

Identification of Characteristic Aroma Components of Thai Fried Chili Paste

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Three forms of Thai fried chili pastes (CP) were prepared, consisting of an unheated CP (UH-CP), a CP heated at 100 °C for 25 min (H25-CP, typical product), and a CP excessively heated for 50 min (H50-CP). The potent odorants in the CPs were investigated by two gas chromatography–olfactometry methods: dynamic headspace dilution analysis (DHDA) and aroma extract dilution analysis (AEDA). DHDA revealed that the predominant odorants in heated CPs were mainly sulfur-containing compounds, followed by lipid-derived compounds, Strecker aldehydes, and Maillard reaction products. Dimethyl sulfide, allyl mercaptan, 2- (or 3-) methylbutanal, allyl methyl sulfide, 2,3-butanedione, 3,3'-thiobis(1-propene), and methyl propyl disulfide were among the most potent headspace odorants detected by DHDA. By AEDA, 2-vinyl-4*H*-1,3-dithiin and diallyl trisulfide had the highest FD factors in H25-CP. On the basis of their high FD factors by both GCO methods, the predominant odorants in H25-CP were 3-vinyl-4*H*-1,2-dithiin, allyl methyl disulfide, and allyl methyl trisulfide. Furthermore, dimethyl trisulfide and diallyl disulfide had the highest odor activity values in H25-CP, suggesting that these were also potent odorants in CP. In addition, methional, 3-methylbutanoic acid, 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone, and 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolon) were indicated as potent thermally derived odorants of H25-CP.

KEYWORDS: Thai fried chili paste (nam phrik phao); aroma-active; odorant; gas chromatography–olfactometry; dynamic headspace dilution analysis; aroma extract dilution analysis

INTRODUCTION

Thai fried chili paste (CP), nam phrik phao, is widely consumed in Thailand. It is used as a condiment in traditional Thai foods such as tom yam (Thai spicy soup). Sometimes, it is used as a spread for breads or crackers. CP has specific flavors derived from its ingredients and thermal processing. The flavor of CP is one of the most important criteria determining consumer choice and acceptance. The ingredients of CP generally include chili powder, garlic, shallot, dried shrimp, tamarind juice, fish sauce, salt, coconut sugar, and soybean oil. Dried shrimp, fish sauce, and shrimp paste used in the preparation of CP provide protein as well as some characteristic marine and dried seafood aromas. In addition, reaction of ingredients via the Maillard reaction can create additional aroma components during heating.

The volatile components of many of the ingredients used in the production of CP have been previously studied. Allylthio-containing volatile compounds, especially diallyl sulfide and diallyl disulfide, have been identified in the volatile flavor of garlic products and are believed to be responsible for the

characteristic flavor of thermally treated garlic products (1). It has been reported that the most abundant volatile compound in garlic is diallyl trisulfide, followed closely by diallyl disulfide and allyl methyl trisulfide (2). Moreover, the volatile oils from raw, baked, and deep fat fried shallots have been studied (3). During heating of shallot, either by baking or deep fat frying, the amount of 2,4-dimethylthiophene, 3,4-dimethylthiophene, methyl 1-propenyl trisulfide, and propyl 1-propenyl trisulfide increased while the amount of saturated alkyl (dimethyl, methyl, propyl, and dipropyl) trisulfides and unsaturated alkyl disulfides decreased. Methyl propyl trisulfide was found at the highest percent content in volatile oils of shallot. Methyl propenyl disulfide and propyl propenyl disulfide were present at lesser amounts, but their changes upon heating were conspicuous (3). In addition, Zimmermann and Schieberle (4) reported that 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone (HDMF; caramel-like), 3-hydroxy-4,5-dimethyl-2-(5*H*)-furanone (sotolon; seasoning-like), and 2- and 3-methylbutanoic acids contribute to the aroma of sweet bell pepper powder. The compounds furfural, 5-methyl-2-(3*H*)-furanone, phenylacetaldehyde, and 5-methylfurfural are the major volatile components in tamarind (5). Furthermore, Fukami and co-workers (6) indicated that 2-methylpropanal, 2-methylbutanal, 2-pentanone, 2-ethylpyridine, dimethyl trisul-

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Table 1. Composition of Thai Fried Chili Paste

| ingredients | % (w/w) |
|--|---------|
| chili powder | 3.74 |
| ground garlic (<i>Allium sativum</i> Linnaeus) | 16.26 |
| ground shallot (<i>Allium ascalonicum</i> Linnaeus) | 19.51 |
| minced dried shrimp | 4.88 |
| tamarind juice | 4.06 |
| fish sauce | 2.44 |
| salt | 0.33 |
| kaphi (shrimp paste) | 5.69 |
| coconut sugar | 23.58 |
| soy bean oil | 19.51 |

fide, 3-(methylthio)propanal (methional), and 3-methylbutanoic acid are principal contributors to the distinctive odor of fish sauce.

The characteristic aroma components of CP have not been previously studied. The purpose of the present study was to identify and compare the chemical nature of aroma-active compounds of unheated CP (UH-CP), a typical CP product heated at 100 °C for 25 min (H25-CP), and excessively heated CP (100 °C for 50 min; H50-CP). The results will aid in establishing baseline data so that defects in CP caused by ingredients or processing may be more clearly detected and characterized.

MATERIALS AND METHODS

Materials. Chili powder, dried shrimp, and shrimp paste were obtained from a local market in Bangkok, Thailand. Garlic, shallot, tamarind juice, fish sauce, salt, coconut sugar, and soybean oil were purchased at a local market in Urbana, IL.

Chemicals. Diethyl ether (anhydrous, 99.8%), sodium chloride (99%), *n*-alkane standards (C6–C30), 2-methyl-3-heptanone (internal standard for neutral fraction), 2-ethylbutyric acid (internal standard for acidic fraction), and 2,4,6-trimethylpyridine (internal standard for basic fraction) were purchased from Aldrich Chemical Co. (St. Louis, MO). Sodium sulfate (99%), sodium hydroxide (98.7%), and hydrochloric acid (36.5%) were obtained from Fisher Scientific (Pittsburgh, PA). Deodorized distilled water was prepared by boiling glass-distilled water to two-thirds of its original volume. The authentic standard compounds listed in Tables 2–4 were obtained from the following commercial sources: **1, 3–5, 7–13, 15, 17, 21, 23, 25, 30, 31, 33, 34, 36, 41, 42, 45, 46, 48, 49, 53, 54, 56, 60, 64, 65, 67, 77, 78, and 80–82** (Aldrich); **14, 47, 55, 71, and 83** (Sigma, St. Louis, MO); **2 and 6** (Fluka, Steinheim, Germany); **26 and 43** (Lancaster, Windham, NH); **74** (Mallinckrodt Baker Inc., Phillipsburg, NJ); **16** (Bedoukian Research Inc. Danbury, CT); **20** (Alfa, Ward Hill, MA); **35** (Pfaltz/Bauer, Waterbury, CT); **69** (Firmenich Co., Princeton, NJ). 2-Acetyl-1-pyrroline (**27**) was obtained from Dr. R. Buttery (USDA, ARS, WRRRC, Albany, CA). (*Z*)-1,5-Octadien-3-one (**32**), (*Z*)-2-nonenal (**43**), and (*E*)-4,5-epoxy-(*E*)-2-decenal (**75**) were synthesized as previously described (7–9).

Sample Preparation. The composition of unheated CP (UH-CP) is presented in Table 1. The apparatus described by Pojjanapimol et al. (10) was used for the heating of CP. Two hundred grams of the mixed ingredients of CP (Table 1) was placed in a three-neck round-bottom flask (1 L) and closed with thermometer, condenser (0 °C), and PTFE stirrer blade assembly. The mixture was heated at 100 °C by using a heating mantle and stirred (50 rpm) for 25 or 50 min to produce H25-CP and H50-CP, respectively. The mixture was immediately cooled in an ice–water bath. The CPs (200 g of mixed CP ingredients) were placed in Corpak clear standard wide-mount bottles and sealed with Teflon-lined closures and then covered with aluminum foil. Samples were prepared in duplicate and kept at –70 °C until further analysis.

Proximate composition (11) of the H25-CP was as follows: moisture, 4.43%; lipid, 24.29%; protein, 6.61%; ash, 3.78%; crude fiber, 1.28%; and carbohydrate, 59.61%.

Dynamic Headspace Dilution Analysis (DHDA). A mixture of 5 g of CP, 45 mL of deodorized distilled water, and 5 μ L of an internal standard solution (containing 1.62 μ g/ μ L 2-ethylbutyric acid, 2.44 μ g/ μ L 2,4,6-trimethylpyridine, and 1.25 μ g/ μ L 2-methyl-3-heptanone in methanol) was homogenized at 14000 rpm for 1 min using an Ultra Turrax Ika T25 basic homogenizer (Janke & Kunkel GmbH & Co., Germany). Five milliliters of the mixture was placed in the three-neck glass purge and trap vessel (280 mL volume, jacketed; Scientific Instrument Services, Ringoes, NJ). The volatiles were purged onto an adsorbent trap (Tenax TA 60/80, 200 mg/trap; Supelco, Bellefonte, PA) using nitrogen (flow rate 20 mL/min, ultrahigh purity). The vessel was maintained at 25 °C by circulating water through the external water jacket. DHDA was performed by varying the headspace purge times (25, 5, and 1 min), as described by Cadwallader and Baek (12). After purging, the desorption tube was removed from the vessel and dry purged with nitrogen gas (flow rate 50 mL/min) for approximately 5 min at room temperature to remove any moisture in the trap.

The thermal desorption system (splitless mode; TDS2; Gerstel GmbH & Co. KG, Germany) was employed to desorb the volatiles from the Tenax trap. This system was connected to a 6890 GC (Agilent Technologies Inc.) equipped with a cooled injection system (CIS4; Gerstel), a flame ionization detector (FID), and an olfactory detector port (ODP2; Gerstel). Volatiles were desorbed at 220 °C into the CIS4 inlet held at –150 °C (solvent vent mode, 50 mL/min helium vent flow) followed by cold splitless injection (inlet heated at 12 °C/s from –150 to 260 °C with final hold time of 10 min; purge valve delay was 1.10 min) of the desorbed volatiles into the GC column. Separations were performed on a polar capillary column (Stabilwax-DA, 15 m \times 0.32 mm i.d.; 0.5 μ m film; Restek, Bellefonte, PA) and a nonpolar column (RTX-5MS, 15 m \times 0.32 mm i.d.; 0.5 μ m film; Restek). The GC oven temperature was programmed from 30 to 225 °C at a rate of 10 °C/min with initial and final hold times of 5 and 15 min, respectively. Helium was used as a carrier gas at a constant flow rate of 2.1 mL/min. The FID and sniffing port temperatures were 250 °C. To prevent drying of the nasal mucosa, humidified air was supplied to the sniff port at 30 mL/min. The end of the capillary column was split between FID and sniff port in the ratio of 1:1 using deactivated fused silica capillaries (1 m \times 0.32 mm i.d.; Restek). Analysis of each dynamic headspace dilution was carried out in triplicate, and GCO was performed by two experienced sniffers. A flavor dilution factor was calculated for each odorant by dividing the highest purge time tested (25 min) by the purge time at which it was last detected by GCO (e.g., either 25, 5, or 1 min) (12).

Direct Solvent Extraction and Solvent-Assisted Flavor Evaporation. A CP sample (20 g) was weighed into Teflon bottle (capacity of 250 mL) equipped with Tefzel closures. The extraction was prepared in duplicate. Deodorized distilled water (100 mL) and 20 μ L of an internal standard solution (containing 1.62 μ g/ μ L 2-ethylbutyric acid, 2.44 μ g/ μ L 2,4,6-trimethylpyridine, and 1.25 μ g/ μ L 2-methyl-3-heptanone in methanol for acidic, basic, and neutral fractions, respectively) were added to the bottles. The mixture was homogenized at 14000 rpm for 1 min using an Ultra Turrax Ika T25 basic homogenizer. Diethyl ether (90 mL) and 10 g of sodium chloride (99%) were added to the bottles. The mixtures were agitated for 30 min on a Roto mix (Thermolyne, type 50800, Dubuque, IA) at 200 rpm. The bottles were then centrifuged at 3000 rpm for 10 min in order to separate the solvent phases, which were subsequently collected into round-bottom flasks. The procedure was repeated two more times with 90 mL of diethyl ether. The solvent phases were combined and then dried over anhydrous sodium sulfate. The extract was concentrated to 100 mL by distillation using a Vigreux column at 40 °C.

Separation of volatile compounds from the CP extract was achieved by using solvent-assisted flavor evaporation (SAFE). The SAFE system was employed to isolate the volatile components of a complex matrix as in the case of CP. This system was selected due to its higher yields of volatile components from fatty matrices and reduced thermal alteration of the flavor components of CP during the isolation (13). The system consisted of two liquid nitrogen-cooled traps (receiving and waste traps), a transfer head, and a 1 L round-bottom flask. The whole system was operated under high vacuum (approximately 10^{-5} Torr). The CP extract (100 mL) was fed through

Table 2. Potent Headspace Odorants of Thai Fried Chili Pastes Determined by Dynamic Headspace Dilution Analysis

| no. ^a | compound | RI ^b | | odor description ^c | FD factor ^d | | |
|------------------|--|-----------------|-----------------|-------------------------------|------------------------|--------|--------|
| | | FFAP | RTX5 | | UH-CP | H25-CP | H50-CP |
| 1 | methanethiol ^e | 696 | <500 | sulfurous, rotten | 5 | 5 | 25 |
| 2 | acetaldehyde ^e | 734 | <500 | pungent, yogurt | 25 | 1 | 1 |
| 3 | dimethyl sulfide ^e | 760 | <500 | fresh corn | 25 | 25 | 25 |
| 4 | 2-methylpropanal ^e | 779 | 549 | dark chocolate | 5 | 5 | 25 |
| 5 | 1-propanethiol ^e | 838 | 616 | meaty | 5 | 5 | 25 |
| 6 | allyl mercaptan ^e | 904 | 608 | meaty, bologna | 25 | 25 | 25 |
| 7/8 | 2/3-methylbutanal ^e | 918 | 645 | dark chocolate | 25 | 25 | 25 |
| 9 | allyl methyl sulfide ^e | 946 | 681 | meaty, fishy | 5 | 25 | 25 |
| 10 | 2,3-butanedione ^e | 990 | 593 | buttery | 25 | 25 | 25 |
| 11 | thiophene ^e | 996 | na ^g | garlic | nd ^h | 5 | 25 |
| 13 | ethyl 3-methylbutanoate ^e | 1061 | 851 | fruit, berry | 5 | 1 | 1 |
| 14 | dimethyl disulfide ^e | 1107 | 775 | sulfurous, rubbery | 1 | 1 | 1 |
| 15 | hexanal ^e | 1086 | 796 | green, cut grass | 5 | 5 | 5 |
| 16 | (Z)-3-hexenal ^e | 1148 | 794 | green, cut leaf | 5 | 5 | 1 |
| 17 | 3,3'-thiobis(1-propene) ^e | 1188 | 868 | sulfurous | 25 | 25 | 25 |
| 18 | 2,4-dimethylthiophene ^f | 1195 | 873 | sulfurous, rubbery | 25 | 5 | 5 |
| 19 | 2-methyl-3-furanthiol ^f | na | 875 | meaty | nd | 5 | 25 |
| 20 | (Z)-4-heptenal ^e | 1237 | 909 | crabby, fishy, fatty | 25 | 5 | 5 |
| 21 | methyl propyl disulfide ^e | 1240 | 920 | sulfurous, meaty | 25 | 25 | 25 |
| 22 | 3,4-dimethylthiophene ^f | 1258 | 880 | garlic, fishy | 1 | 5 | 25 |
| 23 | 1,3-dithiane ^e | 1277 | 931 | sulfurous, rubbery, salty | 5 | 5 | 25 |
| 24 | allyl methyl disulfide ^f | 1288 | 958 | pungent, fresh garlic | 25 | 25 | 25 |
| 25 | octanal ^e | 1290 | 1011 | orange oil | 1 | 5 | 25 |
| 26 | 1-octen-3-one ^e | 1296 | 976 | mushroom | 25 | 25 | 25 |
| 27 | 2-acetyl-1-pyrroline ^f | 1335 | 921 | popcorn | 5 | 25 | 25 |
| 29 | unknown | 1345 | na | roasted | 5 | 5 | 5 |
| 30 | dipropyl disulfide ^e | 1372 | 1138 | sulfurous, garlic | 5 | 5 | 5 |
| 31 | dimethyl trisulfide ^e | 1388 | 969 | sulfurous, garlic | 25 | 25 | 25 |
| 32 | (Z)-1,5-octadien-3-one ^e | 1402 | 986 | metallic | 25 | 25 | 25 |
| 34 | 2-isopropyl-3-methoxy-pyrazine ^e | 1429 | 1187 | green, earthy, soil | 5 | 5 | 1 |
| 35 | propyl hexanoate ^e | 1442 | na | floral, melon | nd | 5 | 5 |
| 36 | methional ^e | 1456 | 902 | potato | 25 | 25 | 25 |
| 37 | (E)-propenyl propyl disulfide ^f | 1450 | na | sulfurous, garlic | 25 | 25 | 25 |
| 39 | unknown | 1461 | na | garlic, green, oily, nutty | 25 | 5 | 1 |
| 41 | diallyl disulfide ^e | 1478 | 1080 | pungent, fresh garlic | 25 | 25 | 25 |
| 43 | (Z)-2-nonenal ^e | 1502 | 1159 | hay | 25 | 5 | 1 |
| 45 | (E)-2-nonenal ^e | 1513 | 1171 | stale, hay | 25 | 25 | 1 |
| 46 | 2-isobutyl-3-methoxy-pyrazine ^e | 1521 | 1174 | bell pepper | 25 | 25 | 1 |
| 47 | benzaldehyde ^e | 1533 | 941 | chili, nutty | nd | 25 | 25 |
| 48 | (Z)-3-nonenal ^e | 1540 | 1095 | melon, cucumber | 5 | 5 | 5 |
| 49 | (E,Z)-2,6-nonadienal ^e | 1586 | 1150 | cucumber | 25 | 5 | 5 |
| 50 | allyl methyl trisulfide ^f | 1592 | 1144 | eggy, meaty, garlic | 25 | 25 | 25 |
| 51 | unknown | 1606 | na | mushroom | nd | 1 | 1 |
| 53 | butanoic acid ^e | 1618 | na | cheesy | nd | 5 | 25 |
| 54 | (E)-2-decenal ^e | 1636 | 1260 | cilantro, fatty | nd | 5 | 1 |
| 55 | phenylacetaldehyde ^e | 1649 | 1046 | dried rose, plastic | 1 | 5 | 5 |
| 56 | 3-methylbutanoic acid ^e | 1655 | na | sweaty, dried fruit | 1 | 5 | 1 |
| 58 | unknown | 1671 | na | garlic, meaty | 25 | 25 | 25 |
| 60 | (E,E)-2,4-nonadienal ^e | 1706 | 1215 | fried, fatty | 5 | 5 | 5 |
| 61 | 3-vinyl-4 <i>H</i> -1,2-dithiin ^f | 1721 | 1193 | pungent, garlic | 25 | 25 | 25 |
| 62 | unknown | 1730 | 1330 | metallic | nd | 5 | 5 |
| 63 | 2-vinyl-1,3-dithiin ^f | 1742 | 1202 | pungent, garlic | 5 | 5 | 25 |
| 64 | (E,Z)-2,6-nonadien-1-ol ^e | 1755 | 1162 | green, cucumber | 1 | 5 | 25 |
| 65 | 2-acetyl-2-thiazoline ^e | 1761 | 1097 | popcorn | nd | nd | 1 |
| 66 | diallyl trisulfide ^f | 1805 | 1305 | pungent, garlic | 5 | 25 | 5 |
| 67 | (E,E)-2,4-decadienal ^e | 1820 | 1319 | fried, fatty | 1 | 1 | 5 |
| 68 | unknown | 1825 | na | brothy | 5 | 5 | 1 |
| 69 | β -damascenone ^e | 1859 | 1390 | apple sauce | 25 | 25 | 25 |
| 70 | 2-vinyl-4 <i>H</i> -1,3-dithiin ^f | 1847 | 1222 | pungent, garlic | 25 | 5 | 5 |
| 74 | phenol ^e | 1974 | na | medicinal, antiseptic | 1 | 5 | 5 |
| 75 | <i>trans</i> -4,5-epoxy-(E)-2-decenal ^f | 2006 | 1378 | metallic | 5 | 1 | 1 |
| 76 | 4-ethylguaiaicol ^f | 2027 | 1288 | smoky, seasoning | 1 | 1 | 1 |
| 80 | <i>o</i> -aminoacetophenone ^e | 2179 | 1351 | corn, tortilla | 1 | 1 | 1 |

^a Numbers correspond to those in Tables 3 and 4. ^b Retention indices (RI) were calculated from GCO results on a FFAP (Stabilwax-DA) or RTX5 (RTX-5MS) column.

^c Odor description at the sniffing port during GCO. ^d Flavor dilution factor was determined on a Stabilwax-DA column, except for compound 19; FD factor = highest purge time tested (25 min) divided by lowest purge time in which odorant was last detected by GCO (25, 5, or 1 min); UH-CP = unheated CP, H25-CP = CP heated at 100 °C for 25 min, and H50-CP = CP heated at 100 °C for 50 min. ^e Compound was positively identified (RI, odor, MS). ^f Compound was tentatively identified (RI, odor). ^g na = not available. ^h nd = no odor detected.

the upper part of the transfer head, and separation occurred when aliquots of the sample were dropped into the round-bottom flask partially submerged in a mild (50 °C) water bath. The extraction

time was approximately 2.5 h. The separated volatiles traveled through the outlet line of the separation head toward the receiving tube, where they were condensed and frozen due to the sudden

Table 3. Potent Odorants (\log_3 FD Factors ≥ 2) in Thai Fried Chili Pastes Determined by Aroma Extract Dilution Analysis

| no. ^a | compound | fraction ⁱ | RI ^b | | odor description ^c | \log_3 FD factors ^d | | |
|------------------|---|-----------------------|-----------------|-----------------|-------------------------------|----------------------------------|-----------------|--------|
| | | | WAX | RTX5 | | UH-CP | H25-CP | H50-CP |
| 7 | 2-methylbutanal ^e | NF | 915 | 650 | dark chocolate | <1 | 2 | 1 |
| 8 | 3-methylbutanal ^e | NF | 920 | 646 | dark chocolate | 1 | 3 | 3 |
| 10 | 2,3-butanedione ^e | AF | 982 | na ^g | buttery | 2 | 3 | 3 |
| 12 | ethyl 2-methylbutanoate ^e | NF | 1046 | na | floral, sweet | 2 | <1 | <1 |
| 14 | dimethyl disulfide ^e | NF | 1077 | 769 | rubbery, garlic | 2 | 3 | 3 |
| 15 | hexanal ^e | NF | 1086 | 796 | green, bug | 1 | 2 | 1 |
| 16 | (Z)-3-hexenal ^e | NF | 1149 | 801 | green, bug | 2 | <1 | <1 |
| 17 | 3,3'-thiobis(1-propene) ^e | NF | 1190 | 854 | garlic, rubbery | 1 | 2 | 1 |
| 20 | (Z)-4-heptenal ^e | NF | 1233 | 904 | fishy, marine | 4 | 3 | 2 |
| 21 | methyl propyl disulfide ^e | NF | 1251 | 914 | sulfurous, meaty | 4 | 4 | 2 |
| 22 | 3,4-dimethylthiophene ^f | NF | 1266 | 886 | garlic salt, rubbery | 5 | 4 | 4 |
| 23 | 1,3-dithiane ^e | NF | 1290 | 931 | garlic | 1 | <1 | 2 |
| 24 | allyl methyl disulfide ^f | NF | 1294 | 954 | pungent, fresh garlic | 5 | 6 | 4 |
| 26 | 1-octen-3-one ^e | NF | 1307 | 979 | mushroom | 5 | 4 | 2 |
| 27 | 2-acetyl-1-pyrroline ^f | BF | 1320 | 918 | popcorn | <1 | 1 | 2 |
| 28 | unknown | NF | 1326 | n.a. | garlic salt, fishy, meaty | 5 | nd ^h | nd |
| 30 | dipropyl disulfide ^e | NF | 1387 | 1135 | sulfurous, garlic | nd | 5 | 1 |
| 31 | dimethyl trisulfide ^e | NF | 1380 | 981 | sulfurous, garlic | 5 | 6 | 5 |
| 33 | 3-ethyl-2,5-dimethylpyrazine ^e | BF | 1428 | 1064 | green, potato, roasted | nd | 3 | <1 |
| 36 | methional ^e | NF | 1448 | 897 | potato | 4 | 5 | 6 |
| 38 | unknown | NF | 1455 | na | green, nutty | <1 | 3 | <1 |
| 40 | unknown | NF | 1462 | na | roasted, meaty, dried shrimp | 4 | 6 | 2 |
| 41 | diallyl disulfide ^e | NF | 1473 | 1080 | pungent, fresh garlic | 5 | 7 | 4 |
| 42 | 2,3-diethyl-5-methylpyrazine ^e | BF | 1473 | 1151 | roasted, potato | 2 | 3 | 1 |
| 44 | diethylmethylpyrazine isomer ^f | BF | 1504 | na | roasted | 2 | nd | nd |
| 45 | (E)-2-nonenal ^e | NF | 1549 | 1164 | floral, melon | 4 | nd | nd |
| 46 | 2-isobutyl-3-methoxypyrazine ^e | NF | 1536 | 1177 | chili | 3 | 4 | 1 |
| 47 | benzaldehyde ^e | NF | 1537 | 953 | chili, roasted | 1 | 5 | 2 |
| 49 | (E,Z)-2,6-nonadienal ^e | NF | 1596 | 1154 | green, cucumber | 4 | 4 | 1 |
| 50 | allyl methyl trisulfide ^f | NF | 1606 | 1169 | eggy, meaty, garlic | 6 | 9 | 6 |
| 52 | unknown | NF | 1614 | na | potato, mushroom | 2 | 3 | 1 |
| 53 | butanoic acid ^e | AF | 1628 | na | cheesy | 3 | 4 | 3 |
| 55 | phenylacetaldehyde ^e | NF | 1655 | 1043 | rosy | 3 | 3 | 2 |
| 56 | 3-methylbutanoic acid ^e | AF | 1673 | na | sweaty, dried fruit | 4 | 5 | 4 |
| 57 | unknown | NF | 1666 | na | melon, floral | 2 | 4 | <1 |
| 59 | dipropyl trisulfide ^f | NF | 1683 | 1356 | meaty, garlic | 6 | 6 | 4 |
| 60 | (E,E)-2,4-nonadienal ^e | NF | 1711 | 1335 | nutty | nd | 1 | <1 |
| 61 | 2-vinyl-4H-1,2-dithiin ^f | NF | 1756 | 1194 | pungent, garlic | 8 | 8 | 2 |
| 63 | 2-vinyl-1,3-dithiane ^f | NF | 1769 | 1202 | garlic | 1 | 5 | 2 |
| 66 | diallyl trisulfide ^f | NF | 1811 | 1301 | pungent, garlic | 6 | 11 | 4 |
| 67 | (E,E)-2,4-decadienal ^e | NF | 1817 | 1335 | nutty, oily | 1 | 3 | <1 |
| 69 | β -damascenone ^e | NF | 1843 | 1374 | apple sauce | 2 | 3 | 1 |
| 70 | 2-vinyl-4H-1,3-dithiin ^f | NF | 1858 | 1236 | pungent, garlic | 9 | 12 | 9 |
| 71 | hexanoic acid ^e | AF | 1862 | na | sweaty | 2 | 2 | 2 |
| 72 | unknown | AF | 1879 | na | brothy, spicy | nd | nd | 2 |
| 73 | unknown | AF | 1914 | na | spicy | nd | 2 | nd |
| 74 | phenol ^e | NF | 2001 | na | inky, metallic | 5 | <1 | <1 |
| 75 | trans-4,5-epoxy-(E)-2-decenal ^f | NF | 2019 | 1381 | metallic | 3 | 2 | 1 |
| 76 | 4-ethylguaiaicol ^f | NF | 2043 | 1288 | smoky, seasoning | 4 | 3 | 2 |
| 77 | 4-hydroxy-2,5-dimethyl-3-(2H)-furanone (HDMF) ^e | AF | 2028 | na | caramel, burnt sugar | 2 | 4 | 5 |
| 78 | p-cresol (4-methylphenol) ^e | NF | 2074 | na | phenolic, dung, stable | 1 | 2 | 1 |
| 79 | unknown | BF | 2105 | 1342 | minty | 1 | 2 | 1 |
| 80 | o-aminoacetophenone ^e | BF | 2236 | 1299 | corn tortilla | 1 | 3 | 2 |
| 81 | 3-hydroxy-4,5-dimethyl-2-(5H)-furanone (sotolon) ^e | AF | 2211 | na | curry, spicy | 3 | 4 | 3 |
| 82 | phenylacetic acid ^e | AF | 2554 | na | rosy | 3 | 3 | 3 |
| 83 | 4-hydroxy-3-methoxybenzoic acid (vanillin) ^e | AF | 2561 | na | vanilla | 3 | 4 | 3 |

^a Numbers correspond to those in **Tables 2** and **4**. ^b Footnote same as **Table 2**. ^c Footnote same as **Table 2**. ^d Footnote same as **Table 2**. ^e Footnote same as **Table 2**. ^f Footnote same as **Table 2**. ^g Footnote same as **Table 2**. ^h Footnote same as **Table 2**. ⁱ Fraction containing odorant.

change of temperature. The tube was then removed and thawed to proceed with the fractionation of the CP extract.

To separate the acidic, basic, and neutral fractions from the extract, the SAFE extract was first concentrated to 30 mL by distillation using a Vigreux column at 40 °C and then placed in a 125 mL separatory funnel. The extract was washed with aqueous NaOH (1 mol/L, 3 × 30 mL), and the organic layer containing the neutral and basic volatiles was collected. The aqueous layer was washed with diethyl ether (2 × 30 mL) and then acidified to pH 2 with 10% (w/v) aqueous HCl and saturated with NaCl. It was then extracted with diethyl ether (3 × 20 mL). The ether layer containing the acidic volatiles was washed with saturated NaCl (2 × 30 mL).

The organic layer containing neutral and basic volatiles was washed with saturated NaCl (2 × 30 mL) and then extracted with aqueous HCl (1 mol/L, 3 × 30 mL). The organic layer containing the neutral volatiles was collected and was washed with saturated NaCl (2 × 30 mL). The aqueous layer containing basic volatiles was washed with diethyl ether (2 × 30 mL) and then adjusted to pH 9 with 10% NaOH solution and saturated with NaCl. The mixture was then extracted with diethyl ether (3 × 20 mL). The ether extract was washed with saturated NaCl (2 × 30 mL), and the ether layer containing the basic volatiles was collected.

Each fraction from above was concentrated under a gentle stream of nitrogen gas to 10 mL, dried over anhydrous Na₂SO₄, and further

Table 4. Concentrations and Odor Activity Values of the Selected^a Potent Odorants in Thai Fried Chili Pastes

| no. ^b | compound | concn ± SD (ng/g) ^c | | | odor threshold (ng/mL) ^d | odor activity value (OAV) ^e | | |
|------------------|---|--------------------------------|--------------|--------------|---------------------------------------|--|---------------|---------------|
| | | UH-CP | H25-CP | H50-CP | | UH-CP | H25-CP | H50-CP |
| 1 | methanethiol ^{g,h} | 212 ± 13a | 792 ± 100b | 908 ± 35b | 0.02 ⁱ (0.06) ^k | 10600 (3533) | 39600 (13200) | 45400 (15133) |
| 3 | dimethyl sulfide ^{f,h} | 63 ± 7a | 408 ± 81b | 507 ± 60b | 0.3 ⁱ (1.2) ^k | 210 (53) | 1360 (340) | 1690 (423) |
| 4 | 2-methylpropanal ^{g,h} | 397 ± 40a | 1019 ± 68b | 1327 ± 165b | 0.1 ⁱ (3.4) ^k | 3970 (117) | 10190 (300) | 13270 (390) |
| 6 | allyl mercaptan ^{f,h} | 141 ± 5a | 242 ± 11a | 477 ± 72b | 0.005 ⁱ | 28200 | 48400 | 95400 |
| 8 | 3-methylbutanal ^{f,h} | 139 ± 14a | 2052 ± 196b | 3144 ± 154c | 0.2 ⁱ (13) ^k | 695 (11) | 10260 (158) | 15720 (242) |
| 9 | allyl methyl sulfide ^{f,h} | 77 ± 12a | 401 ± 50b | 706 ± 132c | na ^m | | | |
| 10 | 2,3-butanedione ^{f,h} | 94 ± 6a | 114 ± 7ab | 172 ± 32b | 2.3 ⁱ (10) ^k | 41 (9) | 50 (11) | 75 (17) |
| 14 | dimethyl disulfide ^{f,i} | 8 ± 0.05a | 27 ± 0.1c | 26 ± 0.2b | 0.16 ⁱ | 50 | 169 | 163 |
| 17 | 3,3'-thiobis(1-propene) ^{f,h} | 105 ± 13a | 390 ± 25b | 555 ± 53c | 32.5 ⁱ | 3 | 12 | 17 |
| 21 | methyl propyl disulfide ^{f,h} | 50 ± 3a | 100 ± 1b | 148 ± 19c | na | | | |
| 22 | 3,4-dimethylthiophene ^{g,h} | 78 ± 2a | 155 ± 2b | 298 ± 37c | na | | | |
| 23 | 1,3-dithiane ^{f,h} | 894 ± 431a | 1736 ± 83b | 2006 ± 98b | na | | | |
| 24 | allyl methyl disulfide ^{g,h} | 2759 ± 78a | 6552 ± 189b | 8182 ± 201c | na | | | |
| 30 | dipropyl disulfide ^{f,i} | 1.75 ± 0.03a | 2.17 ± 1.41a | 1.77 ± 0.05a | na | | | |
| 31 | dimethyl trisulfide ^{f,h} | 1555 ± 35a | 4644 ± 49c | 4450 ± 6b | 0.005 ⁱ (2.5) ^k | 311000 (622) | 928800 (1858) | 890000 (1780) |
| 33 | 3-ethyl-2,5-dimethylpyrazine ^{f,i} | 0.4 ± 0.02a | 0.9 ± 0.2b | 0.5 ± 0.01a | 0.4 ⁱ (24) ^j | 1 (0.02) | 2 (0.04) | 1 (0.02) |
| 36 | methional ^{f,i} | 0.2 ± 0.00a | 1.06 ± 0.1b | 1.22 ± 0.2b | 0.2 ⁱ (0.2) ^j | 1 (1) | 5 (5) | 6 (6) |
| 41 | diallyl disulfide ^{f,h} | 4205 ± 64a | 8202 ± 192b | 8000 ± 408b | 4.3 ⁱ | 978 | 1907 | 1860 |
| 47 | benzaldehyde ^{f,h} | 27 ± 6a | 47 ± 12a | 45 ± 6a | 350 ^j | 0.08 | 0.13 | 0.13 |
| 50 | allyl methyl trisulfide ^{g,h} | 1706 ± 18a | 1835 ± 129a | 1604 ± 126a | na | | | |
| 53 | butanoic acid ^{f,i} | 42 ± 1a | 157 ± 15b | 64 ± 0.1a | 240 ^j (135) ^k | 0.18 (0.31) | 0.65 (1.16) | 0.27 (0.47) |
| 55 | phenylacetaldehyde ^{f,i} | 11 ± 0.01b | 11 ± 1b | 2 ± 0.02a | 4 ^j | 3 | 3 | 0.5 |
| 56 | 3-methylbutanoic acid ^{f,i} | 98 ± 1a | 196 ± 7c | 117 ± 0.2b | 120 ^j (22) ^k | 0.8 (4) | 2 (9) | 1 (5) |
| 59 | dipropyl trisulfide ^{g,i} | 0.3 ± 0.00ab | 0.35 ± 0.00b | 0.27 ± 0.04a | na | | | |
| 61 | 3-vinyl-4 <i>H</i> -1,2-dithiin ^{g,h} | 1108 ± 30a | 1319 ± 12b | 1461 ± 51c | na | | | |
| 63 | 2-vinyl-1,3-dithiane ^{g,i} | 3 ± 0.01a | 11 ± 0.1b | 3 ± 0.03a | na | | | |
| 66 | diallyl trisulfide ^{g,h} | 343 ± 2a | 959 ± 9c | 887 ± 23b | na | | | |
| 70 | 2-vinyl-4 <i>H</i> -1,3-dithiin ^{g,h} | 259 ± 3b | 226 ± 10a | 223 ± 4a | na | | | |
| 74 | phenol ^{f,i} | 22 ± 0.04b | 1 ± 0.1a | 2 ± 0.02a | 5500 ^j | 0.05 | 0.04 | 0.04 |
| 77 | 4-hydroxy-2,5-dimethyl-3-(2 <i>H</i>)-furanone (HDMF) ^{f,i} | 0.4 ± 0.01a | 2.1 ± 0.5b | 2.8 ± 0.15b | 0.03 ⁱ (25) ^k | 13 (0.02) | 70 (0.08) | 93 (0.11) |
| 82 | phenylacetic acid ^{f,i} | 11 ± 0.2a | 14 ± 2a | 11 ± 2a | 1000 ^j | 0.01 | 0.01 | 0.01 |

^a Compounds having high FD factors and detectable by GC-MS were chosen for quantitative analysis. ^b Numbers correspond to those in **Tables 2 and 3**. ^c Average concentration ± standard deviation ($n = 2$). Means in a row followed by different letters are significantly different ($P < 0.05$). ^d Odor detection threshold in water. Numbers in parentheses are odor detection thresholds in sunflower oil. ^e Odor activity value (OAV) was calculated by dividing compound concentration by its published odor detection threshold in water or in sunflower oil. ^f Concentration of compound is based on calibration against authentic reference standard (see text). ^g Semiquantitative concentration = concentration of internal standard × peak area of compound/peak area of the internal standard (see text). ^h Concentration determined by dynamic headspace analysis/GC-MS. ⁱ Concentration determined by direct solvent extraction—solvent-assisted flavor evaporation/GC-MS. ^j Odor threshold reported by Leffingwell (29). ^k Odor threshold reported by van Gemert (45). ^l Odor threshold reported by Burdock (46). ^m na = not available.

concentrated to 100 μ L under a nitrogen gas stream. Samples were prepared in duplicate and kept at -70 °C until analysis.

Aroma Extract Dilution Analysis (AEDA). Each aroma extract fraction was diluted sequentially with diethyl ether in a ratio of 1:3 according to the aroma extract dilution analysis technique (14). Each dilution was kept in a 200 μ L glass insert put inside a 1 mL amber vial equipped with a PTFE-lined screw cap and kept at -70 °C until analyzed.

The GCO system consisted of a 6890 GC (Agilent Technologies Inc.) equipped with a FID, an on-column injector, and an olfactory detection port (DATU Technology Transfer, Geneva, NY). Each aroma extract was injected by cool on-column mode ($+3$ °C temperature tracking mode) into a polar capillary column (Stabilwax, 15 m \times 0.32 mm i.d.; 0.5 μ m film; Restek) or a nonpolar column (RTX-5MS, 15 m \times 0.32 mm i.d.; 0.5 μ m film; Restek). Column effluent was split 1:1 between the FID and olfactory detection port using deactivated fused silica tubing (1 m \times 0.25 mm i.d.; Restek), with both detector temperatures held at 250 °C. The GC oven temperature was programmed from 35 to 225 °C at a rate of 8 °C/min with initial and final hold times of 5 and 15 min, respectively. Helium was used as a carrier gas at a constant flow rate of 2.2 mL/min. Other conditions of GCO have been previously described (15).

Dynamic Headspace Analysis/Gas Chromatography–Mass Spectrometry (DHA/GC-MS). The system used for DHA/GC-MS consisted of a thermal desorption system (TDS2; Gerstel), a CIS4 inlet (Gerstel), and a 6890 GC/5973N mass selective detector (MSD; Agilent Technologies Inc.). The conditions for thermal desorption and injection were the same as previously described for DHDA.

Separations were performed using either a polar capillary column (Stabilwax-DA, 30 m \times 0.25 mm i.d.; 0.5 μ m film; Restek) or a nonpolar column (RTX-5MS, 30 m \times 0.25 mm i.d.; 0.5 μ m film; Restek). The oven temperature was programmed from 35 to 225 °C at a rate of 6 °C/min with initial and final hold times of 5 and 10 min, respectively. Helium was used as carrier gas at a constant rate of 1.0 mL/min. The MSD conditions were as follows: capillary direct interface temperature, 280 °C; ionization energy, 70 eV; mass range, 35–300 amu; electron multiplier voltage, Autotune + 200 V; scan rate, 5.27 scans/s.

Gas Chromatography–Mass Spectrometry. GC-MS of the organic fractions obtained by SAFE were injected using a cool on-column method ($+3$ °C temperature tracking mode) into a 6890 GC/5973N MSD (Agilent Technologies Inc.). Separations were performed using the columns described above for DHA/GC-MS. The oven was programmed from 35 to 225 °C at a rate of 4 °C/min with initial and final hold times of 5 and 20 min, respectively. Helium was used as carrier gas at a constant rate of 1.0 mL/min. The mass selective detector conditions were the same as described for DHA/GC-MS analysis.

Identification of Odorants. For positive identification, retention indices, mass spectra, and odor properties of unknowns were compared with those of authentic standard compounds analyzed under identical conditions. Tentative identifications were based on comparing mass spectra of unknown compounds with those in the National Institute of Standards and Technology (NIST, 2005) mass spectral database or by matching the retention indices values and odor properties of unknowns against those of authentic standards. For linear retention indices (LRI)

calculation, a homologous series of *n*-alkanes (C6–C30 and C6–C22 for polar and nonpolar columns, respectively) were analyzed under the same chromatographic conditions. The linear retention indices (LRI) or retention index (RI) was calculated using a published procedure (16).

Quantification of Selected Compounds. An aqueous mimic matrix for standard solutions was composed of 21.67% (w/w) sucrose, 0.96% (w/w) fructose, 0.95% (w/w) glucose (these were the main sugar contents in coconut sugar (17)), 19.51% (w/w) fresh soybean oil, and 0.33% (w/w) NaCl in odorless water with pH adjusted to 5.96 using 10% aqueous HCl. The stock solution for quantification contained 813 μg of **3**, 972 μg of **6**, 177 μg of **7**, 247 μg of **8**, 372 μg of **9**, 408 μg of **10**, 550 μg of **14**, 461 μg of **17**, 521 μg of **21**, 868 μg of **23**, 472 μg of **30**, 550 μg of **31**, 509 μg of **33**, 735 μg of **36**, 1265 μg of **41**, 368 μg of **47**, 545 μg of **53**, 401 μg of **55**, 481 μg of **56**, 982 μg of **74**, 1334 μg of **77**, and 443 μg of **82** per mL in methanol. Preparation of standard solutions was accomplished by addition of 0 (blank), 1, 25, 50, 100, and 500 μL of stock solution to the matrix (20 g). Each mixture was also spiked with 20 μL of internal standard solution. Sample preparation and GC-MS analysis were performed in the same way as described above for the CP samples. Each standard concentration was measured in duplicate. Concentrations of positively identified compounds were determined using MS response factors and total ion areas for each compound relative to the internal standard, calculated as follows:

$$\text{concn}_i = \text{concn}_{\text{is}} \left(\frac{\text{peak area}(i)}{\text{peak area}(\text{is})} \right) f_i$$

where concn_i and peak area (*i*) are the concentration and total ion peak area, respectively, for compound *i*; concn_{is} and peak area (is) are the concentration and total ion peak area, respectively, of the internal standard; and f_i is the MS response factor of compound *i* calculated using a five-point standard curve. Semiquantitative analysis of compounds **1**, **4**, **22**, **24**, **50**, **59**, **61**, **63**, **66**, and **70** in **Table 4** was conducted by using 2-methyl-3-heptanone as the internal standard without considering calibration factors; that is, $f_i = 1.00$.

Statistical Analysis. Quantitative data were evaluated by the analysis of variance with means separation by least significant difference (LSD) method (SAS, version 9.1, Cary, NC).

RESULTS AND DISCUSSION

Two complementary techniques were applied for the comprehensive gas chromatography–olfactometry (GCO) analysis of the aroma components of the Thai fried chili pastes. Dynamic headspace dilution analysis (DHDA) is a suitable technique for the analysis of odorants of high and intermediate volatility. On the other hand, aroma extract dilution analysis (AEDA) is generally restricted to the analysis of intermediate and semi-volatile odorants, since the highly volatile compounds may be lost during extraction, distillation, and sample workup procedures. In the present study, a total of 63 and 56 odorants were detected by DHDA (**Table 2**) and AEDA (**Table 3**), respectively. Thirty-six common odorants were detected by the two methods. Twenty-seven odorants (**1–6**, **9**, **11**, **13**, **18**, **19**, **25**, **29**, **32**, **34**, **35**, **37**, **39**, **43**, **48**, **51**, **54**, **58**, **62**, **64**, **65**, and **68**) were detected by DHDA only. Meanwhile, AEDA revealed an additional 19 odorants (**12**, **28**, **33**, **38**, **40**, **42**, **44**, **52**, **57**, **59**, **71–73**, **77–79**, and **81–83**) that were not detected by DHDA.

DHDA. In UH-CP, 26 odorants were detected with FD factors of 25, including 13 sulfur-containing compounds (**Table 2**). Many of the sulfur compounds are decomposition products of thiosulfates and are derived from amino acid flavor precursors such as *S*-allyl-L-cysteine sulfoxide (alliin) of the *Allium* family including garlic and shallot (3, 18). Alliin is the most predominant amino acid flavor precursor of garlic (18). The enzyme alliinase hydrolyzed alliin to pyruvate, ammonia, and thiosul-

finite, particularly allicin, after tissue disruptions (18). Allicin is highly unstable and can decompose or rearrange to form secondary products. A variety of sulfides are known to contribute to the characteristic flavor and taste of garlic (18, 19).

The major garlic-derived odorants in the unheated product (UH-CP) were identified as dimethyl sulfide (**3**), allyl methyl disulfide (**24**), dimethyl trisulfide (**31**), diallyl disulfide (**41**), allyl methyl trisulfide (**50**), 3-vinyl-4*H*-1,2-dithiin (**61**), and 2-vinyl-4*H*-1,3-dithiin (**70**). In particular, allyl mercaptan (**6**), which can be generated from alliin through a hydrolysis process or free radical rearrangement (20), imparted a characteristic meaty, garlicky, and bologna-like aroma. This compound was reported as a character-impact odorant in bulgogi (21). Another potent sulfur-containing compound, methyl propyl disulfide (**21**) was reported as a character-impact component of onion (22). The propyl group has been reported as the major allyl group in shallot volatiles (22, 23). (*E*)-Propenyl propyl disulfide (**37**) was the major volatile compound identified in the distilled oil from shallot, and 2,4-dimethylthiophene (**18**) was reported to be the typical constituent of fried shallot (24, 25).

The sulfur-containing compounds with the highest FD factors of 25 in all CP samples were dimethyl sulfide (**3**), allyl mercaptan (**6**), 3,3'-thiobis(1-propene) (**17**), methyl propyl disulfide (**21**), allyl methyl disulfide (**24**), dimethyl trisulfide (**31**), methional (**36**), (*E*)-propenyl propyl disulfide (**37**), diallyl disulfide (**41**), allyl methyl trisulfide (**50**), and 3-vinyl-4*H*-1,2-dithiin (**61**). Among these, dimethyl trisulfide was the most potent aroma-active compound with the highest odor activity value (OAV), followed by allyl mercaptan, diallyl disulfide, and dimethyl sulfide (**Table 4**). These compounds have extremely high OAVs due to their relatively high concentrations and very low detection threshold values. Moreover, allyl methyl disulfide, allyl methyl trisulfide, and 3-vinyl-4*H*-1,2-dithiin had the highest FD factors of 25 in all treatments, which was consistent with their high relative abundance values (**Table 4**), but their OAVs could not be calculated because odor detection threshold values for these compounds are unavailable.

Other predominant aroma compounds with high FD factors of 25 in all CP samples were 2- (3-) methylbutanal (**7/8**, detected as a coeluted peak), 2,3-butanedione (**10**), 1-octen-3-one (**26**), (*Z*)-1,5-octadien-3-one (**32**), and β -damascenone (**69**). 2- and 3-Methylbutanal are Strecker aldehydes derived from isoleucine and leucine, respectively (26). 2,3-Butanedione is a characteristic component of cooked foods and can be thermally generated through the Maillard reaction (27). Although the FD factors of 2- (3-) methylbutanal and 2,3-butanedione in the three CP samples were not different, the concentration of these compounds increased significantly with increasing heating time ($P < 0.05$) and showed the highest concentration in H50-CP (**Table 4**). Therefore, these odorants seemed to be at least partially responsible for the thermally induced changes in CP flavor. 1-Octen-3-one and (*Z*)-1,5-octadien-3-one were reported to contribute to the aroma of fresh crustaceans, and these compounds can be formed by lipid degradation of arachidonic acid and linolenate, respectively (28). β -Damascenone has a very low odor threshold in water (2 $\mu\text{g}/\text{g}$) (29). This compound is believed to be a product of the oxidative degradation of the carotenoid neoxanthin (30) and can be formed by the hydrolysis of glycosides in some natural products such as grapes (31).

The heating of CP lead to the generation of thermally derived aroma compounds such as methanethiol (**1**), 2-methylpropanal (**4**), 1-propanethiol (**5**), thiophene (**11**), 2-methyl-3-furanthiol (**19**), 3,4-dimethylthiophene (**22**), octanal (**25**), benzaldehyde (**47**), butanoic acid (**53**), and (*E,Z*)-2,6-nonadien-1-ol (**64**). The

FD factors of these compounds increased as a result of heating, and they had the highest FD factors in H50-CP. Among these odorants, methanethiol (bp = 6 °C) was detected by DHDA only. A semiquantitative estimate of this compound concentration was made due to difficulties in accurately preparing the reference standard. Methanethiol and 2-methylpropanal had low odor thresholds and relatively high concentrations in three CPs; thus they also may contribute to the overall aroma of the CPs. It was reported that Strecker degradation of valine can lead to the formation of 2-methylpropanal (26). 2-Methylpropanal has been identified as a character-impact odorant in fish sauce (6). 2-Methyl-3-furanthiol was detected only on the nonpolar RTX-5MS column by DHDA and was not detected by AEDA of the solvent extracts. 2-Methyl-3-furanthiol has been identified as an important odorant in a beef-like process flavor (32) and can be perceived at a very low concentration due to its very low odor detection threshold ($t = 0.005\text{--}0.01$ ppb in water (33)). The compounds (*E*)-2-decenal (54), 3-methylbutanoic acid (56), and diallyl trisulfide (66) were detected at higher FD factors in H25-CP than in UH-CP or H50-CP. It was reported that 3-methylbutanoic acid is produced from leucine catabolism via transamination, followed by oxidation steps (34).

AEDA. The results of AEDA for the neutral, basic, and acidic fractions for all CPs are summarized in **Table 3**, and concentration results for selected odorants are presented in **Table 4**. Twelve, 14, and 5 potent odorants with \log_3 FD factors between 5 and 12 were detected in UH-CP, H25-CP, and H50-CP, respectively. Among these, allyl methyl disulfide (24), dimethyl trisulfide (31), methional (36), diallyl disulfide (41), allyl methyl trisulfide (50), dipropyl trisulfide (59), 3-vinyl-4*H*-1,2-dithiin (61), diallyl trisulfide (66), and 2-vinyl-4*H*-1,3-dithiin (70) were the predominant odorants having high \log_3 FD factors in all CPs. On the basis of the results of AEDA, 2-vinyl-4*H*-1,3-dithiin (70) was the most potent odorant with the highest \log_3 FD factors of 9, 12, and 9 in UH-CP, H25-CP, and H50-CP, respectively.

The FD factors and the concentrations of the thermally generated aroma compounds (8, 10, 27, 36, and 77) increased as a result of heating. It is hypothesized that excessive heating of CP (e.g., H50-CP) would cause the formation of more intense potato and caramelized notes as a result of increases in methional (36) and 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone (HDMF; 77). HDMF can be generated from hexoses (for example, glucose or fructose) during the Maillard reaction (35, 36). Methional has been associated with the Strecker degradation of methionine (37). The OAVs and FD factors were consistent for methional and HDMF. On the basis of its high OAV, HDMF was regarded as the predominant thermally induced aroma compound of CP.

The FD factors of sulfur-containing compounds (21, 24, 30, 31, 41, 50, 59, 61, 63, 66, and 70) in the neutral fraction were highest in the CP produced by intermediate heating treatment (H25-CP); then these compounds decreased as a result of excessive heating (i.e., H50-CP). 3-Vinyl-4*H*-1,2-dithiin (61) and 2-vinyl-4*H*-1,3-dithiin (70) were postulated to be thermal degradation products of allicin (19). Due to their high FD factors (\log_3 FD factors ≥ 7) and aroma properties, 2-vinyl-4*H*-1,3-dithiin (70), diallyl trisulfide (66), allyl methyl trisulfide (50), 3-vinyl-4*H*-1,2-dithiin (61), and diallyl disulfide (41) are considered predominant odorants of H25-CP. These compounds are responsible for garlic, sulfurous, pungent, and meaty notes. They have been reported to be the major volatile compounds in thermally treated garlic products (38–40) and may be formed by decomposition and rearrangement of allicin at high temperature (38). Compounds 41, 50, and 66 exhibited the highest

concentration in H25-CP. Moreover, it has been reported that methyl propyl disulfide (21), dipropyl disulfide (30), and dipropyl trisulfide (59) were the character-impact flavor compounds in onion and shallot products (3, 41). Although dimethyl disulfide had a \log_3 FD factor of only 3 in H25-CP, this compound may also contribute to the flavor of CP due to its high OAV.

The FD factors of benzaldehyde (47), (*E,E*)-2,4-decadienal (67), and β -damascenone (69) increased as a result of heating, leading to higher chili/nutty, fatty/fried, and apple sauce notes, respectively, in H25-CP. The FD factors of these compounds decreased due to decomposition caused by excessive heating (i.e., H50-CP). (*E,E*)-2,4-Decadienal has been reported as an oxidation product of linoleic acid and plays an important role in the flavor of deep-fried food (42). (*E,E*)-2,4-Decadienal and β -damascenone, which have extremely low odor detection threshold values of 0.07 and 0.002 in water, respectively (29), were not detected by GC-MS and were, therefore, only tentatively identified using the GCO data.

3-Ethyl-2,5-dimethylpyrazine (33) and 2,3-diethyl-5-methylpyrazine (42) were predominant odorants in the basic fraction of H25-CP. These compounds have characteristic potato and roasted odors. It has been reported that these pyrazines are typical Maillard reaction products formed by interaction of carbonyl (reducing) compounds and amino-containing compounds (43). In particular, 3-ethyl-2,5-dimethylpyrazine was present in the three treatments at concentrations higher than its odor detection threshold value. Because of its high FD factor in the basic fraction, *o*-aminoacetophenone (80) was regarded as a potentially important aroma component of H25-CP. This compound was previously identified as a predominant odorant in tortilla-type corn products, and it may be generated from alkali degradation of tryptophan (44).

With the exception of HDMF, the FD factors of the acidic odorants differed only slightly among the three CPs. Sotolon (81), phenylacetic acid (82), and vanillin (83) had relatively high \log_3 FD factors of 3–4 in all three CPs. Butanoic (53) and 3-methylbutanoic acids (56) were detected at higher \log_3 FD factors in H25-CP, and this finding is consistent with the quantitative data (**Table 4**). 3-Methylbutanoic acid has been previously reported as a major volatile component of bell pepper (4).

The combined results of DHDA and AEDA demonstrate the importance of sulfur-containing odorants in the overall flavor of heated and unheated CP. Especially important are the odorants that originate from garlic and shallot. Thermally derived volatiles, such as those formed by Maillard and Strecker degradation reactions or by further breakdown of sulfur-containing compounds, are also predominant odorants of heated CPs. It is suggested that additional research be conducted to relate the aroma composition of CP to its sensory flavor attributes and consumer acceptability.

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