Production of Some Odor-active Volatiles by 'McIntosh' Apples following Low-ethylene Controlled-atmosphere Storage

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Abstract. The effectiveness of some poststorage treatments in enhancing the flavor components of low-ethylene controlled-atmosphere (LCA) stored 'McIntosh' apples (*Malus domestica* Borkh.) was investigated. Fruits were stored for 9 months in LCA at 3.3C and then exposed to air at 20C and to air, simulated LCA, 100% O₂, or light at 3.3C for up to 4 weeks. Respiration and ethylene production indicated that apples were still in the early stage of ripening after 9 months of storage in LCA. Gas chromatographic analysis for 13 odor-active volatiles revealed the presence of eight. Air at 20C after LCA significantly increased the production of some odor volatiles, while light for up to 3 weeks only slightly increased their concentration. Poststorage exposure to air or 100% O₂ at 3.3C for up to 4 weeks was not effective in enhancing volatile formation.

Controlled atmosphere (CA) is an established method of prolonging the storage life of apples (Smock, 1979). Low-ethylene CA (LCA), where ethylene in the storage atmosphere is maintained at or below 1 ppm, is very effective in further prolonging the storage life of the fruit with minimum losses in flesh firmness, acidity, and soluble solids (Blanpied et al., 1985; Liu and Samelson, 1986; Yahia et al., 1985).

Williams (1979) indicated that flavor is an important quality attribute in CA-stored apples that are firm. Earlier studies (Kidd and West, 1936) concluded that the full characteristic flavor of CA-stored 'Cox's Orange Pippin' apples developed after a short con-

ditioning period in air at 12C. Hatfield (1975) reported that much of the loss of flavor in CA storage could be regained if the apples

were kept at 5 to 15C after storage before being transferred to 20C. However, other studies indicated significant loss in flavor in CA-stored apples (Knee and Sharples, 1981; Streif and Bangerth, 1988; Yahia, 1989; Yahia et al., 1990b, 1985). The severity of CA suppression of flavor components depended on the atmospheric composition and the duration of storage. The lower the O₂ concentration, the higher the CO₂ concentration; and the longer the fruit was kept in CA storage, the greater was the suppression (Knee and Sharples, 1981; Lidster et al., 1983; Patterson et al., 1974; Yahia et al., 1990b, 1985). Simulated LCA storage caused a greater suppression of flavor than conventional CA storage (Yahia, 1989; Yahia et al., 1990b, 1985).

Apple flavor is a complex combination of taste and odor sensations. Although taste and texture are important to apple quality, the presence of trace amounts of volatile components responsible for odor gives the fruit much of its character (Dimick and Hoskin, 1983). About 20 to 40 odor-active volatiles are responsible for apple aroma (Cunningham et al., 1986). These volatiles fall into three classes: the "apple peel-smelling" esters like ethyl 2-methylbutanoate, the lipid

Fig. 1. Effects of poststorage treatments on respiration (A) and ethylene production (B) rates of 'McIntosh' apples following low-ethylene CA storage. Vertical bars represent LSD values at $P = 0.05$.

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Fig. 2. Effects of poststorage treatments on total content of the eight odor-active volatiles detected and concentrations of hexanal, (E)-2-hexenal, hexyl acetate, and butyl hexanoate in 'McIntosh' apples following low-ethylene CA storage. ■, air at 20°C; □, air at 3.3°C; ●, simulated LCA; ○, 100% O₂; △, light. (Note that scales on the ordinates differ for the various volatiles.)

Fig. 3. Effects of poststorage treatments on concentrations of ethyl butanoate, propyl butanoate, butyl butanoate, and ethyl 2-methylbutanoate in 'McIntosh' apples following low-ethylene CA storage. ■, air at 20°C; □, air at 3.3°C; ●, simulated LCA; ○, 100% O₂; △, light. (Note that scales on the ordinates differ for the various volatiles.)

oxidation products like E-2-hexenal, and the terpenoid B-damascenone.

The objective of this study was to evaluate the effect of fruit exposure to air, light, and 100% O₂ on enhancing the production of odor volatiles of 'McIntosh' apples following LCA storage.

'McIntosh' apples were picked according to the method of Liu (1985) and stored in a

commercial LCA room. The room was filled on 22 to 26 Sept. 1984, sealed immediately, and held at 3.3°C. The atmosphere in the room was monitored daily using an Orsat gas analyzer (Orsat, Fisher Scientific, Springfield, N.J.) and averaged 3.3% O₂ and 4.6% CO₂. Ethylene produced by the fruit was removed with KMnO₄/alumina beads for the first 2 months and a "Swingtherm Heated Catalyst Ethylene Converter" afterwards (Blanpied et al., 1985). Ethylene in the room was monitored at various intervals using gas chromatography and averaged $2.42 \pm 1.39 \mu\text{l}\cdot\text{liter}^{-1}$. The room was opened on 22 June 1985. On 24 June, fruits were taken from the LCA room and placed under one of the following five treatments: air at 20°C; air at 3.3°C; simulated LCA at 3.3°C; 100% O₂ at 3.3°C; and light at 3.3°C.

Fruits for air, simulated LCA, and 100% O₂ were put into 19-liter glass jars with ≈ 50 fruits each. Air free from C₂H₄ and CO₂, or a mixture of 3% O₂ + 3% CO₂ + 94% N₂ was humidified and metered at 200 ml·min⁻¹ through each of the air or simulated LCA jars, respectively. Gas samples were collected three times per week from the outlet of each LCA jar, and O₂ and CO₂ contents were measured using an Orsat gas analyzer. The jars with 100% O₂ were ventilated with humidified O₂ at 200 ml·min⁻¹. Apples exposed to light were put for up to 3 weeks at 3.3°C in a chamber composed of a box with nine high-output fluorescent tubes (F48 T12/WW/HO, General Electric) with an average intensity of 7560 lux. The side of the fruit exposed to light was random. Respiration rate was measured for all apples but those in simulated LCA or under light by detecting the CO₂ concentration from the outlet of the jar using a calibrated Beckman Model IR 215 infrared gas analyzer (Beckman Instruments, Somerset, N.J.); data were calculated as milliliters CO₂ per kilogram per hour. Ethylene production was measured for all apples but those under light using a Varian Aerograph Model 3700 gas chromatograph (Varian Analytical Instruments, Sunnyvale, Calif.) equipped with a flame ionization detector and a 0.25 m × 2 mm column packed with activated aluminum oxide. Samples of 10 apples were taken initially and at weekly intervals for analysis of 13 volatiles (Table 1). These volatiles have all been shown to be odor-active in a combined apple extract of various cultivars, including 'McIntosh' (Cunningham et al., 1986). Volatiles were extracted as reported by Yahia et al. (1990a, 1990b). A gas chromatograph equipped with a flame ionization detector and a 12.5 m × 0.36 mm fused silica column coated with 0.53 μm crosslinked methyl silicone was used for volatile analysis. The column was held at 35°C for 3 min, increased 4°C/min to 250°C, and held there for 15 min. The retention indices (Kovats, 1965) of the 13 authentic standards were used to identify all volatiles and as a calibration for quantitative analysis. Retention indices were calculated using n-paraffin hydrocarbon standards containing n-heptane through n-octadecane. Statistical analysis for respiration and ethylene produc-

tion rates was done using analysis of variance and least significant difference test at $P = 0.05$ was used for mean separation. Volatiles values represent one measurement of extract from 10 fruits.

Apples ripened in air at 20°C had the highest rates of respiration (Fig. 1A). Apples kept in simulated LCA produced little ethylene ($< 1 \mu\text{l}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$). Those kept in air at 3.3°C or in 100% O₂ at 3.3°C had intermediate rates of ethylene production, and those kept in air at 20°C had the highest rate (Fig. 1B).

Gas chromatographic analysis of odor-active volatiles revealed the absence of five volatiles, i.e., butyl-, phenyl-, and isopentyl acetate, and butyl propanoate and butyl pentanoate. Although these volatiles were found to be present in some apple cultivars (Dimick and Hoskin, 1983), they were consistently absent from 'McIntosh' and 'Cortland' apples (Yahia, 1989; Yahia et al., 1990a, 1990b, 1985). The total content of volatiles detected increased rapidly during fruit ripening in air at 20°C but remained very low under other conditions and was the lowest under simulated LCA storage (Fig. 2). There were no large differences in the production of hexanal under the different storage conditions except for the unexplained peak in air at 20°C at 7 days. (E)-2-hexenal was lowest in simulated LCA and in air at 3.3°C, slightly higher under light and 100% O₂, and highest in air at 20°C. Hexyl acetate generally decreased at a similar rate under all conditions, except for an increase in air at 20°C at 14 days and in light at 21 days. Butyl hexanoate was not detected in simulated LCA and had increased by 3 weeks of light treatment and by 4 weeks of holding in air at 20°C. Ethyl butanoate content was very low in apples from simulated LCA, slightly higher in those from air at 3.3°C, light, or 100% O₂, and very high in air at 20°C (Fig. 3). Propyl butanoate was produced in small amounts in air at 20°C but was nearly absent under all other conditions. Butyl butanoate was produced in small amounts in simulated LCA and in 100% O₂, and in slightly higher amounts in air at 3.3°C, air at 20°C, or under light. Ethyl 2-methylbutanoate was produced in very small amounts under all conditions except in air at 20°C.

The rates of CO₂ and ethylene production indicated that apples were still in the early stage of ripening after 9 months of storage in LCA. The ability of LCA storage to slow ripening and senescence and to prolong the storage life of apples has been shown by others (Blanpied et al., 1985; Liu, 1985; Liu and Samelson, 1986).

Exposure of apples for 4 weeks to air at 3.3°C after LCA storage was not effective in enhancing the flavor components of the fruit. Air at 20°C significantly increased the production of some flavor volatiles. However, this temperature increases softening and acidity loss of apples (Liu, 1985; Liu and Samelson, 1986). The use of 100% O₂ did not cause any significant stimulation in the production of odor-active volatiles. Frenkel (1978) used high levels of O₂ to accelerate ripening in several fruits and storage organs. The use of high O₂ in combination with eth-

Table 1. Odor-active volatiles analyzed.

Butyl acetate
Pentyl acetate
Iso pentyl acetate
Hexyl acetate
Butyl propanoate
Hexanal
(E)-2-hexenal
Ethyl butanoate
Propyl butanoate
Butyl butanoate
Ethyl 2-methylbutanoate
Butyl pentanoate
Butyl hexanoate

ylene is worth testing to determine its effect on the development of aroma volatiles. Treatment with elevated concentration of ethylene might be effective in enhancing ripening and flavor development after CA storage. After an appropriate storage period, ethylene removal could be stopped, allowing the gas to re-accumulate, or the storeroom could be purged with ethylene. Light slightly stimulated the production of some odor-active volatiles, but the effect was too small for practical application. Knee et al. (1979) found an increase in the headspace concentration of esters, such as butyl and hexyl acetate, by illuminating the apples (cvs. Cox's Orange Pippin, Lady Sudely, and Golden Delicious) with fluorescent light during storage in low-O₂ atmosphere (2% O₂ + 98% N₂ at SC.

Apples are generally accepted by consumers after prolonged storage periods in LCA (Liu, 1985). However, the results presented in this study indicated that content of some important flavor components was very low. The content of these volatiles was lower than in fruits stored in simulated LCA for 8 months (Yahia et al., 1985), possibly because the ethylene scrubbing methods used during LCA storage oxidize hydrocarbons other than ethylene. Exposure to air, light, or 100% O₂ at

3.3°C for 3 to 4 weeks did not improve flavor of 'McIntosh' apples after storage in LCA for 9 months. Only the ripening temperature (20°C) stimulates the production of odor volatiles after storage in LCA. Further studies are needed to understand the mode of action of CA and to evaluate ethylene scrubbing systems for their effects on flavor volatiles.

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