African Journal of Agricultural Research Vol. 6(7), pp. 1771-1778, 4 April, 2011
Available online at http://www.academicjournals.org/AJAR
DOI: 10.5897/AJAR10.1019
ISSN 1991-637X ©2011 Academic Journals

Full Length Research Paper

A comparison of aroma components of pineapple fruits ripened in different seasons

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Accepted 21 February, 2011

Shenwan cultivar of pineapple (*Ananas comosus* L. Merr.) is an important tropical fruit of Guangdong China which is excellent in quality with strong fragrance. The aim of this study was to compare the aroma components among pineapple fruits ripened in different seasons (spring, summer, autumn and winter) by GC-MS. The results showed that there was diversity among the aroma components of pineapple fruits ripened in the four corresponding seasons. Ten kinds of aroma components were detected in spring fruits, including four unique components. The predominant were hexanoic acid methyl ester, 1,3,7-octatriene-3,7-dimethyl and octanoic acid methyl ester with relative content of 38.94, 26.32 and 10.34%, respectively. Nineteen kinds of aroma components were detected in summer fruits, including ten unique components. The predominant were butanoic acid 2-methyl-methylester, hexanoic acid methyl ester, and 2-hydroxy-N-(2-morpholinoethyl)-4-phenylbutanamide with relative content of 24.95, 24.69 and 9.60%. Eleven kinds of aroma components were detected in autumn fruits, including three unique components. The predominant were hexanoic acid methyl ester, butanoic acid 2-methyl-methyl ester and butyric acid methyl ester with relative content of 57.67, 18.52 and 8.76%. Twelve kinds of aroma components were detected in winter fruits, including four unique components. The predominant were hexanoic acid methyl ester, octanoic acid methyl ester and cis-ocimene with relative content of 63.08, 15.82 and 7.78%. The relative contents of methyl 3-(methylthio)-propanpate in the four corresponding fruits were 0.89, 4.09, 0.45 and 0.99%, respectively.

Key words: Pineapple, aroma components, fruits ripened in different seasons.

INTRODUCTION

Pineapple (*Ananas comosus* L. Merr.), cultivated worldwide all around the tropical and subtropical regions for local consumption and international export, is the most important representative of the *Bromeliaceae* family (Van de Poel et al., 2009; Saxena et al., 2009). The pineapple fruit is consumed freshly by many people and used as source of essential mineral elements, nutrients and vitamins. It could easily be processed into jams, alcoholic and nonalcoholic drinks and other confectionaries. Also, pineapple is an important fresh fruit, which is widely cultivated in a few provinces of China. According to the new online database from Ministry of Agriculture of China.

China is one of the leading producers of pineapple with an area of 53500 ha and yields 933633 tonnes in 2008. However, the overwhelming majority of pineapple fruits are sold at a low price. But, the local cultivar 'Shenwan' (0.5 to 0.75 kg per fruit, TSS 17 to 21%) , which is mostly cultivated in Shenwan town of Zhongshan city, Guangdong province of China, is sold for about 1.50 US dollars per kilogram, usually, five times as much as the other varieties in price. Recently, with the use of ethephon for flower induction, pineapple can be fruited, and multiple harvested all in the same year (Van de Poel et al., 2009**)**. According to the local cultivation practices, there are four relatively concentrated maturity periods, April, June, September, and February, which were called, spring fruit, summer fruit, autumn fruit and winter fruit by the local growers, respectively. However, the four corresponding fruits even from the same orchard with

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thesame maturity level are diverse in fragrance because of the difference of climate and environment condition. The summer fruits have very strong fragrance. Consumers prefer summer fruits and make desirable effort to spend much in buying them.

The full-bodied aroma of fruits is one of the important factors attracting consumers and strengthening the marketplace. So, aroma compound analysis plays an important role in the process of quality fruit breeding (Li et al., 2008). With the requirement for high-quality fruit of international market and natural flavor of the food industry, the studies of fruit flavor components and their influencing factors have been paid more attention gradually (Nie et al., 2004). There were some reports on pineapple aroma (Preston et al., 2003; Tokitomo et al., 2005; Akioka and Umano, 2008). Some researches have focused on aroma components of pineapple from different cultivars (Liu et al., 2008) and different maturation degrees (Liu et al., 2009). However, there were few reports on the diversity of pineapple aroma components ripened in different seasons.

In order to appraise the diversity of aroma of pineapple fruits ripened in different seasons and reveal the reason why consumers prefer the summer fruits, this present study was conducted to compare the aroma components of pineapple ripened in four seasons with ‘Shenwan’ pineapple used as materials.

MATERIALS AND METHODS

Sample materials

In this trial, the materials, ‘Shenwan’ pineapple fruits, were grown in ‘Shenwan’ town of Zhongshan city, Guangdong China. The pineapple plants were cultivated in open field with planting density of 45000 plants/ha and were induced for flowers with ethylene (600×), when plant has 40 leaves which were more than 50 cm in length. 3 fruits of each season with full maturity level (fruit peel fully turned yellow) were randomly harvested for materials. Spring fruits were harvested on April 11, 2009, summer fruits harvested on June 11, 2009, autumn fruits harvested on September 23, 2009, winter fruits harvested on February 23, 2009. All the fruits were immediately sent to the laboratory for detection.

Methods

Aroma components were analyzed by SPME/GC-MS. 250 g of fresh pulp from the 3 fruits, after being grinded evenly, were removed into a 500 ml headspace vial. After sealing the vial, the pulp was extracted for 30 min using a solid-phase micro-extraction fiber (CAR/PDMS 75 μm), and then desorption for 3 min at 220℃ and sampling.

GC-MS conditions

Aroma components were analyzed with Trace GC-MS analysis made by Finnigan. The MS apparatus was equipped with HP-1 column (length 30 m, diameter 0.25 mm, film thickness 0.1μm). Column temperature was maintained at 45℃ for 1.0 min. After that, the temperature was increased to 100℃ at a rate of 3℃ per min then to 180℃ at a rate of 10℃ per min. At last, the column temperature was maintained at the final temperature for 5 min. Helium (99.99%, 1.0 ml/min) was used as the carrier gas. The MS was operated with an EI ion source temperature of 170℃, electron energy 70 eV, and photomultiplier tube voltage of 350 V. Mass scanning range was 35 to 335 amu.

Aroma components were tentatively identified by comparing their mass spectrum with the mass spectra of NIST library. The relative content of each component was determined by their peak area.

RESULTS AND DISCUSSION

Total ionic chromatogram of aroma components of pineapple fruits ripened in four corresponding seasons

The GC-MS total ionic chromatograms of aroma components in the four pineapple fruits were presented in Figures 1 to 4. The aroma components were ascertained by searching NIST, and the relative contents were counted based on the apex area.

The compositions of aroma components of pineapple fruits ripened in four corresponding seasons

Quality of fruit is made of its external and internal (morphological-physical, biochemical and organoleptic) factors. With its quality, it has to correspond to wishes of many consumers so that it can satisfy most of their needs, preferences, tastes and habits (Harker et al., 2002). Aroma is one of the essential factors for the evaluation of fruit quality. The aroma of fruit is the result of a complex mixture of esters, alcohols, aldehydes, terpenoid compounds, etc. In this study, a total of 30 components were identified from the pineapple fruits by SPME-GC-MS in the four corresponding fruits (Table 1). In the 30 components, there were 14 esters, 9 alkenes, 2 alkanes, and 5 heterocycles. And esters such as hexanoic acid methyl ester, butanoic acid 2-methyl-methyl ester and octanoic acid methyl ester, were the predominant components in the four corresponding fruits, which agreed with the previous reports (Preston et al., 2003; Elss et al., 2005). There were 5 common aroma components that were identified from the four pineapple fruits, including butanoic acid 2-methyl-methyl ester, hexanoic acid methyl ester, hexanoic acid ethyl ester, octanoic acid methyl ester, and methyl 3-(methylthio)-propanpate. But the aroma components and their relative contents in the four fruits were diverse (Table 2).

Ten components were identified in spring fruits (Table 1), including five esters, three alkenes, and two heterocycles. The relative content of hexanoic acid methyl ester, 38.94%, was the highest in the five esters. The relative content of 1,3,7-octatriene 3,7-dimethyl, (26.32%), was the highest in the three alkenes. Four components, including 1,3,7-octatriene 3,7-dimethyl,

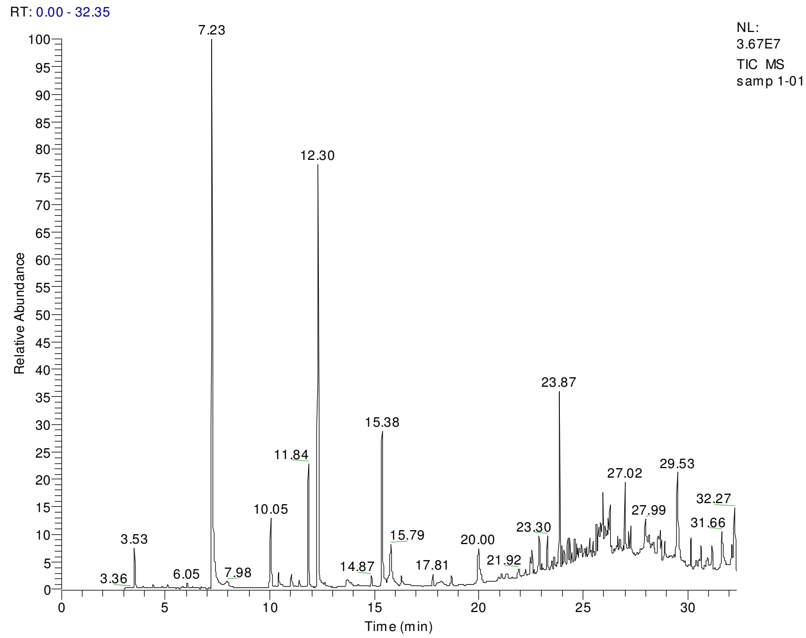

Figure 1. Total GC-MS ionic chromatogram of aroma components of spring fruit.

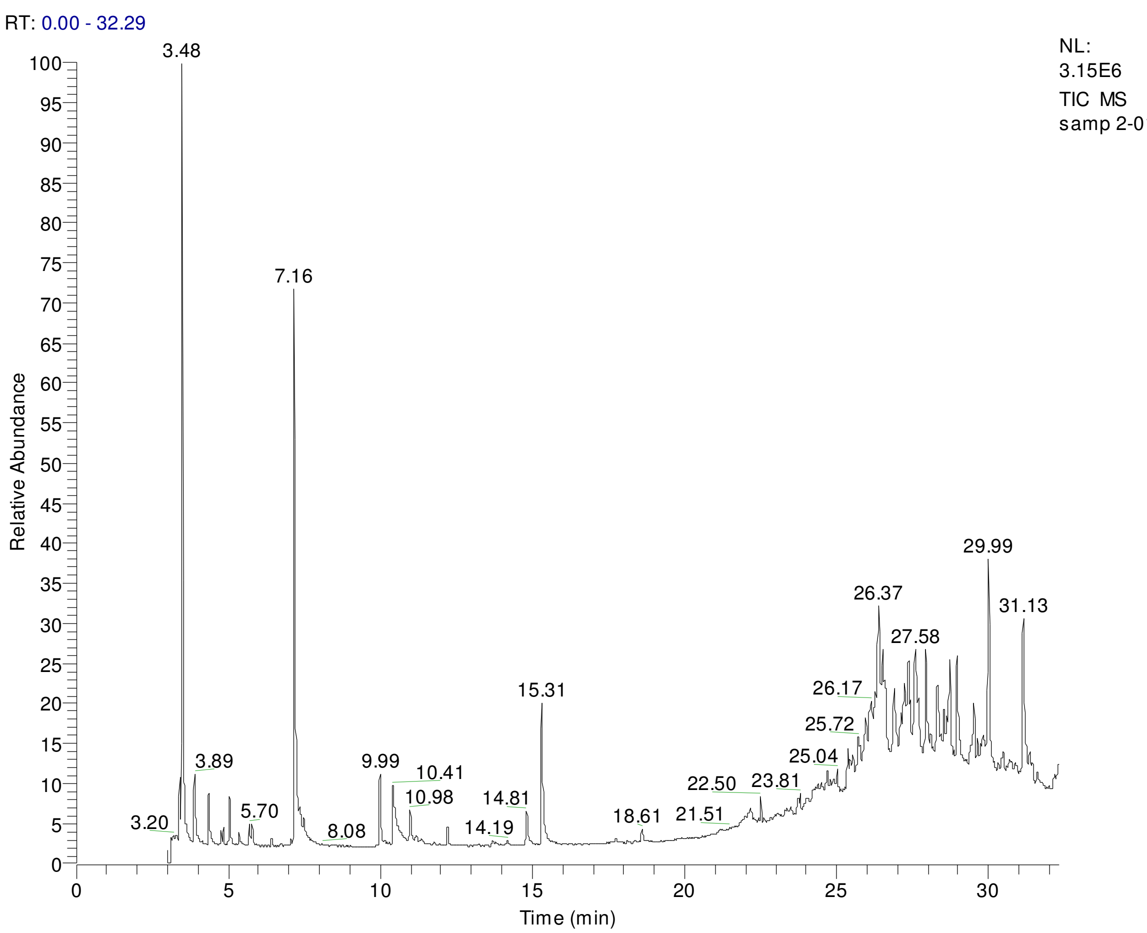

Figure 2. Total GC-MS ionic chromatogram of aroma components of summer fruit.

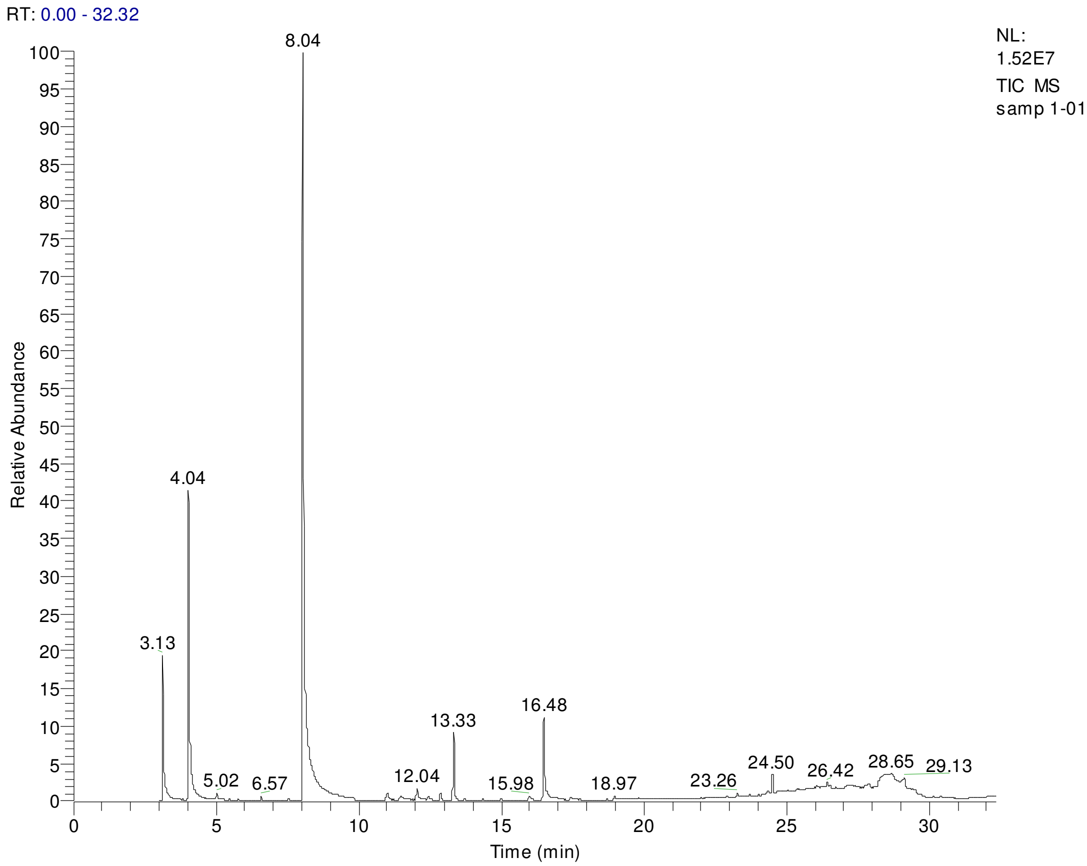

Figure 3. Total GC-MS ionic chromatogram of aroma components of autumn fruit.

relative content of 2.16 and 1.90%, respectively. The relative content of 2-hydroxy-N-(2-morpholinoethyl)-4-phenylbutanamide, (9.60%), was the highest in the three heterocycles. There were ten components which were only identified in summer fruits including acetic acid 2-methylpropyl ester, butanoic acid ethyl ester, butanoic acid 2-methyl-ethyl ester, isoamyl acetate, 2-methylbutyl acetate, heptadecane, eicosane, 3,5,5-trimethyl-2-[2-(4-morpholinyl)ethyl]cyclohex-2-en-1-one, trans-1-(fluoromethyl)-2-vinylcyclopropane, and 2-hydroxy-N-(2-morpholinoethyl)-4-phenylbutanamide.

Eleven components were identified from autumn fruits (Table 1), including eight esters, and three alkenes. The relative content of hexanoic acid methyl ester, (57.67%), was the highest in the eight esters. The relative content of (E)-1,3,6-octatriene 3,7-dimethyl, (4.67%), was the highest in the three alkenes. Three components, including butyric acid methyl ester, tran-ocimene and à-copaene, were only identified in autumn fruits.

Twelve components were identified from the winter fruits including seven esters, and five alkenes (Table 1). The relative content of hexanoic acid methyl ester, (63.08%), was the highest in the seven esters. The relative content of cis-ocimene, (7.78%), was the highest in the five alkenes. Three components including 1,3,5,8-undecatetraene, aromadendrene, and à-muurolene were identified only in winter fruits.

Plants are capable of synthesizing tens to hundreds of thousands of primary and secondary metabolites with diverse biological properties and functions. Plants volatile organic compounds generated from both primary and secondary metabolites are generally low molecular weight lipophilic compounds (Goff and Klee, 2006). Engel et al. (1990) reported that several methyl esters and some characteristic sulphur-containing esters, various hydroxy esters and their corresponding acetoxy esters, as well as a number of lactones were being responsible for the typical pineapple flavor profile. Preston et al. (2003) also reported that sulphur-containing esters, methyl 3-methylthio-propionate and ethyl 3-methylthio-propionate, were the characteristic aroma components of pineapple fruits. But in this present study, only one characteristic sulphur-containing aroma component, methyl 3-methylthio-propionate, was identified from the pineapple fruits. And the relative contents of methyl 3-methylthio-propionate in the four fruits were diverse. The content of methyl 3-methylthio-propionate of summer fruits (4.09%) was the highest, followed by winter fruits (0.99%) and spring fruits (0.89%). That of autumn fruits was the lowest (0.45%). In this study, the relative content

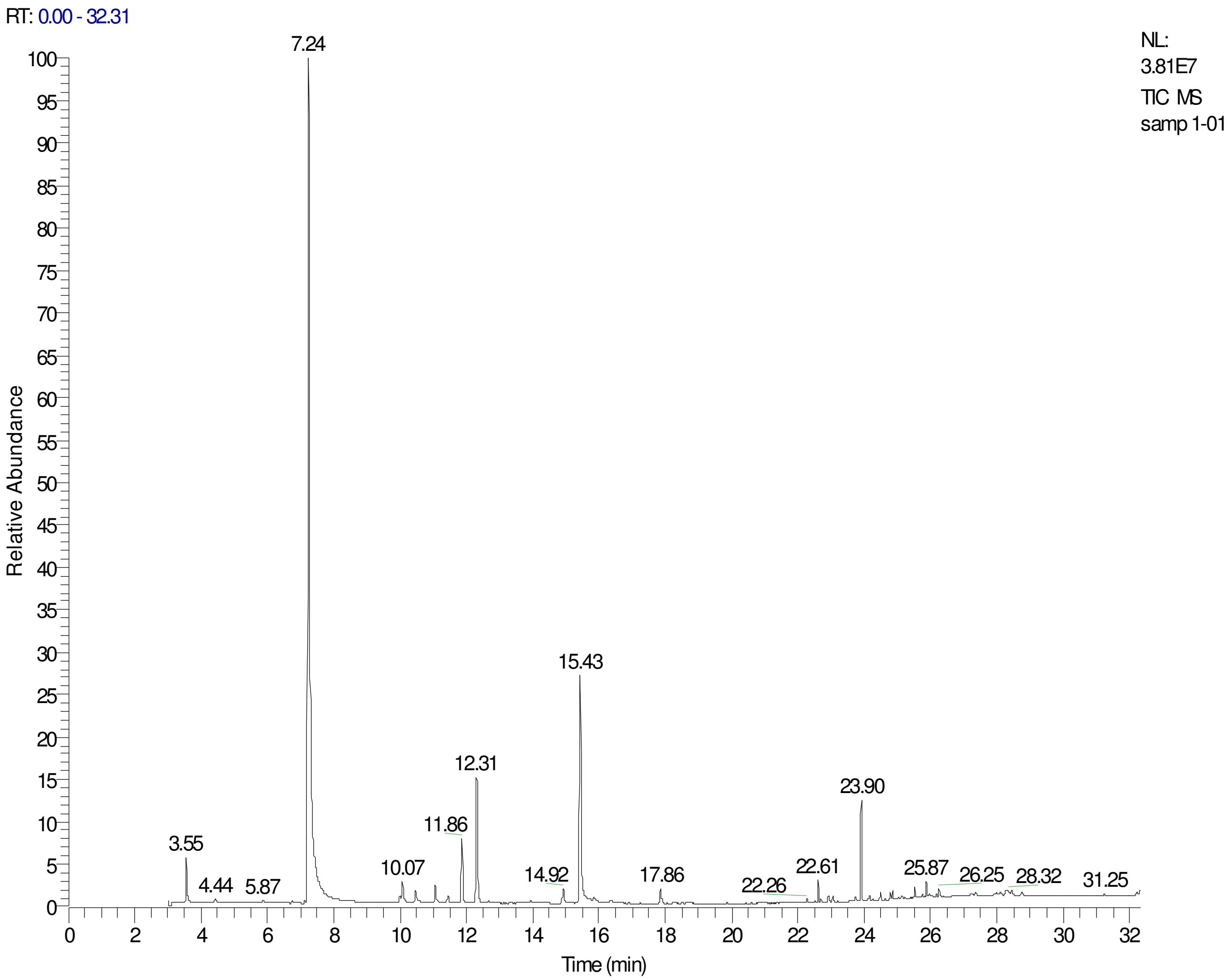

Figure 4. Total GC-MS ionic chromatogram of aroma components of winter fruit.

of characteristic aroma of summer fruits was the highest among the four corresponding fruits. It was probably related to the reason why the summer fruits were best in fragrance and consumers make desirable to them.

Some functional groups such as R-O-R', -C=O, -COOH, -OH, and some atoms such as S, F, P, As, Sb, which are called as odoriphor groups, contribute to fruits fragrance. The components containing more odoriphor groups contribute more to fruits fragrance. In this study, esters and heterocycles are the categories which contain the above odoriphor groups. There were totally 14 kinds of esters and 5 kinds of heterocycles identified from the four corresponding fruits (Table 1). In the four corresponding fruits, there were the most kinds of esters and heterocycles with the highest total relative content (95.22%) in summer fruits. It was probably related to the reason why the summer fruits were best in fragrance and consumers prefer it.

However, fruit aroma volatiles are strongly related to variety (Clara et al., 2005; Sivakumar et al., 2008), environmental conditions (Bravdo, 2001; Wang et al., 2005), cultivation practice (Jia et al., 2005; Voća et al., 2007), harvest date and post-harvest condition (Echeverrìa et al., 2004; Clara et al., 2005; Voća et al., 2007). Volatile aroma emissions were also strongly affected by light exposure and volatile ester formation increased together with increasing light exposure. Sylvie et al. (2000) reported that foliage shade reduced the aroma content of terpenoids from grapes. Mpelasoka and Behboudian (2002) reported that deficit irrigation enhanced volatile production during ripening. Moderate light is helpful for the synthesis of fruit aroma components, and too strong or too weak light will reduce aroma components accumulation (Bureau et al., 2000; Jia et al., 2005). Zhang *et al.* (2006) also reported that the average temperature of growth period was related to the aroma components, and relative high temperature was helpful to aroma synthesis. In this study, the sample

Table 1. Aroma components and relative contents in pineapple fruits ripened in different seasons.

Category	Component name	Molecular formula	Relative content (%)			
			Spring fruit	Summer fruit	Autumn fruit	Winter fruit
Ester	Butyric acid methyl ester	$C_5H_{10}O_2$	—	—	8.76	—
	Butanoic acid 2-methyl-methyl ester	$C_6H_{12}O_2$	2.01	24.95	18.52	2.37
	Pentanoic acid methyl ester	$C_6H_{12}O_2$	—	2.09	0.40	—
	Acetic acid 2-methylpropyl ester	$C_6H_{12}O_2$	—	1.58	—	—
	Butanoic acid ethyl ester	$C_6H_{12}O_2$	—	2.69	—	—
	Hexanoic acid methyl ester	$C_7H_{14}O_2$	38.94	24.69	57.67	63.08
	Butanoic acid 2-methyl-ethyl ester	$C_7H_{14}O_2$	—	1.75	—	—
	Isoamyl acetate	$C_7H_{14}O_2$	—	0.62	—	—
	2-methylbutyl acetate	$C_7H_{14}O_2$	—	0.70	—	—
	Hexanoic acid ethyl ester	$C_8H_{16}O_2$	4.26	3.00	0.65	1.55
	Methyl 3-methylthio- propionate	$C_5H_{10}O_2S$	0.89	4.09	0.45	0.99
	Heptanoic acid methyl ester	$C_8H_{16}O_2$	—	1.33	0.85	1.12
	(Z)-4-octenoic acid methyl ester	$C_9H_{16}O_2$	—	1.72		0.98
	Octanoic acid methyl ester	$C_9H_{18}O_2$	10.34	6.97	6.85	15.82
Alkene	Tran-ocimene	$C_{10}H_{16}$	—	—	0.37	—
	Cis-ocimene	$C_{10}H_{16}$	7.30	—	—	7.78
	1,3,7-octatriene 3,7-dimethyl	$C_{10}H_{16}$	26.32	—	—	—
	(E)-1,3,6-octatriene 3,7-dimethyl	$C_{10}H_{16}$	—	0.61	4.67	3.94
	Alloocimene	$C_{10}H_{16}$	0.91	—	—	—
	1,3,5,8-undecatetraene	$C_{11}H_{18}$	—	—	—	0.87
	Aromadendrene	$C_{15}H_{24}$	—	—	—	0.80
	à-muurolene	$C_{15}H_{24}$	—	—	—	0.64
	à-copaene	$C_{15}H_{24}$	—	—	0.73	—
Alkane	Heptadecane	$C_{17}H_{36}$	—	2.16	—	—
	Eicosane	$C_{20}H_{42}$	—	1.90	—	—
Heterocycle	[1]benzothieno [2,3-c]quinolin-6(5h)-thione	$C_{15}H_9NS_2$	4.49	—	—	—
	2-methoxy[1]benzothieno [2,3-c]quinolin-6(5h)-one	$C_{16}H_{11}NO_2S$	4.48	—	—	—
	3,5,5-trimethyl-2- [2-(4-morpholinyl)ethyl] cyclohex-2-en-1-one	$C_{15}H_{25}NO_2$	—	4.53	—	—
	Trans-1-(fluoromethyl)-2-vinylcyclopropane	C_6H_9F	—	4.91	—	—
	2-hydroxy-N-(2-morpholinoethyl)-4-phenylbutanamide	$C_{16}H_{25}ClN_2O_3$	—	9.60	—	—

— not found or not exist.

Table 2. Aromatic categories and relative contents in pineapple fruits ripened in different seasons.

Category	Relative content (%)				Categories			
	Spring fruit	Summer fruit	Autumn fruit	Winter fruit	Spring fruit	Summer fruit	Autumn fruit	Winter fruit
Ester	56.44	76.18	94.15	85.91	5	13	8	7
Alkene	34.53	0.61	5.77	14.03	3	1	3	5
Alkane	—	4.06	—	—	—	2	—	—
Heterocycle	8.97	19.04	—	—	2	3	—	—

— not found or not exist.

pineapple cultivar was planted in the same orchard with same culture practice. The diversities of aroma components of pineapple fruits ripened in different seasons lie in the different environments (temperature, sunlight, rainfall, etc.) the fruits encountered. The spring and winter fruits were growing in the periods with relatively low temperature. The later growth period of summer fruits were May and June. The average temperature of this period was relatively high with little rainfall and moderate light. The later growth period of autumn fruits were August and September. The average temperature of this period was high, but there was more rainfall and stronger light. Comparing with the other three environments conditions that the fruits encountered, the environment condition of summer fruits was relatively best and benefit to aroma synthesizing. In addition, the whole growth period (from flower induction to harvest) of summer fruits were the longest. In the longest growth period, summer fruits accumulated more nutrition, which was benefit to aroma synthesizing. So in this study, the summer fruits are richest in aroma and best in fragrance, which is related to the environment the summer fruits encountered.

Conclusion

There was diversity among the aroma components of pineapple fruits ripened in spring, summer, autumn, and winter. In the four corresponding fruits, there were the most kinds of aroma components especially esters and heterocycles, with high relative contents of characteristic aroma in summer fruits compared with others. Maybe it is related to the reason why summer fruits smell best in fragrance and consumers prefer to.

ACKNOWLEDGEMENT

This study was supported by the pineapple industry project (3-41) from Ministry of Agriculture of China.

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