Change in Apple Fruit Volatiles after Storage in Atmospheres Inducing Anaerobic Metabolism

James P. Mattheis,*,† David A. Buchanan,† and John K. Fellman‡

Tree Fruit Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, 1104 North Western Avenue, Wenatchee, Washington 98801, and Department of Plant, Soil and Entomological Sciences, University of Idaho, Moscow, Idaho 83843

Delicious apple fruit (*Malus domestica* Borkh.) stored in 0.05% O_2/0.2% CO_2, 1 °C, for 30 days developed large concentrations of ethanol and acetaldehyde. The accumulation of products of anaerobic metabolism resulted in altered synthesis of fruit volatiles, most notably a large increase in the amount of ethyl acetate. Several ethyl esters, not detectable from control fruit, were present in headspace samples collected from apples stored in 0.05% O_2/0.2% CO_2 including ethyl propanoate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl hexanoate, ethyl heptanoate, and ethyl octanoate. The increase in the emission of these compounds was accompanied by a decrease in the amounts of other esters requiring the same carboxylic acid group for synthesis.

INTRODUCTION

The organoleptic quality of apple fruit is dependent on a number of factors including firmness, texture, sweetness, tartness, aroma, and flavor. Aroma and flavor are attributable in part to volatile compounds produced as a result of biosynthetic reactions occurring in the fruit (Guadagni et al., 1971). The predominant volatiles produced by apple fruit are indicative of the stage of fruit development (Drawert et al., 1969; Sapers et al., 1977) and are dependent on several factors including cultivar (Kakiguchi et al., 1986), cultural conditions (Paillard, 1981), and previous storage environment (Patterson et al., 1974; Willaert et al., 1983). Volatiles synthesized by preclimacteric apples are primarily aldehydes (De Pooter et al., 1987) whereas carboxy acid esters of aliphatic alcohols dominate the aroma from postclimacteric apples (Flath et al., 1967; Drawert et al., 1969). Ethanol is produced in ripening apples stored in air (Power and Chestnut, 1920); however, metabolic activity favoring production of ethanol increases during low-oxygen-induced anaerobic respiration (Thomas, 1925). Fruit ethanol concentration can increase several hundredfold depending on the duration of anaerobic respiration and variety of apple (Fidler, 1971; Patterson and Nichols, 1988).

Both physical and biochemical means of ethanol dissipation from apples are possible following return to aerobic metabolism. Ethanol is lost via evaporation (Cossins and Turner, 1959) and also enters various metabolic pathways to be converted to organic acids, amino acids, lipids, and carbohydrates (Cossins and Beevers, 1963). In apple fruit tissue this metabolic process occurs at a slow rate compared to that in carrot disks, pea cotyledons and shoots, castor bean endosperm, corn coleoptiles, potato tubers, and corn shoots (Cossins and Beevers, 1963). Aliphatic alcohols can also serve as substrates for ester synthesis in postclimacteric apples. Ethyl acetate as well as acetaldehyde was synthesized by Cox's Orange Pippin apples exposed to ethanol vapors (Knee and Hatfield, 1981), and additional volatile ethyl esters were identified from Delicious apples following a similar treatment (Berger and Drawert, 1984).

Many apple cultivars are stored commercially for extended periods under refrigerated controlled atmosphere conditions. Typically oxygen is lowered to 1-3% and CO_2 is allowed to accumulate to 1-3% depending on the cultivar being stored. Occasionally, technical problems in these facilities allow O_2 concentrations to fall below the Pasteur point and anaerobic metabolism is induced. Accumulation of ethanol and acetaldehyde can lead to development of off-flavors (Fidler and North, 1971). Dissipation of abnormally high amounts of ethanol and acetaldehyde is therefore essential to preservation of optimal fruit quality of apples.

Periods of anaerobiosis alter the senescence processes in apples and other fruits (MacLean et al., 1969; Itamura, 1986; Kelly and Saltveit, 1988). Because fruit volatile synthesis is altered during ripening and senescence, an investigation of apple volatiles produced after an extended period of anaerobiosis and subsequent recovery in air was conducted.

MATERIALS AND METHODS

Fruit Storage. Delicious apples were obtained from a local commercial warehouse after 4 or 5 months of controlled atmosphere (CA) storage (1.1% O_2/1.0% CO_2, 0.5 °C). Initial volatile samples were taken prior to imposition of the CA treatments. CA treatments were applied in 70-L aluminum chambers fitted with Plexiglas doors. Apples were stored at 1.5% O_2/2.0% CO_2 (control) or 0.05% O_2/0.2% CO_2 (anaerobic). Desired atmospheres were achieved within 2 days of sealing the chambers. O_2 and CO_2 concentrations in the chambers were measured by utilizing an electrochemical O_2 analyzer and an infrared gas analyzer for CO_2. Gas concentrations were adjusted by a microcomputer-controlled chamber monitoring system with N_2, air, and CO_2 supplied from compressed gas cylinders. Storage temperature was 1 °C. Fruits from all treatments (initial, control, anaerobic) were sampled after 1 and 7 days of ripening at 20 °C in air. Apples were removed from storage after 15 or 30 days; volatile analyses for apples stored for 30 days indicated qualitative similarities but quantitative increases from apples stored 15 days. Therefore, results of volatile analyses of fruit stored 30 days are reported.

Volatile Analysis. Apple samples (1 kg) were placed into glass jars (4 L) and sealed by using Teflon lids with two gas ports. Qualitative and quantitative volatile data were obtained by sampling intact fruit to avoid generation of volatiles in response to disruption of tissues (Takeoka et al., 1988). Compressed air, purified by flowing through a column containing potassium permanganate, activated charcoal, calcium hydroxide, and molecular sieve, was passed through the jars at 150 mL min^{-1} for 30

† U.S. Department of Agriculture.
‡ University of Idaho.

0021-8561/91/1439-1602$02.50/0

Table I. Volatiles Detected in Headspace Samples Collected from Whole Delicious Apples[a]

			nL kg^{-1} h^{-1}					
			initial		1.5% O_2		0.05% O_2	
peak	volatile	R_t, min	day 1	day 7	day 1	day 7	day 1	day 7
1	acetone	7.3	1.05	0.91	0.29	0.31	0.21	0.38
2	ethyl acetate	9.3	0	0	0.10	0.17	26.65	16.50
3	ethyl propanoate	12.2	0	0	0	0	0.93	0.85
4	propyl acetate	13.1	0	0	0	0.06	0.28	0.24
5	ethyl butyrate	16.1	0	0	0	0	1.50	0.83
6	ethyl 2-methylbutyrate	16.9	0	0	0	0	2.78	1.99
7	butyl acetate	17.9	0.26	0.89	0.13	0.20	0.21	0.21
8	hexanal	18.3	0.84	0.81	0	0.14	0.04	0.24
9	2-methylbutyl acetate	20.1	2.47	2.08	1.71	2.89	0.65	2.70
10	1-butanol	21.5	0.08	0.05	0.04	0.05	0.07	0.09
11	pentyl acetate	22.5	0.06	0.04	0.03	0.04	0.03	0.03
12	heptanal	23.0	0.34	0.32	0	0	0	0
13	2-methyl-1-butanol	24.0	0.29	0.21	0.20	0.27	0.18	0.44
14	butyl butyrate	24.7	0.06	0.06	0.04	0.09	0.02	0.02
15	butyl 2-methylbutyrate	24.8	0.03	0.04	0.01	0.08	0	0.03
16	ethyl hexanoate	24.9	0	0	0	0	0.64	0.34
17	hexyl acetate	26.4	0.60	0.25	0.40	0.31	0.34	0.21
18	octanal	27.4	0.13	0.25	0	0.05	0	0.05
19	ethyl heptanoate	28.6	0	0	0	0	0.01	0.01
20	6-methyl-5-hepten-2-one	28.7	0.08	0.10	0.04	0.04	0.04	0.02
21	hexyl propanoate	28.8	0	0	0	0.05	0	0.01
22	1-hexanol	29.2	0.05	0.02	0.03	0.02	0.02	0.01
23	nonanal	30.7	0.27	0.46	0.01	0.22	0.02	0.08
24	hexyl butyrate	31.2	0.17	0.07	0.08	0.15	0.01	0.04
25	hexyl 2-methylbutyrate	31.6	0.41	0.08	0.12	0.25	0.03	0.13
26	ethyl octanoate	31.9	0	0	0	0	0.13	0.08
27	decanal	33.9	0	0.51	0.12	0.14	0.11	0.12
28	benzaldehyde	34.8	0.04	0.02	0.01	0.01	0.02	0.01
29	hexyl hexanoate	36.6	0.42	0.20	0.19	0.25	0.08	0.15
	sum		7.66	7.36	3.57	5.83	34.99	25.82
	esters		4.48	3.71	2.81	4.54	34.28	24.37
	aldehydes		1.62	2.35	0.14	0.56	0.19	0.50
	alcohols		0.42	0.28	0.27	0.34	0.27	0.54
	ketones		1.13	1.01	0.33	0.35	0.25	0.40

[a] Values are averages of three 1-kg replicates/treatment. Volatile compounds were analyzed by GC–MS following collection using 50 mg of Tenax GC packed into 10-cm glass tubing. Apples were sampled prior to imposition of CA treatments (initial) and after 1 and 7 days in air at 20 °C following removal from 30 days of storage at 1 °C in 0.05% O_2 0.2% CO_2 or 1.5% O_2 2.0% CO_2.

min and then decreased to 100 mL min^{-1} for 5 min prior to sampling. The volume of headspace collected from each replication was 250 mL.

Volatiles were collected by using traps consisting of glass tubing (10 cm) packed with 50 mg of Tenax TA. Tenax was conditioned prior to use by Soxhlet extraction with methanol for 8 h and subsequent heating at 250 °C for 30 min with a flowing stream of nitrogen at 60 mL min^{-1}. After collection, volatiles were introduced into a GC–MS system via thermal desorption and cryofocusing (Farwell et al., 1979). Each trap was inserted into a carrier gas loop constructed from Teflon-lined stainless steel tubing, Cajun screw-type fittings, and a six-port Hamilton switching valve. Volatiles were desorbed from the trap with a hot air gun at 300 °C, and a 1-m section of fused silica capillary glass tubing was used as a cryoloop inserted into a Dewar of liquid N_2. Following desorption and cryofocusing, volatiles were introduced to the GC by exchanging the liquid N_2 Dewar for a container of hot (100 °C) water. A Hewlett-Packard 5890A-5971A GC–MSD system equipped with a DB-Wax column (J&W Scientific, 60 m, 0.25-μm i.d., 0.25-μm film thickness) was used for analysis. Conditions for chromatography were 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 gas velocity for He carrier 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. Spectra were recorded via a Hewlett-Packard 59970C Chemstation. Initial identification was made by matching against the Wiley/NBS library. Confirmation of identification was made by comparison of sample retention times and spectra with those of standards. Quantification was accomplished by using selected ion monitoring for base peaks and comparing abundance values with those for standards of known concentration.

Ethanol and acetaldehyde were measured according to a headspace method (Lidster et al., 1985). These compounds are not known to be produced in response to wounding and allowed calculation of tissue concentrations rather than rates at which individual volatile compounds evaporated from intact fruit (Knee and Hatfield, 1976). Individual apples were sectioned and placed into a 1-L jar with a septum in the lid. Following a 2-h equilibration period, 1-mL headspace samples were injected into a GC (Hewlett-Packard 5880) with a 0.6-m packed column (3.2-mm i.d., Poropak Q). Temperatures for oven, injector, and FID were 120, 200, and 250 °C, respectively. Flow rates for N_2, H_2, and air were 30, 25, and 300 mL min^{-1}, respectively.

Duplicate experiments were conducted, and similar results were obtained. Values reported are averages from the second experiment.

RESULTS

Volatile samples taken prior to the imposition of CA treatments contained 19 compounds other than ethanol and acetaldehyde (Table I). These compounds consisted of nine esters, five aldehydes, three alcohols, and two ketones. Esters were most prevalent on a concentration basis.

Ethanol and acetaldehyde concentrations increased over the 30-day storage period in 0.05% O_2 (Figures 1 and 2). Apples stored in 1.5% O_2 did not exhibit a similar increase. Concentrations of both ethanol and acetaldehyde in fruit previously stored at 0.05% O_2 declined following 7 additional days of room temperature storage (Figures 1 and 2) but remained in excess of that of 1.5% O_2 stored fruit.

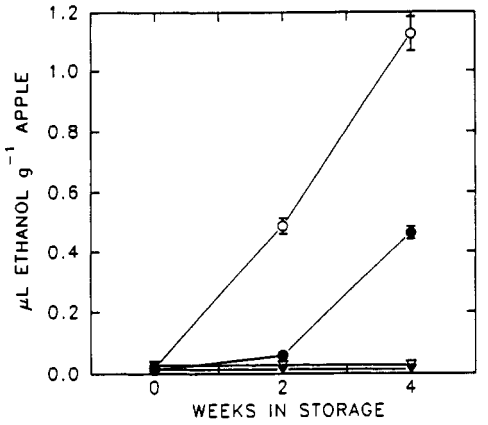

Figure 1. Amount of ethanol in apples stored under low-oxygen atmospheres. Apples were stored under 0.05% O_2/0.2% CO_2 or 1.5% O_2/2.0% CO_2, removed from controlled atmosphere chambers after 2 or 4 weeks, and analyzed after 1 or 7 days in air at 20 °C. 0.05% O_2, 1 day (○), 7 days (●); 1.5% O_2, 1 day (▽), 7 days (▼).

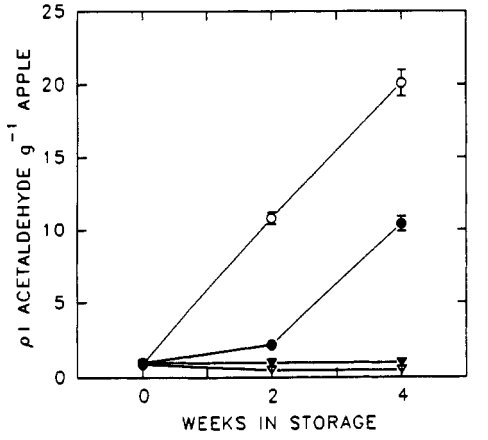

Figure 2. Amount of acetaldehyde in apples stored under low-oxygen atmospheres. Apples were stored under 0.05% O_2/0.2% CO_2 or 1.5% O_2/2.0% CO_2, removed from controlled atmosphere chambers after 2 or 4 weeks, and analyzed after 1 or 7 days in air at 20 °C. 0.05% O_2, 1 day (○), 7 days (●); 1.5% O_2, 1 day (▽), 7 days (▼).

Considerable alterations in the predominant volatiles were observed following 30 days of storage in 0.05% O_2 (Table I). A marked increase in the number and amount of ethyl esters was measured from anaerobic fruit, ethyl acetate being the most prevalent. Several ethyl esters were detected from anaerobic apples that were not found from the CA control or the initial samples. These included ethyl propanoate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl hexanoate, ethyl heptanoate, and ethyl octanoate. Propyl acetate and hexyl propanoate were detected from the CA treatment after 7 days of ripening following removal from storage. A decrease in several esters identified initially was observed from anaerobic apples including the predominant volatile 2-methylbutyl acetate as well as butyl butyrate and hexyl butyrate. When both storage treatments were compared to the initial samples, a decrease in the emission of C_6–C_{10} aldehydes, acetone, and 6-methyl-5-hepten-2-one was observed. The total amount of these compounds detectable from intact apples following both storage treatments did not approach levels from the initial sampling even after an additional 7 days of ripening at room temperature.

DISCUSSION

Because intact fruits were used, actual tissue concentrations of volatiles were not measured (Knee and Hatfield, 1976). Apple fruits have previously been demonstrated to metabolize exogenously applied ethanol to acetaldehyde and a variety of esters (Berger et al., 1984; Knee, 1981). Bartley et al. (1985) identified ethyl acetate as the major ester produced following ethanol treatments of intact apples. The 0.05% oxygen storage treatment resulted in a large accumulation of ethanol in our experiment. This resulted in the production of substantial amounts of ethyl acetate and several other ethyl esters not detectable prior to the storage treatments or after storage in 1.5% O_2. Apparently the large quantity of fruit ethanol produced in response to anaerobiosis is sufficient to displace other alcohols in reactions with the ester forming enzyme(s). This is evident in the reduced amounts of butyl butyrate, butyl 2-methylbutyrate, hexyl acetate, hexyl butyrate, hexyl 2-methylbutyrate, and hexyl hexanoate. All declined in headspace collected from anaerobic apples (Table I) while the corresponding ethyl ester increased from nondetectable levels. The decrease in butyl and hexyl esters emanating from fruit previously stored under anaerobic conditions, also noted by Berger and Drawert (1984) following treatment of apples with ethanol vapors, illustrates the competitive nature of acyl esterification.

The lack of several of these ethyl esters, particularly ethyl 2-methylbutyrate, in the initial and CA samples is also indicative of fruit previously stored in CA. Fruits used in these experiments were obtained from local commercial warehouses and had previously been stored under CA conditions. Lack of volatile synthesis by apples following extended CA storage is a well-documented phenomenon (Guadagni et al., 1971; Patterson et al., 1974) and would account for the lack of considerable ester production by these fruits at the initial sampling. A large increase in the endogenous levels of fruit alcohol, primarily ethanol, resulted in a corresponding increase in fruit ester synthesis. Following an examination of the metabolism of exogenous alcohols by apple fruit, Knee (1981) concluded that the lack of ester production in CA-stored apples was due to a lack of fruit alcohol. The increase in ester production following induction of anaerobiosis in these studies is likely due to the large increase in ethyl alcohol.

Another consequence of anaerobic storage was a decrease in the amount of aldehydes (other than acetaldehyde) and ketones present in headspace samples (Table I). The concentration of aldehydes was also lower in the CA treatment. Apples used in these experiments were obtained from a local warehouse and had been removed from CA and stored in regular cold storage for an unknown period prior to our use. Cold storage in air may have resulted in a greater accumulation of aldehydes and ketones than was subsequently observed following the low-oxygen treatments. De Pooter et al. (1984) reported aldehydes applied as vapors to intact apples were oxidized to the corresponding carboxylic acid in addition to conversion to alcohols. Acetaldehyde can be converted to acetate via acetyl CoA during fermentation; this conversion would allow acetate to be available for subsequent ester formation and would prevent disruption of ester synthesis due to lack of acetate. Conversion to esters would also be an additional route for depletion of acetaldehyde from fruit tissue in addition to evaporation and oxidation.

Volatile samples were collected from intact fruit to minimize generation of compounds due to disruption of tissues. Although samples collected in this manner do not necessarily reflect actual apple tissue concentrations (Knee and Hatfield, 1976), the data provide information that may be useful in the performance of nondestructive

analysis of large lots of apples to determine if exposure to conditions promoting anaerobic metabolic activity has previously occurred.

An increase in fruit ethanol concentration and the number and amounts of ethyl esters was observed following anaerobic storage of Delicious apples. Following 7 days of ripening at 20 °C after removal from storage, the amount of residual ethanol was reduced. In addition to oxidation and diffusion out of the fruit, ethanol was also dissipated via conversion to esters (and acetaldehyde) that are sufficiently volatile to evaporate out of apples to the surrounding atmosphere.

LITERATURE CITED

Bartley, I. M.; Stoker, P. G.; Martin, A. D. E.; Hatfield, S. G. S.; Knee, M. Synthesis of aroma compounds by apples supplied with alcohols and methyl esters of fatty acids. *J. Sci. Food Agric.* **1985**, *36*, 567–574.

Berger, R. G.; Drawert, F. Changes in the composition of volatiles by post-harvest application of alcohols to red delicious apples. *J. Sci. Food Agric.* **1984**, *35*, 1318–1325.

Cossins, E. A.; Beevers, H. Ethanol metabolism in plant tissues. *Plant Physiol.* **1963**, *38*, 375–380.

Cossins, E. A.; Turner, E. R. Utilization of alcohol in germinating pea seedlings. *Nature* **1959**, *183*, 1599–1600.

De Pooter, H. L.; Van Acker, M. R.; Schamp, N. M. Aldehyde metabolism and the aroma quality of stored Golden Delicious apples. *Phytochemistry* **1987**,*26*, 89–92.

Drawert, F.; Heimann, W.; Emberger, R.; Tressl, R. Formation of aroma substances in apples during growth and storage. *Z. Lebensm. Unters. Forsch.* **1969**, *140*, 65–88.

Farwell, S. O.; Gluck, S. J.; Bamesberger, W. L.; Schutte, T. M.; Adams, D. F. Determination of sulfur-containing gases by a deactivated cryogenic enrichment and capillary gas chromatographic system. *Anal. Chem.* **1979**, *51*, 609–615.

Fidler, J. C. The metabolism of acetaldehyde by plant tissues. *J. Exp. Bot.* **1968**, *19*, 41–51.

Fidler, J. C.; North, C. J. The effect of periods of anaerobiosis on the storage of apples. *J. Hortic. Sci.* **1971**, *46*, 231–221.

Flath, R. A.; Black, D. R.; Guadagni, D. G.; McFadden, W. H.; Schultz, T. H. Identification and organoleptic evaluation of compounds in Delicious apple essence. *J. Agric. Food Chem.* **1967**, *15*, 29–35.

Guadagni, D. G.; Bomben, J. L.; Hudson, J. S. Factors influencing the development of aroma in apple peels. *J. Sci. Food Agric.* **1971**, *22*, 110–115.

Itamura, H. Relationship between fruit softening, respiration and ethylene production after deastringent treatment by alcohol in Japanese persimmon (*Diospyras kaki Thunb* var. Hiratanenaski) fruit harvested at various stages. *J. Jpn. Soc. Hortic. Sci.* **1986**, *55*, 89–98.

Kakiguchi, N.; Moriguchi, S.; Fukuda, H.; Ichimura, N.; Kato, Y.; Banba, Y. Composition of volatile compounds of apple fruits in relation to cultivar. *J. Jpn. Soc. Hortic. Sci.* **1986**, *55*, 280–289.

Kelly, M. O.; Saltveit, M. E., Jr. Effect of endogenously synthesized and exogenously applied ethanol on tomato fruit ripening. *Plant Physiol.* **1988**, *88*, 143–147.

Knee, M.; Hatfield, S. G. S. A comparison of methods for measuring the volatile components of apple fruits. *J. Food Technol.* **1976**, *11*, 485–493.

Knee, M.; Hatfield, S. G. S. The metabolism of alcohols by apple fruit tissue. *J. Sci. Food Agric.* **1981**, *32*, 593–600.

Lidster, P. D.; Blanpied, G. D.; Lougheed, E. C. Factors affecting the progressive development of low-oxygen injury in apples. In *Controlled Atmospheres for Storage and Transport of Perishable Agricultural Commodities*; Blankenship, S. M., Ed.; North Carolina State University Press: Raleigh, NC, 1985; pp 57–69.

MacLean, D. C.; Dedolph, R. R.; Dilley, D. R.; Dewey, D. H. Effects of cyclic anaerobiosis on pome fruits. *J. Am. Soc. Hortic. Sci.* **1969**, *94*, 221–223.

Paillard, N. Factors influencing flavour formation in fruit. In *Flavour '81*; Schrier, P., Ed.; de Gruyter: New York, 1981; p 479.

Patterson, B. D.; Hatfield, S. G. S.; Knee, M. Residual effects of controlled atmosphere storage on the production of volatile compounds by two varieties of apples. *J. Sci. Food Agric.* **1974**, *25*, 843–849.

Patterson, M. E.; Nichols, W. C. Metabolic response of 'Delicious' apples to carbon dioxide in anoxic and low-oxygen environments. *HortScience* **1988**, *23*, 866–868.

Power, F. B.; Chestnut, V. K. The odorous constituents of apples. Estimation of acetaldehyde from the ripe fruit. *J. Am. Chem. Soc.* **1920**, *42*, 1509–1525.

Sapers, G. M.; Abbott, J.; Massie, D.; Watada, A.; Finney, E. E., Jr. Volatile composition of McIntosh apple juice as a function of maturity and ripeness indices. *J. Food Sci.* **1977**, *42*, 44–47.

Takeoka, G. R.; Flath, R. A.; Guntert, M.; Jennings, W. Nectarine volatiles: Vacuum steam distillation versus headspace sampling. *J. Agric. Food Chem.* **1988**, *36*, 553–560.

Thomas, M. The controlling influence of carbon dioxide. V. A quantitative study of the production of ethyl alcohol and acetaldehyde by cells of the higher plants in relation to concentration of oxygen and carbon dioxide. *Biochem. J.* **1925**, *19*, 927–947.

Willaert, G. A.; Dirinck, P. J.; DePooter, H. L.; Schamp, N. M. 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 December 10, 1990. Accepted May 29, 1991. Reference to a company name or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

Registry No. Acetone, 67-64-1; ethyl acetate, 141-78-6; ethyl propionate, 105-37-3; propyl acetate, 109-60-4; ethyl butyrate, 105-54-4; ethyl 2-methylbutyrate, 7452-79-1; butyl acetate, 123-86-4; hexanal, 66-25-1; 2-methylbutyl acetate, 624-41-9; 1-butanol, 71-36-3; pentyl acetate, 628-63-7; heptanal, 111-71-7; 2-methyl-1-butanol, 137-32-6; butyl butyrate, 109-21-7; butyl 2-methylbutyrate, 15706-73-7; ethyl hexanoate, 123-66-0; hexyl acetate, 142-92-7; octanal, 124-13-0; ethyl heptanoate, 106-30-9; 6-methyl-5-hepten-2-one, 110-93-0; hexyl propionate, 2445-76-3; 1-hexanol, 111-27-3; nonanal, 124-19-6; hexyl butyrate, 2639-63-6; hexyl 2-methylbutyrate, 10032-15-2; ethyl octanoate, 106-32-1; decanal, 112-31-2; benzaldehyde, 100-52-7; hexyl hexnaoate, 6378-65-0; ethanol, 64-17-5; acetaldehyde, 75-07-0.