Identification of Aroma Compounds in Coconut Sugar

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ABSTRACT

Volatile aroma compounds in coconut sugar were isolated by solvent extraction, and subjected to gas chromatography-mass spectrometry (GC-MS) and GC-olfactometry (GC-O). Total 15 identified aroma compounds were pyrazine, furan, pyran derivatives, ketones, aldehyde, alcohol, acid and sulfur containing compound. The results indicated that the heterocyclic compounds responsible for sweet, burnt, roasty, nutty, smoky and caramel characteristics of coconut sugar, while ketones were responsible for the buttery note. A descriptive sensory analysis was also carried out to identify the aroma attributes of coconut sugar. Nine trained panelists described seven aroma attributes namely caramel, creamy, pandan, vanilla, alcoholic, acidic and smoky. Among the aroma notes, caramel and creamy were dominant, whereas vanilla and acidic had the lowest intensity.

Key words: volatile compound, aroma, coconut sugar, gas chromatography-olfactometry, descriptive sensory analysis

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INTRODUCTION

Coconut sugar, a brown colored sweetener, has been used for centuries by South and South-East Asian. It is traditionally used to prepare sweets and sauce for their characteristic sweet aroma and taste. Coconut sugar is prepared from the sap which is collected from the unopened inflorescence of coconut (*Cocos nucifera*) tree, which is an important member of palm family. Coconut sap contains high amount of sugar (about 9%), protein, minerals and vitamins (Barh and Mazumdar, 2008). During palm sugar preparation, the sap is filtered in a large pan and heated on a wood fired oven. The heating process continue until the desired aroma and color developed. The major reactions occur during the heating process of palm sap are Maillard reaction and caramelisation (Ho *et al*., 2007). These reactions are responsible for the generation of volatile compounds which give the unique flavor of coconut sugar. Apriyantono *et al.* (1996) identified 27 volatile compounds from coconut sugar using gas chromatography-mass spectrometry (GC-MS). The major volatiles were dodecanoic acid, acetic acid, 2-undecanone, decanoic acid, 2-nonanone and 2-furfural. Thermal process volatiles including 2-methyl pyrazine, 2,5-dimethyl pyrazine, 2,6-dimethyl pyrazine and 2-acetyl pyrrole were also found in coconut sugar. The additional high abundance volatiles were 2-butanol, 1,4-diethyl-6,1-butyl-acetate, cyclohexiloctane and N,N-dimethy-2-(diphenylmethoxy)-ethylamine (Purnomo, 2007).

Though few studies have been conducted regarding volatile compounds in coconut sugar, the information on aroma compounds in coconut sugar is not available. Therefore, the present study was carried out with the following objectives: i) to identify the volatile aroma compounds and ii) to describe the aroma attributes by using descriptive sensory analysis.

MATERIALS AND METHODS

1. Material

Commercial coconut sugar produced in August 2013 was collected from Samutsongkhram, Thailand.

2. Analysis of volatile aroma compounds

Coconut sugar (100 g) was dissolved in odorless-distilled water (40 mL) in a glass bottle. The volatile compounds in sugar sample were extracted for 30 minutes. Extraction was performed three times with diethyl ether (100 mL + 100 mL + 50 mL). The combined extract was concentrated to 50 mL using a Vigreux column at 43 °C. The concentrated extract was subjected to a high-vacuum distillation for further cleanup. The distilled extract was concentrated to 10 mL using a Vigreux column before removal of water by using anhydrous sodium sulphate. The extract was further concentrated to 200 μL under gentle nitrogen flow, and kept at - 40 °C until analysis.

Volatile compounds of coconut sugar extract were analyzed by using GC (7890A; Agilent Technologies; California, USA) coupled with Time-of-Flight Mass Spectometer (TOFMS) (Pegasus 4D; LECO®; Michigan, USA). Volatile extract was analyzed on a Stabilwax column (30 m × 0.25 mm id × 0.25 μm film thickness; Restek; Pennsylvania, USA) and a DB-5MS column (30m × 0.25 mm id × 0.25 μm film thickness; Agilent Technologies;California, USA). Cold on-column injection technique with helium as carrier gas at a constant flow rate of 1 mL/min was used. Initial oven temperature was 35 ºC, and held for 5 min.Temperature was increased at 4ºC/min to 225ºC for Stabilwax column and 250 ºC for DB-5MS column, and the holding time was 20 min.

The description of volatile aroma compounds in coconut sugar was performed by using GC-olfactometry (GC-O) by two trained panelists.The effluent divided 1:1 to flame ionization detector (FID) and sniffing port. The extract was applied by cold on-column injection onto Stabilwax and DB-5 (30 m × 0.25 mm id × 0.25 μm film thickness; Agilent Technologies; California, USA) columns. The oven temperature was programmed from 35 ºC to 225 ºC at a rate of 10 ºC/min for Stabilwax column, and to 250 ºC at a rate of 6 ºC/min for DB-5 column. The initial and final holding time were 5 and 20 min, respectively. Helium was used as carrier gas at a constant flow rate of 2 mL/min.

The identification of volatile aroma compounds based on comparison of mass spectra to the National Institute of Standards and Technology (NIST 2.0) mass spectral data base. Additionally, calculated retention index (RI) from two different polarity columns and odor description from GC-O were compared with available data in the literature.

3. Descriptive sensory analysis

Descriptive sensory analysis was performed using nine graduate students (5 males and 4 females, between 24 to 38 years) in the Department of Food Science and Technology, Kasetsart University. The panelists were selected according to their interest, available time and ability to detect and differentiate aroma notes. The panelists were trained 2 hours/day for 15 days. The training program consisted of three sessions: i) development of aroma attributes and definitions, ii) selection of reference standards and their intensities and iii) practicing with different type of palm sugar. Ten grams of coconut sugar and 10 mL of reference standards in glass covered with plastic wrap were supplied to each panelists. A total of seven aroma attributes were generated (Table 1). The intensity of listed aroma attributes were scored on a 15-cm intensity line scale, where 0 referred to none and 15 referred to extremely.

Table 1 Aroma attributes, definitions and corresponding reference standards used for sensory evaluation of coconut sugar.

Aroma attribute	Definition	Reference	Reference intensity
caramel	sweet aromatic associated with the perception of heating or burning sugar	Lin caramel syrup (TRR sugar groups; Bangkok, Thailand)	
		- 6% (w/w) aqueous solution	8
		- 3% (w/w) aqueous solution	4
creamy	an aromatic associated with the milk cream	Best odour butter milk flavor (Best odour Co., Ltd.; Bangkok, Thailand)	
		- 0.6% (w/w) aqueous solution	12
		- 0.3% (w/w) aqueous solution	6
pandan	sweet aromatic associated with boiled pandan leave	5% (v/v) aqueous solution of pandan drink (Preco; Tesco Lotus;Bangkok, Thailand)	7
vanilla	sweet aromatic associated with vanilla or vanillin	0.15% (w/w) aqueous solution of vanilla flavor (Winner's; Greathill Ltd., Bangkok, Thailand)	6
alcoholic	aroma associated with any alcoholic or fermented product	15% (v/v) of absolute ethanol in water	7
acidic	an aromatic associated with the impression of acidic product	5% (v/v) aqueous solution of vinegar (Tiparos; Tang Sang Hah Co., Ltd., Bangkok, Thailand)	5
smoky	an aromatic associated with any type of smoke perception	50 g of burnt coconut husk soaked in 100 mL water	9

RESULTS AND DISCUSSION

1. Volatile aroma compounds in coconut sugar

In this study, 40 volatile compounds including pyrazines, furans, pyrans, aldehydes, ketones, alcohols, acids, phenols and sulfur containing compound were found by GC-MS analysis. Among these volatiles, acetic acid was the most abundance component in coconut sugar. This result match with the previous studies of Apriyantono *et al.* (1996) and Purnomo (2007). Acetic acid was also reported in coconut sap (Purnomo, 2007).

According to the data from GC-O and GC-MS, 15 tentatively identified and 7 unidentified aroma compounds were detected from coconut sugar (Table 2). The majority of aromas were heterocyclic compounds namely 2,5-dimethyl pyrazine (nutty, sweet, roasty note), furfural (smoky, burnt, bread, caramel), 5-methyl furfural (strong burnt sugar, nutty, sweet), 2-furan methanol (caramel, burnt sugar, musty, sweet), 4-methyl-5*H*-furan-2-one (roast, nutty, sweet, caramel), 5-methyl-2-furan methanol (sweet, caramel), maltol (sweet, caramel, cotton candy) and Furaneol®(burnt sugar, caramel, cotton candy).The heterocyclic compounds usually derived from Maillard reaction which occurred during heating process. Numerous studies suggested that these aromas were the determining factor for the typical nutty, roasty, smoky, burnt, sweet and caramel notes (Czerny and Grosch, 2000; Maga, 1979).

Among the identified aroma compounds, acetoin, 2,3-butanedione, 2,3-pentanedione, furfural, 2-furan methanol, 5-methyl furfural, acetic acid and 2,5-dimethyl pyrazine were previously identified as volatile compounds in coconut sugar, palm sugar and palm sap (Apriyantono *et al.*, 1996; Purnomo, 2007; Naknean *et al.*, 2010). Acetoin (buttery note) and acetic acid (sharp vinegar-like) might come from the fermentation of coconut sap or coconut sugar. Acetoin was occured in the presence of fermentable sugar or pyruvic acid (Romano and Suzzi, 1996), and was also identified from palm wine (Lasekan and Abbas, 2010). On the other hand, methional, benzyl alcohol, maltol, 4-methyl-5*H*-furan-2-one and 5-methyl-2-furan methanol have never been reported before as part of volatiles in palm sugar or palm sap.

According to odor description, the aroma compounds in coconut sugar can be categorized into five groups. The first group was represented by 2,5-dimethyl pyrazine, unknown-4, furfural, 5-methyl furfural, 2-furan methanol, 4-methyl-5*H*-furan-2-one, 5-methyl-2-furan methanol, benzyl alcohol, maltol, Furaneol®, unknown-6 and vanillin with sweet, burnt, roasty, nutty, smoky and caramel note. The second group consisted of unknown-1, 2,3-butanedione, 2,3-pentanedione, acetoin and unknown-5 with buttery, cheesy and creamy aroma. Unknown-2 and acetic acid with sharp pungent note represented the third group. Methional with French fries aroma comprised the fourth group.Unknown-3 (ethereal note) and unknown-7 (fenugreek-like) were in the miscellaneous group.

2. Sensory evaluation of coconut sugar

The orthonasal evaluation of aroma attributes in coconut sugar is shown in Figure 1. They were caramel, creamy, pandan, vanilla, alcoholic, acidic and smoky. Caramel and creamy were the highest intensity followed by smoky, pandan and alcoholic. Vanilla and acidic notes had the lowest intensity.

Table 2 Volatile aroma compounds of coconut sugar measured by GC-O.

Compound[a]	Retention index[b]		Odor description[c]
	Stabilwax	DB-5	
unknown-1		<600	buttery
unknown-2		<600	acidic
2,3-butanedione	983	617	buttery, cheesy, creamy
2,3-pentanedione	1064	n.a.	cheesy, soured milk, creamy
acetoin	1294	726	cheese, soured milk, creamy
2,5-dimethyl pyrazine	1347	932	nutty, sweet, roasty
unknown-3	1360	n.a.	ethereal
unknown-4	1367	n.a.	sweet, caramel
unknown-5	1387	n.a.	buttery, cheese
acetic acid	1394	609	sharp pungent, vinegar
methional	1464	899	potato chips, French fries
furfural	1483	n.a.	smoky, burnt, bread, caramel
5-methyl furfural	n.a.	972	strong burnt sugar, nutty, sweet
2-furan methanol	n.a.	854	caramel, burnt sugar, musty, sweet
4-methyl-5*H*-furan-2-one	n.a.	1025	roast, nutty, sweet, caramel
5-methyl-2-furan methanol	n.a.	953	sweet caramel
benzyl alcohol	1835	n.a.	sweet floral
maltol [3-Hydroxy-2-methyl-4*H*-pyran-4-one]	1921	n.a.	sweet, caramel, cotton candy
Furaneol® [2,5-dimethyl-4-hydroxy-3(2*H*)-furanone]	2043	1090	burnt sugar, caramel, cotton candy.
unknown-6	2190	n.a.	burnt sugar
unknown-7	2223	n.a.	fenugreek-like
vanillin [4-Hydroxy-3-methoxy benzaldehyde]	2593	1389	sweet, vanilla

[a] Compounds were tentatively identified by comparing mass spectra to NIST 2.0 data base, retention indices and aroma description to literature data

[b-c] derived from GC-O data

n.a. means not available

The result of sensory analysis agree with the analytical data from GC-MS and GC-O. The caramel and creamy attributes may generate from aroma compounds in group 1 and 2, respectively. The acidic, smoky, and vanilla notes may be attributed to acetic acid, furfural and vanillin, correspondingly.

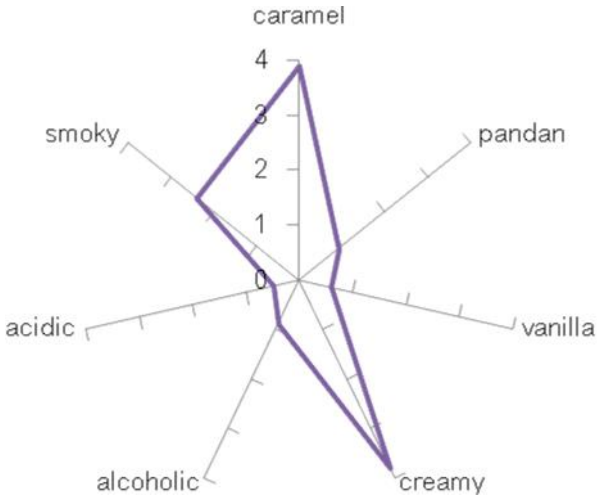

Figure 1 The aroma profile of coconut sugar from descriptive sensory analysis (n=9).

CONCLUSION

The characteristic sweet, burnt sugar, roast, nutty, smoky and caramel notes of coconut sugar were due to the presence of pyrazine, furan and pyran derivatives. Vanillin and benzyl alcohol also had sweet note. Additionally, 2,3-butanedione, 2,3-pentanedione and acetoin responsible for buttery, cheesy and creamy aroma. These information supported by descriptive sensory analysis.

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