Current addres: EPAGRI, Estação Experimental, 89500-000, Caçador, SC, Brazil.

[‡] Current address: USDA, ARS ERRC, 600 E. Mermaid Lane, Wyndmoor, PA 19038.

d'Anjou pears were harvested from commercial orchards in north central Washington state at commercial maturity in September, 1998. One day after harvest, fruit were treated with 0, 0.42, 4.2, or 42 μ mol m⁻³ 1-MCP at 20 °C for 18 h in a 230-L steel container with a steel

lid sealed by a water moat. 1-MCP was applied as a gas generated by mixing EthylBloc powder and buffer solution (BioTechnology for Horticulture Inc., Burr Ridge, IL) in a 150-mL flask. 1-MCP gas was pumped from the flask into the steel container for 20 min via a closed loop. Following treatment, fruit were stored at 1 °C for 2, 4, 6, or 8 months. In 1999, d'Anjou pears were treated the day after harvest with 42 μ mol m⁻³ 1-MCP at 20 °C for 20 h in a 100-m³ CA storage room in Wenatchee, WA. A closed system was used, whereby 1-MCP was generated outside the treatment room and pumped into the room via Tygon tubing. Control fruit were held in a similar room at the same facility. After treatment, samples of control and 1-MCP-treated fruit were transported to the USDA laboratory and stored in air at 1 °C. Concentrations of 1-MCP in the treatment chambers were determined as previously described (*31*).

Responses of 1-MCP-Treated Fruit to Ethylene. d'Anjou fruit from the 1998 harvest were exposed to ethylene for 7 days at 20°C following 2, 4, 6, or 8 months cold storage. Fruit from each treatment were divided into six groups of 6 or 7 fruit (n = 40 fruits per treatment). Each group was placed into a 10-L plexiglass chamber, through which compressed air or air supplemented with 0.45 mmol m⁻³ ethylene flowed continuously at 100 mL min⁻¹. In 1999, d'Anjou pears treated the day after harvest with 0 (control) or 42 μ mol m⁻³ 1-MCP were removed from cold storage after 3, 8, 16, or 24 weeks and exposed to 4-18 mmol m⁻³ ethylene during 7 days at 20 °C, as previously described (5). Control and 1-MCP-treated fruit (n = 40) were divided into six groups of 6 or 7 fruit. Each group was placed into a Ziploc freezer bag (3.8 L) perforated with eight 3-mm holes. A 30-mL syringe filled with pure ethylene was placed into three bags of each treatment and then the bags were sealed. The syringes were fitted with 23-gauge needles cut to 1 cm in length, to allow gradual ethylene release into the bag headspace. Fruit were held in bags at 20 °C for 7 d. Ethylene released from syringes accumulated to 18 mmol m⁻³ 1 day after the bags were sealed and remained greater than 4 mmol m⁻³ during the following 6 days at 20 °C.

Fruit Quality Analysis. Fruit quality and volatile production were evaluated after 1 and 7 days at 20 °C after removal from cold storage. Flesh firmness was measured with a penetrometer fitted with an 8-mm tip (EPT-1; Lake City Technical Products, Kelowna, B. C., Canada). Peel color was measured with a colorimeter (Minolta CR-200, Japan), using CIE illuminant C and an 8-mm diameter aperture. Color values a^* and b^* were converted to hue angle (h°) (32). Measurement of titratable acidity (TA), soluble solids content (SSC), ethylene production, and respiration were as previously described (33). Analysis of other volatile compounds was conducted using dynamic headspace sampling. There were four replicate samples of four to five intact fruit (approximately 1 kg). Purified compressed air flowed at 6 L h⁻¹ through the 4-L jars in which pear fruit were enclosed during sampling. Volatile compounds in the outflow were adsorbed onto 50 mg of 30-50 mesh Tenax TA (Alltech Associates, Deerfield, IL) packed in glass tubing (17.5 cm \times 0.4 cm i.d). Volatile compounds on the Tenax traps were desorbed at 250 °C for 3 min, using a Tekmar 6016 aero trap desorber (Tekmar Co., Cincinnati, OH). After the desorbed sample compounds were condensed at -120 °C, the cryofocusing module was flash heated to 250 °C under a stream of He carrier gas, which carried the analytes into a Hewlett-Packard 5890A/5971A GC-MSD equipped with a DB-Wax column (J&W Scientific, 60 m \times 0.25 mm i.d., 0.25 μ m film thickness). Conditions for chromatography were as follows: initial oven temperature 35 °C held for 5 min, increased to 50 °C at 2 °C min⁻¹, increased to 200 °C at 5 °C min-1, and held for 5 min. Linear velocity of the He carrier gas was 30 cm s⁻¹. Mass spectra were obtained by electron ionization at 70 eV. Transfer line and ion source temperatures were 280 and 180 °C, respectively. Compound identification was made by comparison of spectra of sample compounds with those contained in the Wiley-NBS library and by comparing retention indices of sample compounds and standards. Quantification was performed using selected ion monitoring for base peaks, and quantitative values were calculated using response factors generated with standards.

Superficial scald was visually assessed using a scale from 1, no scald to 7, dark scald and >60 % of the fruit surface affected (11). Core browning, senescent scald, and decay were visually assessed as clear (1) or affected (2).



Figure 1. Ethylene production (A) and respiration rates (B) of d'Anjou pear fruit at harvest and after 2 to 8 months of storage at 1 °C plus 7 days at 20 °C. Fruit were exposed the day of harvest to 0.42, 4.2, and 42 μ mol m⁻³ 1-MCP. Numbers at the top of A and vertical bars in B represent least significant difference (LSD: $\alpha = 0.05$).

Experimental Design and Data Analysis. The experiments were conducted using a completely randomized design, with 20 fruit per storage period per treatment for each quality attribute measured, except 4 replicates of 4 or 5 fruit were used for analysis of respiration, ethylene and volatile production. Data were subjected to ANOVA using SAS (SAS Institute, Raleigh, NC), and means between treatments were separated using Fisher's least significant difference (LSD), $\alpha = 0.05$.

RESULTS

Fruit Response to 1-MCP Concentration. Fruit firmness at harvest was 68 ± 2.8 N (SE) and 70.0 ± 1.7 N in 1998 and 1999, respectively. 1-MCP treatment delayed the increase in ethylene production (Figure 1), and the duration of 1-MCP effects increased with treatment concentration. However, there were no treatment differences in maximum ethylene production. Respiration rates of 1-MCP-treated fruit were lower than controls through 8 months of storage plus 7 days at 20 °C.

All 1-MCP treatments delayed softening (Table 1). The duration of the 1-MCP-induced delay of fruit softening was dependent on treatment concentration and duration of storage and ripening at 20 °C after removal from storage. Firmness of all 1-MCP-treated fruit was higher compared to controls after 2 or 4 months of storage plus 7 days of ripening. The largest differences in firmness between control and 1-MCP-treated fruit were detected after 4 and 6 months of storage plus 1 day at 20 °C and 2 and 4 months of storage plus 7 days at 20 °C. 1-MCP treatment concentration effects were evident after 6 and 8 months of storage plus 1 day at 20 °C and 2, 6, or 8 months of storage plus 7 days at 20 °C. Fruit treated with 0.42 μ mol m⁻³ 1-MCP were softer than fruit treated with 4.2 or 42 μ mol m⁻³. After 6 and 8 months of storage, firmness of d'Anjou fruit treated at 0.42 μ mol m⁻³ 1-MCP was similar to controls and less than that of the higher 1-MCP concentrations 7 days after removal from storage.

Titratable acidity of 1-MCP-treated fruit was higher compared to controls through 8 months of storage (**Table 1**). All 1-MCPtreated fruit were greener (higher h°) than controls after 2 and 4 months of storage, and the difference was greatest after 7 days of ripening at 20 °C. After 6 months, fruit treated with

Table 1. Firmness, Titratable Acidity (TA) and Peel Color (Hue) of d'Anjou Pears after Exposure to 1-MCP and/or Ethylene^a

		1 day		7 days									
				firmne	ess (N)		TA	(%)		hue	e (°)		
1-MCP (μ mol m ⁻³)	firmness (N)	TA (%)	hue (°)	$-C_2H_4$	$+C_2H_4$		$-C_2H_4$	$+C_2H_4$		$-C_2H_4$	$+C_2H_4$		
					2 months								
0	65.1	0.24	112.4	19.2	19.0	NS ^b	0.23	0.23	NS	107.5	106.2	*	
0.42	68.6	0.31	113.3	60.8	57.7	*	0.26	0.23	*	111.8	111.5	NS	
4.2	66.6	0.27	114.4	64.2	61.3	*	0.27	0.26	NS	112.0	111.6	NS	
42	72.2	0.27	113.9	71.9	72.1	NS	0.31	0.31	NS	113.2	112.5	NS	
LSD _{0.05}	2.4	0.01	0.8	2.7	3.1		0.01	0.01		1.3	1.0		
					4 months	5							
0	32.0	0.21	107.0	17.5	17.9	NS	0.20	0.19	*	97.3	96.7	NS	
0.42	63.7	0.25	112.0	50.7	41.8	*	0.22	0.23	NS	110.7	107.8	*	
4.2	65.6	0.25	112.6	66.8	62.5	NS	0.24	0.25	NS	111.9	110.2	NS	
42	62.5	0.25	112.0	51.5	56.8	NS	0.26	0.27	NS	111.3	110.0	NS	
LSD _{0.05}	3.1	0.01	1.1	5.6	4.9		0.01	0.02		1.3	1.2		
					6 month	5							
0	19.1	0.16	97.7	18.1	19.2	NS	0.17	0.15	*	92.6	92.9	NS	
0.42	45.4	0.23	106.2	20.0	20.2	NS	0.19	0.17	*	94.8	94.2	NS	
4.2	66.4	0.23	108.1	28.4	27.1	NS	0.22	0.21	NS	103.8	100.5	*	
42	61.0	0.22	109.8	25.3	27.3	NS	0.20	0.21	NS	101.9	101.6	NS	
LSD _{0.05}	5.6	0.01	1.8	3.0	3.3		0.02	0.03		2.1	2.6		
					8 months	8							
0	18.0	0.14	93.7	16.3	16.3	NS	0.13	0.14	NS	92.1	91.8	NS	
0.42	19.8	0.19	96.2	18.7	17.1	*	0.17	0.15	*	94.2	94.0	NS	
4.2	31.2	0.20	101.6	23.8	19.6	*	0.19	0.18	NS	96.2	94.7	NS	
42	27.7	0.19	100.8	23.5	25.7	NS	0.18	0.19	NS	94.4	95.1	NS	
LSD _{0.05}	4.8	0.01	2.3	3.0	2.7		0.01	0.02		2.1	2.3		

^a Pears were exposed to 1-MCP for 18 h at 20 °C and stored at 1°C for 2–8 months, followed by 1 or 7 days at 20 °C. Fruit were exposed to air ($-C_2H_4$) or air plus 0.45 mmol m⁻³ ethylene ($+C_2H_4$) during the 7 days at 20 °C. Values are means, n=20. ^b Ethylene exposure: NS = nonsignificant, * = significant at $\alpha = 0.05$.

 Table 2. Severity of Physiological Disorders and Decay after 6 and 8

 Months of Storage of d'Anjou Pears^a

6	months		8 months							
1-MCP (µmol m ⁻³)	scald (1–7)	decay (1–2)	scald (1–7)	core browning (1–2)	senescent scald (1–2)	decay (1–2)				
0	5.2	1.4	5.7	1.2	1.2	1.5				
0.42 4.2	1.0	1.1	2.3 1.1	1.1	1.2	1.5				
42 LSD _{0.05}	1.0 0.38	1.0 0.14	1.6 0.92	1.0 0.13	1.0 0.17	1.2 0.22				

^a Fruit were exposed the day after harvest to 1-MCP for 18 h at 20 °C and stored at 1°C for 2 to 8 months, followed by 7 days at 20 °C. Superficial scald (scald) was visually assessed using a scale from 1 = no scald to 7 = dark scald and >60% of the fruit surface affected. Core browning, senescent scald, and decay were visually assessed as clear (1) or affected (2). Values are means, n = 20.

0.42 μ mol m⁻³ 1-MCP were greener than controls but yellower than fruit treated at 4.2 or 42 μ mol m⁻³. After 8 months of storage, color differences due to 1-MCP treatment were detectable, however, all treated fruit had undergone considerable development of yellow color. After 6 months of storage, all 1-MCP treatments prevented superficial scald and reduced or prevented decay compared to untreated controls (**Table 2**). After 8 months, reduction of superficial scald, senescent scald, core browning, and decay by 1-MCP treatment was concentration dependent. Rates of physiological disorders were lowest for fruit treated at 4.2 or 42 μ mol m⁻³ 1-MCP.

A total of 44 volatile compounds, including alcohols, aldehydes, esters, acetic acid, 1 ketone, and 1 hydrocarbon were detected in headspace samples collected from d'Anjou pears (**Tables 3–5**, and **Figure 2**). Esters and alcohols were quantitatively the most abundant, with the major volatile compounds being acetate esters (ethyl, propyl, butyl, pentyl, and hexyl

acetate), butyl and hexyl hexanoate, hexyl 2-methylbutanoate, ethanol, butanol, decanal, and α -farnesene.

Production rates of volatile compounds were dependent on storage duration and 1-MCP treatment. Ester production, particularly that of acetate and propanoate esters as well as methyl, ethyl, and hexyl butanoate, by control fruit peaked after 4 months of storage. However, production of hexyl 2-methylbutanoate, other butanoate esters, ethyl, propyl, butyl, and hexyl hexanoate by control fruit were highest after 2 months of storage. Alcohol production, particularly ethanol, by control fruit increased over storage period. However, production of straight chain C_3 – C_6 alcohols increased between 2 and 4 months of storage plus 7 days at 20 °C then remained similar or decreased. Control fruit ester production was greater than alcohol production following 2 or 4 months of storage but lower after 8 months of storage.

1-MCP treatment delayed the increase in ester and alcohol production. Highest ester and alcohol production by control and 1-MCP-treated fruit occurred after 4 and 8 months, respectively (**Tables 3** and **4**). Maximum production of ethyl, butyl, and hexyl propanoate, hexyl butanoate, and C_4-C_6 alcohols by 1-MCP-treated fruit and controls were similar. In contrast, maximum production rates of branched chain butanoate esters, ethyl, propyl, butyl, and hexyl hexanoate by 1-MCP-treated fruit were lower compared to controls.

Aldehyde production by control and 1-MCP-treated fruit was less than 75 and 25 η mol kg⁻¹ h⁻¹, respectively, through 6 months of storage plus 7 days at 20 °C. After 8 months, aldehyde production increased to approximately 250 and 110 η mol kg⁻¹ h⁻¹ in control and 1-MCP-treated fruit, respectively. The effect of storage duration and 1-MCP treatment on production of individual aldehydes was similar, except that maximum production of benzaldehyde and butanal by control fruit occurred after 2 and 4 months of storage, respectively. 1-MCP treatment also

Table 3. Ester Production by d'Anjou Pear Fruit After Storage at 1 °C Plus 7 Days at 20 °C^a

treatment months		cor	itrol			1-1	MCP			1-MCI	$P + C_2H_4$		
in storage	2	4	6	8	2	4	6	8	2	4	6	8	LSD^b
η mol kg ⁻¹ h ⁻¹													
ethyl acetate	30	175	97	68	0.8	2.9	20	137	1.2	1.8	21	188	37
propyl acetate	9.2	42	19	6.6	0.1	0.3	10	24	0.2	0.6	9.1	31	5.4
butyl acetate	126	326	134	50	1.0	3.1	91	273	1.9	5.5	102	427	37
pentyl acetate	13	32	11	6.8	0.1	0.4	8.5	19	0.2	0.5	10	28	3.9
hexyl acetate	67	167	33	12	3.4	2.2	30	124	3.5	3.1	48	146	22
2-methylpropyl acetate	1.0	2.8	1.4	0.7	NDc	0.1	0.8	2.1	ND	0.1	0.8	2.3	0.4
2-methylbutyl acetate	3.8	5.8	1.7	1.0	0.4	0.5	1.8	5.0	0.6	0.6	2.1	5.7	0.9
ethyl propanoate	0.3	0.5	0.5	0.3	ND	ND	0.1	0.6	ND	0.1	0.1	ND	0.3
propyl propanoate	0.2	0.2	0.2	0.1	ND	ND	0.1	0.2	ND	ND	0.1	ND	0.1
butyl propanoate	0.9	1.6	1.0	1.0	0.1	0.4	1.3	1.4	0.6	0.8	1.3	1.1	0.3
hexyl propanoate	1.5	1.9	1.0	1.0	0.6	0.5	0.9	2.1	0.9	0.8	1.3	1.8	0.4
methyl butanoate	0.5	1.0	0.7	0.3	ND	0.1	0.1	0.4	ND	0.1	0.1	0.4	0.3
ethyl butanoate	1.3	2.1	1.7	1.5	0.2	0.2	0.2	1.5	0.2	0.1	0.4	1.6	0.6
hexyl butanoate	13	17	8.2	7.5	1.8	6.3	6.7	17	12	12	21	15	4.1
butyl butanoate	11	9.6	5.4	4.6	0.3	2.1	6.6	8.3	3.9	7.7	12	7.6	2.1
pentyl butanoate	2.4	2.1	1.4	2.3	0.2	1.2	1.6	2.1	1.7	2.5	3.4	1.6	0.7
ethyl 2-methylbutanoate	0.5	0.1	0.1	0.1	ND	0.1	ND	0.1	ND	0.1	ND	ND	0.3
butyl 2-methylbutanoate	1.7	0.8	0.1	0.2	0.3	0.2	0.1	0.2	0.3	0.1	0.1	0.2	0.2
2-methylbutyl-2-methylbutanoate	0.6	0.2	ND	ND	ND	0.1	ND	ND	ND	ND	ND	ND	0.1
hexyl 2-methylbutanoate	23	9.0	1.9	2.5	3.7	4.3	1.4	4.0	4.2	4.4	3.9	4.2	2.9
ethyl hexanoate	7.5	2.8	1.4	1.1	2.0	ND	0.3	1.1	1.8	0.1	0.6	1.1	2.3
propyl hexanoate	1.3	1.1	0.5	0.3	0.1	0.1	0.4	0.4	0.2	0.4	0.8	0.3	0.2
butyl hexanoate	30	23	11	5.9	2.6	5.5	13	13	9.5	20	38	11	6.2
hexyl hexanoate	22	22	7.5	6.0	2.0	6.1	6.8	10	10	16	28	11	9.9
ethyl octanoate	7.0	2.4	0.6	0.2	1.2	ND	0.5	1.0	1.4	ND	0.8	1.1	2.1
total esters	376	848	340	181	21	37	202	648	54	77	306	886	140

^{*a*} Fruit were exposed to 42 μ mol m⁻³ 1-MCP the day after harvest for 18 h at 20 °C. Exposure to ethylene (0.45 mmol m⁻³) was for 7 days at 20 °C, following removal from cold storage. ^{*b*} Fisher's least significant difference (LSD) for significant treatment × month interaction (α = 0.05). ^c ND = not detected.

Table 4. Alcohol Production by d'Anjou Pear Fruit after Storage at 1 °C Plus 7 Days at 20 °C^a

treatment		CO		1-M	СР		$1-MCP + C_2H_4$						
months in storage	2	4	6	8	2	4	6	8	2	4	6	8	LSD ^b
η mol kg ⁻¹ h ⁻¹		00/		045		40		(07				70/	004
ethanol	84	296	4/4	915	1.6	43	5.7	687	3.3	6.5	39	/86	294
1-propanol	15	40	34	39	0.9	12	3.2	29	1.7	7.1	10	45	7.6
2-methyl-1-propanol	16	15	14	16	1.4	5.5	0.9	14	0.8	1.0	4.9	12	5.9
1-butanol	43	94	74	77	0.7	42	3.9	95	2.4	8.1	40	112	19
2-methyl-1-butanol	5.0	8.1	4.8	8.1	0.3	4.2	1.0	10	0.5	1.8	3.9	9.6	1.9
1-pentanol	0.8	2.0	1.4	2.6	ND ^c	0.8	0.1	2.0	ND	0.3	0.8	2.3	0.7
1-hexanol	12	21	9.1	8.4	0.4	7.6	1.3	24	1.3	3.1	11	34	4.9
total alcohols	176	477	611	1066	5.3	116	16	862	10	28	110	1001	340

^{*a*} Fruit were exposed to 42 μ mol m⁻³ 1-MCP the day after harvest for 18 h at 20 °C. Exposure to ethylene (0.45 mmol m⁻³) was for 7 days at 20 °C, following storage. ^{*b*} Fisher's least significant difference (LSD) for significant treatment × month interaction ($\alpha = 0.05$). ^{*c*} ND = not detected.

reduced acetic acid production from 2 to 6 months of storage. However, there was no effect of 1-MCP treatment on maximum acetic acid production after 8 months of storage.

Higher amounts of the sesquiterpene hydrocarbon α -farnesene were detected 1 day compared to 7 days after removal from cold storage, regardless of storage duration or 1-MCP treatment (**Figure 2**). Production of α -farnesene in control fruit decreased after 4 months of storage but increased in 1-MCP-treated fruit over the 8 month storage period. Control fruit emitted α -farnesene at higher rates than did 1-MCP-treated fruit after 1 day of ripening following 2 and 4 months but at lower rates following 6 and 8 months of storage. Emanation of α -farnesene in 1-MCP-treated fruit remained lower than that in control fruit after 7 days of ripening following 2 to 6 months of storage. Similarly, the production of 6-methyl-5-hepten-2-one after 2 and 4 months of storage was reduced by 1-MCP treatment.

Responses of 1-MCP-Treated Fruit to Ethylene. Ethylene treatment at 0.45 mmol m⁻³ after storage accelerated ripening of fruit treated at 0.42 or 4.2 μ mol m⁻³ 1-MCP and stored for

2, 4, or 8 months (**Table 1**). While exposure to ethylene enhanced softening, yellowing and loss of TA, effects of 1-MCP treatment were not completely negated as 1-MCP-treated fruit exposed to ethylene remained significantly firmer and greener than control fruit. Changes in firmness, TA, and peel color during 7 days at 20 °C were not enhanced by exposure to 0.45 mmol m⁻³ (**Table 1**) or 4–18 mmol m⁻³ (data not presented) ethylene for fruit treated with 42 μ mol m⁻³ 1-MCP.

Effects of exogenous ethylene on volatile production in fruit treated with 42 μ mol m⁻³ 1-MCP were compound specific and dependent on storage duration. Ethylene treatment during post-storage ripening stimulated production of straight chain acetate esters, hexyl propanoate, ethyl butanoate, propanol, hexanol, and all aldehydes after 8 months of storage (**Tables 3–5**). Post-storage exposure of 1-MCP-treated fruit to ethylene also stimulated production of butyl, pentyl, and hexyl butanoate and butyl and hexyl hexanoate after 2, 4, or 6 months of storage (**Table 3**), but had no significant effect on branched chain esters, ethyl, propyl, and butyl propanoate, methyl butanoate, ethyl

Table 5. Aldehyde and Acetic Acid Production by d'Anjou Pear Fruit after Storage at 1 °C Plus 7 Days at 20 °C^a

	control					1-1	ИСР		$1-MCP + C_2H_4$				
treatment months in storage	2	4	6	8	2	4	6	8	2	4	6	8	LSD ^b
η mol kg ⁻¹ h ⁻¹													
butanal	2.3	12	7.4	4.6	0.2	0.4	2.1	8.3	0.3	0.5	2.2	13	2.1
pentanal	0.8	1.0	0.9	2.4	0.2	0.3	0.2	1.2	0.2	0.2	0.2	3.0	0.5
hexanal	2.9	2.1	3.5	11	0.9	0.8	0.9	6.2	0.8	0.8	1.1	10	2.2
heptanal	2.4	1.8	1.7	7.2	0.5	0.8	0.4	2.8	0.3	0.6	0.5	8.2	1.8
octanal	5.2	9.2	12	36	1.3	2.1	1.3	16	0.4	2.3	1.7	30	12
nonanal	10	12	6.4	51	2.6	5.6	1.7	20	1.0	4.8	2.8	60	15
decanal	22	29	14	131	6.3	13	3.6	55	1.6	17	5.8	154	49
benzaldehyde	10	1.6	0.8	5.2	0.4	0.5	0.2	2.1	0.3	0.6	0.2	6.1	4.1
2-furancarboxaldehyde	0.3	0.5	1.7	2.2	0.1	0.2	0.1	1.1	ND ^c	0.1	0.1	3.1	1.7
total aldehydes	56	70	49	251	13	24	10	113	4.9	27	15	288	89
acetic acid	13	18	7.0	17	0.8	4.0	1.6	17	0.6	2.5	1.4	45	6.4

^{*a*} Fruit were exposed to 42 μ mol m⁻³ 1-MCP the day after harvest for 18 h at 20 °C. Exposure to ethylene (0.45 mmol m⁻³) was for 7 days at 20 °C, following removal from storage. ^{*b*} Fisher's least significant difference (LSD) for significant treatment × month interaction ($\alpha = 0.05$). ^{*c*} ND = not detected.



Figure 2. α -Farnesene (A) and 6-methyl-5-hepten-2-one (B) production by d'Anjou pear fruit after 2 to 8 months of storage at 1 °C plus 1 or 7 days at 20 °C. Fruit were exposed the day after harvest to 42 μ mol m⁻³ 1-MCP for 18 h at 20 °C. Vertical bars represent least significant difference (LSD: $\alpha = 0.05$).

hexanoate, and ethyl octanoate, regardless of storage duration. Post-storage treatment with ethylene did not consistently impact volatile production in control fruit (data not shown).

DISCUSSION

Ripening of European pears is characterized by softening, a change in peel color from green to yellow, and development of characteristic taste and aroma related to changes in sugar, organic acid content, and volatile production (*16*, *19*, *34*, *35*). Pear fruit stored under low O_2 and high CO₂ exhibit reduced rates of respiration and ethylene production and a delay in the onset of the climacteric (*16*, *36*, *37*). It is necessary to maintain CO₂ concentration below 1 kPa to prevent physiological disorders such as core browning in d'Anjou pears (*18*, *19*). Offflavors can also develop in pear fruit if exposed to excessively low O_2 and/or high CO₂ concentrations (*16*).

d'Anjou pears treated with 1-MCP also have an extended preclimacteric period with low ethylene production and respiration rates. Fruit ripening is delayed after 1-MCP treatment and treated fruit retain firmness, titratable acidity, and green peel color longer than control fruit, while maintaining the capacity to ripen after long-term storage in air. Additional effects of 1-MCP treatment include reduced development of superficial and senescent scald, core browning, and decay. Development of scald and decay during pear ripening is the first indication of storage life termination (*38*). Reduced development of superficial scald on d'Anjou pears treated with 1-MCP is consistent with results from apple fruit, where reduced production of α -farnesene and 6-methyl-5-hepten-2-one accompanied reduced scald development (*11*–*13*).

The magnitude of responses induced by 1-MCP varied with treatment concentration. Storage life was extended up to 8 months when 1-MCP was applied at 4.2 or 42 μ mol m⁻³ and up to 6 months when applied at 0.42 μ mol m⁻³. 1-MCP treatments at 4.2 or 42 μ mol m⁻³ resulted in similar retention of firmness, TA, and color, indicating the maximum fruit response to 1-MCP was attained between these concentrations. A dose response of 1-MCP for delaying ethylene production was also evident. Fruit treated with 4.2 or 42 μ mol m⁻³ 1-MCP began to produce ethylene 2 and 4 months later than controls, respectively, and fruit treated with 0.42 μ mol m⁻³ had ethylene production lower than controls at 2 and 4 months after treatment.

The profile of volatile compounds produced by ripened d'Anjou pears in the present study was similar to that previously identified (35). Esters are the most abundant volatiles produced by ripening European pears (35, 39, 40). In the present study, esters were the most abundant volatiles produced by control fruit after 2 or 4 months, while alcohols were the most abundant volatiles after 6 or 8 months.

As in other cultivars such as La France (40), Bartlett and Packham's Triumph (35), acetate esters, butyl and hexyl hexanoate are the predominant esters produced by d'Anjou pears. Decadienoate esters that are character impact compounds in pear cultivars with Bartlett-like aroma are produced by d'Anjou pears (35) but were not detected in this study. The lack of detection of decadienoate esters may have been due to the use of Tenax TA as the solid sorbent material in volatile traps. Using standards, we observed decadienoates do not efficiently release from the Tenax traps under the analytical conditions used in this study. Although ethyl 2-methylbutanoate was detected in volatile samples in this study, the chromatographic system used for analysis was not capable of providing information regarding its enatomeric identity identified. Production rates of ethyl acetate, alcohols, and aldehydes by ripened d'Anjou pears were higher in the present study than previously reported. Higher total alcohol production after long-term storage reflected, in part, the increase in ethanol production over the storage period. A considerable increase in ethanol production by pears has also been detected during fruit ripening following

air or CA storage (41). Higher production of alcohols relative to esters by d'Anjou pears stored for 6 or 8 months is in agreement with the suggestion that availability of alcohols may not be the only factor limiting ester production by climacteric fruit (26).

As a consequence of the 1-MCP-induced inhibition of ethylene action, the emanation of esters, alcohols, and aldehydes was also reduced. CA storage of pear fruit or treatment with the ethylene synthesis inhibitor aminoethyoxyvinylglycine also reduces production of volatiles (6, 42, 43). Ethylene treatment earlier in the storage period did not result in enhanced volatile production, indicating that reduced volatile synthesis is a result of inhibition of ethylene action but not the absence of exposure to ethylene. In apples, the synthesis of most ripening-related volatiles requires continuous ethylene action and a high rate of ethylene production (44).

Volatile production by d'Anjou pears treated with1-MCP resumed when fruit started producing ethylene. The increase in volatile production by d'Anjou pear fruit was delayed by 4 to 6 months when treated with 1-MCP at 42 μ mol m⁻³. As previously reported for Fuji cv. apples (26), the production of individual alcohols and esters were differentially inhibited by 1-MCP in d'Anjou pears. For example, production of branched chain butanoate and hexanoate esters by d'Anjou pears was reduced more than acetate esters and alcohols following 1-MCP treatment. The amounts of alcohols, many straight chain esters including ethyl, butyl, and hexyl acetate and the branched chain esters 2-methylpropyl acetate and 2-methylbutyl acetate were similar between controls and 1-MCP-treated fruit at maximum production. Production of other esters, including butyl and hexyl hexanoate and the 2-methylbutanoate esters by 1-MCP-treated fruit, did not exceed 50% of maximum production by controls indicating regulation of ester synthesis in d'Anjou pears is compound specific rather than general for these two structural groups. The impact of storage duration on production of acetate esters was also different compared to that of branched chain butanoate esters and hexanoate esters regardless of 1-MCP treatment, indicating that production of these compounds may be regulated by additional factors.

When d'Anjou pear treated with 1-MCP were at an acceptable maturity for consumption based on firmness (i.e., after 8 months of storage plus 7 days ripening), the quantitative contribution of total alcohols and esters were approximately the same, while at a similar stage of ripening in control fruit (i.e., after 2 or 4 months of storage plus 7 days of ripening) the quantitative contribution of esters were substantially higher than that of alcohols. In contrast, production of all aldehydes by 1-MCP-treated fruit after 8 months of storage was higher than that by control fruit after 2 or 4 months of storage. Further studies are needed to establish the impact of 1-MCP treatment on sensory aroma quality of pears.

Pear fruit treated with 1-MCP eventually soften and emit volatile compounds typical of ripening fruit. These processes occur even after a prolonged delay in the initiation of ripening. Induction of ripening and development of optimum eating quality of d'Anjou pear fruit are achieved upon warm temperature following 60 days of cold storage (4). Preconditioning nonchilled d'Anjou pear fruit to 4.2 mmol m⁻³ ethylene effectively promotes uniform ripening and good flavor quality (5). In the present study, 1-MCP-treated fruit required a longer period of storage at low temperature to ripen and achieve marketable quality. Furthermore, exposure of 1-MCP-treated d'Anjou fruit to 0.45 or 4–18 mmol m⁻³ ethylene did not enhance ripening to a large extent, indicating 1-MCP-treated

pear fruit may not be available for marketing for an extended period after 1-MCP treatment. Control fruit may ripen in its own capacity without exogenous ethylene stimulation after 2 or more months of storage. That may explain why even control fruit did not respond to ethylene after 2 or more months of storage.

In summary, 1-MCP treatment delays ripening of d'Anjou pears. The duration of 1-MCP effects are concentration dependent. 1-MCP at 0.42 μ mol m⁻³ can prevent d'Anjou pear ripening for 4 months, while the threshold concentration of 1-MCP to inhibit fruit ripening for longer storage periods is higher. Exposure of 1-MCP-treated pears to ethylene after storage does not fully reverse the effects of 1-MCP. 1-MCP reduces development of superficial scald, core browning, and decay. When 1-MCP-treated fruit begin to ripen, the ripening process proceeds normally, and qualitative volatile production is similar to untreated fruit.

ACKNOWLEDGMENT

We thank David Buchanan and Janie Countryman for technical assistance and BioTechnology for Horticulture, Inc. for providing 1-MCP.

LITERATURE CITED

- Abeles, F. B.; Morgan, P.; Saltveit, M. E. *Ethylene in plant biology*; Academic Press: San Diego, CA, 1992; pp 182–185.
- (2) Blankenship, S. M.; Richardson, D. G. Development of ethylene biosynthesis and ethylene-induced ripening in d'Anjou pears during the cold requirement for ripening. J. Am. Soc. Hortic. Sci. 1985, 110, 520-523.
- (3) Knee, M. Development of ethylene biosynthesis in pear fruit at -1 °C. J. Exp. Bot. 1987, 38, 1724–1733.
- (4) Chen, P. M.; Mellenthin, W. M. Maturity, chilling requirement, and dessert quality of d'Anjou and 'Bosc' pears. *Acta Hort.* 1982, *124*, 203–210.
- (5) Ma, S. S.; Chen, P. M.; Varga, D. M. Ethylene capsule promotes early ripening of d'Anjou pears packed in modified atmosphere bags. J. Food Qual. 2000, 23, 245–259.
- (6) Romani, R.; Labavitch, J.; Yamashita, T.; Hess, B.; Rae, H. Preharvest AVG treatment of 'Bartlett' pear fruit: Effects on ripening, color change, and volatiles. J. Am. Soc. Hortic. Sci. 1983, 108, 1046–1049.
- (7) Lelièvre, J.-M.; Latché, A.; Jones, B.; Bouzayen, M.; Pech, J.-C. Ethylene and fruit ripening. *Physiol. Plant.* 1997, *101*, 727–739.
- (8) deWild, H. P. J.; Woltering, E. J.; Peppelenbos, H. W. Carbon dioxide and 1-MCP inhibit ethylene production and respiration of pear fruit by different mechanisms. *J. Exp. Bot.* **1999**, *50*, 837–844.
- (9) Lelièvre, J.-M.; Tichit, L.; Dao, P.; Fillion, L.; Nam, Y.-W.; Pech, J.-C.; Latche, A. Effects of chilling on the expression of ethylene biosynthetic genes in Passe-Crassane pear (*Pyrus communis* L.) fruits. *Plant Mol. Biol.* **1997**, *33*, 847–855.
- (10) Gong, Y.; Tian, M. S. Inhibitory effect of diazocyclopentadiene on the development of superficial scald in Granny Smith apple. *Plant Growth Regul.* **1998**, *26*, 117–121.
- (11) Fan, X.; Mattheis, J. P.; Blankenship, S. Development of apple superficial scald, soft scald, core flush, and greasiness is reduced by MCP. J. Agric. Food Chem. **1999**, 47, 3063–3068.
- (12) Rupasinghe H. P. V.; Murr D. P.; Paliyath G.; Skog, L. Inhibitory effect of 1-MCP on ripening and superficial scald development in 'McIntosh' and 'Delicious' apples. *J Hortic. Sci. Biotech.* 2000, *75*, 271–276.
- (13) Watkins, C. B.; Nock, J. F.; Whitaker, B. D. Responses of early, mid, and late season apple cultivars to postharvest application of 1-methylcyclopropene (1-MCP) under air and controlled atmosphere storage conditions. *Postharvest Biol. Technol.* 2000, 19, 17–32.

- (14) Blankenship, S. M.; Dole, J. M. 1-methycyclopropene a review. *Postharvest Biol. Technol.* **2003**, *28*, 1–25.
- (15) Chen, P. M.; Spotts, R. A.; Mellenthin, W. M. Stem-end decay and quality of low oxygen stored d'Anjou pears. J. Am. Soc. Hortic. Sci. 1981, 106, 522–527.
- (16) Kader, A. A. Mode of action of oxygen and carbon dioxide on postharvest physiology of 'Bartlett' pears. *Acta Hort*. **1989**, 258, 161–166.
- (17) Gorny, J. R.; Kader, A. A. Low oxygen and elevated carbon dioxide atmospheres inhibit ethylene biosynthesis in preclimacteric and climacteric apple fruit. J. Am. Soc. Hortic. Sci. 1997, 122, 542–546.
- (18) Richardson, D. G.; Kupferman, E. Controlled atmosphere storage of pears. In *Proceeding of the Seventh International Controlled Atmosphere Research Conference*; Mitcham, E. J., Ed.; University of California: Davis, CA, 1997; Vol. 2, pp 31–35.
- (19) Mitcham, E. J.; Mitchell, F. G. Postharvest handling system for pome fruits. In *Postharvest technology of horticultural crops*, 3rd edition; Kader, A. A., Ed.; University of California: Oakland, CA, 2002; pp 333–344.
- (20) Hansen, E.; Mellenthin, W. M. Factors influencing susceptibility of pears to carbon dioxide injury. *Proc. Am. Soc. Hortic. Sci.* **1962**, 80, 146–153.
- (21) Chen, P. M.; Varga, D. M. Control of superficial scald of Anjou pears by short-term hyper-low oxygen stress as influenced by carbon dioxide concentration. *Tree Fruit Postharvest J.* 1993, *4*, 53–57.
- (22) Sisler, E. C.; Blankenship, S. M. Method of counteracting an ethylene response in plants. US Patent Office, Washington, DC. 1996. US Patent No. 5,518, 988.
- (23) Sisler, E. C.; Serek, M. E. Inhibitors of ethylene response in plants at the receptor level: recent developments. *Physiol. Plant.* **1997**, *100*, 577–582.
- (24) Baritelle, A. L.; Hyde, 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.
- (25) Golding, J. B.; Shearer, D.; Wyllie, S. G.; McGlasson, W. B. Application of 1-MCP and propylene to identify ethylenedependent ripening processes in mature banana fruit. *Postharvest Biol. Technol.* **1998**, *12*, 87–98.
- (26) Fan, X.; Mattheis, J. P. Impact of 1-methylcyclopropene and methyl jasmonate on apple volatile production. J. Agric. Food Chem. 1999, 47, 2847–2853.
- (27) Fan, X.; Argenta, L. C.; Mattheis, J. P. Inhibition of ethylene action by 1-methylcyclopropene prolongs storage life of apricots. *Postharvest Biol. Technol.* 2000, 20, 135–142.
- (28) Fan, X.; Blankenship, S.; Mattheis, J. P. 1-Methylcyclopropene inhibits apple ripening. J. Am. Soc. Hortic. Sci. 1999, 124, 690– 695.
- (29) Mir, N. A.; Curell, E.; Khan, N.; Whitaker, M.; Beaudry, R. M. Harvest maturity, storage temperature, and 1-MCP application frequency alter firmness retention and chlorophyll fluorescence

of 'Redchief Delicious' apples. J. Am. Soc. Hortic. Sci. 2001, 26, 618–624. 19, 17–32.

- (30) Blankenship, S. M.; Sisler, E. C. Ethylene binding site affinity in ripening apples. J. Am. Soc. Hortic. Sci. 1993, 118, 609– 612.
- (31) Fan, X.; Mattheis, J. P.; Roberts, R. G. Biosynthesis of phytoalexin in carrot root requires ethylene action. *Physiol. Plant.* 2000b, *110*, 450–454.
- (32) McGuire, R. G. Reporting of objective color measurements. *HortScience* 1992, 27, 1254–1255.
- (33) Fan, X.; Mattheis, J. P.; Fellman, J. K. Responses of apples to postharvest jasmonate treatments. J. Am. Soc. Hortic. Sci. 1998, 123, 421–425.
- (34) Chen, P. M.; Richardson, D. G.; Mellenthin, W. M. Differences in biochemical composition between 'Beurre d'Anjou' and 'Bosc' pears during fruit development and storage. J. Am. Soc. Hortic. Sci. 1982, 107, 807–812.
- (35) Suwanagul, A.; Richardson, D. G. Identification of headspace volatile compounds from different pear (*Pyrus communis* l.) varieties. *Acta Hort.* **1998**, 475, 605–623.
- (36) Yoshida, T.; Borgic, D. M.; Chen, P. M.; Mielke, E. A. Changes in ethylene, acids, and brown-core development of 'Bartlett' pears in low-oxygen storage. *HortScience* **1986**, *21*, 472–474.
- (37) Maage, F.; Richardson, D. G. Winter pear chilling requirements for auto catalytic ethylene synthesis and ripening: delaying effects of controlled atmosphere storage. *Acta Hortic.* **1998**, 475, 625–627.
- (38) Claypool, L. L. Further studies on controlled atmosphere storage of 'Bartlett' pears. J. Am. Soc. Hortic. Sci. 1973, 98, 289–293.
- (39) Jennings, W. G.; Tressl, R. Production of volatile compounds in the ripening Bartlett pear. *Chem. Microbiol. Technol. Lebesem.* 1974, *3*, 52–55.
- (40) Shiota, H. Changes in the volatile composition of La France pear during maturation. J. Sci. Food Agric. 1990, 52, 421–429.
- (41) 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.
- (42) Fidler, J. C.; North, C. J. Production of volatile organic compounds by pears. J. Sci. Food Agr. 1969, 20, 518–520.
- (43) Chervin, C.; Speirs, J.; Loveys, B.; Patterson, B. D. Influence of low oxygen storage on aroma compounds of whole pears and crushed pear flesh. *Postharvest Biol. Technol.* 2000, *19*, 279– 285.
- (44) Fan, X.; Mattheis, J. P.; Buchanan, D. Continuous requirement of ethylene for apple fruit volatile synthesis. J. Agric. Food Chem. 1998, 46, 1959–1963.

Received for review January 10, 2003. Revised manuscript received March 23, 2003. Accepted April 6, 2003. This work was supported by a grant from the Winter Pear Control Committee and the Rohm and Haas Company.

JF034028G