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<u>Abstract</u>

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'Nam Dok Mai' mangoes 'Maha Chanok' mangoes extraction volatile compounds

Two Thai Mango cultivars 'Maha Chanok' and 'Nam Dok Mai' were studied. Volatile compounds from pulp and peel of 'Maha Chanok' and 'Nam Dok Mai' mango cultivars were extracted using simultaneous distillation-extraction apparatus of Likens-Nickerson, in order to identify and quantify volatile compounds of the samples by gas chromatography-mass spectrometry. Dichloromethane was used as an extraction solvent. The extraction time was 4 h. Terpinolene was the major volatile compound identified from both pulp and peel of 'Maha Chanok' mangoes and caryophyllene was found to be the most abundant volatile compound in pulp and peel of 'Nam Dok Mai' mangoes.

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Introduction

Mango tree, scientifically known as *Mangifera indica* L. which belongs to the *Anacardiaceae* family is an evergreen tree that is widely grown in the tropical and subtropical regions. Mango is one of the best known choices of fruit in the tropics. Many cultivars of mangoes are grown in Thailand, India, Pakistan, China, Mexico and Brazil. Each cultivar has its own distinctive shape, size, color, aroma, flavor and pulp consistency (Ansari *et al.*, 2004). 'Nam Dok Mai' is one of the most famous and consumed cultivars in Thailand. It is oval-shaped with a sharp-pointed tip, its ripe fruits are golden-yellow with deep yellow flesh, and the taste is sweet, slightly sour and scented (Thai Mango - Ma-Muang, 2008).

Thai Mangoes are available in the market from March to June. They can be divided into two categories; mangoes that are eaten green and mangoes that are eaten ripe. Some of the most popular Thai mangoes are; 'Nam Dok Mai', 'Aok Rong', 'Keaw Sa-Woi and 'Rad'. 'Nam Dok Mai' and 'Aok Rong' are sweet and are very popular for their use in one of Thailand's best desserts – mango with sticky rice. By contrast, 'Keaw Sa-Woi' and 'Rad' are best eaten raw with sweet fish sauce (Thai Mango - Ma-Muang, 2008).

Since Thai mangoes are very popular, they are widely consumed domestically and exported, it is of great importance to study the qualities of these mangoes. Other than the high nutritional value and delicious taste, size, shape, flavour and aroma are also critical factors when it comes to consumer acceptability (Negoias *et al.*, 2008). The consumer can easily detect the aroma not only in the pulp but also in the unpeeled ripened mangoes especially 'Nam Dok Mai' and 'Maha Chanok' mangoes.

Many volatile compounds from different mango cultivars such as 'Aok Rong', 'Nam Dok Mai' and 'Rad mangos' were studied by Chitsamphanshvej (2007) using headspace extraction technique. The most abundant volatile compounds found in 'Aok Rong', 'Nam Dok Mai' and 'Rad mangos' are α -terpinolene, cis-ocimene, and trans-ocimene, respectively. However, little attention was paid to the volatile compounds in the peel of mangoes especially in the 'Maha Chanok' cultivar.

The aim of this study was to identify and to quantify volatile compounds or aroma compounds in both pulp and peel of 'Nam Dok Mai' and 'Maha Chanok'. For this experiment Likens-Nickerson Simultaneous distillation-extraction (LNSDE) was used to isolate volatile compounds from mango samples. Gas Chromatography Mass Spectrometry (GC/MS) was used to separate, identify and quantify these compounds.

Materials and Methods

Raw materials

'Nam Dok Mai' and 'Maha Chanok' mangos were purchased from local markets in Bangkok. Samples were washed and peeled before analysis.

Determination of volatile compounds

A modified Likens- Nickerson apparatus was used for extraction of volatile compounds from pulp and peels of 'Nam Dok Mai' and 'Maha Chanok' mangoes. Extraction of pulp and peel was carried out in triplicates. For pulp extraction, 250 g of fresh mangos were used by taking 50 grams of flesh from 5 mangos. For peel extraction, 55 g of fresh mangos were used by taking 11 grams of peel from 5 mangos

Samples were cut into fine pieces. The extraction was carried on for 4 h following the method described by Laohaprasit *et al.* (2009). The extract filtered (filter paper Macherey-Nagel MN617, 100 mm) then transferred into amber bottles. The bottles were covered with aluminum foil and stored in the freezer until further analysis.

Identification of volatile compounds

Hewlett Packard (Agilent Technologies) HP-7890A gas chromatograph equipped with an HP 5975C mass-selective detector was used for the analysis of volatile compounds. The sample (4 μ l) was injected into the machine in split-less mode. Capillary column of model HP-5 MS; 30m x 0.25 mm (film thickness 0.25 μ m) was used to separate the volatile compounds. The oven temperature was programmed to stay at 40°C for 5 mins, and then increase at the rate of 10°C/min to rise to 220°C and remain constant at 220°C for 5 mins. The carrier gas used at the flow rate of 1mL/min was helium gas.

Electronimpact mass spectra were recorded at 70 eV while the temperature of ion source was at 230°C. NIST/NBS mass spectral library was used to identify the extracted compounds. The internal standard method was used for quantification. Tridecane (C13) was used as an internal standard.

The amounts of volatile compounds were calculated using the following equation:

$$Conc(c) = \left(\frac{A(C)}{W(S)}\right) \times \left(\frac{W(IS)}{A(IS)}\right)$$

where Conc (C) is the concentration of compound, A(C) is the peak area of compound C, A(IS) is the peak area of internal standard, W(S) is the weight of the samples and W(IS) is the weight of the internal standard added.

Results and Discussion

The volatile compounds of both pulp and peel of both mango cultivars were determined. The results are shown in Table 1. A total of 16 volatile compounds were found in the pulp of 'Maha Chanok' mangoes. These include ethyl butanoate, ethyl isovalerate, α -pinene, β -pinene, α -phellandrene, δ -3-carene, α -terpinene, sylvestrene, cis- β -ocimene, γ -terpinene, terpinolene, trans- β -damascene, caryophyllene, α -caryophyllene, caryophyllene (I1) and β -selinene. Terpinolene was found to be the major volatile compound followed by β -3-carene.

A total of 15 volatile compounds were found in the peel of 'Maha Chanok' mangoes including ethyl butanoate, ethyl isovalerate, α -pinene, α -phellandrene, δ -3-carene, α -terpinene, octanol<n->, terpinolene, ethyl octanoate, ethyl trans-4-decenoate, trans- β -damascene, caryophyllene, α -caryophyllene, β -selinene and δ -cadinene. Terpinolene was the most abundant volatile compound found in the peel of 'Maha Chanok' mangoes while δ -3-carene was found to be the second most abundant volatile compound followed by ethyl octanoate.

A total of 18 volatile compounds were found in the pulp of 'Nam Dok Mai' mangoes. These volatile compounds are 3-hexanol, 2-hexanol, trans-2-hexenal, cis-3-hexenol, trans- β -ocimene, cis- β -ocimene, copaene, β -elemene, caryophyllene, β -gurjenene, α -guaiene, α -caryophyllene, γ -muurolene, γ -amorphene, α -muurolene, α -bulnesene, γ -cardinene and δ -cadinene. Caryophyllene was the most abundant volatile compound followed by trans- β -ocimene and γ -amorphene.

A total of 26 compounds were found in peel of 'Nam Dok Mai' mangoes. These 26 compounds are cis-3-hexenol, limonene, trans- β -ocimene, bezene acetaldehyde, cis- β -ocimene, ocimene<allo>, dodecane, δ -elemene, α -cubebene, vlangene, β-bourbonene, β-elemene, carvophyllene, β -gurjenene, α -guaiene, α -caryophyllene, germacrene γ -muurolene, γ -amorphene, D. α -muurolene, α -bulnesene, γ -cardinene, δ -cadinene, α -cadinene, germacrene B and hexadecane<n->. Caryophyllene was found to be the most abundant volatile compounds in the peel of 'Nam Dok Mai' mangoes followed by germacrene D and α-caryophyllene, respectively.

Comparison between volatile compounds from pulp and peel of 'Maha Chanok' cultivar

A total of 16 volatile compounds were found in the pulp of this cultivar while 15 volatile compounds were found in the peel of 'Maha Chanok' mangoes.

Table 1. Comparison of volatile compounds in pulp and p	peel of Maha
Chanok and Nam Dok Mai mango cultivars	

	Maha Chanok	Maha Chanok	Nam Dok Mai	Nam Dok Ma	
Volatile compounds	Flesh	Peel	Flesh	Peel	
	Concentration (ppm)				
3-Hexanol	n.d.	n.d.	0.10	n.d.	
2-Hexanol	n.d.	n.d.	0.23	n.d	
Ethyl Butanoate	0.01	0.17	n.d.	n.d.	
Ethylisovalerate	0.02	0.33	n.d.	n.d.	
α-Pinene	0.14	0.12	n.d.	n.d.	
β-Pinene	0.22	n.d.	n.d.	n.d.	
α-Phellandrene	0.15	0.07	n.d.	n.d.	
δ-3-Carene	4.31	3.38	n.d.	n.d.	
α-Terpinene	0.41	0.21	n.d.	n.d.	
Sylvestrene	0.46	n.d.	n.d.	n.d.	
trans-2-Hexenal	n.d.	n.d.	0.15	n.d.	
cis-3-Hexenol	n.d.	n.d.	0.36	0.37	
<i>trans</i> -β-Ocimene	n.d.	n.d.	1.31	n.d.	
<i>cis</i> -β-Ocimene	0.35	n.d.	0.20	0.51	
y-Terpinene	0.07	n.d.	n.d.	n.d.	
Octanol <n-></n->	n.d.	0.05	n.d.	n.d.	
Terpinolene	10.56	5.37	n.d.	n.d.	
Ethyloctanoate	n.d.	1.40	n.d.	n.d.	
Ethyltrans-4					
decenoate	n.d.	0.24	n.d.	n.d.	
<i>trans</i> -β-Damascene	0.04	0.14	n.d.	n.d.	
Copaene	n.d.	n.d.	0.05	n.d.	
Limonene	n.d.	n.d.	n.d.	0.10	
trans-β-Ocimene	n.d.	n.d.	n.d.	4.05	
Bezene acetaldehyde	n.d.	n.d.	n.d.	0.11	
Ocimene <allo></allo>	n.d.	n.d.	n.d.	0.10	
Dodecane	n.d.	n.d.	n.d.	0.21	
δ-Elemene	n.d.	n.d.	n.d.	0.13	
α-Cubebene	n.d.	n.d.	n.d.	0.10	
Ylangene	n.d.	n.d.	n.d.	0.17	
β-Bourbonene	n.d.	n.d.	n.d.	0.18	
βElemene	n.d.	n.d.	0.06	1.77	
β-Gurjenene	n.d.	n.d.	0.05	0.29	
Caryophyllene	0.10	0.84	1.94	10.66	
α-Guaiene	n.d.	n.d.	0.05	0.29	
Caryophyllene	0.10	n.d.	n.d.	n.d.	
œCaryophyllene	0.05	0.44	0.84	4.87	
β-Selinene	1.03	0.69	n.d.	n.d.	
y-Muurolene	n.d.	n.d.	0.08	0.27	
y-Amorphene	n.d.	n.d.	1.23	3.08	
Germacrene D	n.d.	n.d.	n.d.	5.80	
a-Muurolene	n.d.	n.d.	0.18	0.46	
α-Bulnesene	n.d.	n.d.	0.15	1.62	
y-Cardinene	n.d.	n.d.	0.04	0.70	
δ-Cadinene	n.d.	0.37	0.18	2.39	
α⊡Cadinene	n.d.	n.d.	n.d.	0.35	
Germacrene B	n.d.	n.d.	n.d.	0.48	
Hexadecane <n-></n->	n.d.	n.d.	n.d.	0.24	

n.d. not detectable

*Data are averages of three extractions

Volatile compounds that were found in both pulp and peel were ethyl butanoate, ethyl isovalerate, α -pinene, α -phellandrene, δ -3-carene, α -terpinene, terpinolene, trans- β damascene, caryophyllene, α -caryophyllene and β -selinene.

Additional volatile compounds found in the pulp were β -pinene, sylvestrene, cis- β -ocimene, γ -terpinene and caryophyllene. Volatile compounds found in the peel but not in the pulp were octanol<n->, ethyl octanoate, ethyl trans-4-decenoate and δ -cadinene. Terpinolene was the major volatile compounds of both pulp and peel followed by δ -3-carene. Terpinolene found in pulp was also found in peel. This shows the aroma of ripe mangoes does not

only come from the pulp. Aroma of ripened mangoes may be detected without peeling. While δ -3-carene, which was indicated to be the second most abundant volatile compound found in both pulp and peel, was found in close amount.

In addition, α -caryophyllene was found abundant in the peel more than in the pulp from both mangoes varieties. In other fruits, terpenes are also found in the peel more than in the pulp as supported by Gozlekci *et al.* (2011) and Qiao *et al.* (2010).

Comparison between volatile compounds from pulp and peel of 'Nam Dok Mai' mangoes

A total of 18 volatile compounds were found in the pulp of 'Nam Dok Mai' mangoes while 26 were found in the peel of 'Nam Dok Mai' mangoes. Volatile compounds found in both pulp and peel were cis-3hexenol, cis- β -ocimene, β -elemene, caryophyllene, β -gurjenene, α -guaiene, α -caryophyllene, γ -muurolene, γ -amorphene, α -muurolene, α -bulnesene, γ -cardinene and δ -cadinene. Five other volatile compounds were found in the pulp but not in the peel, these were 3-hexanol, 2-hexanol, trans-2hexenal, trans- β -ocimene and copaene.

Besides the 13 volatile compounds found in both pulp and peel, 13 additional compounds were found in the peel. These were limonene, benzene acetaldehyde, ocimene<allo>, dodecane, δ -elemene, ylangene, β -bourbonene, germacrene D, α -cadinene, germacrene B and hexadecane<n->. Tenfold amount of caryophyllene was found in peel in comparison to pulp. The number of volatile compounds found in peel was higher than that of those found in the pulp. It could be concluded that the peel of 'Nam Dok Mai' mangoes plays a very important role in giving it its distinctive aroma.

Comparison between compounds in the pulp of 'Maha Chanok' and 'Nam Dok Mai' cultivars

A total of 16 volatile compounds were found in the pulp of 'Maha Chanok' mangoes while 18 volatile compounds were found in pulp of 'Nam Dok Mai' mangoes. Three common volatile compounds were found in the pulp of 'Maha Chanok' and 'Nam Dok Mai' mangoes, these were cis- β -ocimene, caryophyllene and α -caryophyllene. Terpinolene was the most abundant compound found in the pulp of' Maha Chanok' mangoes while caryophyllene was the most abundant compound found in the pulp of 'Nam Dok Mai' mangoes.

Comparison between the peel of 'Maha Chanok' and 'Nam Dok Mai' mango

A total of 15 volatile compounds were found in

peel of 'Maha Chanok' mangoes while 26 compounds were found in peel of 'Nam Dok Mai' mangoes. The most abundant volatile compound found in the peel of 'Maha Chanok' mango was terpinolene while that of 'Nam Dok Mai' mango was caryophyllene. Caryophyllene, α -caryophyllene and δ -cadinene were the only volatile compounds that were found in peels of both 'Maha Chanok' and 'Nam Dok Mai' mangoes.

Both varieties of mangoes have different organoleptic properties as different varieties of volatile compounds were found in each cultivar. Also, the volatile compounds in abundance were different. Caryophyllene has a spicy, terpenic and woody odor. The taste is woody, pepper-like spicy with a citrus background. It is an oily liquid that is colorless to pale yellow in color (The good scents company, 2010a). Terpinolene is a clear liquid that is colorless. It has a herbal odour that is sweet, piney citrus and fresh with a tinge of woody lemon peel. The taste is lime-like, woody, terpy with a slight tough of floral and herbal (The good scents company, 2010b). δ-3-Carene has a sweet citrus odour (The good scents company, 2010c). Ethyl octanoate has an odour and taste that is sweet, waxy, creamy, waxy, fruity and pineapples like (The good scents company, 2010d).

Conclusion

Two different mango cultivars; 'Maha Chanok' and 'Nam Dok Mai' studied in this project were found to have different constituents of volatile compounds resulting in their distinctive aromas. Terpinolene was the major compound of 'Maha Chanok' mango while that in 'Nam Dok Mai' was caryophyllene. The pulp of these two cultivars had 3 common volatile compounds; cis-β-ocimene, caryophyllene and α -caryophyllene. The peels were also found to share 3 volatile compounds; cis- β -ocimene, caryophyllene and α -caryophyllene. The most abundant volatile compounds found in the pulp and in the peels of 'Maha Chanok' mangoes were terpinolene and δ -3carene, respectively. A total of 16 volatile compounds were found in the pulp of 'Maha Chanok' mangoes and the peel. A total of 18 volatile compounds were found in the pulp of 'Nam Dok Mai' mango while 26 were found in the peels. Caryophyllene was the major compound of pulp and peels of 'Nam Dok Mai' mango.

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