Contribution of roasted grains and seeds in aroma of oleang
(Thai coffee drink)

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Abstract: Oleang, a Thai coffee drink, contained roasted robusta coffee and several roasted grains and seeds. In this research the typical ingredients of oleang that were robusta coffee, corn, soybean, rice, sesame and brown sugar, were roasted and studied for their volatile compounds. Coffee, corn, sesame, and brown sugar were roasted at 220°C for 20 min and soybean and rice were roasted at 240°C for 20 min. Major aroma compounds from roasted corn were 2-furfurylthiol, furfural, 2-methoxyphenol, hexanal, and alkylpyrazines. Soybean contributed mostly pyrazines and phenols similar to those of coffee. The roasted rice had strong sulfurous and burnt characteristics but was low in concentrations of the volatile compounds. The roasted sesame was most abundant in the numbers of aroma compounds provided dimethyl trisulfide, dimethyl disulfide, 2-furfurylthiol, 3-ethyl-2,5-dimethylpyrazine, and 2-methoxyphenol to oleang. Sixteen oleang formulations were evaluated for their sensory preference. The samples were composed of 5% brown sugar, coffee (50, 60, 70, and 80%) with various corn: soybean: rice: sesame ratios (2:3:0:0, 3:2:0:0, 3:1:1:0, and 3:1:0:1). The most preferred formulation for oleang was 50% coffee, 5% brown sugar, and 45% grain mixture that had the corn: soybean: rice: sesame ratio of 3:1:1:0.

Keywords: Oleang, Thai coffee, aroma compounds, roasted corn, roasted soybean

Introduction

Thai coffee drink known as “oleang” is popular in Thai restaurants around the world. Oleang is prepared from the mixture of robusta coffee, brown sugar, and various grains and seeds, generally corn, soybean, rice and sesame. There is no specific formulation or document written about the ingredients of oleang. The amounts of coffee in the formulations printed on the product labels can be varied from 20 to 80%. The grain and seed compositions are varied from manufacturers to manufacturers with corn and soybean are the two major components.

Oleang has the unique aroma, a combination of a coffee aroma and the special roast and smoky notes from high roasted grains and seeds. Consumers who try to prepare Thai coffee drink from high roasted robusta coffee alone usually fail to imitate the unique roasted aroma of oleang. During the production, all grains and seeds are roasted in the extreme conditions until the color of the seeds change to dark brown. Literatures on the aroma compounds of grains and seeds roasted under the extreme conditions are limited.

In contrast, the aroma compounds in coffee have been extensively studied and reviewed (Flament, 2002; Buffo and Cardelli-Freire, 2004). The volatile compounds of coffee are very complex containing more than 700 components, of which about 20 compounds are aroma impact compounds. In Arabica coffee the most prominent aroma compounds are 2-furfurylthiol, 4-vinylguaiacol, alkylpyrazines, furanone, acetaldehyde, propanal, methyl propanal, and 2-, and 3-methylbutanal (Czerny et al., 1999).

In the moderate roasted corn, potent aroma compounds are 2-acetyl-1-pyrroline, 2,4-decadienal, 2-furfurylthiol, 4-vinyl-2-methoxyphenol (Schieberle, 1991), 2-propionyl-1-pyrroline, dimethyl disulfide (Buttery et al., 1997), 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, acetylpyrazine, phenol, guaiacol, and 5-methyl-2-phenol-2-hexanal (Manley et al., 1974). Roasting of soybean increased 2-methylpyrazine, 2,5-, 2,6-, 2,3-dimethylpyrazines, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine, and tetramethylpyrazine concentrations (Jung et al., 1997).

Key odorants in the roasted rice are pyrazines and carbonyl compounds, i.e., 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 2,4-ethyl-3-methylpyrazine, acetaldehyde, propionaldehyde, iso-butyraldehyde and isovaleraldehyde (Cheigh et al., 1975).

Roasting of sesame generated sulfur volatiles such as 2-furfurylthiol, 2-phenylethylthiol, 4,5-dimethylisothiazole, 4,5-dimethylthiazole, 2-propyl-4-methylthiazole, and 2-butyl-5-methylthiazole (Schieberle, 1996; Shimoda et al., 1997). Roasted sesame is also rich in pyrazines, i.e., 2-ethyl-3,5-dimethylpyrazine, acetylpyrazine, alkylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethyl-
6-methylpyrazine, 2-ethyl-5-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine (Schieberle, 1996; Ryu et al., 1999). The other important compounds are 2-methoxyphenol, 4-vinyl-2-methoxyphenol, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, 2-pentylypridine, 2,4-decadienal, 2-acetyl-1-pyrrrole, and pyrrole-2-carboxaldehyde. Again, previous investigations were done on moderately roasted samples.

The objectives of this work were to investigate the aroma components in the extremely roasted grains and seeds used in oleang production as well as to study the preferred formulations of oleang to be used as a guideline for a future production.

Materials and Methods

Raw materials and chemicals
Robusta coffee from southern Thailand was obtained from Quality Coffee Products (Thailand), Ltd. Corn, soybean, and sesame were obtained from the Department of Agriculture, Ministry of Agriculture and Cooperative. Jasmine rice (Khao Dawk Mali 105) was purchased from a local supermarket in Bangkok. Corn, sesame, and brown sugar, 500 g each, were roasted separately in an oven at 220°C for 20 min. Soybean and rice, 500 g each, were roasted at 240°C for 20 min. The roasted samples were packed and vacuum sealed in the laminated aluminium foil bags and stored at -40°C for further analyses.

Analytical-grade solvents were purchased from J.T. Baker (Phillipburg, NJ). 2-Methyl-3-heptanone was from Aldrich Chemical Co. (Milwaukee, WI) and anhydrous sodium sulfate was from Merck (Darmstadt, Germany).

Isolation of volatile compounds
Volatile compounds were isolated from the roasted ingredients grounded with dry ice. The isolation method was adapted from the method by Ryu et al. (1999) using the simultaneous distillation extraction (SDE). Sample (40 g) was mixed with 250 mL odor-free distilled-deionized water and 10 µL of the internal standard, 2-methyl-3-heptanone solution (0.2 mg/mL). SDE was carried out for 3 h using 40 mL dichloromethane as the extraction solvent. The extract was concentrated to 10 mL under a nitrogen stream and dried over anhydrous sodium sulfate before further concentrated to 1 mL. The final extracts were kept in the amber glass vials with Teflon lined caps at -40°C. All samples were extracted in duplicate.

Gas chromatography-mass spectrometry
The GC-MS system consisted of an HP6890 and a GC/5973 mass selective detector (MSD, Agilent Technologies, Inc., Palo Alto, USA). The extract (1 µL) was injected into the split injection port at the split ratio of 1:10. The separations of volatile compounds were performed on a fused silica capillary column (HP-Innowax, 60 m x 0.25 mm x 0.5 µm film thickness, Agilent Technologies, Inc.). Helium was used as carrier gas at a constant flow of 40 cm/s. The oven temperature was programmed from 40°C to 250°C at the rate of 3°C/min. The MSD conditions were as follows: capillary direct interface temperature, 280°C; ionization energy, 70 eV; mass range, 30-300 a.m.u; and the scan rate, 2.74 scans/s.

Gas chromatography-olfactometry (GCO)
The odor descriptions of volatile compounds in this study were described by using GCO. The system consisted of a GC, HP5890 (Agilent Technologies, Inc.) equipped with a flame ionization detector (FID), a sniffing port (SGE International, Victoria, Australia), and a split injector. The concentrated extract (1 µL) was injected into a capillary column (HP-Innowax 15 m x 0.32 mm x 0.5 µm film thickness). The GC oven temperature was programmed in the same condition as GC-MS. Two trained panelists sniffed the volatile components at the sniff port for the odor descriptions.

Identification and quantification of odorants
Identifications were done tentatively based on comparing mass spectra with Wiley 275 mass spectrum library, odor description from GCO data, and comparison of retention indices (RI) of the compounds with those in the literatures. Retention indices were calculated based on the retention times of a series of n-alkanes (C5-C30, Aldrich, St. Louis, USA). Concentrations were calculated based on the relative concentration of the internal standard, 2-methyl-3-heptanone. Odor activity value (OAV) was calculated by dividing compound concentration by its published odor detection threshold.

Preparation of oleang
Various oleang formulations were prepared in different ratios of roasted coffee, grains and seeds. The coffee added was varied at 50, 60, 70, and 80% with the roasted grain and seed mixtures of 45, 35, 25, and 15%. The roasted grain and seed mixtures were prepared with the ratios of corn: soybean: rice: sesame at 2:3:0:0, 3:2:0:0, 3:1:1:0 and 3:1:0:1. Roasted brown cane sugar (5%) was added to all samples.
Sensory evaluation

Oleang formulations were prepared using 40 g of roasted ingredients. Water (125 mL) was heated to 95°C and pour onto the ingredients. The extract was cooled down to 4°C prior to the sensory evaluation. Twenty four panelists who regularly drank oleang performed a preference test using a 9-point hedonic scale (9=like extremely, 7=like moderately, 5=neitherlike nor dislike, 4=dislike slightly, 3=dislike moderately, 1=dislike extremely).

Statistical analysis

ANOVA was used to indicate the significant differences between mean values of the different results. A comparison between samples and fermentation time was performed using Duncan’s multiple range test. Significant level was established at $P < 0.05$.

Results and Discussions

Volatile compounds

In this research, coffee, corn, sesame, and brown sugar were roasted at 220°C for 20 min. Roasting soybean and rice at the same condition was not enough to generate the distinctive roasted aroma. Soybean and rice, therefore, were roasted at the higher temperature at 240°C for 20 min. The roasted corn had popcorn aroma characteristic and the roasted sesame had a slightly burnt note. The roasted soybean had coffee aroma characteristic and the roasted rice was sulfurous and burnt.

Volatile compound compositions of the high roasted corn, soybean, rice and sesame are shown in Table 1. The major aroma compounds that had high OAV in corn were 2-furfurylthiol (roasted), nonanal, hexanal (green), 2-methoxyphenol (roasted chili), furfural (sweet), and a few alkylpyrazines. The aroma descriptions in the parentheses were perceived through the GCO. 2-Furfurylthiol was one of the compounds that have most impact on the overall coffee aroma characteristic (Flament, 2002). 2-Furfurylthiol was perceived as freshly roasted coffee at 0.01-0.5 ppb but caused the coffee to be stale with the sulfurous note at the higher concentrations of 1-10 ppb (Tressl and Silwar, 1981). Corn is the major grain commonly used in the commercial oleang formulations. Addition of roasted corn to coffee provided several extra volatile compounds. By comparison of the data in Table 1 and Table 2, the volatiles compounds in the roasted corn that were not detected in our coffee sample were 2-methylthiazole (green vegetable), 2-furfurylthiol, ethenylthiophene (burnt, roasted), 2-thiophene carboxaldehyde (nutty), 1,4-dimethylbenzene, butylbenzene, nonanal, 2-methyltetrahydrofuran-3-none (burnt sugar), methylpyrazine, ethylpyrazine (peanut), 2-vinylpyrazine, 2-methyl-6-vinylpyrazine, and 1H-pyrrole (slightly pungent). Most of these compounds were also previously reported in the roasted coffee (Flament, 2002). Our coffee sample might contain these compounds but at low concentrations. Addition of the roasted corn to the coffee increased the concentration of the compounds previously mentioned leading to more of the roast and nutty characteristic to the oleang.

The roasted soybean had overall aroma characteristic similar to that of coffee. Its volatiles were not as complex as those in corn. Major aroma compounds in roasted soybean were 3-ethyl-2,5 dimethylpyrazine, 2-ethyl-3,5-dimethylpyrazine, and 2-methoxyphenol. The compounds in the roasted soybean sample that were not found in coffee were 2-methyl-1-butanol, 3-methyl-1-butanol, 1H-pyrrole, benzaldehyde, and 2-formyl-1-methylpyrrole (Table 1 and Table 2). It should be noted that the roasted soybean contained low amounts of sulfur containing compounds. Thus, it had the roasted, coffee-like, and burnt characteristics without the rubbery note. Addition of soybean can substitute coffee but it did not provide the extra volatiles that distinct oleang from the typical coffee.

The roasted rice sample, composed of only few volatile components, had strong sulfurous and burnt characteristic. The total volatile concentration of the roasted rice sample was the lowest among the roasted grains and seeds. Even though the rice sample was roasted at the higher temperature than coffee, corn, and sesame, the condition was not enough to generate high amount of volatile compounds. The compounds that formed could have low threshold values. There were four unknown compounds that were detected by GCO but were not detected by MSD. Those compounds had roasted and smoky (RI=1245 and 1255), rubbery (RI=1269), and pandan (RI=1350) characteristics. The last one with the RI of 1350 was probably 2-acetyl-1-pyrorine that is the character-impact compound in pandan leaves and the fragrant rice. The roasted rice sample had hexanal, dimethyl disulfide (cabbage), and 2-pentylfuran (beany) as its major aroma component. The compounds that were not found in the robusta coffee sample were dimethyl disulfide, 2-heptanone, 2-pentylfuran, cyclohexan, and 1H-pyrrole. Rice provided sulfur compounds to the oleang mixture but it contributed less impact on the aroma when compared to sesame.

Among all seeds in this study, sesame was the most abundant in the numbers of aroma compounds. It was rich in sulfur-containing compounds and...
pyrazines that had low threshold values. The major compounds that contributed to aroma were dimethyl trisulfide, dimethyl disulfide, 2-furfurylthiol, 2-acetyl-4-methylthiazole (smoky), 2-vinylpyrazine (green, burnt), 2-methyl-6-vinylpyrazine, 2-acetylpyrazine (popcorn, nutty), and two unknowns with burnt characteristic (RI=1202 and 1581). The use of the high roasted sesame seed in oleang formulation is usually limited to 5%. The data suggested that the small use of sesame provided volatile sulfur compounds that added the roasted, sulfurous, and burnt notes to the mixture.

The commercial oleang usually contained 5% of the compounds that contributed to aroma.

### Table 1. Concentrations of volatile components (μg/g) of oleang ingredients roasted for 20 min

<table>
<thead>
<tr>
<th>Compound</th>
<th>RI</th>
<th>Threshold* (μg/g)</th>
<th>Corn</th>
<th>Soybean</th>
<th>Rice</th>
<th>Sesame</th>
</tr>
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<tbody>
<tr>
<td>chloroform</td>
<td>1010</td>
<td>1051</td>
<td>3054</td>
<td>3060</td>
<td>3022</td>
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<td>2-methylfuran</td>
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<td>1335</td>
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<tr>
<td>1-methylfuran</td>
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</tr>
</tbody>
</table>

*Threshold values were determined by gas chromatography-mass spectrometry (GC-MS) and were expressed as the concentration of each compound in μg/g. The threshold values were determined under the condition that the concentration of each compound was 100 ng/mL in water. The threshold values were calculated by using the limit of detection (LOD) and the limit of quantification (LOQ) for each compound. The LOD was defined as the concentration of each compound that produces a signal-to-noise ratio of 3, and the LOQ was defined as the concentration of each compound that produces a signal-to-noise ratio of 10. The threshold values were calculated by using the LOD and the LOQ for each compound.
brown sugar. Heating brown sugar at 220°C for 20 min generated an overall caramel odor. The major aroma compound was 2,3-pentanedione (buttery) that was not found in the roasted grain and seed samples. Brown sugar contributes caramel and buttery notes to oleang mixture. In manufacturing of oleang, coffee and brown sugar maybe roasted together. Roasting coffee with sugar results in higher concentrations of various volatiles and intensifies nutty, roast, earthy, burnt, and caramel notes to coffee (Sanz et al., 2002).

**Sensory evaluation**

Preference test was performed using 24 panelists. The formulations were prepared based on the information on the labels variety of commercial products. Our previous unpublished study indicated that using coffee lower than 50% was not acceptable by the panelists and using 100% coffee in the formulation did not generate the pleasant smoky aroma of oleang. From Table 3, the panelists mostly preferred the oleang sample no. 3 that contained only 50% coffee and 45% grain mixture (corn:soybean:rice = 3:1:1:0) with 5% brown sugar. The score 6.7 meant that the panelists slightly preferred the mixture. The other preferred samples were the samples no. 1, 4, 10, and 16. It should be noted that three out of five preferred samples contained only 50% coffee and 45% mixture of roasted grains.

**Conclusion**

The preferred oleang formulations in this experiment contained the highest content (45%) of the roasted grains and seeds that provide the unique roast and burnt characteristic. The high roasted corn plays an important role in generating the roast and burnt aroma components. The other ingredients are important in the balancing of pyrazines, phenols, and sulfur-containing compounds. Sesame and rice provides the volatile sulfur-containing compounds.
that enhances the sulfurous, roast, and burnt notes to the mixture. The high roasted soybean had the aroma similar to that of coffee. It can be used mainly to substitute coffee to lower the cost but do not provide the unique roast and burnt characteristic to oleang.

Acknowledgement

The authors would like to thank the Graduate School, Kasetsart University for partially financially supporting the project; Department of Agriculture, Ministry of Agriculture and Cooperative and Quality Coffee Products (Thailand), Ltd. for providing raw materials used in this study.

References


