Stripped Corn Oil Controls Scald and Maintains Volatile Production Potential in Golden Supreme and Delicious Apples

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Effects of stripped (α-tocopherol < 5 mg L^{-1}) corn oil on flesh firmness, skin color, acidity, soluble solids content (SSC), scald, and fruit volatiles during 6 months at 0 °C were studied using Golden Supreme and Delicious apples. Treatment with 10% oil emulsion reduced production of ethylene, α-farnesene, and major volatile esters in the first 3 months of storage, but this trend reversed after 5 months. After 6 months at 0 °C plus 7 days at 20 °C, oil-treated fruit were firmer and greener and had higher levels of titratable acidity than the controls. In addition, control fruit developed 27% and 42% scald in Golden Supreme and Delicious apples, respectively, whereas oil-treated fruit were free from scald. Soluble solids content and ethanol production were unaffected by oil treatment.

Keywords: *Corn oil; ethylene; α-farnesene; volatile esters; ethanol; Malus sylvestris var. domestica*

INTRODUCTION

Volatile compounds are the major constituents of fruit aroma and, as such, are important in defining fruit quality (Dimick and Hoskin, 1983). In climacteric fruit, such as apples, volatile production during fruit ripening is associated with ethylene (Fan et al., 1998; Mir et al., 1999; Ju and Curry, 2000b), and ethylene inhibitors such as aminoethoxyvinylglycine (Bangerth and Streif, 1987; Ju and Bramlage, 2000) and 1-methylcyclopropene (Fan and Mattheis, 1999) inhibit volatile production. When apples and pears are stored in air at 0 °C, α-farnesene, one of the major volatiles (Fallik et al., 1997; Paliyath et al. 1997; Ju and Curry, 2000a,b), reaches a maximum after 3 or 4 months and decreases thereafter (Huelin and Coggiola, 1970; Watkins et al., 1993). Controlled atmosphere (CA) storage, although delaying fruit senescence, reduces volatile production as compared with fruit stored in regular air (RA) storage (Brackmann et al., 1993; Streif and Bangerth, 1988). Therefore, developing technologies that prolong storage life of fruit in RA storage without reducing volatile production and aroma is an important objective.

Treating with plant oil at harvest may be a viable option for maintaining fruit quality in RA storage. Not only does it reduce scald (Ju et al., 2000), maintain fruit firmness and titratable acidity (TA), and inhibit degreening (Ju and Curry, 2000a; Ju et al., 2000), but also it delays peak production of ethylene and α-farnesene, resulting in higher α-farnesene production in later stored fruit (Ju and Curry, unpublished data), thereby improving volatile production and fruit aroma after prolonged storage. Whereas α-farnesene is synthesized through the mevalonate pathway (Rupasinghe et al., 1998; Ju and Curry, 2000a), it is thought that the major volatile esters produced by ripening fruit arise primarily from lipid oxidation or oxidation products (Paillard, 1990; Rowan et al., 1999). Effect of oil treatment on the production of volatile esters has not been studied.

By nature, oil emulsion treatment is similar to other fruit coatings (Ju et al., 2000). Treating fruit with wax or synthetic polymers also reduces ethylene production and inhibits fruit softening and chlorophyll degradation due to the modified internal atmosphere by these treatments (Hagenmaier and Shaw, 1992; Saftner et al., 1998). A major disadvantage of these coatings has been the potential for fruit anaerobiosis with the associated accumulation of ethanol and subsequent development of off-flavors (Hagenmaier and Shaw, 1992). Although no substantial off-flavor was detected by sensory evaluation in oil-treated fruit after prolonged storage (Ju and Curry, unpublished data), a quantitative measurement of ethanol in oil-treated fruit has not been made. The objective of this study, therefore, was to investigate the effect of oil treatment on scald development, flesh firmness, skin color, TA, and production of volatiles, including ethanol, in Golden Supreme and Delicious apples.

MATERIALS AND METHODS

Plant Materials and Treatments. Golden Supreme and Delicious apples [*Malus sylvestris* (L.) Mill. var. *domestica* (Borkh.) Mansf.] were harvested on Aug 20 and Sept 23, 1998, respectively. Concentrated emulsion containing 60% stripped (α-tocopherol reduced to <5 mg L^{-1}) corn oil (Aldrich, Milwaukee, WI) was made by mixing 6 parts corn oil, 1 part Tween 60, and 3 parts hot water (90 °C) with vigorous stirring (Ju et al., 2000). The emulsion was diluted to 10% with water and used for fruit treatment. At harvest, 10 fruits from each of three replications (trees) were used for flesh firmness, skin color, TA, and soluble solids content (SSC) determination, 10 were used for measurement of internal ethylene concentration, and 10 were used for measurement of ethylene and volatile production. Two hundred and fifty fruits in each replication were dipped in the oil emulsion for 3 min, allowed to air-dry at 20 °C, placed in cardboard boxes on fiber trays, and stored at 0 °C for 6 months. Untreated fruit stored similarly in separate boxes served as controls. Each month following treatment, 20 fruits from each replication were removed from cold storage. Ten were used for measurement of internal ethylene and ethanol concentration and 10 were used for ethylene and volatile production. Sampling was done immediately after removal from storage. After 6 months, the rest

10.1021/jf991278h
Published on Web 05/27/2000

Table 1. Effects of Stripped Corn Oil Treatment on Flesh Firmness, Skin Color, Titratable Acidity (TA), and Scald in Delicious and Golden Supreme Apples[a]

		skin color				scald	
treatment	firmness (*N*)	*L**	hue°	*C**	TA (% malic acid)	(%)	score
			Golden Supreme				
at harvest	86.8 a[b]	72.3 c	113 a	43.5 a	0.45 a		
after 6 months at 0 °C and 7 days at 20 °C							
control	69.3 c	79.2 a	87 c	39.2 c	0.30 c	27 a	2.1
oil	80.5 b	76.1 b	108 b	41.9 b	0.38 b	0 b	
			Delicious				
at harvest	89.8 a	51.6 c	48 b	27.6 b	0.37 a		
after 6 months at 0 °C and 7 days at 20 °C							
control	71.6 c	63.2 a	57 a	34.2 a	0.21 c	42 a	2.7
oil	82.1 b	56.1 b	50 b	29.1 b	0.30 b	0 b	

[a] Golden Supreme was harvested on Aug 20, and Delicious was harvested on Sept 23, 1999. [b] Mean separation in the same column for each cultivar by Duncan's new multiple range test at $P \leq 0.05$.

of the fruit were removed from cold storage and placed in a ripening room at 20 °C for 7 days and used for measurements of skin color, flesh firmness, TA, SSC, and scald.

Fruit Quality Evaluation. Fruit skin color, flesh firmness, SSC, and TA were quantified both at harvest and after cold storage plus 7 days at 20 °C using 3 replications of 10 fruits. Fruit skin color was measured by the *L**, *a**, *b** system using a Minolta Chrome Meter (DP-301, Minolta, Osaka, Japan) and the CIELAB values *a** and *b** reported as chroma and hue angle (McGuire, 1992). Flesh firmness was measured with an Electronic Pressure Tester (EPT-1, Lake City Tech. Products Inc., Kelowna, BC, Canada) equipped with an 11-mm tip. Readings were made on two paired sides of each fruit. SSC was assessed with a Digital Refractometer (PR-1, Atago Co. Ltd., Japan) on a combined sample of juice extracted from 10 fruits in each replicate. TA was measured by titrating 5 mL of juice extracted from 10 fruits in each replicate using a Standard pH meter (PHM 82, Radiometer American, Cleveland, OH) in conjunction with a titrator (TTT 80, Radiometer American, Cleveland, OH), and the results were expressed as percent malic acid equivalents.

At least 100 fruits in each of the three replications were used for scald evaluation. Scald was recorded both as percent incidence and as intensity (scald score) (Ju and Bramlage, 2000). Fruits were first graded according to the scalded area of fruit surface using the scale: 0 = none, 1 = 1 to 10%, 2 = 11 to 33%, 3 = 34 to 66%, and 4 = 67 to 100%. Scald incidence was calculated as the percent of scalded fruit of the total number of fruit evaluated. Scald score was calculated as the mean of the scale ratings for each individual scald affected fruit. Higher scald score represents fruit with larger surface area affected by scald.

Measurement of Volatile Production. Gas chromatography−mass spectrometry (GC-MS) with a solid phase micro extraction (SPME) method as described previously (Ju and Curry, 2000a) was used to measure volatiles. Six fruits from each replication were placed in a 4-L glass jar at 20 °C. The jars were connected to a flow-through system with a flow rate of 100 mL min^{-1}. After a 2-h equilibration, 0.5 mL of air was taken for ethylene, and at the same time, a 100-μm poly(dimethylsiloxane) (PDMS) probe (Supelco, Bellefonte, PA) was introduced into each jar and allowed to adsorb volatiles for 10 min. The probe was inserted immediately into the injection port of a gas chromatograph (HP 5890, Hewlett-Packard, San Fernando, CA). Adsorbed volatiles were allowed to desorb for 3 min in the injector with a constant temperature of 250 °C. The oven temperature was increased from 35 to 250 °C at a rate of 50 °C min^{-1} and then held for 4 min. Helium was used as carrier gas, and the head pressure was maintained to give a constant flow rate of 1 mL min^{-1}. Analysis was conducted using a Hewlett-Packard wide bore capillary column (30 m length × 0.25 mm i.d.) with a splitless injection. Volatiles were identified by analysis of fragmentation profiles using a Hewlett-Packard 5971 MS detector combined with confirmatory library matches. Only the seven major peaks, butyl butanoate, hexyl acetate, hexyl propanoate, butyl hexanoate, hexyl butyrate, hexyl hexanoate, and α-farnesene were quantified. α-Farnesene was quantified using the abundance of characteristic ion 93 and reported as units per kilogram of fresh weight per hour. A reading of 1000 in abundance was defined as one unit. Other volatiles were measured using standards (Sigma, St. Louis, MO) and presented as micromoles per kilogram hour.

For internal ethylene or ethanol measurements, a 0.5-mL air sample was taken from the cavity of individual fruits, and gas chromatography with a glass column (610 × 3.2 mm i.d.) packed with Porapak Q (90−100 mesh) was used. Oven and injector temperatures were 50 °C for ethylene and 115 °C for ethanol. Flame ionization detector temperature was 200 °C, and gas flows for N_2 carrier, H_2, and air were 30, 30, and 300 mL min^{-1}, respectively.

Statistical Analysis. Data were subjected to analysis of variance procedures using SAS Statistical Software (SAS Inst. Inc., Cary, NC). In tables, means were separated using Duncan's new multiple range test at $P \leq 0.05$ when variance analysis indicated significance. In figures, means were compared by HSD using Tukey's Sudentized range test at $P \leq 0.05$. Only results significant at $P \leq 0.05$ are discussed.

RESULTS

Effects of Oil Treatment on Fruit Quality. As compared with the controls, oil-treated fruit of both cultivars had higher flesh firmness and TA and more green color after 6 months of storage (Table 1). Oil-treated fruit had no scald, while control fruit developed 27 and 42% scald in Golden Supreme and Delicious samples, respectively. Treatment did not affect SSC (data not shown).

Effects of Oil Treatment on Volatile Production. Trends in ethylene and α-farnesene production between Golden Supreme and Delicious samples were similar, thus only data from Delicious samples are presented in Figure 1. Ethylene and α-farnesene production in controls showed patterns typical of climacteric fruit, increasing in early storage and decreasing in late storage. Oil treatment inhibited both ethylene and α-farnesene production in the first 3 months but increased it after 5 months of storage. Internal ethylene concentrations in control and treated fruit were similar (data not shown).

In general, production of the major volatile esters (butyl butanoate, hexyl acetate, hexyl propanoate, butyl hexanoate, hexyl butyrate, and hexyl hexanoate) in both cultivars showed similar trends. Therefore, the sum of

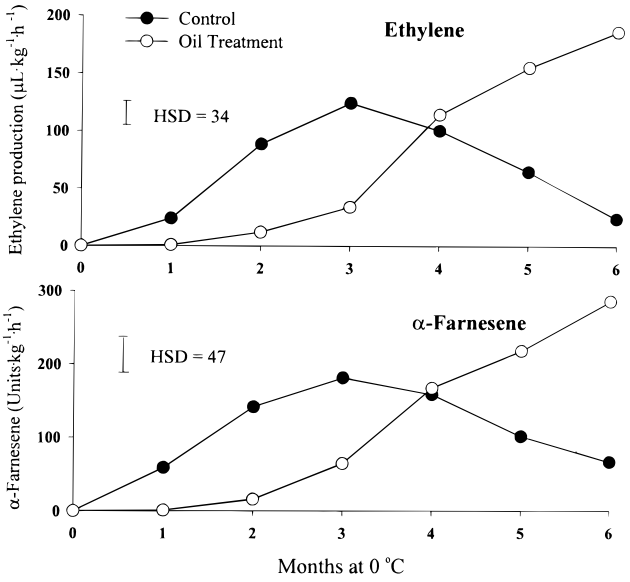

Figure 1. Effects of stripped corn oil treatment on ethylene and α-farnesene production in Delicious apples. Fruits were harvested on Sept 23, 1998.

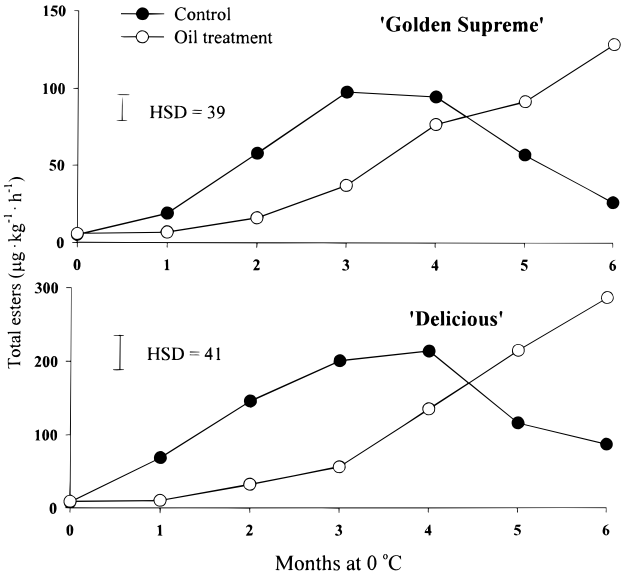

Figure 2. Effects of stripped corn oil treatment on volatile production in Golden Supreme and Delicious apples. Golden Supreme and Delicious apples were harvested on Aug 20 and Sept 23, 1998, respectively. Trends among butyl butanoate, hexyl acetate, hexyl propanoate, butyl hexanoate, hexyl butyrate, and hexyl hexanoate were similar, and data were the sum of all the esters measured.

these esters from Delicious or Golden Supreme samples is presented in Figure 2. Total ester production paralleled changes in ethylene, increasing in early storage and decreasing in late storage. Oil treatment reduced ester production in the first 3 months and increased it after 5 months of storage.

Concentrations of ethanol in untreated fruit was low in early storage and increased in late storage (Figure 3). Oil treatment did not affect ethanol accumulation during 6 months of storage in either cultivar.

DISCUSSION

Oil treatment inhibited scald and maintained flesh firmness, skin color, and TA in Golden Supreme and

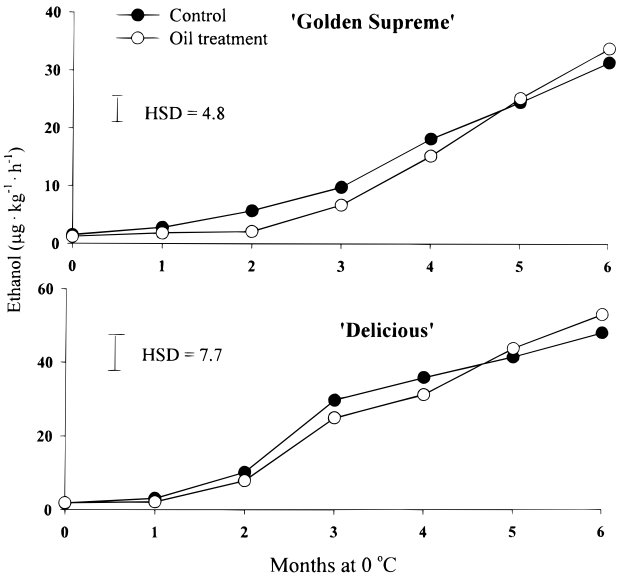

Figure 3. Effects of stripped corn oil treatment on ethanol accumulation in Golden Supreme and Delicious apples. Golden Supreme and Delicious apples were harvested on Aug 20 and Sept 23, 1998, respectively.

Delicious apples (Table 1). These effects on fruit quality are similar to those from trials in which other cultivars were used (Ju et al., 2000). In addition, oil treatment inhibited both α-farnesene and total ester production in the first 3 months but increased it after 5 months storage (Figures 1 and 2). Ethanol levels were not affected by oil treatment. Therefore, oil treatment not only maintains fruit quality by retaining flesh firmness, skin color, and TA, and controlling scald but also improves fruit quality by allowing sufficient levels of flavor volatiles to develop by the end of storage. Although fruit exhibited greasiness on the surface when wiped with plant oils (Scott et al., 1995), they showed no greasiness when dipped in oil emulsion, either at treatment or after prolonged storage. Informal sensory evaluation indicated no off-flavor or flavor originating from plant oil. Considering its low cost and organic nature, stripped corn oil or other plant oils (Ju et al., 2000) could have a huge potential in preserving organic fruits and could be an alternative to diphenylamine in conventional fruit storage.

The mechanism whereby oil treatment alters volatile production in apples is not clear but may involve several factors. First, volatile production in apples is associated with ripening (Vanoli et al., 1995; Song and Bangerth, 1996). Normally, as ripening progresses to senescence, the volatile production potential decreases (Lidster et al., 1983; Willaert et al., 1983). Oil treatment retards fruit ripening and delays fruit senescence as indicated by higher flesh firmness, greener skin color, and higher levels of TA (Table 1, Ju and Curry, 2000a; Ju et al., 2000); therefore, a higher potential of volatile production may be maintained due to less advanced fruit senescence. Second, both α-farnesene and ester production in apples are mediated by ethylene (Fan et al., 1998; Mir et al., 1999; Ju and Curry, 2000b). Oil treatment inhibits ethylene production in early storage but not in late storage (Figure 1), which may contribute to the inhibition of volatile production in the first 3 months and promotion thereof in late storage. The mechanism by which plant oil inhibits ethylene production, however, is not clear. It has been suggested that a modified

internal atmosphere plays an important role in inhibiting ethylene production and fruit ripening in wax or other polymer-coated fruits (Hagenmaier and Shaw, 1992; Banks et al., 1993; Saftner et al., 1998); thus, it is very likely that plant oil-treated fruit share a similar mechanism. Third, because volatile esters produced by ripening fruit are thought to arise primarily from lipid oxidation products (Paillard, 1990; Rowan et al., 1999), increasing the concentration of triacylglycerides available for cellular metabolism could stimulate the degradation of triacylglycerides, thereby releasing fatty acids and thus providing substrates for volatile production. Because scalded apples produce less volatile than healthy fruit, and diphenylamine-treated Cortland apples produce more esters than untreated controls (Mir and Beaudry, 1999), the higher ester production potential in plant oil-treated fruit may also be related to its reduced scald.

Fruit coated with wax or other polymers often develop off-flavors after prolonged storage (Hagenmaier and Shaw, 1992), which have been explained primarily as responses to changes in concentrations of internal CO_2 and O_2 (Banks et al., 1993; Saftner et al., 1998). In our experiment, in contrast, oil treatment had no effect on ethanol accumulation after 6 months of storage (Figure 3), indicating that oil treatment may have higher air permeability than other coating materials. In trials in which grapefruits were treated with safflower oil, the resistance to O_2 (21.9×10^3 s cm^{-1}) was half, and the resistance to CO_2 (14.1×10^3 s cm^{-1}) was equal to that of the commercial wax (McDonald et al., 1993). Another possibility is that a portion of the oil on treated fruit surfaces may be absorbed by cells during storage and thus gradually reduce its resistance to air exchange, whereas other waxes or polymers remain on the fruit surface during storage. Further study is needed to examine these possibilities.

ACKNOWLEDGMENT

We are grateful to Carol Duplaga, Carol Pavelko, Doris Frederick, Dave Buchanan, and Dr. Rodney Roberts from the Tree Fruit Research Laboratory, USDA-ARS, Wenatchee, WA, for their technical support.

LITERATURE CITED

Bangerth, F.; Streif, J. Effects of aminoethoxyvinylglycine and low-pressure storage on the post-storage production of aroma volatiles by 'Golden Delicious' apples. *J. Sci. Food Agr.* **1987**, *41*, 351−360.

Banks, N. H.; Dadzie, B. K.; Cleland, D. J. Reducing gas exchange of fruits with surface coatings. *Postharvest Biol. Technol.* **1993**, *3*, 269−284.

Brackmann, A.; Streif, J.; Bangerth, F. Relationship between a reduced aroma production and lipid metabolism of apples after long-term controlled-atmosphere storage. *J. Am. Soc. Hortic. Sci.* **1993**, *118*, 243−247.

Dimick, P. S.; Hoskin, J. C. Review of apple flavor-state of the art. *CRC Crit. Rev. Food Sci. Nutr.* **1983**, *18*, 387−409.

Fan, X.; Mattheis, J. P. Impact of 1-methylcyclopropene and methyl jasmonate on apple volatile production. *J. Agric. Food Chem.* **1999**, *47*, 2847−2853.

Fan, X.; Mattheis, J. P.; Buchanan, D. Continuous requirement of ethylene for apple fruit volatile synthesis. *J. Agric. Food Chem.* **1998**, *46*, 1959−1963.

Fallik, E.; Archbold, D. D.; Hamilton-kemp, T. R.; Loughrin, J. H.; Collins, R. W. Heat treatment temporarily inhibits aroma volatile compound emission from 'Golden Delicious' apples. *J. Agric. Food Chem.* **1997**, *45*, 4038−4041.

Hagenmaier, R. D.; Shaw, P. E. Gas permeability of fruit coating waxes. *J. Am. Soc. Hortic. Sci.* **1992**, *117*, 105−109.

Huelin, F. E.; Coggiola, I. M. Superficial scald, a functional disorder of stored apples. VI. Evaporation of farnesene from the fruit. *J. Sci. Food Agric.* **1970**, *21*, 82−86.

Ju, Z.; Bramlage, W. J. Cuticular phenolics and scald development in 'Delicious' apples. *J. Am. Soc. Hortic. Sci.* **2000**, in press.

Ju, Z.; Curry, E. A. Lovastatin inhibits α-farnesene synthesis without affecting ethylene production during fruit ripening in 'Golden Supreme' apples. *J. Am. Soc. Hortic. Sci.* **2000a**, *125*, 105−110.

Ju, Z.; Curry, E. A. Evidence that α-farnesene biosynthesis during fruit ripening is mediated by ethylene regulated gene expression in apples. *Postharvest Biol. Technol.* **2000b**, *19*, 9−16.

Ju, Z.; Duan, Y.; Ju, Z. Mono-, di-, and tri-acylglycerols and phospholipids from plant oils inhibit scald development in 'Delicious' apples. *Postharvest Biol. Technol.* **2000**, *19*, 1−7.

Lidster, P. D.; Lightfoot, H. J.; McRea, K. B. Production and regeneration of principle volatiles in apples stored in modified atmosphere and air. *J. Food Sci.* **1983**, *48*, 400−410.

McDonald, R. E.; McCollum, T. G.; Nordby, H. E. Temperature conditioning and surface treatments of grapefruit affect expression of chilling injury and gas diffusion. *J. Am. Soc. Hortic. Sci.* **1993**, *118*, 490−496.

McGuire, R. G. Reporting of objective color measurements. *HortScience* **1992**, *27*, 1254−1255.

Mir, N. A.; Beaudry, R. Effects of superficial scald suppression by diphenylamine application on volatile evolution by stored 'Cortland' apple fruit. *J. Agric. Food Chem.* **1999**, *47*, 7−11.

Mir, N. A.; Perez, R.; Schwallier, P.; Beaudry, R. Relationship between ethylene response manipulation and volatile production in 'Jonagold' variety apples. *J. Agric. Food Chem.* **1999**, *47*, 2653−2659.

Paillard, N. M. M. The flavour of apples, pears and quinces. In *Food Flavours Part C. The Flavour of Fruit.* Marton. I. D., MacLeod, A. J., Eds.; Elsevier: Amsterdam, The Netherlands, 1990; pp 1−41.

Paliyath, G.; Whiting, M. D.; Stasiak, M. A.; Murr, D. P.; Clegg, B. S. Volatile production and fruit quality during development of superficial scald in Red Delicious apples. *Food Res. Int.* **1997**, *30*, 95−103.

Rowan, D. D.; Allen, J. M.; Fielder, S.; Hunt, M. B. Biosynthesis of straight-chain ester volatiles in 'Red Delicious' and 'Granny Smith' apples using deuterium-labeled precursors. *J. Agric. Food Chem.* **1999**, *47*, 2553−2562.

Rupasinghe, H. P. V.; Paliyath, G.; Murr, D. P. Biosynthesis of α-farnesene and its relation to superficial scald development in 'Delicious' apples. *J. Am. Soc. Hortic. Sci.* **1998**, *123*, 882−886.

Saftner, R. A.; Conway, W. S. Effects of postharvest calcium and fruit coating treatments on postharvest life, quality maintenance, and fruit-surface injury in 'Golden Delicious' apples. *J. Am. Soc. Hortic. Sci.* **1998**, *123*, 294−298.

Scott, K. J.; Yuen, C. M. C.; Kim, G. H. Reduction of superficial scald of apples with vegetable oils. *Postharvest Biol. Technol.* **1995**, *6*, 219−223.

Song, J.; Bangerth, F. The effect of harvest date on aroma compound production from 'Golden Delicious' apple fruit and relationship to respiration and ethylene production. *Postharvest Biol. Technol.* **1996**, *8*, 259−269.

Streif, J.; Bangerth, F. Production of volatile aroma substances by 'Golden Delicious' apple fruits after storage for various times in different CO_2 and O_2 concentrations. *J. Hortic. Sci.* **1988**, *63*, 193−199.

Vanoli, M.; Visai, C.; Rizzolo, A. The influence of harvest date on the volatile composition of 'Starkspur Golden' apples. *Postharvest Biol. Technol.* **1995**, *6*, 225−234.

Watkins, C. B.; Barden, C. L.; Bramlage, W. J. Relationships among α-farnesene, conjugated trienes and ethylene pro-

duction with superficial scald development of apples. *Acta Hortic.* **1993**, *343*, 155−160.

Willaert, G. A.; Dirinck, P. J.; DePooter, H. L.; Schamp, N. N. Objective measurement of aroma quality of 'Golden Delicious' apples as a function of controlled-atmosphere storage time. *J. Agric. Food Chem*. **1983**, *31*, 809−813.

Received for review November 24, 1999. Revised manuscript received March 15, 2000. Accepted March 31, 2000. This research was supported by the Washington Fruit Tree Research Commission.

JF991278H