ODOR-ACTIVE VOLATILES IN MCINTOSH APPLES STORED IN SIMULATED LOW-ETHYLENE CONTROLLED ATMOSPHERE.

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Introduction

The benefits of controlled atmosphere (CA) storage to prolong the life of apples is well established. Although the physiological and biochemical basis of CA is not completely understood, it has been observed that CA suppresses flavor in apples (7). The severity of suppression depends on both the atmospheric composition and the length of storage. The higher the CO_2, the lower the O_2 content, and the longer the fruit is kept under CA storage, the greater is the flavor suppression (9). Liu (10) has reported that low ethylene controlled atmosphere (LCA) storage was even more effective than conventional CA storage in preserving the firmness of McIntosh apples. However, the anecdotal observations that fruit stored under LCA do not develop full flavor potential must be examined because flavor is a major part of apple quality.

Odor, an important part of flavor, is caused by volatiles that emanate from the fruit. Almost 300 volatiles have been identified in apples (5) but most display little or no odor-activity at the concentrations found in the fruit (4). Recently, the most odor-active volatiles in apples were determined (4) and a quantitative method for the analysis of some of them has been developed (2). In this study some of the volatiles present in McIntosh apples were measured during LCA storage and after the fruit was removed from LCA.

Materials and Methods

Apples, *Malus domestica* Borkh, cv McIntosh, were harvested on September 28, 1984, from a mature standard-size tree grown on a Cornell University orchard in Ithaca, New York. Optimum maturity was determined by the method of Liu (10). The tree was sprayed about two months before harvest with 1000 ppm daminozide™. At harvest, three replicate samples of 40 apples were examined for internal ethylene by gas chromatography using a .30 m x 2 mm column packed with activated aluminum oxide. Flesh firmness was measured with the skin removed using an 'Effegi' fruit penetrometer equipped with an 11 mm plunger. The soluble solids were measured with a hand refractometer.

After harvest apples were either ripened in air at 20°C for four weeks and sampled every three days, or held in air at 3.3°C for four months and sampled every two weeks. Fruit for LCA were put into 19 L glass jars at 3.3°C with a flow-through system. Pre-mixed CA gases containing 3% O_2 + 3% CO_2 + 94% N_2 were humidified and metered through each jar at 200 ml/min. and monitored every day. The ethylene production, measured periodically, was always below 0.4 ppm. Fruit from LCA were sampled every four weeks for about eight months and then ripened in air at 20°C for four weeks and sampled every three days. Apples stored at 3.3°C and LCA were held at 20°C overnight before analysis.

Twenty-two odor-active volatiles were selected for this study including 20 esters and two aldehydes (Table 1). A sample of 10 (1-1.5 kg) apples were tested for flesh firmness. Then they were cut and pressed under methanol to inhibit enzymatic changes, using a hydraulic press with a stainless steel basket (Figure1). The odor-active volatiles were analyzed using N*O*V*A* (Non-polar Odor-active Volatile Analysis) outlined in Figure 1. The juice was extracted with Freon 113 (1,1,2-trichloro-1, 2,2-triflouroethane)

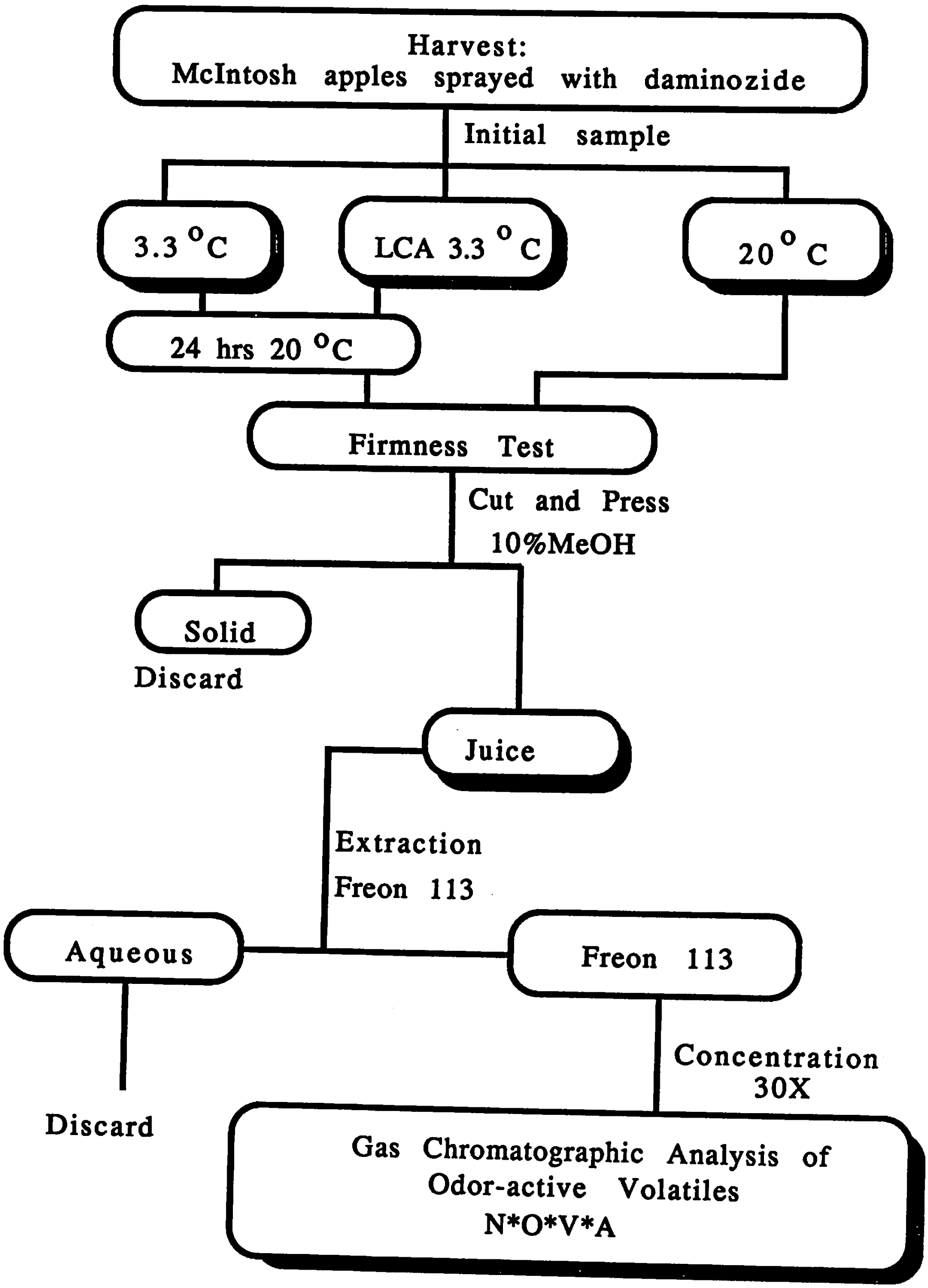

Figure 1 A flow diagram of the experiment.

with stirring (60 rpm for 30 minutes). The Freon 113 layer was separated, dried using $MgSO_4$, and concentrated in a rotary evaporator at 35°C (0.5 atm) to a 30 fold concentrate. Extracts were stored in amber glass bottles at 0°C until they were analyzed on a gas chromatograph equipped with a flame ionization detector and a 25 m x 0.36 mm fused silica column coated with 0.53 microns crosslinked methyl silicone (OV101). The column temperature was held at 35°C for 8 mi. and then increased 3°C/min to 250°C and held 15 min. The retention indices (8) of authentic standards were used to identify all 22 volatiles. Fourteen were verified by mass spectrometry (table 1). Retention indices (RI) were calculated using a n-paraffin hydrocarbon standard containing n-heptane (C7) through n-octadecane (C18). Mass spectra were obtained with an HP5985 quadrapole mass spectrometer with the same column used for gas chromatographic analysis.

Table 1. The odor-active volatiles analyzed and their method of identification. RI represents OV101 retention index and GC-MS represents gas chromatography- mass spectroscopy.

Compound	RI	GC-MS	Compound	RI	GC-MS
hexanal	+	-	methyl 2-methylbutanoate	+	+
(z)-2-hexenal	+	+	ethyl 2-methylbutanoate	+	+
			propyl 2-methylbutanoate	+	+
butyl acetate	+	-	butyl 2-methylbutanoate	+	+
pentyl acetate	+	-	pentyl 2-methylbutanote	+	+
hexyl acetate	+	-	hexyl 2-methylbutanoate	+	+
propyl propanoate	+	+	ethyl pentanoate	+	+
butyl propanoate	+	-	butyl pentanoate	+	-
pentyl propanoate	+	-			
			methyl hexanoate	+	+
methyl butanoate	+	+	butyl hexanoate	+	-
ethyl butanoate	+	+	hexyl hexanoate	+	+
propyl butanoate	+	+			

Results and Discussion

The apples at harvest had an average internal ethylene content of 0.16 ppm, an average firmness of 72.2 Newtons and 11.4% soluble solids. As shown in Figure 2, LCA storage was very effective in retaining the firmness of apples. In comparison, the fruit softened slowly when stored in air at 3.3°C and more rapidly in air at 20°C.

As shown in Figure 3, LCA storage severely suppressed the total production of odor-active volatiles. However, when apples were transferred from LCA to air at 20°C, they produced as much total volatiles as comparable apples did in air at 20°C before storage. The 22 compounds listed in Table 1 include 20 esters and 2 aldehydes that have been reported to be among the most important odor-active volatiles in apples (4,5). However, the similarity in the total amount of odor-active volatiles does not necessarily indicate a similarity in odor because the contribution each volatile makes to the odor is different. Butyl acetate, pentyl acetate, propyl propanoate, butyl propanoate, penty propanoate and pentyl 2-methylbutanoate were not detected in any of the samples.

The formation of hexanal, (Z)-2-hexenal, hexyl acetate, butyl pentanoate and methyl 2-methylbutanoate was not suppressed by LCA storage. For example, apples in LCA storage and in air at 3.3°C produced similar amounts of hexanal (Figure 4). Also, similar (Z)-2-hexenal levels were found in apples held in air at 20°C before and after LCA storage. Other volatiles which include most of the butanoates, 2-methylbutanoates and hexanoates were either severely or completely suppressed by LCA. For instance, the production of butyl hexanoate increased rapidly in air at 20°C and gradually in air at 3.3°C , but did not significantly increase during LCA (Figure 5). The production of ethyl butanoate was completely inhibited by LCA storage (Figure 6).

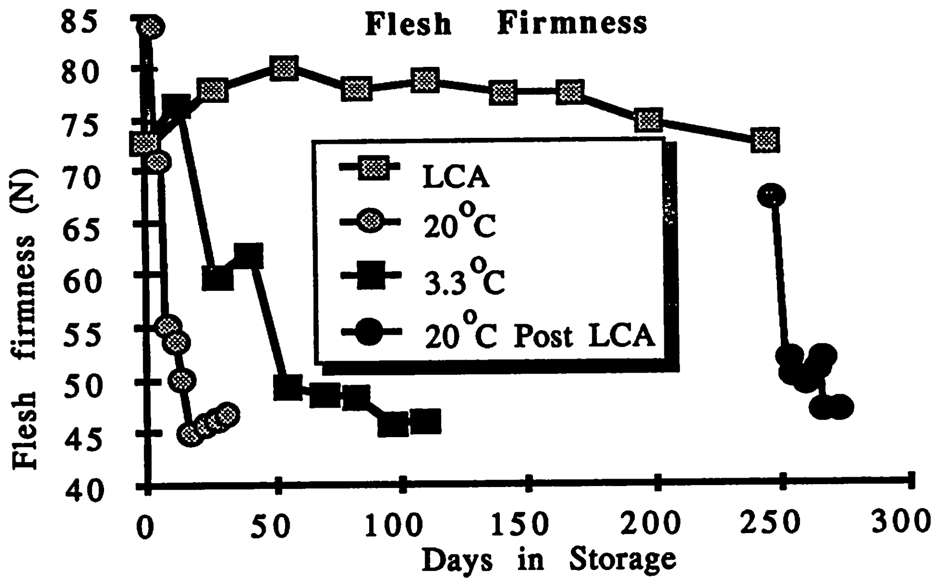

Figure 2 Flesh firmness of McIntosh apples stored under various storage environments.

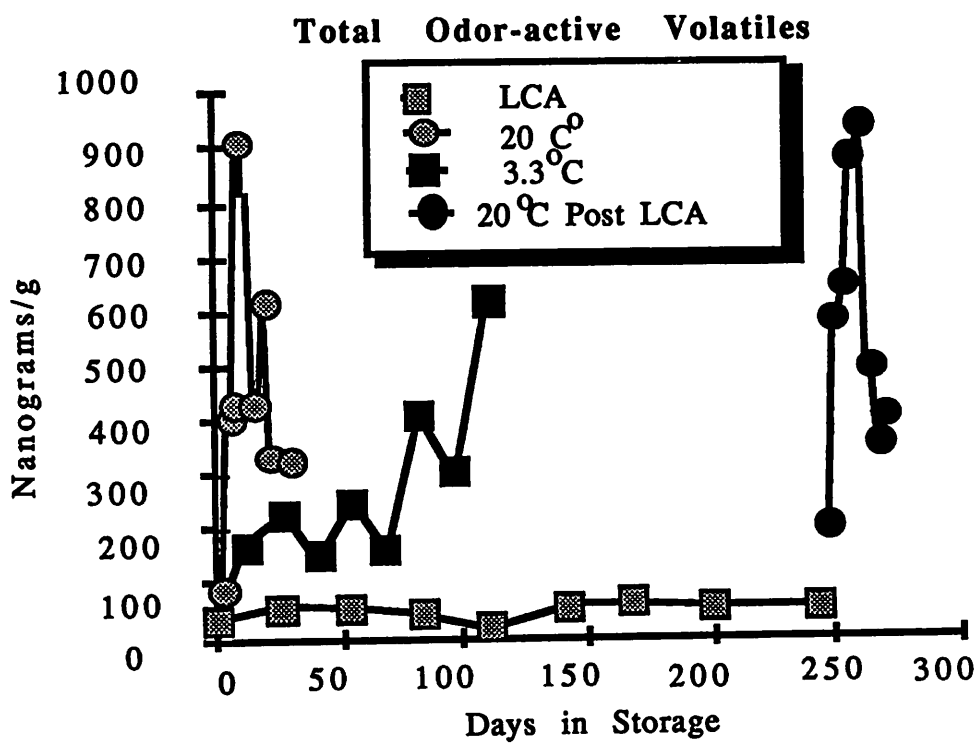

Figure 3 The production of total odor-active volatiles by McIntosh apples stored unrer various storage environments.

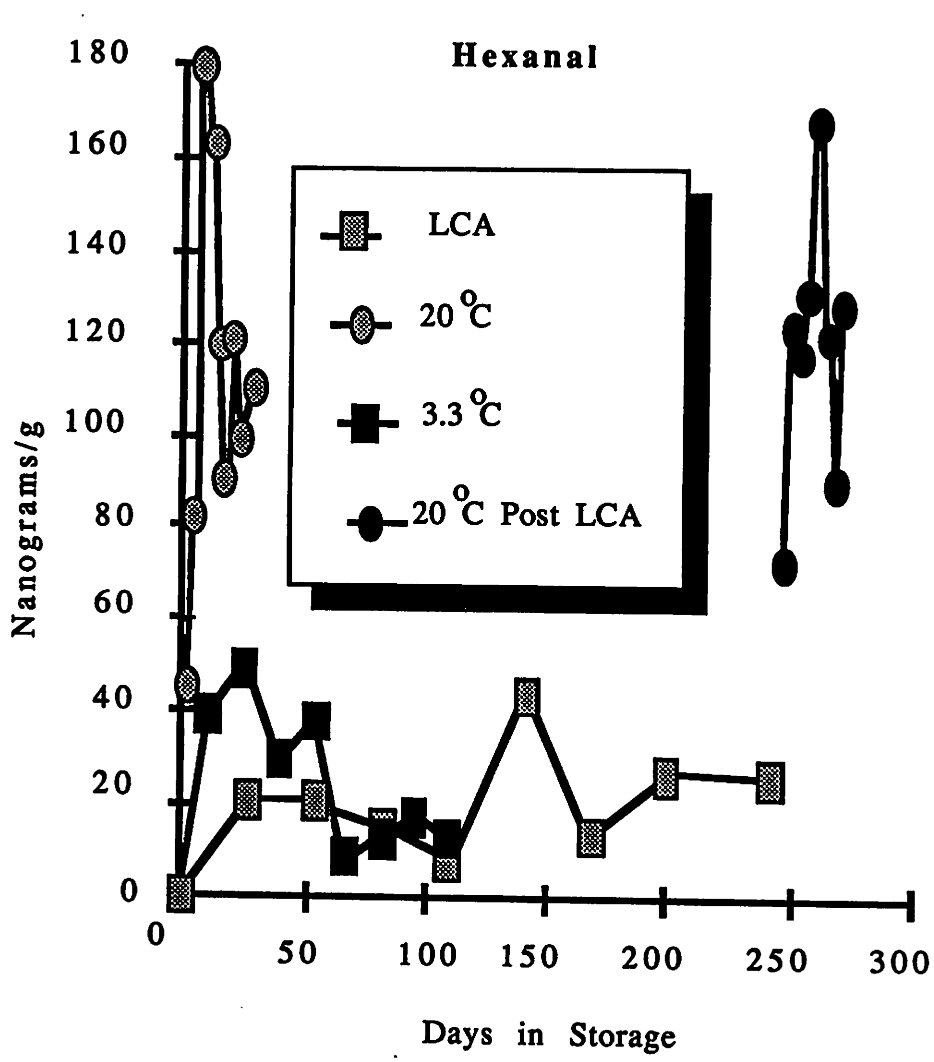

Figure 4 The production of hexanal by McIntosh apples stored under various storage environments.

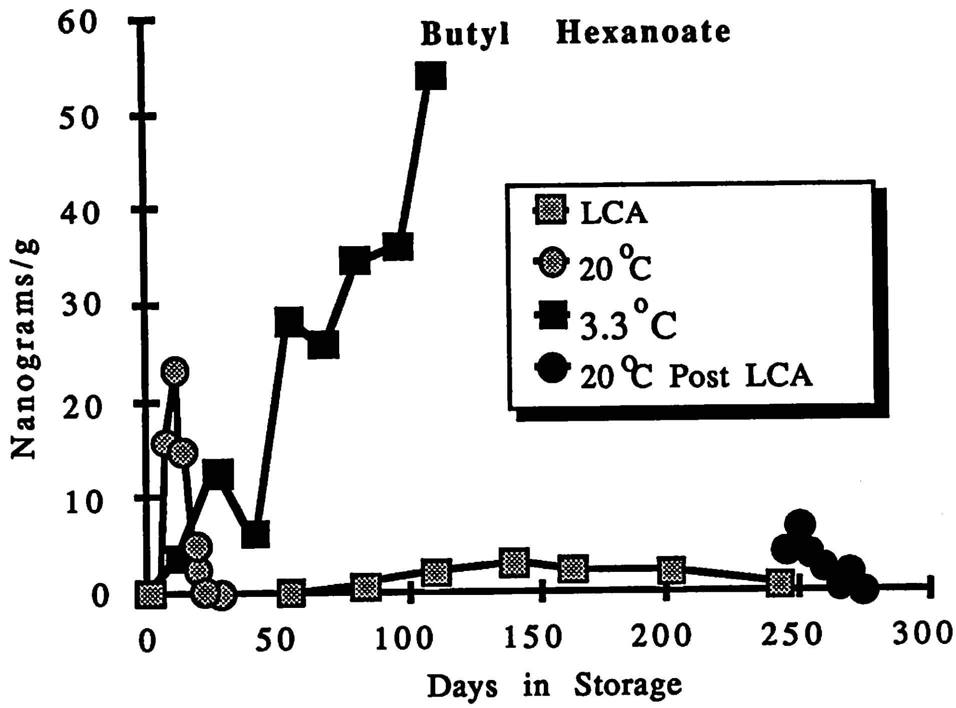

Figure 5 The production of butyl hexanoate by McIntosh apples stored under various storage environments.

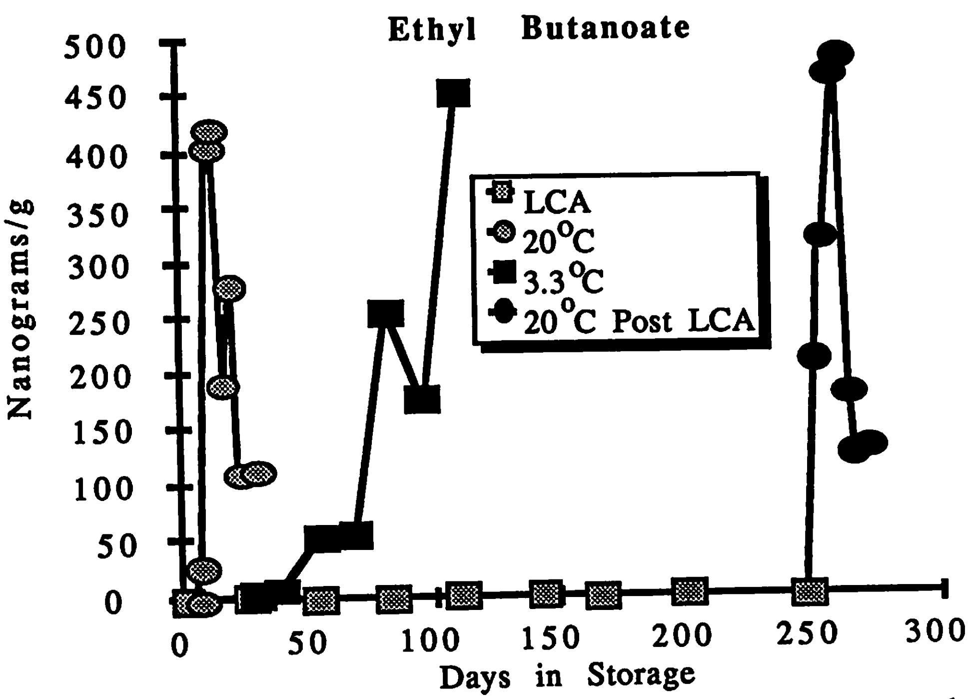

Figure 6 The production of ethyl butanoate by McIntosh apples stored under various environments.

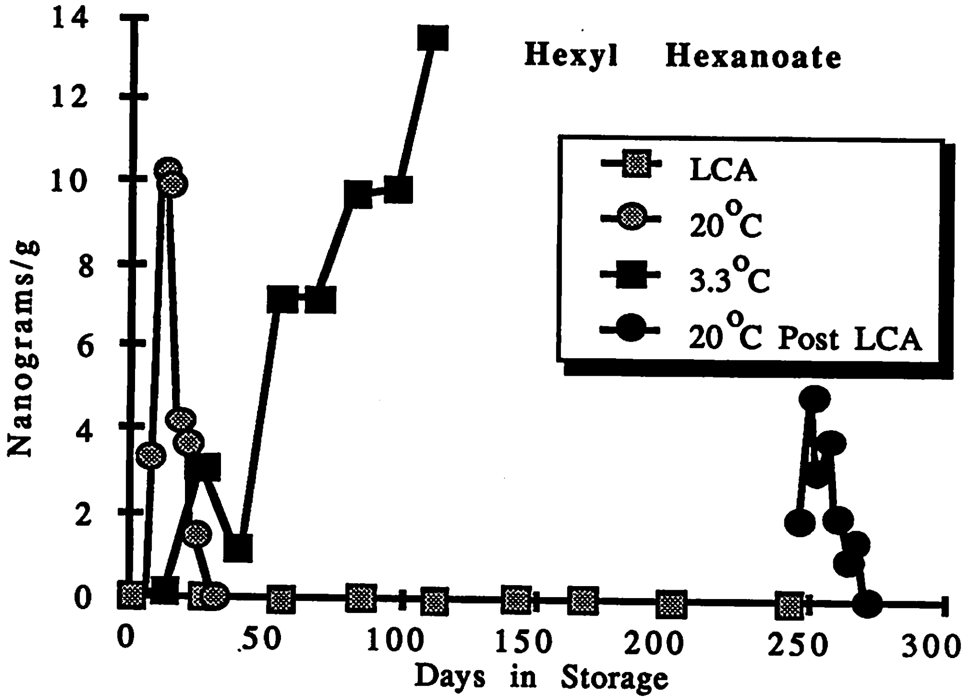

Figure 7 The production of hexyl hexanoate by McIntosh apples stored under various storage environments.

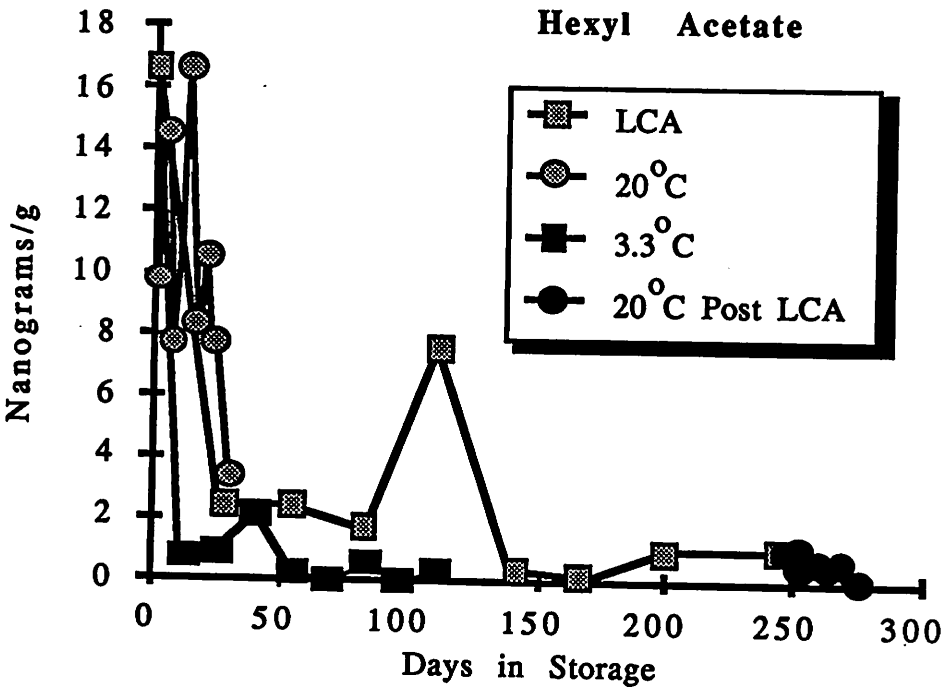

Figure 8 The production of hexyl acetate by McIntosh apples stored under various storage environments.

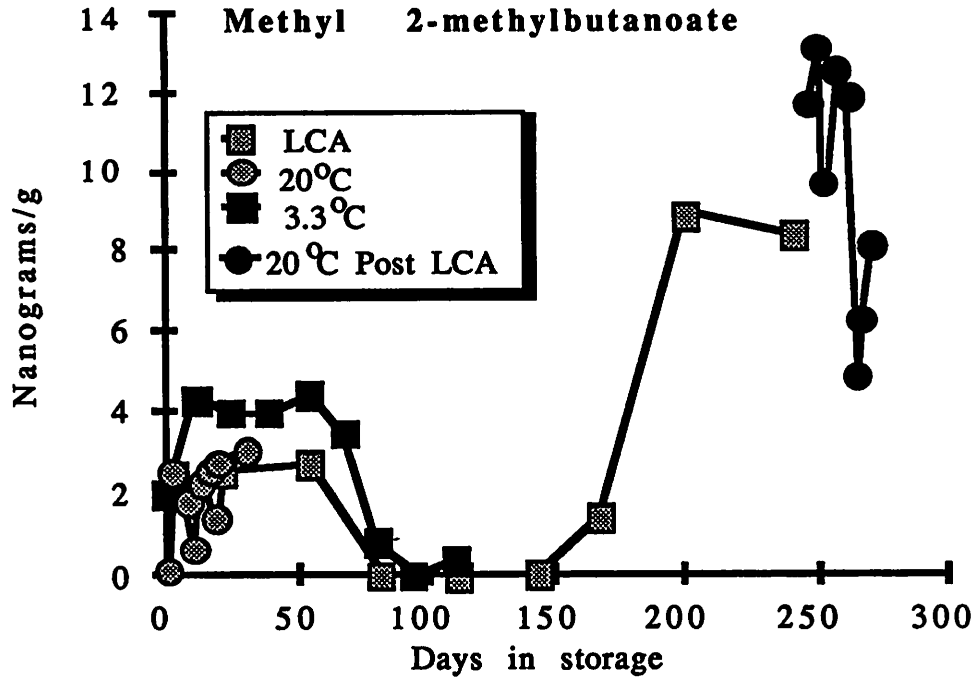

Figure 9 The production of methyl 2-methylbutanoate by McIntosh apples stored under various storage environments.

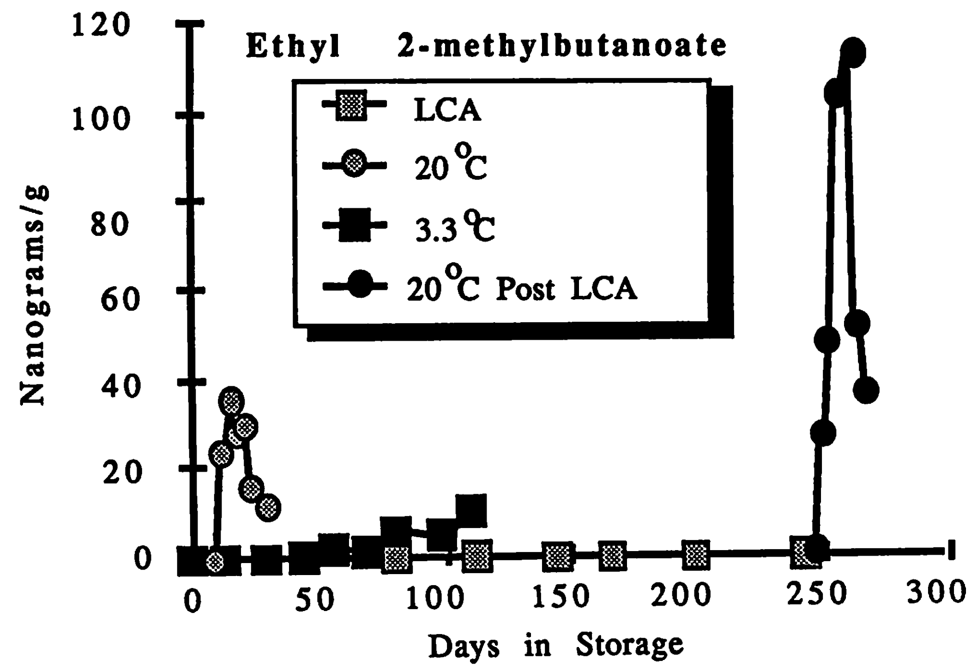

Figure 10 The production of ethyl 2-methylbutanoate by McIntosh apples stored under various storage environments.

McIntosh apples, after being stored in LCA for 8 months, still had the ability to produce most of the odor-volatiles when they were transferred to air at 20°C. For instance, apples before and after storage produced similar amounts of ethyl butanoate in air at 20°C (Figure 6). Apples after LCA storage produced about one half of the hexyl hexanoate of the pre-storage apples in air at 20°C (Figure 7). On the other hand, LCA storage had a residual effect on suppressing the production of butyl hexanoate (Figure 5) and hexyl acetate (Figure 8). It is also interesting that apples after LCA storage, produced more ethyl pentanoate, methyl 2-methylbutanoate (Figure 9), and ethyl 2-methylbutanoate (Figure 10) than apples before storage.

Since ethyl 2-methylbutanoate has been described as the character-impact in apple flavor (6) and since it has a very low odor threshold (0.1ppb.), the increase in its production may have particular importance.

Conclusion

LCA storage did not suppress the production of lipid oxidation products such as the aldehydes hexanal and (Z)-2-hexenal. On the other hand, LCA storage did suppress the production of short chain esters. This suppression was reversed when the apples were transferred from LCA to air at 20°C. Further research into the production of odor-active volatiles and their precursors during CA storage should lead to a better understanding of the effects of CA on the flavor of apples.

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