Volatile Components of Wampee Fruits [*Clausena lansium* (Lour.) Skeels] Treated by Different Drying Conditions

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Abstract

The objective of this study was to compare the composition of volatile compounds of 4 different drying methods of wampee fruits growing in Thailand, (a) sun drying at ambient temperature (between 30-39 °C ; (b) drying in a hot air oven at 45 °C; (c) drying in a hot air oven at 60 °C; (d) drying in a vacuum oven at 45 °C. The volatile compounds were isolated by a hydro-distillation extraction apparatus and analyzed by GC-MS with a HP-5MS column. Fifty-three components were detected, including 17 monoterpene hydrocarbons, 14 sesquiterpene hydrocarbons, 10 alcohols, 3 aldehydes, 4 ketones, 1 carboxylic acid, and 4 terpene oxides. The relative peak areas of major components of this oil were sabinene(33.68-66.73%),α-pinene(9.57-13.35%), 1-phellandrene(5.77-10.76%), and myrcene(3.20-4.50%).

Keywords: wampee, volatile, GC-MS, monoterpene hydrocarbons, sesquiterpene hydrocarbons, sabinene, 1-phellandrene, hydro-distillation extraction.

1.Introduction

Volatile compounds are the most sensitive components in the process of food drying. The effect of drying on the composition of volatile constituents of various aromatic plants and vegetables has been the subject of numerous studies, which show that the changes in concentrations of the volatile compounds during drying depend on several factors, such as the drying method and parameters that are characteristic of the product subjected to drying [1].

Wampee [*Clausena lansium* (Lour.) Skeels] is a minor member of the Rutaceae and distant relative of the citrus fruits originated in southern China. The Chinese people introduced it to the north of Thailand 100 years ago in Nan Province. It has many vernacular names and most are derived from the Chinese *huang-p'i-kuo,* in Thailand it is *mafai jeen,*(มะไฟจีน) and the fruits ripen in May-July. The common name is wampee. The fruits taste similarly to grapefruits, when ripe, resemble a diminutive lemon, and are about 2.0 cm in diameter (Figure 1). It contains 1 – 3 seeds and the pulp is slightly sour. When fully ripe, it can be eaten with the peel. The pulp can be added to fruit cups, gelatins or other desserts, or made into pies, jams or jellies. A carbonated beverage resembling champagnes is made by fermenting the fruit with sugar [2], but the most popular product is dried wampee. Dried wampee is currently produced in Thailand as a sweet preserved fruit. The fruit is said to be used as a medicine for stomach upsets and indigestion, for coughs, as folkloric uses in the

Figure 1 Wampee *(Clausena lansium* (Lour.) Skeels).

Philippines for influenza, colds and abdominal colic pains [3]. In general, the fruits are sold at a price of approximately 25 Baht./kg.

Drying of fruits is commonly done in different parts of the world to improve the storage quality and to preserve the fruit for consumption during off seasons. As a result of drying, the water activity of fruit product is decreased, whereby chances of microbial spoilage are minimized [4]. Dried whole wampee is a unique product, consumed mainly in the northern part of Thailand. However, no reports were available on systematic drying of wampee fruit, nor on the changes that occur in its aroma profile as a result of processing, though the fruit is valued mainly for its flavor and aroma. The objectives in this study are to determine the changes in volatile aroma components of dried wampee fruit, using different types of driers.

2. Materials and methods

2.1. Plant material

The fresh wampee fruits were collected in May 2004 in Nan Province located in the northern part of Thailand. The initial samples were divided into five batches. One was stored frozen at –18 °C for fresh analysis. The remaining batches were dried by using one of the following different drying methods: (a) sun drying at ambient temperature (30-39 °C); (b) drying in a hot air oven at 45 °C; (c) drying in a hot air oven at 60 °C; (d) drying in a vacuum oven at 45 °C. The samples were dried until the moisture content reached approximately 16 % dry basis (calculation based on initial moisture content and weight loss, (mass of moisture/mass of dry solid) x 100.

2.2. Extraction of volatiles

The Clevenger-type apparatus [5] hydro-distillation extraction was used for extraction and concentration of volatiles. The wampee fruit samples, 500 g of fresh fruit or 200 g dried fruit was put into a round bottomed flask with 500 ml of distilled water. Five drops of silicone were added as antifoam. The distillation process was carried out for 6 h. The distillate was dried over anhydrous sodium sulfate. Dried distillate was concentrated under a stream of nitrogen and stored in 2 ml vials at –18 °C until analysis. The extract of each sample was submitted to gas chromatography-mass spectrometer (GC-MS) analyses.

2.3. GC-MS analysis

A GC-MS (Agilent 6890 and HP 5973 mass-selective detector, Agilent Technologies, Inc., Wilmington, DE 19808, USA.) equipped with a fuse silica capillary column, HP-5MS, with 5%-Phenyl methylpolysiloxane as non-polar stationary phase (30 m x 0.25 mm i.d. x 0.25 μm film thickness, Agilent Technologies) was utilized for analysis of volatiles obtained from distillation of wampee fruits. The samples (1 μL) were injected with a split ratio of 10:1. The injection port temperature was 250 °C. The column temperature program started at 40 °C upon injection. The temperature was increased at a rate of 3 °C /min to 100 °C, and then increased at a rate of 5 °C/min to 230 °C, and held for 2 min. Purified helium gas at a flow rate of 1 mL/min was used as the GC carrier gas. The mass spectrometer was operated in the electron impact (EI) mode with an electron energy of 70 eV; ion source temperature, 230 °C; quadrupole temperature, 150 °C; mass range *m/z* 35-400; scan rate, 0.25 s/scan; EM voltage, 1423 V. the GC-MS transfer line was set to 280 °C.

2.4. GC-MS data analysis

Identification of volatile components was performed by matching their mass spectra with reference spectra in the Wiley 275 Mass Spectral Library (Revision C.00.00) and the NIST 98 Mass Spectral Library (Revision D.01.00/1.6d), both purchased from Agilent Technologies. Quantitative analysis of each volatile component in percent was performed by peak area normalization measurement.

3.Results and discussion

The volatile fractions from wampee fruit samples were isolated by hydro-distillation to obtain aroma compounds. They were transparent yellowish oils in appearance, lighter than water and having a floral-fresh-lemon odor. The essential oil yield during extraction from vacuum dried sample, compared to the oil obtained from fresh fruit, was about 82% higher. The yield of oil from wampee fruit was 0.11 and 0.62 ml for 100 g fresh and vacuum dried fruits, respectively (Table 1). In order to study the effect of drying method on volatile compounds of wampee fruit, the volatile compound in the essential oils of the fresh fruit was compared with those found in different drying methods. Using the mass spectral matching against library standards, the results are shown in Table 2.

Table 1 Yields of oil in fresh fruit and dried wampee by sun dried, vacuum dried at 45 °C, hot air dried at 45 °C, and hot air dried at 60 °C.

Sample No.	Fruit/sample	Moisture(%)	Essential oil (ml/100 g)	
			dried fruit basis	fresh fruit basis
1.	Fresh	72.05	0.11	0.11
2.	Sun-dried	15.75	0.50	0.16
3.	Vacuum dried at 45	15.50	0.62	0.20
4.	Hot air dried at 45 °C	14.85	0.35	0.11
5.	Hot air dried at 60 °C	15.40	0.35	0.12

Fifty-three compounds could be identified in all 5 essential wampee fruit oils, using GC-MS with a HP-5MS column which represent about 97.40-99.07 % of the total relative area. The wampee fruit essential oil consists of a mixture of monoterpene hydrocarbons, sesquiterpene hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, and terpene oxides. No esters were detected in the examined fruit samples. All wampee oils were nearly similar in their main compositions. They consist mainly of monoterpene hydrocarbons (fresh fruit; 94.48%, hot air dried at 45 °C; 92.59%, hot air dried at 60 °C; 92.88%, vacuum dried at 45 °C; 94.13%,and sun-dried;94.05%).Themonoterpene hydrocarbons in fresh fruit, hot air dried at 45 °C, hot air dried at 60 °C, vacuum dried at 45 °C, and sun-dried oil were distinctly dominated by sabinene, constituting about 66.73, 33.68, 41.13, 64.48 and 63.18% of the oils' composition, respectively. It is accompanied by significant amounts of α-pinene (11.74, 12.33, 12.02, 13.35, and 9.57%), 1-phellandrene (7.25, 5.77, 6.15, 7.79, and 10.76%), and myrcene (4.27, 4.07, 4.50, 3.65, and 3.20%). Except for 2 samples the hot air dried at 45 °C and hot air dried at 60 °C contained large amounts of β-phellandrene, 33.34 and 25.06%, respectively.

The major alcohols were α-terpineol (1.00-1.79%), 3-cyclohexen-1-ol (0.80-1.04%) and fenchol (0.13-0.23%). Only one compound of the sesquiterpene hydrocarbon; isosativene was present in all samples in small amounts (0.07-0.30%)

In the fresh fruit, there were 27 components in this oil, amounting to 99.07 % of the relative area. Ten monoterpene hydrocarbons, 2 sesquiterpene hydrocarbons, 7 alcohols, 1 aldehyde, 3 ketones, 1 carboxylic acid, and 3 terpene oxides were found. The monoterpene hydrocarbons fractions (94.48%) dominated the essential oil sample. Sabinene (66.7%), α-pinene (11.7%), 1-phellandrene (7.2%), and myrcene (4.3%) were the major components. The oxygenated components represented 4.3% of the total oil with α-terpineol (1.18%) and 2-cyclohexen-1-one (1.02%) as the main components. The sesquiterpene hydrocarbons were smaller with isosativene (0.13%) and curcumene (0.03%).

Three components; curcumene (0.03%), α-campholene aldehyde (0.06%), and α-pinene oxide (0.06%) were lost or changed to other compounds after drying.

Table 2 Volatile compounds identified in the wampee essential oils; fresh fruit, hot air dried at 45 °C, hot air dried at 60 °C, vacuum dried at 45 °C, and sun-dried, in order of their retention time (t_R) using HP-5MS non-polar column.

Compounds	t_R (Min)	% Relative peak area				
		resh fruit	Hot air 45°C	Hot air 60°C	Vacuum 45°C	un-dried
Monoterpene hydrocarbons						
1. d-limonene	9.029	-	-	-	-	0.03
2. tricyclene	9.144	-	-	-	0.04	-
3. α-thujene	9.433	-	-	0.04	0.05	-
4. α-pinene	9.750	11.74	12.33	12.02	13.35	9.57
5. camphene	10.274	0.54	0.73	0.65	1.09	0.76
6. β-pinene	11.520	-	-	-	-	0.10
7. myrcene	12.390	4.27	4.07	4.50	3.65	3.20
8. 1-phellandrene	12.939	7.25	5.77	6.15	7.79	10.76
9. δ-3-carene	13.145	-	-	0.22	-	-
10. 3-carene	13.150	0.22	0.20	-	-	-
11. 4- carene	13.511	1.92	1.21	1.66	1.65	3.58
12. sabinene	14.400	66.73	33.68	41.13	64.48	63.18
13. β-phellandrene	14.526	-	33.34	25.06	-	-
14. β-fenchene	16.112	0.04	-	0.02	-	0.03
15. γ-terpinene	19.373	1.60	1.26	1.24	1.88	2.49
16. α-fenchene	19.676	0.17	-	0.19	0.15	0.18
17. trans-ocimene	27.380	-	-	-	-	0.17
total		94.48	92.59	92.88	94.13	94.05
Sesquiterpene hydrocarbons						
1. 1H-3a, 7-methanoazulene	29.606	-	-	-	0.04	0.19
2. isosativene	29.851	0.13	0.10	0.07	0.30	0.19
3. bergamotene	30.303	-	-	-	0.03	-
4. tran-β-farnesene	30.924	-	-	-	-	0.05
5. naphthalene	31.443	-	0.10	0.05	-	-
6. α-muurolene	31.534	-	0.03	-	-	-
7. curcumene	31.650	0.03	-	-	-	-
8. β-biabolene	32.304	-	-	0.04	-	-
9. β-farnesene	32.314	-	-	-	0.04	-
10. cis-calamenene	32.679	-	0.04	-	-	-
11. δ-cadinene	32.679	-	-	0.02	-	-
12. valencene 2	34.208	-	-	-	0.03	-
13. aromadendrene	35.076	-	-	-	0.04	-
14. γ-curcumene	36.329	-	-	-	-	0.04
total		0.16	0.27	0.18	0.48	0.47
Alcohols						
1. 1-pentanol	7.576	-	0.05	-	-	-
2. 1-octanol	7.610	-	-	0.03	-	-
3. linalol	17.584	0.38	-	0.31	0.16	0.24
4. fenchol	18.084	0.18	0.23	0.21	0.12	0.13

(continued on next page)

Table 2 (continued).

Compounds	t_R (Min)	% Relative peak area				
		resh fruit	Hot air 45°C	Hot air 60°C	Vacuum 45°C	un-dried
5. Isoborneol	20.590	0.05	-	0.06	-	0.08
6. 3-cyclohexen-1-ol	21.128	0.80	0.85	0.99	0.94	1.04
7. p-menth-2-en-1-ol	21.407	0.07	-	-	-	0.04
8. α-terpineol	21.835	1.18	1.23	1.17	1.00	1.79
9. Santalol	27.077	-	-	-	0.21	-
10. limonyl alcohol	27.076	0.07	-	0.07	-	-
total		2.73	2.36	2.84	2.43	3.32
Aldehydes						
1. α-campholene aldehyde	17.295	0.06	-	-	-	-
2. Benzaldehyde	24.023	-	-	0.05	-	-
3. Phellandral	25.278	-	0.07	-	0.08	0.19
total		0.06	0.07	0.05	0.08	0.19
Ketones						
1. Pulegone	20.984	0.13	-	-	0.15	-
2. 2-cyclohexen-1-one	21.566	1.02	1.34	1.07	0.90	0.43
3. carvota acetone	24.244	-	-	-	-	0.05
4. Piperitone	24.518	0.08	-	0.13	-	-
total		1.23	1.34	1.20	1.05	0.48
Carboxylic acids						
1. acetic acid	25.591	0.13	0.11	0.07	0.14	0.17
total		0.13	0.11	0.07	0.14	0.17
Terpene oxides						
1. cis-linalol oxide	16.208	-	0.07	-	0.08	-
2. α-pinene oxide	17.295	0.06	-	-	-	-
3. cis-limonene oxide	19.041	0.10	0.13	0.09	0.10	-
4. phellandrene epoxide	22.378	0.12	-	0.09	0.09	0.12
total		0.28	0.20	0.18	0.27	0.12
Total identified		99.07	96.94	97.40	98.58	98.80

Thirteen components remaining after different drying methods were; α-pinene, camphene, myrcene, 1-phellandrene, 4- careen, sabinene, γ-terpinene, isosativene, fenchol, 3-cyclohexen-1-ol, α-terpineol, 2-cyclohexen-1-one, and acetic acid.

Probably, some of the identified compounds were formed or produced during drying and extraction of the samples, especially, alcohols, and aldehydes. No relationship was found between the retention of volatile compounds by fresh fruit and different drying processes. After acuum drying, 7 new compounds; tricyclene (0.04%), 1H-3a,7-methanoazulene (0.04%), bergamotene (0.03%), β-farnesene (0.04%), valencene 2 (0.03%), aromadendrene (0.04%), and santalol (0.21%) were produced.

After sun drying, 6 new compounds; d-limonene (0.03%), β-pinene (0.1%), trans-ocimene (0.17%), tran-β-farnesene (0.05%), γ-curcumene (0.04%), and carvota acetone (0.05%) were produced. After hot air drying at 60 °C, 5 new compounds; δ-3-carene(0.22%), β-biabolene (0.04%), δ-cadinene (0.02%), 1-octanol (0.03%), and benzaldehyde (0.05%) were produced.

After hot air drying at 45 °C, 3 new compounds; α-muurolene (0.03%), cis-calamenene (0.04%), and 1-pentanol (0.05%) were produced.

Earlier compositional studies of wild wampee essential oils in Hainan Island, China

found phellandrene (54.8%), limonene (23.6%), and *p*-menth-1-en-4-0l (7.5%) in the seed, β-santalol, 9-octadecenamide and sinensal in the flowers [6]. Therefore, many of the volatile compounds identified using GC-MS are being reported for the first time.

4. Conclusion

In conclusion, it is reported that the wampee fruit essential oil consists of a mixture of monoterpene hydrocarbons, sesquiterpene hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, and terpene oxides. No esters were detected in the examined fruit samples. All of the wampee oils were nearly similar in their main compositions. They consist mainly of monoterpene hydrocarbon (sabinene, α-pinene, 1-phellandrene, and myrcene).

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