Volatile components and sensory characteristics of Thai traditional fermented shrimp pastes during fermentation periods

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Abstract Headspace-volatile components and sensory characteristics, including color, Maillard reaction products and free amino acid profiles, of two types of Thai traditional fermented shrimp paste, Kapi Ta Dam and Kapi Ta Deang, were investigated during the fermentation periods up to 6 months. The results showed that the colors of both products were changed with a decrease in CIELAB values over the fermentation period, except for yellowness of Kapi Ta Deang. Essential amino acids such as lysine and leucine and non-essential amino acids such as glutamic acid and alanine were found to be predominant free-amino acids in the products. After headspace volatile component extraction of the product was carried out using a SPME fiber coated with DVB/CAR/PDMS and analyzed by GC-MS, the main compounds responsible for distinct volatiles in the products were N-containing compounds, especially pyrazines which give roasted nutty odor. The results of sensory evaluation from panelists also suggest that fermentation period had an effect

on sensory characteristics of the fermented shrimp pastes. Moreover, the sensory perceptions of the products would associate with their color, the Maillard reaction products, amino acid profiles and volatile compounds.

Keywords Fermented shrimp pastes · Volatile compounds · Solid-phase microextraction · GC-MS · Quantitative descriptive analysis

Introduction

In Thailand, fermented shrimp paste or Kapi is a key ingredient in chili pastes, curry pastes and sauces. Kapi available in Thailand has two different types, Kapi Ta Dam (black paste) and Kapi Ta Deang (red paste), which are classified according to the source of raw materials and product characteristics. Kapi Ta Dam is produced by fermentation of mysid shrimps (*M. orientalis* and *A. indicus*) harvested in mangrove channel (Pengchumrus and Upanoi 2005). Kapi Ta Deang is produced by fermentation of planktonic shrimps (*Acetes* sp.) harvested in the coastal area of the Andaman Sea (Pengchumrus and Upanoi 2005). Both Kapis are made by mixing the shrimps with salt for approximately 20 % (w/w) and then homogenizing them before natural fermentation at ambient temperature for 7–10 days. After that, the shrimp pastes are packed and fermented under the ambient temperature for further ripening up to 6 months.

Fat or lipid plays a key role as a precursor of volatile compounds and aroma compounds in meat products (Olivares et al. 2009). Protein in foods can also interact with flavor components and influences on flavor and aroma perceptions in foods (Pérez-Juan et al. 2008). The aroma and taste characteristics of a fermented food are primarily due to protein and lipid degradation by autolytic and bacterial enzymes as well as chemical reactions during fermentation (Cha and Cadwallader

Research highlights • Flavor profiles of fermented shrimp pastes were firstly reported using SPME technique.

- Pyrazines were main volatile compounds of the products.
- Fermentation process influenced on flavor profile and sensory attributes of the product.

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1995). Consequently, fermentation and ripening process are responsible for development of volatile components and sensory characteristics in fermented food products (Gao et al. 2010).

Study of volatile compounds of fermented shrimp paste has been previously reported by Cha and Cadwallader (1995). They examined the volatile components in fermented shrimp pastes using simultaneous steam distillation-solvent extraction/gas chromatography/mass spectrometry (SDE/GC/MS). They found that N-containing compounds were abundant compounds in fermented shrimp paste and could be influential flavor characteristics of the shrimp paste. However, SDE requires several steps to extract and concentrate volatile compounds. It is time-consuming and expensive with requiring a large amount of sample (Giri et al. 2010). Solid-phase microextraction (SPME) is a potential sample preparation technique because it is easy to use, inexpensive and compatible with a range of analytical instruments. Moreover, it is simplicity, speed, solvent-free, high sensitivity, small sample volume, relatively low cost and simple automation (Vas and Vêkey 2004). Reports on the application of SPME for volatile compounds analysis in various fermented foods include fish miso (Giri et al. 2010), dry-fermented sausages (Marco et al. 2004) and vegetarian soybean kapi (Wittanalai et al. 2011), but fermented shrimp paste has not been revealed. Therefore, the goal of the present study was to investigate the changes in volatile components of the natural fermented shrimp pastes by GC-MS with the SPME technique as well as their sensory attributes.

Materials and methods

Materials

Two types of Thai traditional fermented shrimp pastes; Kapi Ta Dam (Kp-B0) and Kapi Ta Deang (Kp-R0) were obtained from three different factories at KhaoPra Thong, Kuraburi, Phang Nga, Thailand. Both products were allowed to further ferment at 30 °C for 2, 4 and 6 months and defined as Kp-B2/4/6 and Kp-R2/4/6, respectively and stored at −20 °C until required. All samples were left at room temperature (30 ±2 °C) before the experiment.

Color measurement

All samples were subjected to CIELAB colorimetric L^* (lightness), a^* (redness-greenness) and b^* (yellowness-blueness) measurement using a Hunter Lab UltraScan XE colorimeter (HunterLab, Reston, VA, USA) with Universal software version 4.10. Each sample was well mixed, packed in a clear polyethylene bag and measured at 3 different locations. The average values of the measurement were reported.

Determination of developed brown color

The extracts of all samples were prepared by mixing the samples with distilled water (pH 7.0) at a ratio of 1:5 (w/v). The mixtures were homogenized and shaken at 150 rpm on an orbital shaker for 1 h at 30 °C, followed by centrifugation at 8400×*g* for 10 min at 4 °C to remove undesired debris. Each sample solution was diluted with distilled water at the same dilution to obtain an appropriate concentration before measured at absorbance of 280, 294 and 420 nm by a spectrophotometer (Varian Cary 50 UV-Vis; Agilent Technologies).

Free amino acid analysis

Free amino acid profiles of all Kapi samples were determined according to the method previously described by Liu et al. (1995) using High Performance Liquid Chromatography (HPLC; Agilent Technologies, Santa Clara, CA, USA) coupled with a fluorescence detector at the Central Instrument Facility, Faculty of Science, Mahidol University, Thailand. The analytical column was a reverse phase C18 column (Novo-Pak, 150 × 3.9 mm i.d. and 4 μm particle size, Waters, Milford, MA, USA). Amino acid standards were used for peak identification and quantification. Amino acid compositions were expressed as mg amino acid per 100 mg sample.

Analysis of volatile components

Extraction of volatile compounds

Volatile components were extracted and analyzed using modified method from Giri et al. (2010). Three grams of each Kapi sample were weighted and transferred to a 20-mL headspace vial with a polytetrafluoroethylene/silicone liner sealed tightly with an aluminium cap (Supelco, Bellefonte, PA, USA). The vial was incubated at 50 °C for 10 min with an agitation speed of 500 rpm. Headspace volatile components were adsorbed for another 20 min by a 2 cm-50/30 μm Divinylbenzene/CarboxenTM/Polydimethylsiloxane StableFlexTM (DVB/CAR/PDMS) SPME fiber (Supelco) which has strong retention to volatiles with a molecular mass range of 40–275 and low polarity. The fiber was subject to an injection port 7890A Gas Chromatography (GC; Agilent Technologies) for desorption of the absorbed volatile components for 20 min at 250 °C with the purge valve off (splitless mode). The fiber was pre-treated at the injection port under 240 °C for 60 min before each analysis.

Gas chromatography condition and identification of volatile compounds

The headspace volatile components were separated and identified using Gas chromatography with a mass selective

detector (GC-MSD) equipped with an autosample (CTC Analytics CombiPAL; Agilent Technologies, Redwood, CA, USA). The compounds were separated in a DB-WAX capillary column (30 m × 0.32 mm i.d., 0.5 µm film thickness; JandW Scientific, Folsom, CA, USA). Helium was used as the carrier gas with column inlet pressure of 11 kPa at a flow rate of 1.5 mL/min. The GC oven temperature was programmed from 40 °C for 3 min holding time to 220 °C at the rate of 5 °C/min. The volatile compounds were identified using a mass selective detector (5975C inert KL EI/CI MSD) with a Triple-Axis detector (Agilent Technologies). The mass spectra of volatile compounds were obtained by electron ionization (EI) at 70 eV and the scan range of 40–350 amu. The compounds were identified by comparison with mass spectra from the library databases (National Institute of Standards or NIST and Wiley 275), Kovats retention time indices (RIs) and retention times. The retention times of *n*-alkanes series (C₈ – C₂₀) (FlukaChemika, Buchs, Switzerland) were used to determine the RIs. The odor notes of each volatile compound were identified from several authentic online databases including <http://www.flavornet.org> and <http://www.odour.org.uk>.

Sensory evaluation

The quantitative descriptive analysis (QDA) procedure was used to evaluate the sensory attributes of the fermented shrimp pastes during the fermentation periods. Fifty one panelists, consisting of 13 males and 38 females at their ages between 23- and 59-year-old, were semi-trained consumers who were acquaintance with the fermented shrimp pastes in the local production area. They evaluated the samples in 4 majors attributes; color, odor (fishy, roast, pungent and rancid), taste (saltiness, sourness, umami and bitterness) and overall acceptance. Each attribute was described in detail for the panelists before evaluation. The panelists scored the intensity of odor and taste attributes on a line scale from 0 to 7, in which 7 was the highest intensity and 0 was no detection. They also evaluated color and overall acceptance of the product on the scale, which 7 was the most acceptable and 0 was unacceptable. The scale is easily describable by semi-trained consumers and popularly used to evaluate any food attributes in local food factories as the seven points tends to be a good balance between having enough points of discrimination without having to maintain too many response options. Both Kapi Ta Dam and Kapi Ta Deang at fermentation time of 0, 2, 4 and 6 months were presented to the panelists in clear polypropylene cups covered tightly with lids. Eight samples were coded with random 3-digit numbers and introduced to the panelists into 2 sessions. Firstly, a set of 4 samples from Kapi Ta Dam (Kp-B 0/2/4/6) was introduced to the panelist. After the first session was done, the presentation was followed by Kapi Ta Deang samples (Kp-R 0/2/4/6) at the same manner. Plain bread or cracker and water were instructed to rinse between samples.

Statistical analysis

All data was analyzed for analysis of variance (ANOVA) using SPSS software version 11.5 (SPSS, Illinois, USA). Significance of means was determined using the Duncan's Multiple Range Test (DMRT) at a 95 % significant difference ($p < 0.05$).

Results and discussions

Color

The colorimetric changes in Kapi Ta Dam (Kp-B) and Kapi Ta Deang (Kp-R) during the fermentation periods are shown in Fig. 1. Both Kapi products were darker in appearance with prolonged fermentation time (data not shown). The CIELAB values also showed that fermentation time affected lightness (L^*), redness (a^*) and yellowness (b^*) of the products (Fig. 1). All color parameters decreased during the initial fermentation period and then remained constant after the second month of fermentation, except for the b^* value of Kapi Ta Deang (Kp-R) samples. The decrease in L^* values demonstrated that darker color with browning pigments was formed due to the Maillard reaction. Increasing in Maillard reaction products and its intermediates were also reported in Philippine salt-fermented shrimp paste during the fermentation period (Peralta et al. 2008). In addition, browning color which was referred as a protein-lipid browning complex can be formed by the reaction of oxidized lipids with amino acids and proteins (Sikorski and Haard 2007). Bozkurt and Bayram (2006) revealed that the decreasing in L^* value was correlated to moisture content and water activity (a_w) of the product. It is in agreement with the previous results showing that the 6-month fermented products had lower water activity than the initial products at month 0 (a_w of 0.62 and 0.65, respectively) (Kleekayai et al. 2015).

The decrease of the redness (a^*) and yellowness (b^*) values could be due to degradation of carotenoids in the products. The degradation of carotenoids was found in salt-fermented sauce from shrimp processing by-products during the prolonged fermentation (Kim et al. 2003). The increase of yellowness value of Kapi Ta Deang products could be the coincidence of the Maillard yellow-brown pigment formation and the degradation of carotenoids. Therefore, the different raw material and production process used influenced on the product characteristics of both Kapi Ta Dam and Kapi Ta Deang.

Brown color development

As observed on sample appearance (Fig. 1), the changes of yellowness and lightness values indicated brown color

Fig. 1 Changes in CIELAB colorimetric values of Kapi Ta Dam and Kapi Ta Deang at month 0 (Kp-B0 and Kp-R0) and the fermented products at months 2–6 (Kp-B2/4/6 and Kp-R2/4/6). A, B, C and a, b, c indicate significant difference within each Kapi types at $p < 0.05$

formation of the products during fermentation periods. In this study, absorbance at 280 and 294 nm represented the formation of non-fluorescence Maillard reaction intermediate products, while the absorbance at 420 nm showed the browning intensity of late Maillard reaction products (Matmaroh et al. 2006). During the fermentation period, an increase of the intermediate products was observed in both samples as shown in OD 280 nm raised up to the fourth month of fermentation (Table 1). The Maillard reaction intermediate products could act as a precursor of the late Maillard reaction products which were browning pigments (Ajandouz et al. 2001). Different profiles of the intermediate products and browning intensity of both Kapi types were observed. The browning intensity at OD 420 nm showed an increased trend in Kapi Ta Deang samples (Kp-R) through the fermentation periods. This result

Table 1 Changes in brown color of the aqueous extract of the raw materials of Kapi Ta Dam and Kapi Ta Deang (B and R), their initial products (Kp-B0 and Kp-R0) and their fermented products at months 2–6 (Kp-B2/4/6 and Kp-R2/4/6)

Sample	OD 280 nm	OD 294 nm	OD 420 nm
B	1.858 ± 0.229 ^b	6.220 ± 0.023 ^a	0.218 ± 0.024 ^a
Kp-B0	1.168 ± 0.110 ^a	4.654 ± 0.136 ^a	0.432 ± 0.001 ^d
Kp-B2	1.471 ± 0.044 ^b	6.282 ± 0.221 ^b	0.503 ± 0.002 ^c
Kp-B4	2.840 ± 0.130 ^c	8.750 ± 0.048 ^c	0.311 ± 0.009 ^b
Kp-B6	1.469 ± 0.398 ^b	9.556 ± 0.091 ^d	0.454 ± 0.004 ^c
R	1.081 ± 0.044 ^a	2.263 ± 0.332 ^a	0.098 ± 0.001 ^a
Kp-R0	0.849 ± 0.109 ^a	5.573 ± 0.001 ^b	0.158 ± 0.014 ^b
Kp-R2	2.087 ± 0.397 ^b	6.537 ± 0.482 ^b	0.178 ± 0.004 ^b
Kp-R4	3.133 ± 0.115 ^c	9.208 ± 0.416 ^c	0.428 ± 0.023 ^c
Kp-R6	2.322 ± 0.054 ^b	10.206 ± 0.371 ^c	0.500 ± 0.025 ^d

The results are mean ± SD ($n = 3$) and different superscript letters in the same column are significantly different at $p < 0.05$

is in agreement with b^* values in Fig. 1. Kapi Ta Dam had the highest intensity of browning pigment at the second month of fermentation, however. Their difference would be possibly because some intermediate products were converted to the final brown compounds, while some intermediates were still generated in the products (Matmaroh et al. 2006).

Free amino acid content

Free amino acids found in the fermented Kapi Ta Dam and Kapi Ta Deang samples from months 0–6 are shown in Table 2. Data shows that a raw material affected amounts of free amino acids in the products. Kp-R0 had higher free amino acids than Kp-B0 which is in agreement with protein content and total and free amino acid profiles in both Kapi types as shown in the previous study (Kleekayai et al. 2015). Among free amino acids, glutamic acid was found to be predominant in both samples, although its amounts remained relatively constant during the fermentation period. Other major free amino acids found in both samples were lysine, leucine, aspartic acid, glycine and arginine. Most of them increased with the prolonged fermentation period in Kapi Ta Dam. However, in Kapi Ta Deang, most free amino acids were declined at the end of fermentation. Changes in each free amino acid during a fermentation period could be due to protein decomposition and transformation of free amino acids to amines, volatile acids and other nitrogenous compounds by bacterial metabolisms and/or enzymatic reactions including transamination and oxidative deamination (Peralta et al. 2008). Moreover, they would be correlated to the formation of Maillard reaction products during the fermentation period as observed by brown color development in Kapi Ta Deang, in particular (Table 1). Glutamic acid, the most abundant free amino acid in the fermented shrimp paste products, has been reported to

Table 2 Free amino acid content in Kapi Ta Dam and Kapi Ta Deang of the initial product (Kp-B0 and Kp-R0) and the fermented products at months 2–6 (Kp-B2/4/6 and Kp-R2/4/6)

Amino acid (mg/100 mg)	Kp-B0	Kp-B2	Kp-B4	Kp-B6	Kp-R0	Kp-R2	Kp-R4	Kp-R6
<i>Essential amino acids</i>								
Histidine	0.09	0.08	0.14	0.11	0.21	0.20	0.13	0.11
Threonine	0.26	0.30	0.33	0.35	0.39	0.49	0.37	0.39
Tyrosine	0.25	0.32	0.70	0.73	0.54	0.67	0.61	0.66
Valine	0.39	0.36	0.76	0.76	0.69	0.79	0.55	0.57
Methionine	0.13	0.12	0.43	0.39	0.39	0.45	0.32	0.34
Lysine	0.64	0.65	1.09	1.14	1.04	1.17	0.94	1.06
Isoleucine	0.32	0.28	0.74	0.72	0.60	0.73	0.47	0.52
Leucine	0.65	0.58	1.29	1.24	1.15	1.36	0.91	0.98
Phenylalanine	0.29	0.29	0.67	0.64	0.58	0.68	0.51	0.54
<i>Non-essential amino acids</i>								
Aspartic acid	0.49	0.60	1.04	1.14	0.45	0.71	0.89	0.96
Serine	0.20	0.23	0.11	0.13	0.20	0.29	0.19	0.21
Glutamic acid	1.42	1.53	1.46	1.56	1.37	1.61	1.61	1.71
Glycine	0.40	0.40	0.93	0.90	1.04	1.07	0.73	0.72
Arginine	0.65	0.59	0.52	0.55	0.89	0.97	0.87	0.90
Alanine	0.71	0.79	1.20	1.24	1.28	1.38	1.19	1.22
Proline	0.33	0.35	0.51	0.50	0.57	0.57	0.51	0.52
<i>Total</i>	7.22	7.47	11.92	12.10	11.39	13.14	10.80	11.41

associate with the ‘umami’ taste in other similar products such as fermented shrimp processing by-product and fish products (Kim et al. 2003).

Volatile components

Gas chromatograms of headspace volatile compounds in Kapi Ta Dam and Kapi Ta Deang at different fermentation times are shown in Fig. 2. Maximal total volatile compounds were detected on both Kapi types at month 6 with 56 and 54 volatiles which of 23 and 25 volatiles were positively identified in all samples of Kapi Ta Dam and Kapi Ta Deang as shown in Table 3. Among the identified volatiles, N-containing compounds, aromatic compounds and alcohols were predominant volatile groups in the fermented shrimp pastes. The major volatile compounds, i.e. trimethylamine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethyl-3-ethylpyrazine, 2-ethyl-5-methylpyrazine, 2-methylbutyric acid, 3-methyl butanal, 3-methylbutanol and dimethyl trisulfide, were detected around 5 to 36.5 % of total volatile compounds in both Kapi types.

N-containing compounds, especially pyrazines, were the most abundant group found in the fermented shrimp pastes with approximately up to 70 % of total volatile compounds. These compounds contribute in many flavors and aromas of various foods including fermented products e.g. fish miso, fish paste, shrimp paste, fermented soybean paste and vegetarian

soybean paste (Cha and Cadwallader 1995; Giri et al. 2010; Wittanalai et al. 2011). The formation of pyrazines has been reported to associate with the Maillard reaction through the Strecker degradation as various nitrogen sources including amino acids as a precursor (Nursten 2005) and metabolic activities of microorganisms during fermentation (Labuda 2009). This group of compounds is generally nutty, musty and roasting odor notes (Müller and Rappert 2010). In the present study, among pyrazines group, 2,5-dimethyl-3-ethylpyrazine, 2,5-dimethyl pyrazine and 2,6-dimethylpyrazine were predominantly present in months 2 to 6 of both Kapi types. Moreover, trimethylamine, giving fishy odor, was the major volatile in the initial samples (Kp-B0 and Kp-R0). It is developed by microbial reduction of trimethylamine oxide and is normally found in aged fresh marines (Josephson 1991). However, it was dramatically decreased after prolonged fermentation.

Aromatic compounds, which have been hypothesized to be formed by carotenoids as a precursor of toluene and benzene derivatives, are typically found in fish and shellfish pastes (Borenstein and Bunnell 1966). In both Kapi types, phenol was found at a large amount in the initial samples (Kp-B0 and Kp-R0) and then decreased with fermentation time. In particular, it could not be detected in Kapi Ta Dam at months 4 and 6 (Kp-B4 and Kp-B6). In addition, toluene was present in a small amount in all samples of both Kapi types. Besides, indole was identified only in Kapi Ta Deang (Kp-R) samples.

Fig. 2 Chromatograms of volatile compounds obtained by SPME GC-MSD of Kapi Ta Dam at **a** month 0 (Kp-B0), **b** month 2 (Kp-B2), **c** month 4 (Kp-B4) and **d** month 6 (Kp-B6) and Kapi Ta Deang at **e** month 0 (Kp-R0), **f** month 2 (Kp-R2), **g** month 4 (Kp-R4) and **h** month 6 (Kp-R6)

Fig. 2 continued.

Table 3 Headspace volatile compounds of Kapi Ta Dam at months 0, 2, 4 and 6 (Kp-B0, Kp-B2, Kp-B4 and Kp-B6) and Kapi Ta Deang at months 0, 2, 4 and 6 (Kp-R0, Kp-R2, Kp-R4 and Kp-R6) extracted by 50/30 µm DVB/CAR/PDMS

Kapi Ta Dam							
Peak no.	Compound ^a	KI ^b	% Relative peak area ^c				Odor description
			Kp-B0	Kp-B2	Kp-B4	Kp-B6	
<i>Aldehyde (2)</i>							
2	3-Methylbutanal	866	10.87	4.31	2.35	2.80	almond, cheese, malty
24	Benzaldehyde	1526	3.86	1.68	nd	nd	almond, burnt sugar
<i>Ketone (1)</i>							
9	2-Heptanone	1192	1.65	1.62	0.80	0.74	fruity, blue cheese
<i>Alcohols (5)</i>							
6	2-Methyl-1-propanol	1107	0.70	1.56	0.36	0.55	wine, solvent, bitter
8	1-Penten-3-ol	1175	2.35	0.27	0.62	0.68	fishy, pungent
10	3-Methyl-1-butanol	1222	6.04	9.84	1.21	1.97	whisky, malt, burnt
11	1-Pentanol	1265	1.56	0.55	0.35	0.44	balsamic
27	2-Phenylethanol	1918	0.43	0.32	0.51	0.65	honey, sweet, rose
<i>Aromatic compounds (2)</i>							
3	Toluene	1047	1.53	0.67	0.58	0.63	sweet, pungent
28	Phenol	1997	4.82	1.97	nd	nd	phenol
<i>N-Containing compounds (9)</i>							
1	Trimethylamine	677	16.61	6.65	4.58	4.48	fishy, ammonia
12	2-Methylpyrazine	1277	nd	2.23	0.71	0.70	nutty, roasted
15	2-Ethylpyridine	1294	0.88	nd	0.25	0.17	grassy, fishy
17	2,5-Dimethylpyrazine	1339	5.26	26.64	18.94	16.06	roasted nut
19	2-Ethyl-6-methylpyrazine	1400	1.05	3.07	1.96	1.98	roasted, nutty
20	Trimethylpyrazine	1416	1.14	2.36	5.74	5.50	roasted nut, musty
21	2,5-Dimethyl-3-ethylpyrazine	1459	3.39	4.52	36.49	31.53	roasted, potato
22	3,5-Dimethyl-3-ethylpyrazine	1473	nd	nd	0.78	0.72	potato, nutty
23	2,3,5-Trimethyl-6-ethylpyrazine	1525	nd	nd	6.92	6.19	baked potato, roasted cocoa bean
<i>Ester (1)</i>							
16	3-Methyl-3-methylbutyl butanoate	1301	nd	1.12	nd	0.22	fruity, apple odor
<i>S-Containing compounds (2)</i>							
4	Dimethyl disulfide	1080	0.27	1.42	0.90	2.30	onion, cabbage
18	Dimethyl trisulfide	1383	0.08	0.26	0.79	4.53	fishy
<i>Acid (1)</i>							
26	2-Methyl butanoic acid	1675	4.37	8.72	0.83	2.32	cheese, sweet
Kapi Ta Deang							
Peak no.	Compound ^a	KI ^b	% Relative peak area ^c				Odor description
			Kp-R0	Kp-R2	Kp-R4	Kp-R6	
<i>Aldehyde (2)</i>							
2	3-Methylbutanal	866	6.90	5.49	2.47	2.11	almond, cheese, malty
5	(E)-2-methyl-2-butenal	1107	0.74	0.71	1.08	0.85	wine, solvent, bitter
<i>Ketones (2)</i>							
9	2-Heptanone	1192	2.32	2.40	nd	nd	fruity, blue cheese
14	2-Octanone	1293	0.40	0.55	nd	nd	fruity, musty
<i>Alcohols (4)</i>							
8	1-Penten-3-ol	1175	1.70	1.60	nd	0.11	fishy, pungent
10	3-Methyl-1-butanol	1222	2.10	3.20	5.64	3.81	whisky, malt, burnt
11	1-Pentanol	1265	0.97	0.79	0.36	0.31	balsamic
27	2-Phenylethanol	1918	0.20	0.16	0.81	0.81	honey, sweet, rose
<i>Aromatic compounds (3)</i>							
3	Toluene	1047	1.21	1.48	0.38	0.27	sweet, pungent

Table 3 (continued)

28	Phenol	1997	11.53	9.98	4.85	4.91	phenol
29	Indole	2435	2.01	1.18	0.33	0.29	month ball, burnt
<i>N-Containing compounds (8)</i>							
1	Trimethylamine	677	27.85	15.14	7.70	7.44	fishy, ammonia
12	2-Methylpyrazine	1277	nd	0.53	0.31	0.28	nutty, roasted
17	2,6-Dimethylpyrazine	1341	3.64	12.82	18.33	14.26	nutty, roasted
19	2-Ethyl-5-methylpyrazine	1398	14.81	14.78	2.46	2.30	fruity, sweet
20	Trimethylpyrazine	1416	0.93	1.83	2.40	2.17	roasted nut, musty
21	2,5-Dimethyl-3-ethylpyrazine	1458	4.52	9.38	11.71	10.24	roasted, potato
22	3,5-Dimethyl-3-ethylpyrazine	1474	nd	nd	0.41	0.36	potato, nutty
23	2,3,5-Trimethyl-6-ethylpyrazine	1525	nd	nd	2.90	2.60	baked potato, roasted cocoa bean
<i>Ester (3)</i>							
7	2-Methylbutyl acetate	1138	0.36	0.33	0.15	0.10	fruity
13	2-Methylbutyl-3-methylbutanoate	1286	nd	nd	1.03	1.08	fruity, wine
16	3-Methyl-3-methylbutyl butanoate	1301	nd	nd	1.04	1.07	fruity, apple odor
<i>S-Containing compounds (2)</i>							
4	Dimethyl disulfide	1080	1.20	4.53	4.13	7.86	onion, putrid
18	Dimethyl trisulfide	1383	0.79	2.04	4.98	8.52	fishy
<i>Acid (2)</i>							
25	2-Methyl propanoic acid	1573	1.00	0.73	1.94	2.44	cheesy
26	2-Methyl butanoic acid	1674	1.14	1.47	10.38	12.80	cheese, sweet

^a Compounds by order of their Kovats indices in chemical classes

^b Kovats indices of unknown compounds on the DB-WAX column

^c Percentage of relative peak area of total peak; nd, Not detected

^d Odor description of each compounds was obtained from www.flavornet.org/www.odour.org

Indoles have been considered to be a product from catabolism of tryptophan (Mateo and Zumalacárregui 1996).

Dimethyl disulfide and dimethyl trisulfide were only two S-containing compounds detected in both Kapi Ta Dam and Kapi Ta Deang samples. In Kapi Ta Dam, development of dimethyl trisulfide was noticed when dimethyl disulfide was detected at a lower amount and was maximal at month 6 (Table 3). For Kapi Ta Deang, both dimethyl disulfide and dimethyl trisulfide showed an increased trend with fermentation time (Table 3). The presence of these S-containing compounds could be the flavor characteristic of the fermented shrimp paste because of their low threshold values between 0.16–12 ppb and 0.005–0.01 ppb of dimethyl disulfide and dimethyl trisulfide, respectively (Schutte 1975). The formation of S-containing volatile compounds has been proposed to associate with S-containing amino acids, i.e. cysteine and methionine degradation by microbial enzyme as well as their thermal degradation (Varlet and Fernandez 2010).

Aldehydes, ketones and alcohols are generally produced from oxidative cleavages of the lipids and the degradation of amino acids and saccharides (Wittanalai et al. 2011). Alcohols were another dominant group in fermented shrimp pastes but they were detected in a relatively low amount. This is in agreement with the report of Cha and Cadwallader (1995) that alcohols were found at a large amount in fish paste but lower in shrimp paste. The results showed that the alcohols levels of Kapi Ta Dam were higher than those of Kapi Ta Deang. Among this group, 3-methylbutanol was the most abundance detected in both Kapi types and reached maximal in Kp-B2

and Kp-R4 (Table 3). In addition, some lactic acid bacteria have been reported to produce a large amount of 3-methylbutanol from phenylalanine, valine and leucine (Helinck et al. 2004). Moreover, the amounts of alcohols were found to correlate with aldehyde levels in the fermented shrimp pastes in this study.

Aldehydes were considered to enhance the flavor quality which associated with sweet, fruity, nutty and caramel-like odors (Fors 1983). These compounds can be generated by lipid oxidation and degradation during fermentation (Ames and Macleod 1984). Among aldehydes, 3-methylbutanal was found to be the highest amount in both Kapi Ta Dam and Kapi Ta Deang. It was maximal at the beginning of fermentation and then decreased with fermentation time. Steinhaus and Schieberle (2007) proposed that 3-methylbutanal and 2-methylbutanal were the most important odorants in soy sauce and primarily produced by microbial actions via branched-chain amino acid biosynthesis pathways of leucine, valine and isoleucine. Moreover, the activity of aminopeptidase from *Tetragenococcus halophilus*, found in Indonesian 'Terasi' shrimp paste (Kobayashi et al. 2003) and fish sauce, was closely related to the formation of these volatile compounds (Udomsil et al. 2010). In addition, 3-methylbutanal has been reported to be originated from the Strecker degradation of certain amino acids (Giri et al. 2010). Benzaldehyde (peak no. 24, Table 3) was found only in Kapi Ta Dam in the first 2 months of fermentation (Kp-B0 and Kp-B2), while it was not clearly found in Kapi Ta Deang (Fig. 2). It was also found in fish sauce (Udomsil et al. 2010).

Benzaldehyde was typically generated from the Strecker degradation of phenylalanine and associated to almond-like odor (Andersen and Hinrichsen 1995). Microbial fermentation by *Lactobacillus plantarum* URL-LcL1 could also convert phenylalanine to phenylpyruvic acid which was subsequently transformed to benzaldehyde (Groot and Bont 1998).

A few ketones were detected in both Kapi types. Although 2,3-butanedione was previously reported in a high amount in shrimp paste (Cha and Cawallader 1995), but it could not be found in the present study using DVB/CAR/PDMS extraction. Only two ketones were positively identified in the fermented shrimp pastes. A rapid decrease of 2-heptanone was observed in both Kapi types after the second month of fermentation. Interestingly, in Kapi Ta Deang, both ketone compounds were not detected at the months 4 and 6 as 2-octanone. Ketones can be generated by microbial enzymatic actions on lipids and/or amino acids, or by the Maillard reaction.

2-Methylbutanoic acid, giving cheesy and sweet note, was the most abundance among identified acids in both Kapi types. In Kapi Ta Deang, it increased with increasing fermentation time. Additionally, 2-methylpropanoic acid was found only in Kapi Ta Deang at a lower amount than 2-methylbutanoic acid. This compound gives pungent butterfat-like odor but not as unpleasant (O'Neil 2006). These short chain fatty acids, 2-methylpropanoic acid and 2-methylbutanoic acid, have been considered to be the products of microbial metabolism of valine and isoleucine, respectively (Mateo and Zumalacárregui 1996). These acids may also have a positive impact on aroma due to their conversion into fruity esters (Stahnke 1994), although, their corresponding ester derivatives were detected in a low amount at around 1 % of total volatiles (Table 3). The major ester found in both Kapi types was a series of butanoate esters, giving fruity odor, which was in an agreement with the previous report (Cha and Cadwallader 1995). In Kapi Ta Dam, only 3-methyl-3-methylbutanoate was positively identified and was maximal at the second month of fermentation. Most esters were found in Kapi Ta Deang samples of the last 2 months (Kp-B4 and Kp-B6). Esters may be generated from esterification of various alcohols and carboxylic acids formed by microbial and enzymatic decomposition of lipids (Cha and Cadwallader 1995; Wittanalai et al. 2011). Moreover, Chung et al. (2005) proposed that branch short-chain aldehydes and their corresponding alcohols and acids were mainly produced from branch-chain amino acids via the Ehrlich pathway by the action of various microbial enzymes during fermentation.

It is interesting that microbial metabolisms of amino acids, lipid oxidation and degradation probably play an important role in flavor formation of the fermented shrimp pastes. However, the impact of any compounds on the aroma attributes of the products depends on not only the relative abundance but also the threshold value

of each volatile compound. Furthermore, SPME extraction may not get entire volatile compounds in the samples as much as direct extraction technique. Fiber type and the preconditioning condition could also affect volatile compounds recovered by the SPME technique.

Sensory characterization

The sensory profiles of both Kapi Ta Dam and Kapi Ta Deang during fermentation periods are shown in Fig. 3a, b, respectively. The sensory attributes included both desirable and undesirable odors and tastes. Both Kapi types showed similar profiles. Kp-B0 had the highest scores of overall acceptance, roast odor and umami, while Kapi Ta Dam samples at months 2–6 were no significantly difference in those attributes, except for roast odor in Kp-B6 (Fig. 3a). Kapi Ta Deang at months 0 and 2 (Kp-R0 and Kp-R2) showed no significant difference in all attributes and had higher scores than the samples at months 4 and 6 (Fig. 3b). Color appearance in all samples was found to relate to lightness value (Fig. 1), non-fluorescence Maillard reaction intermediate products and the browning intensity at OD 294 and 420 nm, respectively (Table 1). It was also noted that the samples with higher lightness value (Fig. 1) seemed to be more acceptable by panelists for fermented shrimp paste product. The fishy odor associated with trimethylamine identified in the headspace volatile compounds in both Kapi types has a low threshold value. The panelists could not, thus,

Fig. 3 Sensory profiles of **a** Kapi Ta Dam (Kp-B) and **b** Kapi Ta Deang (Kp-R) during fermentation periods of 0, 2, 4 and 6 months (Kp-B0/2/4/6 and Kp-R0/2/4/6, respectively)

distinguish fishy odor intensity of each sample. The higher pleasant attributes scores of Kp-B0, Kp-R0 and Kp-R2 could correlate to the presence of 3-methylbutanal, giving pleasant almond-like and cheesy odors, at relative amount in those samples (Table 3). It is also observed that pungent and rancid scores of the further fermented samples were higher than those of the initial product possibly due to light catalyst lipid oxidation, as the samples stored in a clear container. Saltiness, sourness and umami in both Kapi types had not changed much throughout the prolonged fermentation as confirmed by relatively constant salt contents and acidity (pH) in the products as shown in the previous study (Kleekayai et al. 2015) and unchanged glutamic acid levels, a precursor of umami taste, in both Kapi types (Table 2).

Conclusions

In both Kapi Ta Dam and Kapi Ta Deang, glutamic acid was the major free amino acid which was associated with umami taste in the products. Among identified volatiles, N-containing compounds, S-containing compounds, esters and aldehydes mainly contributed to flavor characteristics of the fermented shrimp pastes. The development of those aroma attributes in the fermented shrimp pastes at longer fermentation time was observed. Color appearance and volatile compounds identified in the fermented shrimp pastes affected the overall acceptance of panelists. To improve the desirable flavor of fermented shrimp paste, the fermentation condition and microbial starter would be developed.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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