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Volatile Aroma Compounds in Jasmine Rice as Affected by Degrees of Milling

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Summary Jasmine rice (Khao Dawk Mali 105) is popular because of its pleasant unique aroma. Milling is an important step in order to produce various types of edible rice. The distribution of volatile aroma compounds in rice especially, endosperm and bran fractions are different. Hence, the purpose of this study was to determine the volatile aroma compounds of low-milled and high-milled Jasmine rice that affect the aroma quality of cooked rice. The new crop of Jasmine paddy was used in this study. Volatile aroma compounds in raw and cooked rice with two degrees of milling, i.e., low-milled rice (2–4% rice bran) and high-milled rice (11–13% rice bran) were investigated. The raw and cooked samples were extracted with dichloromethane and analyzed by gas chromatography-time of flight mass spectrophotometer (GC-TOFMS). The amount of volatile aroma compounds in rice was decreased with high milling. 3-Penten-2-ol (green odor), the most abundant compound in raw rice, was the lowest amount in high-milled rice. On the other hand, the high-milled rice bran had the highest amount of this compound. After cooking, more types of volatile aroma compounds were detected. 2-Acetyl-1-pyrroline (2AP) (pandan-like, popcorn-like) was the most abundant in cooked rice. Meanwhile, hexanal was the highest amount in cooked rice bran. However, 2AP was the potent aroma compound with the highest odor activity values in both raw and cooked rice with low and high milling degree as well as in rice bran.
Key Words Jasmine rice, rice bran, degrees of milling, 2-Acetyl-1-pyrroline

Jasmine rice or Khao Dawk Mali 105 (KDML 105) is the most important aromatic long grain rice variety in Thailand. KDML 105 can produce the aroma during cooking, as well as growing in the fields. The volatile compounds in aromatic rice have been identified more than 200 compounds. 2-Acetyl-1-pyrroline (2AP), a popcorn-like or pandan-like aroma compound was the important aroma compound in cooked aromatic rice (*1*). After harvest, paddy is dehulled in order to get brown rice. Milling is one of the important steps of rice process to produce various types of rice grain. As the degree of milling increased, the partial surface of rice bran and endosperm are removed. The different degree of milled rice has the different chemical compounds. Moreover, milling level has affected to overall aroma in cooked short grain rice and its sensory evaluation (*2*).

Lipids and proteins are predominantly found in rice bran (*3*). The rice bran which is the by-product from milling also has the aroma characteristic. The residual from rice bran in milled rice can also affect the aroma in cooked rice (*4*).

The distribution of rice bran layer and partial endosperm which affect to overall aroma in KDML 105 has not been assessed. Therefore, the objectives of this study were to identify and compare the volatile aroma compounds in milled rice and rice bran at different degrees of milling.

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Matherials and Methods

Materials. Khao Dawk Mali 105 (KDML105) paddy, harvested in year 2018 was obtained from Agricultural Marketing Co-Operative in the northeastern region of Thailand.

Sample preparation. Paddy was dehulled using rubber rolls to obtain brown rice. The brown rice was milled using horizontal abrasive whitening machine with 2 levels of milling; low-milled (2–4% of removed rice bran) and high-milled (11–13% of removed rice bran) (*4*).

Moisture content. The moisture content of rice and rice bran was analyzed using hot air oven 130±3˚C for 1 h until stable weight (*5*).

Heat treatment of raw milled rice and rice bran. The amount of 50 g of low-milled and high-milled rice was added with deodorized water at the ratio of 1:1.5 and 1:1.2, respectively, and steamed in rice cooker for 40 min. For rice bran, each 30 g of low-milled and high-milled degree was added with deodorized water at the same ratio as rice.

Extraction of volatile compounds. The rice sample was immersed with liquid nitrogen before grinding. 50 and 30 g of grinded rice and rice bran was spiked with 25 and 15 μL of 2-methyl-3-heptanone (1.18 mg/10 mL in methanol) as internal standard and extracted with

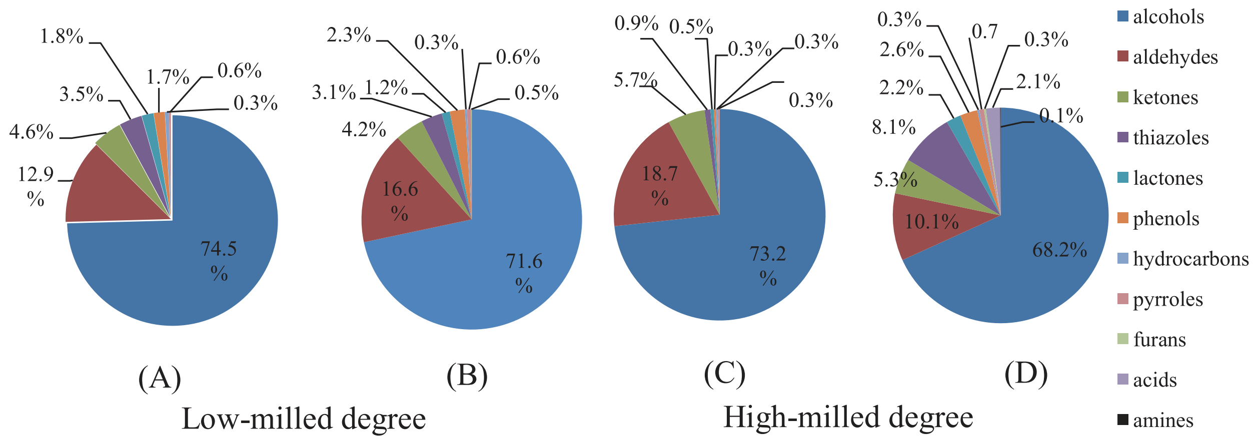

Fig. 1. Relative concentration (%) of volatile aroma groups in low- milled rice (A) and rice bran (B) and high-milled rice (C) and rice bran (D) (raw).

Table 1. Relative concentration of selected volatile aroma compounds with the most abundant/the highest OAVs in low-milled and high-milled rice and rice bran.

Volatile compounds	Odor description*	RI	Relative concentration (ng/g)							
			Low-milled degree				High-milled degree			
			RR	RRB	CR	CRB	RR	RRB	CR	CRB
hexanal	green	<1100	50.8^{a,B}	155.6^{b,A}	45.8^{a,B}	392.1^{b,A}	44.6^{b,B}	304.3^{a,A}	52.1^{b,B}	819.2^{a,A}
3-penten-2-ol	green	1188	421.2^{a,A}	1,406.3^{b,A}	59.3^{a,A}	143.6^{b,A}	243.3^{b,A}	4,632.7^{a,A}	36.9^{b,A}	116.1^{a,A}
heptanal	green, fruity	1194	n.d.	5.2^{b}	1.6^{a,B}	34.1^{b,A}	n.d.	13.0^{a}	1.7^{a,B}	70.3^{a,A}
octanal	green, fruity	1307	2.8^{a,B}	6.2^{b,A}	3.4^{a,B}	48.1^{b,A}	0.2^{a,A}	40.7^{a,A}	3.5^{a,B}	138.2^{a,A}
2-acetyl-1-pyrroline	popcorn-like, pandan-like	1344	1.5^{a,B}	13.0^{b,A}	287.2^{a,A}	94.2^{b,B}	1.1^{a,B}	53.9^{a,A}	206.5^{b,A}	140.7^{a,B}
nonanal	green, soapy	1395	21.4^{a,B}	96.6^{b,A}	42.8^{a,B}	185.7^{b,A}	17.7^{b,B}	166.8^{a,A}	45.5^{a,B}	225.2^{a,A}
cis-linalool oxide	sweet, floral	1423	n.d.	2.7^{b}	n.d.	7.3^{b}	n.d.	15.7^{a}	n.d.	8.9^{a}
γ-butyrolactone	sweet, coconut	1642	4.3^{a,B}	13.1^{b,A}	8.1^{a,B}	26.9^{b,A}	0.6^{a,B}	68.4^{a,A}	8.2^{a,B}	66.8^{a,A}
2-acetylthiazole	roasty, nutty	1653	n.d.	n.d.	n.d.	29.4^{b}	n.d.	n.d.	n.d.	49.4^{a}
2(5*H*)-furanone	sweet, burnt	1774	n.d.	n.d.	6.6^{a,A}	25.4^{b,A}	n.d.	n.d.	4.0^{a,A}	54.4^{a,A}
hexanoic acid	sweaty	1864	n.d.	n.d.	n.d.	18.8^{b}	n.d.	130.9	n.d.	156.8^{a}

* odor description (*12*).
n.d.: not detected.
a-b with different letter was significantly different in degrees of milling comparison.
A-B with different letter was significantly different in rice and rice bran within the same degree of milling.
RR=raw rice, RRB=raw rice bran, CR=cooked rice and CRB=cooked rice bran.

dichloromethane at ambient temperature for 1 h, equipped with high speed shaker. Extraction was carried out 3 times. The extract was concentrated using Vigreux column and further purified with high-vacuum distillation (under 10^{-5} torr). Then, the extract was dried with anhydrous Na_2SO_4. It was concentrated to 250 μL and kept at -80°C in amber vial until analysis.

Analysis of volatile compounds by gas chromatography—time of flight mass spectrometer (GC-TOFMS). Before analysis by using GC (7890A; Agilent Technologies; California, USA) coupled with TOFMS (Pegasus 4D; LECO®; Michigan, USA), the extract was concentrated to 200 μL. Volatile compounds were analyzed by cool on-column technique with oven tracking mode. The 1 μL of extract was injected. The volatile compounds were analyzed on polar capillary column (Stabilwax®; 30 m×0.25 mm i.d.×0.25 μm film thickness; Restek; Pennsylvania, USA). The GC oven temperature was programmed as following: initial temperature of 35°C held for 5 min, raised at a rate of 4°C/min to 225°C, and then held at this temperature for 15 min. The carrier gas was helium at a constant flow rate of 1 mL/min.

Identification and quantification of volatile aroma compounds. The identification was based on comparison of retention index (RI). The RI was determined for each volatile compound against *n*-alkane reference standards (C6-C30), then matched with literatures on the same polar column and mass spectra of each volatile compound against NIST 02 mass spectral libraries. The relative concentration was reported as ng/g (ppb). Odor activity values (OAVs) of identified compound was calculated as the ratio between the concentration and the

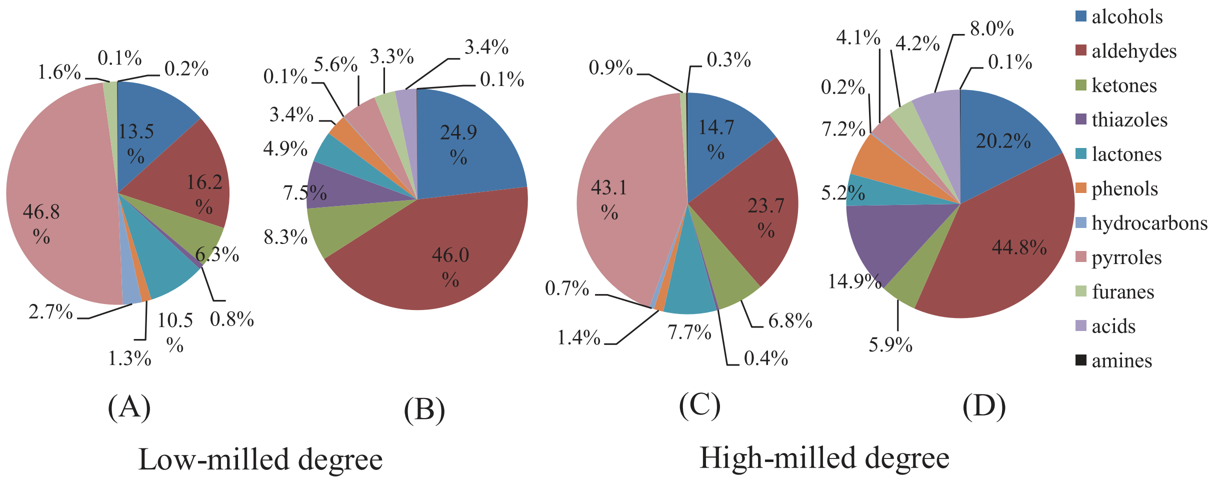

Fig. 2. Relative concentration (%) of volatile aroma groups in low- milled rice (A) and rice bran (B) and high-milled rice (C) and rice bran (D) (cooked).

odor threshold in air from the literatures.

Statistical analysis. The study was performed triplicate. Completely randomized design (CRD) was used. Pair sample *t*-test was conducted ($p<0.05$). Statistical analysis was performed using SPSS v.17 (SPSS Inc., USA).

Results

Effect of degrees of milling on volatile aroma compounds in raw rice and rice bran

The amount of volatile aroma compounds in raw rice bran was higher than in milled rice for both low and high milling. Alcohols, aldehydes, ketones and thiazoles were predominant groups of identified compounds in low-milled and high-milled rice as well as rice bran (Fig. 1). Alcohols had the highest percentage of volatile aroma compounds. Among all the alcohols, 3-penten-2-ol (green odor) was the largest amount. The second major group was aldehydes. In aromatic rice, most of aldehydes provided undesirable aroma with green aroma. Hexanal was the highest content. 2AP, the key aroma compound of Jasmine rice, was found in both rice and rice bran. In addition, *cis*-linalool oxide and hexanoic acid were found in rice bran. They are responsible for floral and sweaty notes, respectively.

The OAV was used to identify the potent aroma compounds (OAVs>1) which might contribute to the overall aroma of food. 2AP was the aroma compound with the highest OAVs in both milled rice and rice bran (OAVs=75 and 650 in low-milled rice and rice bran and OAVs=55 and 2,695 in high-milled rice and rice bran).

Effect of heat treatment on volatile aroma compounds in rice and rice bran

The heat treatment from steam-cooking increased the concentrations of volatile aroma compounds (Table 1). For both degrees of milling, the amount of volatile aroma compounds in rice bran was higher than those of rice. Pyrrole was the major group of aroma compounds in rice. 2AP was the largest amount in cooked rice. Meanwhile, aldehydes were the predominant group and hexanal was the most abundant in rice bran (Fig. 2). For lactones, oxidation product by heat inducing, might partly contribute to the sweet and coconut-like odor. Some furanes such as furfural and 2(5*H*)-furanone were detected due to heat generation. Hexanoic acid and 2-acetythiazole were found only in rice bran. In addition, 2AP was the major potent aroma compound with the highest OAVs in both rice and rice bran after heat treatment. (OAVs=14,360 and 4,710 in low-milled and OAVs=10,325 and 7,035 in high-milled rice and rice bran).

Discussion

The amount of volatile aroma compounds in rice bran was higher than in milled rice. Furthermore, the volatile compounds in high-milled rice bran were higher due to more chemical composition in bran (*3*, *4*). The presence of 3-penten-2-ol might be the product from degradation of lipid and carbohydrate (*6*). Moreover, the alcohols, methyl ketones, aldehydes and lactones could result from fatty acid (*7*) which reported in rice and rice bran (*8*). Some furanes were the product of amino acid and reducing sugar via Maillard reaction, including 2-acethylthiazole (*9*). Furthermore, *cis*-linalool oxide was generated by the glycoside of linalool oxides. The glycation bond might be cleaved by β-D-glucosidase which found in rice bran (*10*). In addition, hexanoic acid was the product from oxidation of hexanal in aromatic rice (*11*). 2AP was found in both rice and rice bran. 2AP in raw rice was higher than in rice bran. Meanwhile, 2AP in rice bran was lower after steam-cooking. This might due to aroma release from bran in powder form by heat treatment. Therefore, 2AP in bran was more heat sensitive than in rice. Furthermore, *cis*-linalool oxide, 2-acetylthiazole and hexanoic acid (Table 1) were detected in rice bran.

This indicated that these volatile aroma compounds seemed to be in bran and outer layer of endosperm fraction.

Conclusion

2-Acetyl-1-pyrroline was the most potent aroma compound with the highest OAV in both raw and cooked rice at low and high degree of milling as well as in rice bran. On the other hand, hexanal, undesirable aroma in aromatic rice, was the second potent aroma compound in high-milled rice bran. Therefore, the degrees of milling would play an important role in the aroma quality of the aromatic rice due to the residual volatile aroma compound in rice bran.

Disclosure of State of COI

No conflicts of interest to be declared.

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