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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 iso-valeraldehyde (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-

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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(2*H*)-furanone, 2-pentylpyridine, 2,4-decadienal, 2-acetyl-1-pyrroline, 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 (C_5-C_{30}, 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 1*H*-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, 1*H*-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-pyroline 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, cyclohexanal, and 1*H*-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

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

Compound	*RI* [a]	*Threshold* [b] *(ng/g)*	*Corn*		*Soybean*		*Rice*		*Sesame*	
			Concn. [c]	*OAV*	*Concn.*	*OAV*	*Concn.*	*OAV*	*Concn.*	*OAV*
chloroform	1007	*n.a.*	2,913.22	*n.a.*	-	-	7,318.58	*n.a.*	4,550.32	*n.a.*
thiophene	1010	84 [d]	289.27	3,443	-	-	-	-	615.12	7,322
toluene	1022	*n.a.*	437.83	*n.a.*	-	-	-	-	-	-
dimethyl disulfide	1051	12 [e]	-	-	-	-	126.08	10,506	5,541.80	461,186
2-vinylfuran	1058	*n.a.*	-	-	-	-	-		230.15	*n.a.*
hexanal	1068	4.5 [e]	779.44	173,208	215.32	47,848	1,146.76	254,835	256.17	56,926
2-methylthiophene	1078	3,000 [f]	312.35	104	-	-	-	-	403.82	134
1,4-dimethylbenzene	1101	*n.a.*	303.49	*n.a.*	-	-	-	-	-	-
3-methylthiophene	1101	5 [f]	-	-	-	-	-	-	302.26	60,452
methylethyl disulfide	1118	*n.a.*	-	-	-	-	-	-	291.69	*n.a.*
1-methylpyrrole	1129	*n.a.*	321.21	*n.a.*	424.64	*n.a.*	131.65	*n.a.*	653.87	*n.a.*
2-vinyl-5-methylfuran	1134	*n.a.*	-	-	-	-	-	-	396.34	*n.a.*
4,5-dimethyloxazole	1139	*n.a.*	-	-	-	-	-	-	141.51	*n.a.*
1-ethylpyrrole	1162	*n.a.*	-	-	-	-	-	-	611.45	*n.a.*
pyridine	1174	2,000 [e]	-	-	566.50	283	-	-	1,426.82	713
2-heptanone	1158	140 [e]	-	-	-	-	729.30	923	-	-
2-methyl-1-butanol	1187	4150	-	-	93.47	22	-	-	-	-
3-methyl-1-butanol	1189	1055	-	-	475.12	450	-	-	-	-
2-pentylfuran	1198	6 [e]	-	-	-	-	292.93	48,821	-	-
pyrazine	1201	18,000 [e]	2,436.46	135	-	-	-	-	1,399.67	77
Unknown	1202	*n.a.*	-	-	-	-	-	-	286.18	-
2-methylpyridine	1205	*n.a.*	-	-	-	-	-	-	225.99	*n.a.*
2-methylthiazole	1218	*n.a.*	312.35	*n.a.*	-	-	-	-	905.78	*n.a.*
thiazole	1229	3,100 [d]	-	-	-	-	-	-	1,572.98	507
2-methyltetrahydrofuran-3-none	1242	*n.a.*	214.21	*n.a.*	-	-	-	-	-	-
methylpyrazine	1264	60,000 [e]	5,848.35	97	-	-	-	-	13,544.63	225
4-methylthiazole	1265	*n.a.*	568.02	*n.a.*	-	-	-	-	3,523.83	*n.a.*
butylbenzene	1269	*n.a.*	261.51	*n.a.*	-	-	-	-	-	-
2,4-dimethylthiazole	1293	*n.a.*	-	-	-	-	-	-	705.95	*n.a.*
2-ethylpyrazine	1306	4,000 [g]	3,843.37	960	-	-	-	-	-	-
2,5-dimethylpyrazine	1319	1,700 [e]	750.03	441	-	-	-	-	-	-
ethenylthiophene	1312	*n.a.*	319.95	*n.a.*	-	-	-	-	-	-
2,6-dimethylpyrazine	1325	1,500 [e]	-	-	-	-	-	-	2,348.35	1,565
2,3-dimethylpyrazine	1330	2,500 [e]	766.38	306	-	-	-	-	765.05	306
dimethyl trisulfide	1331	0.01 [e]	-	-	-	-	-	-	1,692.78	1.6×10^{8}
2-ethyl-6-methylpyrazine	1362	40 [e]	1,660.60	41,515	-	-	-	-	1,949.93	48,748
2-ethyl-5-methylpyrazine	1369	100 [e]	319.04	3,190	-	-	-	-	1,148.12	11,481
cyclohexanol	1378	3,500 [d]	-	-	-	-	101.96		-	-
2-ethyl-3-methylpyrazine	1383	130 [h]	625.45	4,811	1,352.70	10,405	-	-	1,075.20	8,270
2-furfurylthiol	1405	0.005 [i]	407.96	8.1×10^{7}	-	-	-	-	475.21	9.5×10^{7}
2,6-diethylpyrazine	1410	6 [j]	417.91	69,651	345.28	57,546	-	-	193.79	32,298
2-vinylpyrazine	1413	700 [e]	927.55	1,325	-	-	-	-	304.21	434
3-ethyl-2,5-dimethylpyrazine	1434	8.6 [g]	360.54	41,923	5,732.21	6.6×10^{6}	-	-	1,930.47	2.2×10^{6}
2-ethyl-3,5-dimethylpyrazine	1440	0.04 [e]	-	-	1,798.39	4.4×10^{7}	-	-	-	-
furfural	1455	3,000 [e]	169,956.15	56,652	672.03	224	-	-	4,071.10	1,357
2-methyl-6-vinylpyrazine	1463	*n.a.*	303.57	*n.a.*	-	-	-	-	234.57	*n.a.*
3,5-diethyl-2-methylpyrazine	1466	*n.a.*	-	-	993.46	*n.a.*	-	-	-	-
1*H*-pyrrole	1488	*n.a.*	4,232.01	*n.a.*	1,864.84	*n.a.*	117.26	*n.a.*	5,041.86	*n.a.*
nonanal	1508	1 [e]	1,648.88	1.6×10^{6}	-	-	-	-	-	-
dimethyl-2-vinylpyrazine	1511	*n.a.*	-	-	-	-	-	-	140.02	*n.a.*
benzaldehyde	1521	350 [e]	-	-	189.18	540	-	-	810.74	2,316
furfurylacetate	1531	100	-	-	-	-	-	-	331.13	3,331
2-methylpyrrole	1537	*n.a.*	-	-	-	-	-	-	260.88	*n.a.*
5-methylfurfural	1575	6,000 [d]	2,764.02	460	945.49	157	-	-	1,894.06	315
Unknown	1581	*n.a.*	-	-	-	-	-	-	244.35	*n.a.*
dimethyl sulfoxide	1603	*n.a.*	-	-	-	-	-	-	468.92	*n.a.*
2-formyl-1-methylpyrrole	1606	*n.a.*	-	-	259.23	*n.a.*	-	-	-	-
2-acetylpyrazine	1609	62 [k]	-	-	-	-	-	-	247.95	3,999
1-phenylethanone	1627	*n.a.*	-	-	-	-	-	-	358.22	*n.a.*
2-acetyl-4-methylthiazole	1668	*n.a.*	-	-	-	-	-	-	386.01	*n.a.*
2-furanmethanol	1671	5,000	1,866.82	373	291.52	58	-	-	1,526.33	305
4-ethyl-2-methoxypyrrole	1680	*n.a.*	-	-	-	-	-	-	138.66	*n.a.*
2-methoxyphenol	1869	3 [e]	225.15	75,050	2,439.54	8.1×10^{6}	-	-	3,936.59	1.3×10^{7}
2-pyrrolyl-methylketone	1967	170,000	-	-	-	-	-	-	204.38	<1
2-methoxy-5-vinylphenol	2190	*n.a.*	1,802.31	*n.a.*	-	-	-	-	-	-
4-vinyl-2-methoxyphenol	2227	3 [e]	-	-	-	-	-	-	191.32	63,773

[a]Retention indices (RI) were determined on HP-Innowax column. [b]Threshold in water. [c]Relative concentration (average, n = 2). [d]van Gemart (2003). [e]Buttery and Ling (1998). [f]Galetto and Hoffmann (1976). [g]Buttery *et al.* (1997). [h]Buttery and Ling (1972). [i]Tressl (1989). [j]Guadagni *et al.* (1972). [k]Fors (1983). OAV=odor active value, *n.a.*= not available, - = no compound detected.

pyrazines that had low threshold values. The major compounds that contributed to aroma were dimethyl trisulfide, dimethyl disulfide, 2-furfurylthiol, 3-ethyl-2,5-dimethylpyrazine, and 2-methoxyphenol. Compounds from sesame that were not found in coffee sample were dimethyl disulfide, 3-methylthiophene (sulfurous), methyl ethyl disulfide (rubbery, roasted), 2-methylthiazole (green vegetable), thiazole (musty), 2,4-dimethylthiazole, dimethyl trisulfide (sulfurous), 2-furfurylthiol (burnt), dimethyl sulfoxide, 2-acetyl-4-methylthiazole (roasted, burnt), 2-methylfuran (burnt), 2-methylpyridine (popcorn), 1*H*-pyrrole, benzaldehyde, 2-methylpyrrole, furfuryl propionate (nutty), 1-phenylethanone, 4-ethyl-2-methoxypyrrole, 4-vinyl-2-methoxyphenol (smoky), 2-vinylpyrazine (green, burnt), 2-methyl-6-vinylpyrazine , 2-acetylpyrazine (popcorn, nutty), and two unknowns with burnt characteristic (RI=1202 and RI=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. Over use of sesame in the formulation can deviate overall coffee aroma.

The commercial oleang usually contained 5%

Table 2. Concentrations of volatile components and OAV of coffee roasted for 20 min

Compound	*RI* [a]	*Threshold* [b] *(ng/g)*	*Concn.* [c] *(µg/g)*	*OAV*
chloroform	1007	*n.a.*	1,357.08	*n.a.*
3-methylbutanoic acid	1009	250 [d]	126.87	453
thiophene	1010	84 [d]	186.93	2,225
2,3-pentanedione	1050	20 [e]	272.19	13,609
toluene	1022	*n.a.*	80.71	*n.a.*
1-methylpyrrole	1129	*n.a.*	504.38	*n.a.*
2-vinylfuran	1058	*n.a.*	91.75	*n.a.*
hexanal	1068	4.5 [e]	72.51	16,113
2-methylthiophene	1078	5 [f]	102.00	20,400
2-methoxymethylfuran	1123	*n.a.*	239.62	*n.a.*
2-vinyl-5-methylfuran	1134	*n.a.*	123.98	*n.a.*
4,5-dimethyloxazole	1139	*n.a.*	66.64	*n.a.*
1-ethylpyrrole	1162	*n.a.*	63.16	*n.a.*
cyclopentanone	1170	51,100 [d]	73.79	1
pyridine	1174	2,000 [e]	1,868.92	934
pyrazine	1201	18,000 [e]	266.52	14
2-methoxymethylfuran	1223	*n.a.*	239.62	*n.a.*
styrene (vinylbenzene)	1229	80 [d]	98.11	1,225
1-butylpyrrole	1232	*n.a.*	78.74	*n.a.*
methylpyrazine	1264	60,000 [e]	2,036.81	33
4-methylthiazole	1265	*n.a.*	112.06	*n.a.*
3-methylpyridine	1284	*n.a.*	75.97	*n.a.*
2,5-dimethylpyrazine	1319	1,700 [e]	517.54	30
2,6-dimethylpyrazine	1325	1,500 [e]	948.93	363
2,3-dimethylpyrazine	1330	2,500 [e]	270.58	676,450
2-ethyl-6-methylpyrazine	1362	40 [e]	532.86	13,321
3-ethypyridine	1365	*n.a.*	223.29	*n.a.*
2-ethyl-5-methylpyrazine	1369	100 [e]	338.31	3,383
2-ethyl-3-methylpyrazine	1383	130 [h]	252.72	1,944
2,6-diethylpyrazine	1410	6 [i]	82.45	13,741
3-ethyl-2,5-dimethylpyrazine	1434	8.6 [g]	367.17	42,694
2-ethyl-3,5-dimethylpyrazine	1440	0.04 [e]	153.22	383,500
furfural	1455	3,000 [e]	203.07	67
2-furfurylmethylsulfide	1460	*n.a.*	386.51	*n.a.*
3,5-diethyl-2-methylpyrazine	1466	*n.a.*	108.42	*n.a.*
furfurylacetate	1531	100	804.70	8,047
5-methylfurfural	1575	500 [g]	157.69	1,609
2,2'-methylene bis furan	1588	*n.a.*	328.43	*n.a.*
2-formyl-1-methylpyrrole	1615	*n.a.*	123.96	*n.a.*
5-methylfuran	1656	*n.a.*	46.74	*n.a.*
2-furanmethanol	1671	5,000	853.47	170
N-furfurylpyrrole	1824	100 [g]	195.50	1,955
2-methoxyphenol	1869	3 [e]	271.87	90,623
unknown	1976	*n.a.*	170.36	*n.a.*
phenol	2012	5,500 [d]	572.83	97
4-ethyl-2-methoxyphenol	2024	50 [j]	685.51	13,710
4-vinyl-2-methoxyphenol (*p*-vinylguaiacol)	2210	3 [e]	606.32	202,106

[a]Retention indices (RI) were determined on HP-Innowax column. [b]Threshold in water. [c]Relative concentration (average, n = 2). [d]van Gemart (2003). [e]Buttery and Ling (1998). [f]Galetto and Hoffmann (1976). [g]Buttery *et al*. (1997). [h]Buttery and Ling (1972). [i]Guadagni *et al*. (19). [j]Etievant (1991). OAV=odor active value, *n.a.*= not available.

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: sesame =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.

Table 3. Overall preference of oleang formulations with brown sugar and various coffee and grain compositions

No.	Brown sugar (%)	Coffee (%)	Corn : Soy : Rice : Sesame (%)	Corn : Soy : Rice : Sesame (ratio)	Overall Preference
1	5	50	45	2 : 3 : 0 : 0	5.99 [abc] *
2				3 : 2 : 0 : 0	5.49 [bcde]
3				3 : 1 : 1 : 0	6.70 [a]
4				3 : 1 : 0 : 1	5.89 [abcd]
5	5	60	35	2 : 3 : 0 : 0	5.37 [bcde]
6				3 : 2 : 0 : 0	5.68 [bcde]
7				3 : 1 : 1 : 0	5.60 [bcde]
8				3 : 1 : 0 : 1	5.01 [de]
9	5	70	25	2 : 3 : 0 : 0	5.47 [bcde]
10				3 : 2 : 0 : 0	5.80 [abcd]
11				3 : 1 : 1 : 0	4.99 [de]
12				3 : 1 : 0 : 1	5.14 [cde]
13	5	80	15	2 : 3 : 0 : 0	4.80 [e]
14				3 : 2 : 0 : 0	5.24 [bcde]
15				3 : 1 : 1 : 0	5.26 [bcde]
16				3 : 1 : 0 : 1	6.10 [ab]

* 9=Like extremely, 7=like moderately, 5=neither like nor dislike, 4=dislike slightly, 3=dislike moderately, 1=dislike extremely. Score with the same letter are not significantly different at p>0.05.

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.

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