

Aroma volatile profiles of Thai green chili paste (*Nam Prig Noom*) preserved by ultra-high pressure, pasteurization and sterilization

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Article history

Received: 25 December 2012

Received in revised form:

20 February 2013

Accepted: 27 February 2013

Abstract

Volatile components of untreated, pressurized, pasteurized and sterilized Thai green chili paste (*Nam Prig Noom*) were extracted by solid phase microextraction (SPME) and identified by gas chromatography–mass spectrometry (GC–MS). The chromatograms showed that sulfide compounds such as diallyl sulfide, allyl methyl disulfide and allyl methyl trisulfide in untreated *Nam Prig Noom* were the largest group among all quantified volatiles, and their increases were mostly enhanced by thermal processes. Besides sulfides, other compounds generated by heat included 3-methyl-2(5H)-furanone, 2-hexyl-5-methyl-[2H]-furan-3-one, 2-methyl-tetradecane and 1,2-dimethyl cyclohexane. Most desirable esters and sulfides such as 2-methylbutanoate, 4-methylpentanoate and diallyl sulfide were greatly retained in pressurized products, while an undesirable volatile from Maillard reaction such as 2-hexyl-5-methyl-[2H]-furan-3-one disappeared after pressurization. In addition, benzaldehyde was present with the highest amount among various aldehydes. Besides benzaldehyde, other volatiles diminished under processing including aldehyde class, ester class (methyl salicylate and 4-methylpentanoate), acid class and hydrocarbon class (limonene, 2-methyl tridecane and alpha-longipinene). Some volatiles were relatively stable in all treatments such as 3,4-dimethylthiophene, methyl propyl disulfide, alpha-himachalene and gamma-himachalene.

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Keywords

Thai green chili paste

Volatile compounds

High pressure processing

Pasteurization

Sterilization

Introduction

Green chili paste or *Nam Prig Noom*, a traditional dish of the northern region of Thailand, has a unique aroma. Since it receives large consumer demand with traded value of 500 kg/day (Ruanma, 2008), *Nam Prig Noom* is not only restricted to the northern region but also distributed throughout the country. Although several formulas of *Nam Prig Noom* have been developed, the main ingredients such as baked or roasted chili (*Capsicum annuum* Linn.), shallot (*Allium cepa* Linn.) and garlic (*Alliaceae sativum* Linn.) are analogous (Apichartsrangkoon and Jedsadapaisid, 2009). *Nam Prig Noom* is made of roasted chili and shallot with the skin peeled out after roasting. They are subsequently ground with blanched garlic and other seasoning. *Nam Prig Noom* is usually freshly made prior to selling, because it has rather short shelf-life which can be kept for less than a day at room temperature or less than three days at

refrigerator (Apichartsrangkoon and Jedsadapaisid, 2009). To extend its shelf-life, conventional pasteurization or sterilization were consistently applied, but these processes could impair the flavor, color, texture and nutritional values of the chili paste. Ultra-high pressure developed to preserve better food quality could gain high potential for processing *Nam Prig Noom* to meet the consumer requirement. Chaikham and Apichartsrangkoon (2012) observed that pressurized longan juice at 500 MPa with 25°C for 20 min displayed brighter color and more vivid transparency than those untreated and thermal treated juices.

Flavor aroma of *Nam Prig Noom* partially derives from green chili. Srisajjalertwaja *et al.* (2012) found seventy-two volatile components in untreated Thai green chili (cv. *Chakrapad*) with the most abundant volatiles of hydrocarbons, esters and alcohols. Other volatile classes were aldehydes, ketones, sulfur-containing compounds, furans and pyrazine.

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Some volatiles lost, while others generated on baking. Rotsatchakul *et al.* (2008) also found major volatiles in Thai fried chili paste (*Nam Prig Phao*) such as dimethyl sulfide, allyl mercaptan, 2-(or 3-) methylbutanal, allyl methyl sulfide, 2,3-butandione, 3,3'-thiobis(1-propene) and methyl propyl disulfide.

Volatile compounds were found in other chili and ingredients. For instance, Toontom *et al.* (2012) found 8 groups of volatile compounds in Chee Fah chili (*Capsicum annuum* Linn. var. *acuminatum* Fingerh.) including acids, alcohols, ketones, aldehydes, esters, pyrroles, furans and hydrocarbons. Mazida *et al.* (2005) found usual aroma compounds in fresh pepper such as 2,3-butanedione, 1-penten-3-one, hexanal, 3-carene, beta-ocimen, octanal, *trans*-2-hexenal, 2-isobutyl-3-methoxypyrazine and linalool. Elmore *et al.* (2008) identified volatiles of fresh and baked Thai green chili as well as detected high concentration of 3-methyl-1-butanol and 4-methyl-1-pentanol. Besides chili, another essential ingredient was garlic having strong flavor and containing major volatiles such as diallyl trisulfide, diallyl disulfide and allyl methyl trisulfide (Calvo-Gómez *et al.*, 2004). Heated garlic also contained large amount of diallyl sulfide and diallyl disulfide compounds (Lawson *et al.*, 1991). The volatiles in fresh and heated shallots had also been studied. For instance, Wu *et al.* (1982) found the amount of 2,4-dimethylthiophene, 3,4-dimethylthiophene, methyl 1-propenyl trisulfide and propyl 1-propenyl trisulfide in baked or deep fried shallots increased in comparison to fresh shallot, while the amount of saturated alkyls (dimethyl, methyl, propyl and dipropyl) trisulfides and unsaturated alkyl disulfides decreased. In addition, methyl propyl trisulfide was found predominantly in volatile oils of shallot followed by methyl propenyl disulfide and propyl propenyl disulfide. Apichartsrangkoon *et al.* (2009) noted that flavor components including some sulfur-containing compounds could lose or be transformed during heating. Some minor ingredients of *Nam Prig Noom* included fish sauce, a flavor enhancer. Fukami *et al.* (2002) detected 2-methylpropanal, 2-methylbutanal, 2-pentanone, 2-ethylpyridine, dimethyl trisulfide, 3-(methylthio) propanal (methional) and 3-methylbutanoic acid in fish sauce which were the principal contributors to the distinctive odor of this sauce.

It is interesting in studying the volatile aroma characteristic of pressurized (300 or 600 MPa/30 or 50°C/40 min), pasteurized (95°C/5 min) and sterilized (121°C/4 min) *Nam Prig Noom* in comparison with untreated sample. Apichartsrangkoon *et al.* (2009), who compared various processed pennywort

juices by pressurization (400 MPa/<30°C/20 min), pasteurization (90°C/3 min) and sterilization (121°C/4 min) and found that pressurization better retained some volatile compounds including acyclic alcohols, aldehydes and oxygenated monoterpenoids than pasteurization and sterilization; while other aroma compounds including ketones, sulfur-containing compounds and furans were significantly generated in pasteurized and sterilized products.

Materials and Methods

Preparation of *Nam Prig Noom*

Green chili (cv. *Chakrapad*), shallot and garlic, purchased from local market in Chiang Mai province, Thailand. Green chili and shallot were baked at 210°C for 20 min and 10 min, respectively by a conduction oven (SZUTIC, model YXD-40S/YXD-60S/YXD-90S, Guangdong, China); garlic was blanched at 100°C for 50 s. All ingredients were peeled, minced and blended with fish sauce for 5-10 min by a JIADE blender (medel JM-200, Taipei, China). The formula of *Nam Prig Noom* was the mixture of cooked green chili, shallot, garlic and fish sauce at the ratio of 6.5:1:1.5:1 (w/w) (Apichartsrangkoon and Jedsadapaisid, 2009).

Preparation of processed *Nam Prig Noom*

For pasteurization, a 100 g of *Nam Prig Noom* was filled into a retort pouch, sealed and immersed in boiling water until the inside temperature reached 90 ± 5°C and hold for 3 min; for sterilization, the pouch was transferred to a spray retort (FMC FoodTech, Alfa Laval, Fontanil Cornillon, France) and heated to 121°C for 4 min ($F_0 = 4$). Both processed samples were immersed in cooling water and cooled down to 25°C. For pressurization, a 100 g sample was filled into a laminated bag (nylon plus polyethylene, Royal Can Industries, Thailand) and subsequently subjected to pressure at 300 or 600 MPa for 30 or 50°C with holding time 20 min. The high pressure vessel was a 'Food Lab' high pressure rig (Stansted Fluid Power, model 900, Stansted, UK). The rate of pressure increase was about 330 MPa/min. During this high pressure treatment an adiabatic increase in temperature occurs. At ambient temperature (25°C), the monitored cell temperature increased by about 11°C up to 600 MPa but decreased to the set equilibrium value in less than 5 min. The pressure transmitting medium was a mixture of castor oil and 98 % ethanol at the ratio of 20:80 (v/v) (Chaikhram and Apichartsrangkoon, 2012). All processed samples were kept at 4°C for further analysis. Picture of untreated *Nam Prig Noom* is shown in Figure 1.



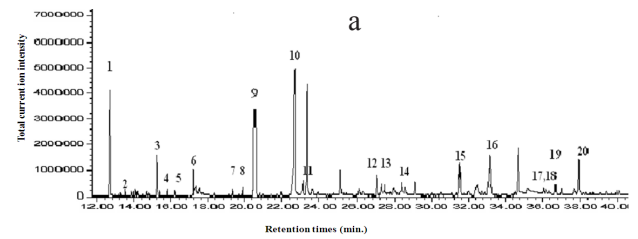
Figure 1. Light photography image of untreated *Nam Prig Noom*

Determination of volatile aroma compounds

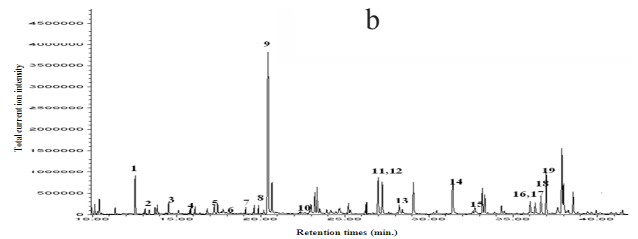
Five grams of untreated or processed *Nam Prig Noom* were transferred into a 60 mL screw-capped amber glass vials (Supelco, Bellefonte, PA, USA). The headspace was extracted at 35°C for 45 min by solid phase microextraction (SPME) fiber, by using a 50/30 µm divinylbenzene (DVB)/carboxen on polydimethylsiloxane (PDMS) fiber (Supelco, Bellefonte, USA). Extract compounds were then analyzed by Gas chromatography–mass spectrometry (GC–MS, HP5972 MSD with HP5890 GC, Agilent, CA) by using a VF–5MS column (60 m × 0.25 µm ID, 0.25 µm in film thickness). The volatile compounds were desorbed from the SPME fiber by heating at 250°C for 3 min, with an initial oven temperature 40°C (2 min) rising to 250°C at 4°C/min. A 1,2-dichlorobenzene as an internal standard (1 µL of a solution in methanol, 130 ng/mL) was injected into GC–MS prior to the injection of samples. Carrier gas was helium at 21 psi., and the mass spectrometer scanned from *m/z* 400 to *m/z* 29 at a scanning rate of 2.05 scans/s (Srisajjalertwaja *et al.*, 2012).

Identification and quantification of volatile aroma compounds

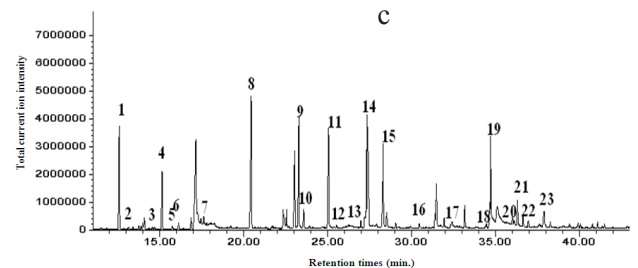
The GC–MS was calibrated daily by running 0.1 µL of a 100 ppm standard mixture of n-alkanes (C5–C25). Qualities of volatile compounds were identified by comparing linear retention indices (LRI) with those of authentic compounds and mass spectra of compounds by comparison with the bibliographic data of known compounds from the mass spectral database (NIST/EPA/NIH Mass Spectral Library, 2005; Adams, 2007). Approximate quantities of each compound were determined by comparison of its area to the integrated peaks of the total ion chromatogram and calculated by comparing peak area with that of the 1,2-dichlorobenzene internal standard. The chromatograms of total volatile compounds in untreated and processed *Nam Prig Noom* are shown in Figure 2.



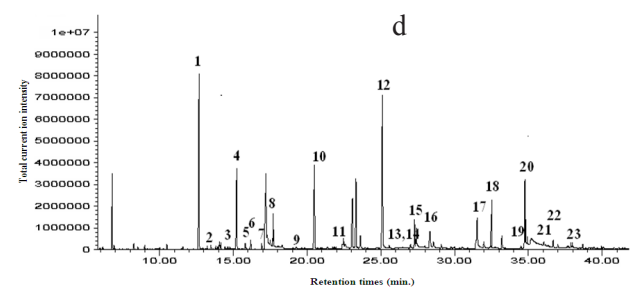
1) diallyl sulfide, 2) 3,4-dimethylthiophene, 3) allyl methyl disulfide, 4) methyl propyl disulfide, 5) 2,3-dimethylthiophene, 6) benzaldehyde, 7) limonene, 8) *cis*-1-nitro-1-propene, 9) 1,2-dichlorobenzene, 10) allyl isothiocyanate, 11) dipropyl disulfide, 12) 2-methyl butanoate, 13) methyl salicylate, 14) hexyl 3-methylbutanoate, 15) 4-methyl pentanoate, 16) 2-methyltridecane, 17) 2-methyltetradecane, 18) alpha-himachalene, 19) 3-buten-2-one and 20) gamma-himachalene



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1) diallyl sulfide, 2) 3,4-dimethylthiophene, 3) 2,5-dimethyl thiophene, 4) allyl methyl disulfide, 5) methyl propyl disulfide, 6) 2,3-dimethylthiophene, 7) dimethyl trisulfide, 8) 1,2-dichlorobenzene, 9) allyl isothiocyanate, 10) dipropyl disulfide, 11) allyl methyl trisulfide, 12) methyl propyl trisulfide, 13) 2-methylbutanoate, 14) 3-vinyl-[4H]-1,2-dithiin, 15) 2-vinyl-[4H]-1,3-dithiin, 16) 4-methylpentanoate, 17) 3,3'-thiobis-1-propene, 18) tetradecane, 19) 1,2,3,4-tetrahiopane, 20) 2-hexyl-5-methyl-[2H]-furan-3-one, 21) 2-methyl-tetradecane, 22) alpha-himachalene and 23) gamma-himachalene



1) diallyl sulfide, 2) 3,4-dimethylthiophene, 3) 2,5-dimethyl thiophene, 4) allyl methyl disulfide, 5) methyl propyl disulfide, 6) 2,3-dimethylthiophene, 7) 2,3-dihydrofuran, 8) dimethyl trisulfide, 9) allyl methyl sulfide, 10) 1,2-dichlorobenzene, 11) 1,2-dithiocyclopentane, 12) allyl methyl trisulfide, 13) methyl propyl trisulfide, 14) 1,2-dimethyl cyclohexane, 15) 3-vinyl-[4H]-1,2-dithiin, 16) 2-vinyl-[4H]-1,3-dithiin, 17) diallyl trisulfide, 18) 3,3'-thiobis-1-propene, 19) tetradecane, 20) 1,2,3,4-tetrahiopane, 21) 2-hexyl-5-methyl-[2H]-furan-3-one, 22) 2-methyl-tetradecane and 23) gamma-himachalene

Figure 2. GC-MS Chromatograms of total volatile compounds in processed *Nam Prig Noom*: a) untreated sample, b) pressurized sample at 600 MPa and 30°C for 20 min, c) pasteurized sample at 90°C for 2 min and d) sterilized sample at 121°C for 4 min

Statistical analysis

All data were the means of triplicate determinations with individual duplication (*n* = 6). Analysis of variance (ANOVA) was carried out

Table 1. Concentrations of selected volatile compounds in untreated and processed *Nam Prig Noom*

LRI**	Volatile compounds (ng/5 g sample)*	Pressurized <i>Nam Prig Noom</i>				Pasteurized <i>Nam Prig Noom</i>	Sterilized <i>Nam Prig Noom</i>
		Untreated <i>Nam Prig Noom</i>	at 30° C		at 50° C		
			300 MPa	600 MPa	300 MPa	600 MPa	
Aldehydes (7)							
801	hexanal	4.73 ± 0.18 ^a	3.27 ± 1.93 ^a	4.36 ± 0.11 ^a	3.18 ± 1.02 ^a	4.61 ± 0.99 ^a	nf ^b
826	2-ethyl- <i>trans</i> -2-butanal	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	9.95 ± 3.56 ^a
957	[<i>E</i>]-2-hexenal ^{ns}	3.04 ± 1.54	6.42 ± 5.13	5.50 ± 4.17	4.44 ± 2.81	5.32 ± 3.79	5.21 ± 2.18
966	benzaldehyde	27.69 ± 10.61 ^a	4.09 ± 0.24 ^b	4.79 ± 0.15 ^b	4.21 ± 1.10 ^b	3.97 ± 0.54 ^b	2.72 ± 0.26 ^c
989	[<i>E</i>]-2-pentenal	4.45 ± 2.45 ^a	nf ^b	nf ^b	nf ^b	nf ^b	2.50 ± 0.50 ^c
1049	benzeneacetaldehyde	3.50 ± 2.28 ^a	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b
1058	[<i>E</i>]-2-octenal ^{ns}	2.05 ± 1.34 ^a	2.33 ± 1.25	2.11 ± 0.21	2.79 ± 0.62	3.56 ± 1.85	3.18 ± 2.94
Ketones (4)							
828	3-methyl-2(5H)-furanone	2.24 ± 1.58 ^d	2.38 ± 0.37 ^d	3.01 ± 1.52 ^{cd}	2.86 ± 0.15 ^c	4.99 ± 1.04 ^b	6.05 ± 0.18 ^b
977	1-octen-3-one	2.53 ± 0.79 ^b	4.97 ± 3.81 ^b	4.09 ± 1.78 ^b	5.23 ± 3.20 ^b	4.28 ± 1.78 ^b	7.73 ± 1.26 ^a
1443	2-hexyl-5-methyl-[2H]-furan-3-one	5.91 ± 2.12 ^c	nf ^d	nf ^d	nf ^d	nf ^d	12.81 ± 3.24 ^b
1487	3-buten-2-one	13.87 ± 7.34 ^a	12.45 ± 6.63 ^a	15.28 ± 6.73 ^a	4.72 ± 0.58 ^b	3.73 ± 1.66 ^b	1.85 ± 1.19 ^b
Esters (4)							
1196	2-methylbutanoate	21.10 ± 3.85 ^b	27.59 ± 1.20 ^a	23.80 ± 2.64 ^b	18.12 ± 3.36 ^c	10.50 ± 5.33 ^c	10.69 ± 2.11 ^d
1202	methylsalicylate	17.54 ± 5.39 ^a	14.46 ± 3.45 ^{ab}	12.23 ± 1.23 ^{bc}	10.52 ± 1.23 ^b	4.42 ± 1.69 ^c	nf ^d
1247	hexyl-3-methylbutanoate	14.81 ± 2.19 ^a	14.37 ± 0.82 ^a	15.76 ± 1.07 ^a	10.06 ± 0.14 ^b	4.32 ± 3.34 ^c	2.04 ± 0.97 ^c
1311	4-methylpentanoate	25.46 ± 2.01 ^a	23.90 ± 2.99 ^a	19.95 ± 6.32 ^a	18.56 ± 7.32 ^{ab}	18.23 ± 5.02 ^{ab}	11.54 ± 3.39 ^b
Alcohol (1)							
1508	2,6-ditertiarybutyl-4-methylphenol(BHT) ^{ns}	5.56 ± 4.30	8.49 ± 5.04	3.62 ± 3.36	9.82 ± 1.18	3.80 ± 2.33	11.32 ± 7.15
Acids (2)							
1106	butanoic acid	8.32 ± 1.14 ^a	7.63 ± 1.69 ^a	7.95 ± 2.16 ^a	6.33 ± 1.03 ^a	6.23 ± 1.83 ^a	nf ^b
1152	2-methylpropanoic acid	4.02 ± 2.19 ^a	3.83 ± 0.37 ^a	4.72 ± 1.71 ^a	3.94 ± 0.24 ^a	4.75 ± 0.70 ^a	nf ^b
Sulfide compounds (17)							
858	diallyl sulfide	109.48 ± 10.40 ^b	28.18 ± 4.73 ^d	24.57 ± 2.65 ^d	8.43 ± 2.62 ^e	8.65 ± 5.34 ^e	79.73 ± 13.00 ^e
877	3,4-dimethylthiophene ^{ns}	13.41 ± 2.41	12.76 ± 1.42	11.90 ± 2.11	13.09 ± 1.47	13.74 ± 2.53	12.12 ± 2.66
905	2,5-dimethylthiophene	5.18 ± 1.96 ^b	4.79 ± 2.81 ^b	4.47 ± 0.13 ^b	4.28 ± 2.55 ^b	3.69 ± 0.57 ^b	12.65 ± 0.67 ^a
918	allyl methyl disulfide	41.37 ± 16.03 ^b	14.58 ± 1.98 ^c	12.57 ± 3.83 ^c	5.46 ± 2.69 ^d	2.14 ± 0.34 ^e	48.80 ± 16.04 ^b
933	methyl propyl disulfide ^{ns}	14.25 ± 2.01	11.99 ± 3.12	11.48 ± 4.65	12.01 ± 6.56	11.47 ± 3.89	16.41 ± 4.25
940	2,3-dimethylthiophene ^{ns}	13.97 ± 4.87	11.20 ± 2.04	11.15 ± 5.07	12.87 ± 2.84	14.52 ± 3.11	15.52 ± 2.66
974	dimethyltrisulfide	6.53 ± 0.79 ^b	5.90 ± 2.52 ^b	4.50 ± 1.57 ^b	3.21 ± 2.25 ^{bc}	2.14 ± 1.11 ^c	22.69 ± 9.79 ^a
1006	allyl methyl sulfide	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	5.18 ± 0.52 ^a
1090	1,2-dithiocyclopentane	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	19.16 ± 3.68 ^a
1103	allyl isothiocyanate	129.09 ± 23.05 ^a	9.89 ± 0.78 ^c	9.40 ± 1.76 ^c	6.92 ± 0.56 ^d	5.84 ± 1.20 ^d	99.49 ± 37.45 ^b
1111	dipropyl disulfide	21.35 ± 1.94 ^a	nf ^d	nf ^d	nf ^d	nf ^d	19.26 ± 10.21 ^b
1149	allyl methyltrisulfide	nf ^c	nf ^c	nf ^c	nf ^c	nf ^c	89.25 ± 26.46 ^b
1161	methylpropyltrisulfide	nf ^c	nf ^c	nf ^c	nf ^c	nf ^c	10.22 ± 1.41 ^b
1191	1-pentyl-2-propyl-cyclopentane	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	6.45 ± 1.90 ^a
1313	diallyl trisulfide	nf ^c	nf ^c	nf ^c	nf ^c	nf ^c	2.38 ± 0.13 ^b
1339	3,3'-thiobis-1-propene	nf ^c	nf ^c	nf ^c	nf ^c	nf ^c	20.46 ± 8.92 ^b
1401	1,2,3,4-tetra thiepane	52.31 ± 6.71 ^b	nf ^c	nf ^c	nf ^c	nf ^c	72.57 ± 3.52 ^a
Hydrocarbon compounds (12)							
1030	limonene	13.74 ± 3.02 ^a	11.98 ± 1.07 ^a	11.40 ± 0.57 ^a	nf ^b	nf ^b	nf ^b
1033	alpha-pinene	nf ^c	0.72 ± 0.67 ^d	1.58 ± 0.41 ^d	1.46 ± 0.15 ^d	1.73 ± 0.15 ^d	2.60 ± 0.36 ^a
1044	<i>cis</i> -beta-ocimene ^{ns}	3.28 ± 1.16	3.46 ± 1.28	2.51 ± 2.18	4.02 ± 1.97	3.17 ± 1.26	2.45 ± 1.88
1180	1,2-dimethylcyclohexane	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	10.69 ± 2.36 ^a
1191	1-pentyl-2-propyl-cyclopentane	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	6.45 ± 1.90 ^a
1360	2-methyltridecane	30.04 ± 5.34 ^a	11.23 ± 8.29 ^b	7.39 ± 1.27 ^b	7.05 ± 2.90 ^b	5.29 ± 0.85 ^b	9.97 ± 6.99 ^b
1364	alpha-longipinen ^{ns}	8.18 ± 3.52	5.98 ± 2.25	4.91 ± 3.29	6.54 ± 1.93	4.05 ± 2.26	4.82 ± 3.99
1380	alpha-silangene ^{ns}	2.09 ± 1.11	1.00 ± 0.15	1.12 ± 1.06	1.45 ± 0.68	1.42 ± 1.16	3.53 ± 2.15
1395	tetra decane	6.93 ± 3.32 ^a	1.31 ± 0.22 ^d	2.04 ± 1.11 ^d	1.82 ± 1.30 ^d	1.41 ± 0.80 ^d	11.73 ± 1.63 ^b
1459	2-methyl-tetra decane	15.21 ± 3.54 ^b	5.10 ± 1.24 ^c	6.20 ± 0.15 ^c	6.22 ± 1.74 ^c	6.20 ± 2.21 ^c	17.07 ± 7.04 ^b
1468	alpha-himachalene ^{ns}	10.48 ± 2.11	8.62 ± 3.53	9.90 ± 4.32	8.41 ± 2.86	7.95 ± 5.04	10.05 ± 3.34
1496	gamma-himachalene ^{ns}	14.05 ± 6.99	10.30 ± 4.02	14.28 ± 7.41	13.78 ± 3.10	13.12 ± 7.81	17.18 ± 9.58
Miscellaneous (5)							
972	2,3-dihydrofuran	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	12.69 ± 2.21 ^a
1083	<i>cis</i> -1-nitro-1-propene	15.23 ± 4.16 ^a	16.81 ± 8.95 ^a	14.29 ± 4.30 ^a	18.05 ± 7.32 ^a	16.09 ± 5.28 ^a	5.74 ± 2.66 ^a
1177	2-methoxy-3-isobutylpyrazine	3.28 ± 0.67 ^a	3.22 ± 2.56 ^a	3.41 ± 0.83 ^a	2.82 ± 1.32 ^a	2.79 ± 1.52 ^a	nf ^b
1206	3-vinyl-4H-1,2-dithiin	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	95.03 ± 17.56 ^a
1228	2-vinyl-4H-1,3-dithiin	nf ^b	nf ^b	nf ^b	nf ^b	nf ^b	72.36 ± 11.52 ^a

* Approximate quantities (ng) in headspace for 5 g sample is estimated by comparison with 100 ng of 1,2-dichlorobenzene as an internal standard

** LRI is Linear Retention Index on a VF5-MS column. nf = not found.

Components followed by different letters within each row are significantly different (P < 0.05). Components were the means of triplications.

by using SPSS Version 14.0, and determination of significant differences among treatment means was done by Duncan's multiple range tests (P < 0.05).

Results and Discussion

The flavor compounds in *Nam Prig Noom* treated by pressurization, pasteurization and sterilization are shown in Table 1. Various selected volatile compounds displayed in this study were 7 aldehydes, 4 ketones, 4 esters, 1 alcohol, 2 acids, 17 sulfide compounds, 12 hydrocarbon compounds and 5 miscellaneous. Among the quantified volatiles, sulfide compounds were the largest groups.

In addition, the major volatiles of *Nam Prig Noom* distributed in various treatment conditions could be clarified as follows. Untreated sample exhibited the largest contents of allyl isothiocyanate, diallyl sulfide and 1,2,3,4-tetra thiepane. The most abundant volatiles in pressurized products were 2-methylbutanoate, 4-methylpentanoate and diallyl sulfide. Pasteurized and sterilized products displayed major flavor components of allyl isothiocyanate,

dithiin, diallyl sulfide, allyl methyl trisulfide and allyl methyl disulfide.

Aldehydes

Six aldehyde compounds were detected from untreated *Nam Prig Noom*, and had been sequenced from the highest concentration as follows: benzaldehyde, hexanal, [*E*]-2-pentenal, benzeneacetaldehyde, [*E*]-2-hexenal and [*E*]-2-octenal. Two aldehyde compounds were relatively stable on processing such as [*E*]-2-hexenal and [*E*]-2-octenal, while benzaldehyde significantly diminished (P < 0.05) by 85% and 91% from high pressure and thermal processes, respectively. It was worth noting that thermal process gave rise to loss of desirable hexanal or reduction of benzaldehyde, while 2-ethyl-*trans*-2-butanal was generated. Two volatiles, [*E*]-2-pentenal and benzeneacetaldehyde, disappeared on processing. Van Ruth *et al.* (1995) reported that hexanal liberated grassy odor in pepper. Table 1 shows that high pressure could preserve this volatile, whereas thermal process decomposed it. Benzaldehyde, slight water soluble, is the major contributor of flavor of fish

sauce, while [*E*]-2-hexenal found in all samples might derive from shallot (McIver *et al.*, 1982; Yaws, 1999; Fukami *et al.*, 2002; Zhang *et al.*, 2006; Pham *et al.*, 2008). Other researchers observed that the amount of hexanal significantly increased during pressurization of tomato juice at 500 MPa for 3 min (Porretta, 1995). This might be due to the catalyzed oxidation products of unsaturated fatty acids by lipoxidase (Whitfield and Shipton, 1966; Barra *et al.*, 2007; Oomah and Liang, 2007). Rotsatchakul *et al.* (2008) found that hexanal was present in both untreated and fried chili pastes at 100°C for 25 and 50 min, while Toontom *et al.* (2012) noticed that hexanal in chili disappeared after drying.

Ketones

Four ketones were found in untreated *Nam Prig Noom* as orderly quantified, 3-buten-2-one, 2-hexyl-5-methyl-[2H]-furan-3-one, 1-octen-3-one and 3-methyl-2(5H)-furanone. Concentration of 3-buten-2-one in untreated and pressurized at 30°C products were parallel. This heat-labile compound significantly decreased ($P < 0.05$) by 71% and 87% after pressurization at 50°C and pasteurization, respectively, while sterilization led to loss of this volatile. Srisajjalertwaja *et al.* (2012) found that ketone group such as 1-penten-3-one in green chili reduced or lost after baking at 180-250°C for 20 min. Volatile, 1-octen-3-one and 3-buten-2-one disappeared from sterilized *Nam Prig Noom*, whereas 3-methyl-2(5H)-furanone and 2-hexyl-5-methyl-[2H]-furan-3-one increased significantly ($P < 0.05$) by 270% and 200% respectively upon sterilization, which indicated that these undesirable volatiles were thermal generated compounds through Maillard modification (Mottram *et al.*, 1998) Rotsatchakul *et al.* (2008) also found 1-octen-3-one in both of untreated and heated (100°C for 25 and 50 min) Thai fried chili pastes. The 1-octen-3-one was the product of lipid oxidation and liberated mushroom-like aroma (Karahadian and Johnson, 1993).

Esters

Four esters were present in untreated and processed *Nam Prig Noom*. Most abundant esters found in untreated and processed samples were 4-methylpentanoate and 2-methylbutanoate along with methyl salicylate and hexyl 3-methylbutanoate. These esters significantly diminished ($P < 0.05$) or disappeared according to treatment severity which suggested that 4-methylpentanoate and methyl salicylate were heat sensitive components. Yusuf and Bewaji (2011) detected high concentration of 2-methylbutanoate from fermented garlic extract

under lower pressure treatment, whereas under higher pressure and temperature, this volatile diminished. They also noticed that methyl salicylate disappeared as a result of heating fermented garlic extract. Lamikanra and Richard (2002) stated that lost of ester compounds in fruits and vegetables corresponded to a loss of freshness or fruity aromas. Table 1 showed that most of these desirable esters diminished or lost through thermal processes, while high pressure better preserved them.

Alcohols and acids

In alcohol class, 2,6-ditertibuthyl-4-methylphenol was stable in all processed and untreated chili pastes, while Srisajjalertwaja *et al.* (2012) found that alcohol such as geraniol remained in baked chili at 180 and 250°C for 20 min.

Butanoic acid and 2-methyl propanoic acid were detected only in untreated and pressurized samples. This suggested that they were thermal sensitive compounds. On the other hand, Rotsatchakul *et al.* (2008) found butanoic acid in Thai fried chili paste heated at 100°C for 25 and 50 min but could not found in unprocessed sample. Moreover, Toontom *et al.* (2012) also found 2-methyl propanoic acid in sun-dried chili but could not detect in freeze-dried, air-dried and unprocessed samples.

Sulfide compounds

Seventeen sulfides were detected and the most abundant compounds were diallyl sulfide, allyl isothiocyanate, allyl methyl disulfide and 1,2,3,4-tetrathiepane. Fisher and Scott (1997) stated that isothiocyanates deriving from non-volatile precursor, appeared during mechanical cell injury and gave pungent aroma in cruciferous plants, such as horseradish, mustard, kohlrabi and cabbage. In addition, sulfides being stable in all *Nam Prig Noom* were 3,4-dimethylthiophene, methyl propyl disulfide and 2,3-dimethylthiophene. Moreover, diallyl sulfide, allyl methyl disulfide and allyl isothiocyanate in pressurized sample significantly decreased ($P < 0.05$) by 74-95%, whereas sulfides disappeared from pressurized samples including allyl methyl sulfide, 1,2-dithiocyclopentane, dipropyl disulfide, allyl methyl trisulfide, methyl propyl trisulfide, 1-pentyl-2-propyl-cyclopentane, diallyl trisulfide, 3,3'-thiobis-1-propene and 1,2,3,4-tetrathiepane. On the other hand, sulfides which significantly increased ($P < 0.05$) under thermal process especially those treated with sterilization included diallyl sulfide, 2,5-dimethyl thiophene, allyl methyl disulfide, dimethyl trisulfide, allyl methyl sulfide, 1,2-dithiocyclopentane, allyl methyl trisulfide, methyl propyl trisulfide, 1-pentyl-

2-propyl-cyclopentane, diallyl trisulfide, 3,3'-thiobis-1-propene and 1,2,3,4-tetrathiepane. Disulfides and trisulfides of allium plants such as garlic and shallot arise from sulfenic acids generated enzymatically (allinase enzyme) from cysteine sulfoxides during chopping, blending or mechanically injuring the cell walls (Fisher and Scott, 1997). Several researchers had identified diallyl sulfide, diallyl trisulfide, dimethyl trisulfide, dipropyl disulfide, methyl propyl disulfide, methyl propyl trisulfide, 3,4-dimethylthiophene, 2,5-dimethyl thiophene in garlic and shallot products. They also found high concentration of methyl propyl trisulfide in shallot (Wu *et al.*, 1982; Chu and Hsu, 2001; Calvo-Gómez *et al.*, 2004; Zhang *et al.*, 2006). Wu *et al.* (1982) noticed that either baked or deep fried shallots led to an increase of 3,4-dimethylthiophene while dimethyl trisulfide decreased. However, Fukami *et al.* (2002) and Pham *et al.* (2008) found that dimethyl trisulfide was also one of the major flavor of fish sauce; hence it was present in all untreated and processed *Nam Prig Noom* since all samples were mixed with fish sauce.

In overall, thermally derived compounds displayed in Table 1 were allyl methyl sulfide, allyl methyl trisulfide, methyl propyl trisulfide, diallyl trisulfide and 3,3'-triobis-1-propene. Excessive heating such as in sterilization could lead to the formation of volatile compounds including, 1,2-dithiocyclopentane and 1-phenyl-2-propyl-cyclopentane. Apichartsrangkoon *et al.* (2009) and Wongfhun *et al.* (2010) stated that the increase of product's flavor components might be a result of heat activation of flavor precursors or the release of flavor compounds bound to cell membranes or macromolecules. For instance, on heating, dimethyl trisulfide, diallyl trisulfide, allyl methyl trisulfide and allyl methyl disulfide could be generated from diallyl thiosulfinate and/or allyl methyl thiosulfinate. This sulfur group usually had the great flavor impact because it bound strongly to the olfactory receptors (Fisher and Scott, 1997).

Hydrocarbon compounds

Twelve hydrocarbons were found. Hydrocarbons which were significantly stable ($P > 0.05$) under processing included *cis*-beta-ocimene, alpha-longipinene, alpha-ylangene, alpha-himachalene and gamma-himachalene. Limonene was the only hydrocarbon that disappeared from thermal treated products, while hydrocarbons which increased or generated on thermal treatment were alpha-pinene, tetradecane and 2-methyl-tetradecane, along with 1,2-dimethyl cyclohexane and 1-pentyl-2-propyl-cyclopentane existing in sterilized samples only.

Limonene is the common aroma compound in various citrus fruits and *Allium* species (Zhang *et al.*, 2006). In this investigation, limonene was relatively thermal labile, hence it was found only in pressure treated products, while 2-methyl tridecane and tetradecane were present in untreated and processed *Nam Prig Noom*, particularly sterilized sample. In general, tetradecane was found in fermented garlic and chili as well as in freeze-dried and air-dried chilies, whereas 2-methyl tridecane existed in sun-dried chili (Yusuf and Bewaji, 2011; Toontom *et al.*, 2012).

Alpha-pinene in processed *Nam Prig Noom* was probably produced during high pressure and thermal treatments, while 1,2-dimethyl cyclohexane and 1-pentyl-2-propyl cyclopentane in sterilized samples could be generated by heat treatment. Other compounds including alpha-pinene, tetradecane and 2-methyl tetradecane increased as a result of heating, while 2-methyl tridecane decreased as a result of high pressure and thermal treatments.

Other miscellaneous compounds

Other compounds including *cis*-1-nitro-1-propene and 2-methoxy-3-isobutyl pyrazine disappeared on thermal treatments, whereas 2,3-dihydrofuran, 3-vinyl-[4H]-1,2-dithiin and 2-vinyl-[4H]-1,3-dithiin were produced from thermal processes. Rotsatchakul *et al.* (2008) found 2-vinyl-[4H]-1,3-dithiin in untreated and fried chili pastes also a major volatile compound in garlic (Dembitsky *et al.*, 2007). However, 2-vinyl-[4H]-1,3-dithiin, 3-vinyl-[4H]-1,2-dithiin and 2,3 dihydrofuran in this study were found only in pasteurized and sterilized *Nam Prig Noom* which indicated that these might be thermally generated compounds. In contrast, 2-methoxy-3-isobutyl pyrazine and *cis*-1-nitro-1-propene disappeared in pasteurized and sterilized batches which might be due to excessive heating that caused decomposition of the compounds. Yu and Chiang (1986) found that pasteurization (75°C/40 s) of passion fruit juice caused about 45% loss of flavor volatile compounds based on total volatiles.

Conclusion

GC-MS chromatograms showed that sulfide compounds such as diallyl sulfide, allyl methyl disulfide and allyl methyl trisulfide in *Nam Prig Noom* were the largest groups among all quantified volatiles; and their increases were mostly enhanced by thermal processes. Besides sulfides, other compounds generated by heat included 3-methyl-2(5H)-furanone, 2-hexyl-5-methyl-[2H]-furan-3-one, 2-methyl-tetradecane and 1,2-dimethyl

cyclohexane. Most desirable esters and sulfides such as 2-methylbutanoate, 4-methylpentanoate and diallyl sulfide were greatly retained in pressurized products, while an undesirable volatile from Maillard reaction such as 2-hexyl-5-methyl-[2H]-furan-3-one disappeared after pressurization. In addition, benzaldehyde, the predominant compounds in aldehyde group, along with ester class (methyl salicylate and 4-methylpentanoate), acid class, hydrocarbon class (limonene, 2-methyl tridecane and alpha-longipinene) diminished according to treatment conditions.

Acknowledgements

The authors would like to thank the Thai Ministry of Education for their financial support. A special thank is also given to Professor Dr. Donald S. Mottram, Dr. Stephen J. Elmore and Mr. Andrew T. Dodson, Department of Food and Nutritional Sciences, University of Reading, Reading, UK for their kind assistance and advice on GC-MS analysis.

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