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Volatile Aromatic Constituents of Tree Ripened and Mature Green 'Irwin' Mango Fruits during Low Temperature Storage

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Changes in volatile aroma constituents of tree ripened (TR) and mature green (MG) 'Irwin' mangoes stored at 5°C for 20 and 30 days were determined by headspace solid phase microextraction/gas chromatography-mass spectrometry. Terpenes were the major volatile compounds of 'Irwin' mangoes, amongst which α-terpinolene was likely the main volatile compound responsible for the typical sweet aroma of this cultivar. Storage at low temperature caused a negligible reduction in terpenes of both TR and MG fruits. However, storage induced a significant increase in the production of off-odors. Off-odors were detected more often in MG fruits and appeared after 20 days, whereas in TR fruits they were observed after 30 days of storage. The occurrence of heptenal, decenal, heptanol, and nonenal that are likely responsible for the generation of off-odors in the pulp during the low temperature storage, are likely due to the increased biosynthesis of those aldehydes rather than the reduction of terpenes.

Key Words: aroma, Irwin, low temperature storage, mango, solid phase micro extraction (SPME).

Introduction

Shelf life of tropical fruit such as mango as depends on the storage conditions, maturity at harvest and on physical and pathological damage of fruits. Short term storage of fresh mango fruits is possible by modifying the storage atmosphere (temperature, humidity, oxygen, ethylene and carbon dioxide) to reduce respiration and transpiration of fruits (Beaudry et al., 1992; Yahia, 1998). However, failure to develop color, loss of texture and development of off-flavors are the major problems in long term storage of mangoes. Most studies on low temperature and controlled atmosphere storages report the loss of aroma in various fruits during storage (Ke and Kader, 1990; Maul et al., 2000; MacDonald et al., 1996). The generation of off-flavors during controlled atmosphere storage of mango has been attributed to the production of ethanol and acetaldehyde (Bender et al., 2000). Response to controlled atmosphere storage depends on the stage of ripening and cultivars (Bender et al., 2000). Tree ripened mangoes produced higher aromatic volatiles are able to tolerate lower temperatures under controlled atmospheres than mature green ones (Bender et al., 2000). Higher ethanol and acetaldehyde production and lower terpenes and hexanal also occurred in mangoes stored at 25% CO_2 atmosphere (Bender et al., 2000). Increased activities of pyruvate decarboxylase and alcohol dehydrogenase during hypoxia (Ke et al., 1994) of controlled atmosphere storage were responsible for the increased acetaldehyde and ethanol concentrations (Bender et al., 2000). Higher lipoxygenase activity was observed when pear fruits were stored at low temperature (Lara et al., 2003). Higher mono and sesquiterpene biosynthesis developed in 'Kensington Pride' fruits ripened at 20°C (Lalel et al., 2004a). A positive correlation was also seen between fatty acids and sesquiterpenes, alcohols and esters.

Reduction in hexanoate and propanoate esters was observed when apples were stored at 1°C for 20 weeks (Plotto et al., 2000); but a greater reduction occurred under controlled atmosphere. Generation of off-flavors, reduction in ripe tomato flavor, increase in methanol, and reduction in hexenal and hexanal have been observed during low temperature storage of tomato (Maul et al., 2000); under similar conditions, irreversible changes in the activities of ethylene biosynthetic enzymes were observed (Bender et al., 2000). In this study the change in volatile aromatic compounds during low temperature storage at 5°C of tree-ripened and mature green mangoes were evaluated.

Materials and Methods

1. Plant material

Tree ripened (TR) and mature green (MG) mangoes

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('Irwin') grown in green houses on Okinawa island of Japan were procured in June 2002. Uniform fruits, selected for the experiment, were dipped in acidic electrolysed water (pH 2.6, oxidation reduction potential 1100 mV, free available chlorine) (Al-Haq et al., 2002) and hot water (46–48°C) for 10 min each to reduce the fruit rot during the storage. Ten TR fruits were set aside as soon as they arrived as the "no storage" group, while 20 TR fruits were stored at 5°C and a relative humidity of 75–80% for 20 and 30 days. Ten MG fruits were ripened at room temperature (25°C) for 4–7 days until edible. A total of 20 MG fruits were stored at 5°C for 20 and 30 days and then ripened for 4–7 days at room temperature until edible.

2. Extraction of volatile constituents

Volatile aromatic constituents were extracted from the headspace of pulp homogenate using solid phase micro extraction (SPME) technique that uses polymer-coated silica fibers which adsorbs the volatiles. In this study we used Divinylbenzene/Carboxen/Poly (dimethylsiloxane) polymer for adsorption of volatiles. A 20-g homogenate of fruit pulp was diluted to 60 mL with distilled water and poured into a 100 mL conical flask. The SPME fiber (100 μm film) was exposed to the headspace overnight at a temperature of 30°C. Aroma volatiles were identified using GS-MS. The GC effluents were sniffed to identify the odors of the major volatile constituents of mango.

3. Gas chromatography conditions

The mango volatiles were separated on DB-5MS column (J&W Scientific Inc., USA), 30 m × 0.32 mm i.d. (0.5 μm film) coated with phenyl methylpolysiloxane, using a Gas Chromatograph model 17A (Shimadzu Co., Japan). Column oven temperature was programmed to initially remain at 60°C for 6 min, rise at a rate of 5°C/min, and maintain a final temperature of 230°C for 6 min. Injector and detector temperatures were maintained at 230 and 250°C respectively. Gas chromatograph-mass spectra were analyzed using the same column and temperature program. Mass units were monitored from 40 to 350 at 70 eV. Compounds were identified by comparing the mass spectra with that of NIST (National Institute of Standards and Technology) library.

Results and Discussion

The relative percentages (each peak area against total peak area) of volatile compounds of TR and MG mangoes (Table 1) reveal that the terpenes are the major volatile group of 'Irwin' mangoes. 3-Carene, the most abundant terpene, was followed by α-terpinolene, myrcene, and limonene. Aldehydes and alcohols followed terpenes. Among sesquiterpenes, α-caryophyllene was the major one followed by α-copaene and humulene. Lower alcohol production during low temperature storage may be due to the reduction in respiration (Shivashankara et al., 2004). Reduction in alcohols and an increase in aldehydes have been observed when 'Kensington pride' mangoes were ripened at 15°C as compared to ripening at 30°C (Lalel et al., 2004a). Lower ethanol production under low temperature storage was also reported for orange (Ke and Kader, 1990) and mango (Bender et al., 2000). Lower ethanol and hexanal concentrations were found in the same study when TR mangoes were stored at 8°C when compared to those stored at 12°C in the ambient atmosphere.

Fruit aroma was the main component that changed during the storage at low temperature. Even though the fruits maintained good functional properties and acceptable total soluble solids and acidity, they would not be accepted if their aroma was bad. Sniffing of GC effluents indicated that α-terpinolene was the major contributor for the typical sweet aroma of this cultivar, whereas heptenal, heptanol, nonenal, nonadienal, and decenal were the main volatiles responsible for the development of off-odors in mango during storage. 2,6-Nonadienal and (*E*)-2-nonenal were responsible for the cucumber odor of mangoes. Heptenal and nonenal concentrations increased with the storage duration. Similar changes were observed when table-ripe tomato fruits were stored at 5°C for 8 days, compared those stored at 20°C (Maul et al., 2000). Lower ripening temperatures also increased aldehyde production in mango (Lalel et al., 2004b). The stages of harvest of TR and MG mangoes had no significant effect on volatile composition at room temperature.

1. Tree ripened fruits

The relative percentage of total terpenes did not differ significantly during the storage period, but the percentage of aldehydes increased notably, whereas the percentage of alcohols decreased. There was an increase in the relative percentage of sesquiterpenes, caryophyllene, and humulene during the storage but the percentage of α-copaene decreased. A significant reduction in concentration of major terpenes was not reported when tree ripened 'Tommy Atkins' mangoes were stored at 12 and 8°C (Bender et al., 2000).

The production of off-odors in TR mangoes stored for 30 days at 5°C may be attributable to the higher production of some of the aldehydes especially (*E*)-2-nonenal and not to the reduction in terpenes.

2. Mature green fruits

Terpenes were found to be the most abundant compounds in the pulp of the MG fruits stored and ripened at room temperature. In fruits exposed to low temperatures for 20 days, aldehydes were the most abundant volatiles. MG fruits stored up to 30 days were not analyzed for aroma because off-odors were noticed after 20 days of storage. The percentage of terpenes decreased significantly with the storage.

The generation of off-odors in MG fruits stored at low

Table 1. Relative percentage of volatile compounds of tree ripened and mature green 'Irwin' mangoes.

Retention time (min)	Volatile compounds	KI[z]	Tree ripened[y]			Mature green[x]		Odor quality
			NS	20DS	30DS	RT	20DS RT	
1.39	Ethanol		5.03	4.12	2.34	8.46	6.12	Yeast
4.21	Hexanal	721	0.13	0.09	0	0.13	0.11	Greens
5.90	Ethyl benzene	868	0.34	0.31	0.04	0.46	0.06	
6.21	*p*-Xylene	875	0.49	0.38	0.08	0.53	0.08	Rubbery
9.23	α-Pinene	944	0.15	0.16	0.14	0.16	0.05	Grass
10.17	2-Heptenal	964	0.34	0.35	0.47	0.18	0.30	Bad puddled soil
10.68	1-Heptanol	975	0.05	0.04	0	0.05	0	Fishy
10.86	*m*-Cymene	978	0.10	0.12	0.11	0.10	0.03	
11.46	Myrcene	989	2.43	2.40	2.31	2.29	1.36	Grass
12.32	3-Carene	1008	34.10	34.80	33.60	35.70	24.41	Leafy
12.94	*p*-Cymene	1026	0.31	0.32	0.47	0.32	0.36	
13.09	Limonene	1030	1.73	1.63	1.64	1.67	1.70	Lime
13.15	β-Phellandrene	1032	0.90	0.79	0.80	0.83	0.33	
13.71	(*E*)-Ocimene	1048	0.19	0.21	0.23	0.17	0.08	Mango leaf
14.17	γ-Terpinene	1060	0.17	0.19	0.21	0.14	0.36	Over ripe
14.72	1-Octanol	1074	0.14	0.07	0	0.13	0.18	Mushroom
15.07	Allocimene	1083	0.47	0.44	0.46	0.45	0.36	Grassy
15.23	α-Terpinolene	1087	3.82	3.73	3.71	3.65	2.65	Mango fruity
15.44	Isopropenyltoluene	1092	0.33	0.40	0.42	0.50	0.43	
15.52	4-Nonenal	1094	1.12	1.44	0.82	0.79	1.00	Floral
15.92	Nonanal	1105	0.52	0.82	0.58	0.60	0.88	Strong floral
16.30	Phenylethyl alcohol	1117	0	0	0	0.29	0.11	Off-odor
17.41	(*Z*)-3-Nonen-1-ol	1150	0.38	0.39	0.48	0.27	0.42	Bug + cucumber
17.68	2,6-Nonadienal	1158	8.93	9.02	8.41	6.81	15.23	Strong cucumber
17.95	(*E*)-2-Nonenal	1166	3.28	20.12	23.89	7.34	26.73	Stinking bug
18.21	1-Nonanol	1173	3.92	2.23	0.73	0	0.11	Creamy
18.26	*trans*-Hexenyl butyrate	1175	3.13	1.06	0	5.55	0.14	Butter
19.43	Decanal	1208	0.21	0.22	0.22	0.15	0.40	Off-odor
21.27	(*E*)-2-Decenal	1266	0.10	0.10	0.11	0.11	0.40	Off-odor
24.71	α-Copaene	1354	0.55	0.31	0	1.17	0.12	Sweet fruity
26.16	Caryophyllene	1430	0.67	1.22	1.33	1.55	1.31	Sweet fruity
27.16	Humulene	1466	0.57	0.93	1.02	1.20	0.82	Strong sweet fruity
30.76	Hexadecane	1600	0.18	0.17	0.34	0.21	0.06	Sweet fruity
33.24	Heptadecane	1665	0.30	0.25	0	0.33	0.17	Sweet fruity
Terpenes			46.16	47.19	45.97	49.40	33.12	
Aldehydes			14.61	32.15	34.48	16.12	45.05	
Alcohols			9.51	6.85	3.54	9.19	6.93	
Esters			3.13	1.06	0	5.55	0.14	
Others			1.63	1.50	0.87	2.03	0.80	
Total			75.04	88.75	84.86	83.40	86.04	

[z] KI, Kovats Index.
[y] NS, No storage; 20DS, Stored at 5°C for 20 days; 30DS, Stored at 5°C for 30 days.
[x] RT, stored at room temperature till the fruits are ripen; 20DS RT, Stored at 5°C for 20 days and at room temperature till the fruits are ripen.

temperature paralleled the significant increase in aldehydes as observed in TR fruits. Major aldehydes responsible for the development of off-odor were, 2,6-nonadienal, (*E*)-2-nonenal, 1-nonanol, (*Z*)-3-nonen-1-ol, nonanal, decanal and (*E*)-2-decenal. Higher production of aldehydes in MG fruits might be attributed to the higher production of fatty acid and lipid breakdown as the result of low temperature storage. More fatty acid was produced by fruits during the first 5 days of ripening at 15°C compared to those ripened at 25°C (Lalel et al, 2004b). Higher aldehydes in fruits stored at low temperatures might also be related to the higher lipoxygenase activity (Lara et al., 2003).

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Literature Cited

Al-Haq, M. I., Y. Seo, S. Oshita and Y. Kawagoe. 2002. Disinfection effects of electrolyzed oxidizing water on suppressing fruit rot of pear caused by *Bortyosphaeria berengeriana*. Food Res. Int. 35: 657–664.

Beaudry, R. M., A. C. Cameron, A. Shirazi and D. L. Dostal-Lange. 1992. Modified atmosphere packaging of blueberry fruit: Effect of temperature on package oxygen and carbon dioxide. J. Amer. Soc. Hort. Sci. 117: 436–441.

Bender, R. J., J. K. Brecht, E. A. Baldwin and T. M. M. Malundo. 2000. Aroma volatiles of mature-green and tree-ripe tommy atkins mangoes after controlled atmosphere vs. air storage. HortScience 35: 684–686.

Ke, D. and A. A. Kader. 1990. Tolerance of Valencia oranges to controlled atmospheres as determined by physiological responses and quality attributes. J. Amer. Soc. Hort. Sci. 115: 779–783.

Ke, D., E. Yahia, M. Mateos and A. A. Kader. 1994. Ethanolic fermentation of 'bartlett' pears as influenced by ripening stage and atmospheric composition. J. Amer. Soc. Hort. Sci. 119: 976–982.

Lalel, H. J. D., Z. Singh and S. C. Tan. 2004a. Ripening temperatures influence biosynthesis of aroma volatile compounds in Kensington pride mango fruit. J. Hort. Sci. Biotech. 79: 146–157.

Lalel, H. J. D., Z. Singh and S. C. Tan. 2004b. The role of ethylene in mango fruit aroma volatiles biosynthesis. J. Hort. Sci. Biotech. 78: 485–496.

Lara, I., R. M. Miro, T. Fuentes, G. Sayez, J. Graell and M. L. Lopez. 2003. Biosynthesis of volatile compounds in pear fruit stored under long-term controlled atmosphere conditions. Postharvest Biol. and Tech. 29: 129–139.

Maul, F., S. A. Sargent, C. A. Sims, E. A. Baldwin, M. O. Balaban and W. Huber. 2000. Tomato flavor and aroma quality as affected by storage temperature. J. Food Sci. 65: 1228–1237.

McDonald, R. E., T. G. McCollum and E. A. Baldwin. 1996. Prestorage heat treatments influence free sterols and flavor volatiles of tomatoes at chilling temperature. J. Amer. Soc. Hort. Sci. 121: 531–536.

Plotto, A., M. R. McDaniel and J. P. Mattheis. 2000. Characterization of Changes in gala apple aroma during storage using osme analysis, a gas chromatography-olfactometry technique. J. Amer. Soc. Hort. Sci. 125: 714–722.

Shivashankara, K. S., S. Isobe, M. I. Al-Haq, M. Takenaka and T. Shiina. 2004. Fruit antioxidant activity, ascorbic acid, total phenol, quercetin and carotene of Irwin mango fruits stored at low temperature after high electric field pretreatment. J. Agric. Food Chem. 52: 1281–1286.

Yahia, E. M. 1998. Modified and controlled atmospheres for tropical fruits. Hort. Rev. 22: 123–183.

樹上完熟および緑熟マンゴー（'Irwin'）の低温貯蔵における揮発性香気成分

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樹上完熟（tree ripened, TR）および緑熟（mature green, MG）マンゴーの 20 および 30 日の低温貯蔵（5 ℃）中の揮発性香気成分の変化について，ヘッドスペース固相マイクロ抽出／ガスクロマトグラフィー質量分析法により評価した．テルペン類は 'Irwin' マンゴーの主要な香気成分であり，テルペンの中でも α-テルピノレンがこの品種のマンゴーの典型的な甘い香気を発する揮発性成分であると考えられた．低温貯蔵による TR および MG マンゴー両者におけるテルペン類の減少はわずかであった．しかしながら，マンゴーの低温貯蔵によりオフフレーバーが顕著に発生した．オフフレーバーは MG マンゴーにおいて低温貯蔵 20 日後に，TR マンゴーにおいては 30 日後に現れ，MG マンゴーにより多く見られた．ヘプタナール，デセナール，ヘプタノールおよびノネナールはマンゴーの低温貯蔵中のオフフレーバーの発生に関わっていると考えられた．マンゴー果肉のオフフレーバーはテルペン類の減少によるのではなく，ヘプタナール，デセナール，ヘプタノールおよびノネナールが生合成されてこれらが増加することにより発生すると考えられた．