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The Effects of Roasting Time of Unfermented Cocoa Liquor Using the Oil Bath Methods on Physicochemical Properties and Volatile Compound Profiles

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ABSTRACT

This study aimed to measure the effect of roasting time on physicochemical properties and volatile compounds of unfermented cocoa liquor roasted with an oil bath method. Physicochemical properties (pH, temperature, and color), flavor, and volatile compounds were analyzed. The results showed that the longer the roasting time the higher the unfermented cocoa liquor's temperature, °Hue, and ΔE value, but lower pH and L value. There were 126 volatile compounds obtained by various roasting time, identified as pyrazines (12), aldehydes (16), esters (1), alcohols (31), acids (15), hydrocarbons (11), ketones (19), and others (21). At 15, 20, and 25 minutes of roasting time, 69, 74, and 67 volatile compounds, respectively, were identified. Volatile compounds' profiles were indicated to be strongly influenced by roasting time. The largest area and highest number of compounds, such as pyrazines and aldehydes, were obtained at 20 minutes, which was also the only time the esters were identified. As well as the time showed a very strong flavor described by panelists.

Keywords: Flavor; oil bath; physicochemical; unfermented cocoa liquor

INTRODUCTION

Cocoa is the main raw material of chocolate products whose popularity in the world relies to its distinctive flavor. The flavor precursor formation occurs during the fermentation process (Camu *et al*., 2008), but in Indonesia cocoa beans produced are dominated by the unfermented cocoa beans with a range of about 93% (Pusdatin, 2013). It has advantages as antioxidants source due to the high content of polyphenols as much as 12–18% in dry beans (Ioannou *et al*., 2012). Due to its potential becoming a health beneficial product and its equal flavor to fermented cocoa, unfermented cocoa needs to be developed. The flavor development of cocoa beans was done during roasting. Conventional roasting on beans is widely used, but the results are inconsistent due to diverse beans size for the reaction to proceeds well (Misnawi *et al*., 2005). Therefore beans size should be uniform, liquor form with a smaller size affected the temperature so that it can be affected directly the intensity of the Maillard reaction that occurs during roasting, a reaction between reducing sugars and amino acids generating chocolate flavor components, such as pyrazines, alcohols, esters, aldehydes, ketones, furans, thiazoles, pyrones, acid, amine, oxazoles, pyroles and ether (Jinap *et al*., 1998; Nazaruddin *et al*., 2006; Noor-Soffalina *et al*., 2009). An alternative solution is the roasting of cocoa bean into liquor form using oil bath method. The method can be considered to optimize the roasting process since the heat transfer among liquor becomes more optimal and the reaction rate is under control. The reaction rate is strongly influenced by roasting temperature and time, these two parameters must be well determined.

In conventional roasting, three degrees of roasting are usually applied on beans. The roasting degree of cocoa beans varies depending on the applied of the end product (Afoakwa, 2010). Cocoa bean roasted at low

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degree (110 °C for 60 minutes), medium (140 °C for 40 minutes) and high (190 °C for 15 minutes) (Utami et al., 2017). However, optimum roasting time of cocoa liquor in oil bath roasting is still unknown. Therefore, the effect of roasting time on physicochemical cocoa liquor roasted by oil bath method was observed. Roasting in liquor form allows more homogenous distribution of flavor precursor interactions and ease connection between flavor compounds due to the reduction of size differences among beans. Various reports on flavor compounds of fermented cocoa beans have been published, but not of those of unfermented cocoa beans (Afoakwa, 2010; Bonvehí, 2005; Climaco Alvarez, 2016; Farah & Zaibunnisa, 2012; Wiesława Krysiak, *et al.,* 2013; Rodriguez-Campos et al., 2012). Accordingly, this study was also aimed to identify volatile compounds of unfermented cocoa liquor obtained by various oil bath roasting times.

METHODS

The materials used in this study were the unfermented dry cocoa beans obtained from a plantation in Gunung Kidul, Yogyakarta, Indonesia. Cooking oil (Sania) was bought at the supermarket and cocoa butter was obtained from Indonesian Coffee and Cocoa Research Institute (ICCRI). The instruments used in this research were a vessel (Shuma Stainless steel), deep fryer, pH meter (pH HM 30 G), thermocouple type K, spectrophotometer (Spectronic 200 Thermo Scientific), chromameter (Konica Minolta CR 400 Osaka Japan), a set of the sensory analyzer, and SPME-GC/MS (Agilent Technologies 6890N-5793 Network GC–MS system (Agilent Technologies, Santa Clara, CA, USA).

Sample Preparation and Oil Bath Roasting

Unfermented dry cocoa beans were peeled, and then the nibs were milled using a meat grinder (in/out process 22 times) to obtain unroasted cocoa liquor (50–70 µm). Six liters of cooking oil, as the medium of heat transfer, was poured into the roaster. The stainless steel container as a roaster vessel was placed into the roaster which has been filled with cooking oil so that the roaster vessel sinks slightly in the cooking oil. After that, the roaster temperature was set to 170 °C, and then 2.6 g of cocoa butter was added into the roaster vessel until it melted. After that 100 g of unroasted cocoa liquor was put into cocoa butter system while stirring using a hand mixer in 5, 10, 15, 20 and 25 minutes. Roasting was done triplicate for each roasting times.

pH and Temperature Measurement

pH was determined according to Indonesia National Standard (SNI, 2008), while temperature during roasting was measured by thermocouple (type K).

Browning Intensity

Browning intensity of unfermented cocoa liquor roasted was determined using the method of Supriyanto&Marseno (2010) with slight modifications. Fifty milligrams of unfermented cocoa liquor roasted and 50 ml of ethanol 50% were added to erlenmeyer with lid, then dissolved by sonicator at room temperature, and then filtered with whatman filter paper No 1. The filtrate obtained was read by UV Vis spectrophotometer at 420 nm.

Color

Color of unfermented cocoa liquor roasted was determined using the method of Supriyanto *et al*. (2014). The color was expressed in L*, L* expresses luminance and changes from 0 for black to 100 for white. ^{o}Hue = arctan (b*/a*) a* (negative values indicate green and positive values indicate red), b* (negative values indicates blue and positive values indicate yellow). Remarkable °Hue values are: 0^{o} (red), 270° (or -90°, blue), 90° (yellow), 45° (orange) and 180 ° (green). The colorimetric difference ΔE was obtained through the equation: ΔE = . Measurement of color per samples was repeated by five readings. Each of the treatment was measured in triplicate.

Sensory Analysis

Sensory analysis was conducted by 20 semi-trained panelists with flavor as the tested parameter, using a scoring test with interval score 1 (very weak) up to 5 (very strong). The odor description of strong is distinctive of chocolate flavor notes. Among five roasting times, three periods showed strong to very strong scores were selected for volatile compound profile identification.

Volatile Compound Profiles

Static headspace isolation of volatile compounds was performed using solid phase micro extraction (SPME) for 45 min at 55 °C onto a polydimethylsiloxanedivinylbenzene, 65 µm fiber (Supelco, Bellefonte, PA, USA). Approximately 5 g cocoa liquor was previously heated to 55 °C and intermittently stirred for 45 min for headspace equilibration. Each experiment had control sample made by stirring an empty vial under the same conditions. Volatile compounds were desorbed (5 min) into the split less injector (250 °C) of GC Agilent 7890A and MS 5795C with triple axis detector (Agilent Technologies, Santa Clara, CA, USA) and separated on a J&W 60 m DB-Wax capillary column (0.22 mm id., 0.25 μm film thickness). Carrier gas was hydrogen with 1.8ml/min flow rate. The temperature program was: at 40 °C; 5 °C min^{-1} to 200 °C for 15 min. Compounds were fragmented using electron-impact ionization (70 eV), with source temperature of 230 °C, scan range of 33–550 amu and scan rate of 2 s^{-1}. Components were identified based on comparison of mass spectra with those of spectral libraries NIST 05 and Wiley 7N Registry of GC Mass Spectral Database (John Wiley, New York, USA) (Afoakwa *et al*., 2009).

Statistical Analysis

Results in tables and figures are presented as mean ± standard deviation of analyses done in triplicate. Physicochemical data obtained were tabulated and analyzed using variance analysis (ANOVA). Differences among samples would be tested using Least Significant Different (LSD) with the significance level set at α = 0.05.

RESULT AND DISCUSSION

Physicochemical Characteristics on Unfermented Cocoa Liquor

One of the basic technological operation in cocoa bean processing affecting the quality of cocoa derivative products is roasting (Oracz & Nebesny, 2014). It determines the character of the chemical and physical processes that occurred inside the beans, and the final products quality (Wieslawa Krysiak & Motyl-Patelska, 2006). Roasting process which highly influenced by the roasting time causes physicochemical changes such as temperature, pH, color and flavor. Table 1 showed that the longer the roasting time the higher cocoa liquor temperature, with the highest was obtained at 25 minutes as influenced by heat energy from the roaster. Increasing heat energy with longer roasting time caused heat transfer from cocoa liquor system to its surface, led to higher temperature, which generally increased the rate of Maillard reaction (Durmaz & Gökmen, 2010). High temperatures were ideal for Maillard reactions, the reaction occurred at 80–160 °C (Fennema, 2007). In this study, it showed by the final temperature measurement during roasting cocoa liquor using the oil bath methods at 115.5–143 °C.

High roasting temperature decreases acidity, especially the volatile acids with low boiling point, such as acetic acid, thus cocoa beans became less acidic (Afoakwa *et al*., 2009; Frauendorfer & Schieberle, 2008). Longer roasting time also led to lower pH with range of 6.5 to 6.0, closely related to volatile and non-volatile organic acid contents. Lower acidity was probably caused organic acids breakdown, especially the non-volatiles. As mentioned by Afoakwa *et al*. (2009), volatile acids evaporation during roasting might reduce acidity, sourness, and bitterness of cocoa beans.

Roasting time also affected cocoa beans color as interpreted by the value of L, °Hue and ΔE. The table 1 showed that longer roasting time reduced L value. The decline indicated darker color of roasted cocoa liquor. In addition, browning intensity value was also increased with longer roasting time, which was probably due to the increase in brown pigment formation from Maillard reactions (melanoidins), thermal oxidation and polymerization of polyphenols to form tannins and strecker degradation reactions during roasting (Wiesława Krysiak *et al*., 2013; Patras *et al*., 2010)"container-title":"Journal of Food Quality","page":"21-31","volume":"36","issue":"1","source":"Wiley Online Library","abstract":"The cacao bean of the Ivory Coast variety was convectionally roasted. The influence of parameters of air (temperature from the scope T = 110–150C, the speed of its flow v = 0.5 and 1.0 m/s, and the relative humidity = 0.3–0.8% or 2 and 5.0%. Several components might significantly affect colors, such as polyphenols, anthocyanins, and proteins that easily form colloid and generally contain reducing groups causing red to blue appearance. Other important component affected roasted cocoa liquor was °Hue, the degree of color combinations of yellow (a) and red (b) from the Hunter system. Results also showed that longer roasting time led to higher °Hue. Roasting time greatly induced color change, seen from higher ΔE value with the longer roasting time at the range of 1.45 to 7.53.

Increasing temperature, pH decrease, and color changes with longer roasting time contributed to cocoa liquor flavor. Flavors in cocoa were the result of complex reactions of amino acids, peptides and sugars and possible involvement of flavonoid during roasting. The results showed that panelist description on unfermented cocoa liquor roasted flavor ranging from 2.4 to 3.45, indicated that the flavor was a weak until highly strong. The highest value was obtained by 20 minutes roasting, while those obtained at 5 minutes as the lowest. In general, the longer roasting time the higher the flavor of unfermented cocoa liquor roasted, as indicated by higher value of panelist description. As mentioned by Fisher & Scott (1997), several flavor reactions and protein deamination products including empyreumatic compounds will increase with the higher

Table 1. Physicochemical characteristics on unfermented cocoa liquor

Time	Temperature	pH	Browning index	L	ΔE	°Hue	Flavor
5	115.5±7.97^{a}	6.5±0.06^{d}	0.197±0.001^{a}	33.69±0.12^{e}	1.45±0.39^{a}	0.65±0.00^{a}	2.4±1.10^{a}
10	132.6±5.11^{b}	6.3±0.06^{c}	0.207±0.001^{a}	31.24±0.20^{d}	3.19±0.61^{b}	0.63±0.01^{a}	2.45±0.99^{a}
15	137.6±3.24^{b}	6.2±0.10^{b}	0.388±0.002^{b}	28.78±0.07^{c}	5.69±0.62^{c}	0.70±0.05^{c}	2.65±0.93^{a}
20	142.1±0.84^{c}	6.2±0.06^{a}	0.497±0.001^{c}	27.99±0.62^{b}	6.65±1.15^{d}	0.74±0.03^{c}	3.45±0.83^{b}
25	143.0±2.00^{c}	6.0±0.06^{a}	0.552±0.012^{c}	27.08±0.19^{a}	7.53±0.24^{e}	0.77±0.01^{d}	2.60±0.87a

Results are presented as mean ± standard deviation; all of the analyses were done in triplicate. Means with same superscript in the same column are not significantly different according to least significant differences test at α = 0.05.

temperature received by the material through Maillard reaction. Among several flavors component formed by the reaction, heterocyclic compound has the most significant contribution, such as furan, triazole, oxazoles, pyrrole, pyridine, and alkylpyrazine (Bonvehí, 2005).

Volatile Compounds Profile

Volatile compound identification was performed using solid phase micro extraction (SPME) GC-MS. This study used unfermented cocoa beans roasted in liquor form at various roasting time using oil bath method. The results showed 126 volatile compounds on unfermented cocoa liquor obtained by various roasting time, consisted of pyrazines (12), aldehydes (16), ester (1), alcohols (31), acids (15), hydrocarbons (11), ketones (19), and others (21). On the other hand, Jinap *et al*. (1998) found 48 volatile compounds on fermented cocoa bean using oven (conventional). These results indicate that the number of volatile compounds on liquor roasting using the oil bath method was higher than bean roasting using conventional methods. Among several flavors compound formed by Maillard reaction, heterocyclic compounds had the highest contribution to cocoa flavor compounds, including furans, triazoles, oxazoles, pyrrole, pyridine, and alkylpyrazine (Serra Bonvehí&Ventura Coll, 2002; Ziegleder, 2009).

In respective roasting times of 15, 20 and 25 minutes, 69, 74 and 67 volatile compounds were identified. At 15 minute roasting, pyrazines (10), aldehydes (9), alcohols (16), hydrocarbons (5), acids (10), ketones (8) and others (11) were found, while after 20 minutes, pyrazines (12), aldehyde (12), ester (1), alcohols (13), hydrocarbons (6), acids (9), ketones (13) and others (8) were found. Similarly, 25 minutes roasting generated pyrazines (9), aldehydes (6), alcohols (16), hydrocarbons (6), acids (13), ketones (12) and others (5). The longer the roasting time the higher the number of volatile compounds, but decreased at 25-minutes-roasting. This result closely related to kinetics the formation of the Maillard reaction flavor compounds with the longer roasting time. This is also to the effect of higher temperatures which affect the intensity of the Maillard reaction. However, the decrease of the volatile compounds at 25 minutes roasting showed that the volatile flavor compounds polymerized formed melanoidin compounds in the final stage of the Maillard reaction (Jousse *et al*., 2002; Van Boekel *et al*., 2006). The results of unfermented cocoa liquor volatile compounds were presented in unit area and odor description of each compounds (Table 2).

Table. 2. Unit area and odor description of volatile compounds in unfermented cocoa liquor obtained by various oil bath roasting time

Number	Compound	Unit area			Odor description*
		15 minutes	20 minutes	25 minutes	
Pyrazines					
1	Pyrazine, 2,5-dimethyl-	19661915	17897487	12942649	nutty, peanut, musty, earthy, powdery, slightly roasted with a cocoa powder nuance
2	Pyrazine, methyl-	9131831	6704698	6458070	nutty, brown, nut skin, musty, pyrazine and coffee a slight roasted
3	Pyrazine, ethyl-	3182817	2910273	2141622	roasted potato

Number	Compound	Unit area			Odor description*
		15 minutes	20 minutes	25 minutes	
4	Pyrazine, 2,3-dimethyl-	1956393	1653807	1556904	musty, cocoa powdery and roasted with potato and coffee nuances
5	Pyrazine, trimethyl-	5644237	5075911	4614531	nutty, musty, powder cocoa, potato and musty
6	Pyrazine, 3-ethyl-2,5-dimethyl-	4452561	5689969	3589366	potato, cocoa roasted and nutty
7	Pyrazine, tetramethyl-	9777103	8400467	8008964	nutty, musty and vanilla with dry, brown cocoa nuance
8	Pyrazine, 2-ethyl-6-methyl-	2281814	2460154	1657946	Roasted, hazelnut roasted hazelnut, nutty
9	Pyrazine, ethenyl-	1267861	1407817		-
10	2-Acetyl-3-methylpyrazine	nd	874913	nd	roasted, nutty, vegetable, grain toasted grain, grain, nutty
11	Pyrazine, 2-ethyl-5-methyl-	nd	12062675	nd	coffee bean, nutty
12	Pyrazine, 2-ethenyl-6-methyl-	1165023	1078949	1010633	-
	Total	**58521555**	**66217120**	**41980685**	
Esters					
1	Acetic acid, 2-phenylethyl ester	nd	1538417	nd	Honey, floral
Aldehydes					
1	Butanal, 3-methyl-	60353498	19065427	24097587	Chocolate, ethereal, aldehydic, peach, fatty
2	Benzeneacetaldehyde	7237624	3824261	3168822	honey, floral rose, powdery, fermentedchocolate with a slight earthy nuance
3	Furfural	4315273	4581755	nd	sweet, brown, woody, bready, caramellic, with a slight phenolic nuance
4	Nonanal	11931802	nd	9191940	waxy, aldehyde, citrus, with a slightly green, lemon peel like
5	2-Octenal, (E)-	1165590	1184693	nd	fresh, cucumber, fatty, green, herbal banana, waxy, green, leafy
6	Benzaldehyde	6398537	5917405	5361024	almond, fruity, powdery, nutty
7	2-Decenal, (E)-	nd	2935115	2573231	sweet, aldehydic, orange, waxy
8	2,4-Decadienal, (E,E)-	2127482	3597748	nd	Oily, cucumber, melon, citrus, pumpkin, nutty
9	Butanal	nd	3518315	nd	-
10	2-Dodecenal	nd	1161150	nd	green, citrus, fruity, mandarin, orange, herbal
11	2,4-Decadienal	nd	nd	2312894	orange, sweet, fresh, citrus, fatty, green
12	2-Butenal, 3-phenyl-	nd	955664	nd	Sweet
13	1H-Pyrrole-2-carboxaldehyde	nd	791463	nd	Sweet, candy, and honey flavor
14	Octanal	nd	1898833	nd	aldehydic, green, peely, citrus, orange
15	2-Butenal, 2-phenyl	702190	nd	nd	Sweet
16	2-Undecenal, E-	804232	nd	nd	waxy, aldehydic, green, citrus, meaty
	Total	**95036228**	**49431829**	**46705498**	

Number	Compound	Unit area			Odor description*
		15 minutes	20 minutes	25 minutes	
Alcohols					
1	1-Butanol, 3-methyl-, acetate	3961029	nd	2394772	Fruity, grape
2	2-Hexanol, 3-methyl-	nd	7191984	nd	
3	1-Butanol, 3-methyl-	2902656	1201901	3837368	Malty, chocolate
4	2-Heptanol	13594637	14473280	12567035	fruity greenearthybitter
5	2-Octanol	11016319	nd	nd	fresh, spicy, green, woody, herbal, earthy
6	3-Ethyl-2-pentanol	8267062	nd	nd	-
7	2-Hexanol, 3,4-dimethyl-	2028520	nd	nd	-
8	1,3-Dioxan-5-ol	924692	nd	nd	-
9	1,2-Ethanediol, diacetate	1297810	nd	nd	-
10	2-Heptanol, 6-methyl-	5458374	nd	nd	waxy, fatty, citrus
11	2-Nonanol	2750722	nd	nd	waxygreen creamy citrusorange cheesyfruity
12	2,3-Butanediol, [R-(R*,R*)]-	78712813	nd	22865447	-
13	Phenylethyl Alcohol	796667	12040639	10819968	sweet, floral, bready with a rosy honey nuance
14	2,3-Butanediol	55365371	46287177	14970663	fruity, creamy, buttery
15	2-Furanmethanol	4740057	3357379	3102019	-
16	Benzenemethanol, α-methyl-	759255	nd	nd	-
17	3-Buten-2-ol, 2-methyl-	7105743	nd	nd	herbal, earthy,oily
18	Benzyl Alcohol	nd	2288268	1738560	Sweet, floral, fruity with chemical nuance
19	1-Pentanol, 3,4-dimethyl-	nd	3438996	nd	-
20	2-Pentadecanol	nd	12221164	nd	-
21	2-Pentanol, 4-methyl-	nd	15403624	20273492	pungent, alcoholic
22	3-Ethyl-2-heptanol	nd	3133829	nd	-
23	1,2-Ethanediol, monobenzoate	nd	1377765	nd	-
24	4-Methylimidazole-2,5-diethanol	nd	877832	nd	-
25	2-Pentanol	nd	nd	6309041	alcoholic, fusel, fermented, musty, sweet, winey, banana ripe banana, apple
26	3-Ethyl-3-methyl-2-pentanol	nd	nd	73872818	-
27	1-Heptanol	nd	nd	3909252	musty, pungent, leafy, green, vegetable, fruity, apple, banana
28	2-Hexanol	nd	nd	11756545	chemical, winey, fruity, fatty, terpenic, cauliflower
29	2-Heptanol, 3-methyl-	nd	nd	2809660	-
30	2-Pentanol, 3-methyl-	nd	nd	2334166	-
31	Benzeneacetaldehyde, α-ethylidene-	nd	nd	822358	-
	Total	**199681727**	**123293838**	**194383164**	

Number	Compound	Unit area			Odor description*
		15 minutes	20 minutes	25 minutes	
Acids					
1	Acetic acid	52516603	24314486	26546210	Sharp pungent sour vinegar
2	Butanoic acid, 3-methyl-	nd	19774102	22028257	-
3	Propanoic acid, 2-methyl-	16546607	8603800	9254990	Floral
4	Acetic acid, hydroxy-	nd	nd	2107136	-
5	Butanoic acid	nd	1462956	2252853	acidic, sour, cheesy, dairy, creamy, fruity
6	Butanoic acid, anhydride	nd	3544391	nd	butter
7	Pentanoic acid	nd	nd	1473241	-
8	Hexanoic acid	6000900	6939664	8362320	cheesy, fruity, phenolic, fatty, goaty
9	Hexanoic acid, 2-ethyl-	3397483	4772511	3842763	-
10	Octanoic Acid	449949	1012675	353878	rancid, soapy, cheesy, fatty, brandy
11	Hexanoic acid, 3,5,5-trimethyl-	nd	1106304	880621	-
12	Propanoic acid	1619791	nd	nd	acidic, dairy, fruity
13	Propanedioic acid, propyl-	nd	1410109	nd	-
14	Pentanoic acid, 3-methyl-	34538559	nd	nd	-
15	3,3-Dimethylheptanoic acid	1006093	nd	nd	-
	Total	**116075985**	**72940998**	**77102269**	
Hydrocarbons					
1	β-Myrcene	11777863	nd	14444468	-
2	Eicosane	nd	2933548	nd	Waxy
3	trans-β-Ocimene	9169000	8280719	8882656	green, tropical, woody, floral, vegetable
4	4-trans,6-cis-Allocimene	6248251	5548311	5773306	terpene, sweet, fresh, floral
5	Naphthalene	2179777	2794132	1856530	pungent, dry, tarry
6	β-Ocimene	3162147	nd	nd	green, tropical, woody, floral, vegetable
7	α-Ocimene	nd	nd	2671155	fruity, floral, wet cloth
8	1-Hexene, 3,3-dimethyl-	nd	nd	1042848	-
9	β-Pinene	nd	12503533	nd	cooling, woody, pine, terpenic, fresh, minty, eucalyptus, camphoreous, spicy, peppery, nutmeg
10	Nonane, 2-methyl-5-propyl-	nd	1603316	nd	-
11	cis-β-Ocimene	nd	2341784	nd	sweet herbal
	Total	**32537038**	**36005343**	**34670963**	
Ketons					
1	2-Heptanone	101637519	105018277	116838758	cheesy, fruity, coconut, waxy, green
2	Acetophenone	4383987	2801839	2932580	sweet, pungent, hawthorn, mimosa, almond, acacia chemical
3	Cyclobutanone, 2-ethyl-	6933251	nd	1947896	-
4	2-Nonanone	952296	913878	913145	cheesy, green, fruity, dairy, dirty, buttery
5	2,2,3-Trimethyl-1-phenyl-3-buten-1-one	nd	2586175	nd	-

Number	Compound	Unit area			Odor description*
		15 minutes	20 minutes	25 minutes	
6	2-Butanone, 3-methyl-	nd	nd	939913	camphor
7	Butyrolactone	10205522	11263851	9061093	-
8	Pyranone	2854167	4706813	4847336	-
9	Ethanone, 1-(1H-pyrrol-2-yl)-	nd	nd	2610159	-
10	Ethanone, 1-(2-furanyl)-	nd	2576202	nd	-
11	[1,3]Diazepan-2,4-dione	2252763	nd	nd	
12	2-Butanone, 3-hydroxy-	nd	720344	nd	-
13	2(3H)-Furanone, dihydro-3-hydroxy-4,4-dimethyl-	nd	nd	3412847	-
14	2H-Pyran-2-one, tetrahydro-	836547	1042121	nd	-
15	Pantolactone	nd	1419263	1033423	cotton candy
16	2-Pyrrolidinone	nd	6288766	4348169	-
17	2-Pyrrolidinone, 1-propyl-	nd	nd	567064	-
18	2-Pyrazolin-5-one, 1,3-dimethyl-	nd	1119158	nd	-
19	2-Pyrrolidinone, 1-butyl-	nd	708874	nd	-
	Total	**130056052**	**141165561**	**149452383**	
Others					
1	2-Acetyl-1H-pyrrole	nd	3851909	nd	sweet, musty, nutty, tea
2	Maltol	nd	780926	nd	sweet, cotton, candy, caramellic, jammy, fruity, berry
3	Phenol, 2-methyl-	1763045	nd	nd	meaty, onion, garlic, sulfurous, eggy
4	Linalool oxide	922493	nd	nd	green, floral, fatty, woody, fermented, herbal, fruity, berry
5	1-Anthracenamine	964595	nd	nd	-
6	Hydrazine, (2-methylpropyl)-	2750464	2843888	nd	-
7	Mellein	2779220	nd	nd	-
8	Propane, 2-ethoxy-	nd	2669326	nd	-
9	Octaethylene glycol	606565	nd	nd	-
10	1-Methoxy-5-trifluoroacetoxyhexane	17964229	nd	nd	-
11	Octane, 1-methoxy-	1206732	nd	nd	-
12	Carbazole, 2,3,6-trimethyl-	nd	686023	nd	-
13	1-Butyne, 4-methoxy-	nd	2672581	nd	-
14	5-(p-Aminophenyl)-4-(p-tolyl)-2-thiazolamine	nd	nd	5996719	-
15	Hexane, 3-methoxy-	nd	nd	3105981	-
16	Isobenzofuran	2954036	nd	nd	-
17	Pyrrole, 4-ethyl-2-methyl-	nd	1726113	nd	-
18	Piperazine, 2-methyl-	nd	nd	1807664	-
19	Oxime-, methoxy-phenyl-	2841942	2232329	1701349	-
20	2-Hexene, 1-methoxy-, (E)-	832110	nd	nd	-
21	2-Anthracenamine	nd	nd	531778	-
	Total	**35585431**	**17463095**	**13143491**	

*Source : (Anonymous, 2016)

Pyrazines

Pyrazines are those of the most important volatile compounds in roasted cocoa, represent about 40% for flavor (Aculey *et al.*, 2010; Owusu *et al.*, 2012). Pyrazines formation occurs through Maillard reaction. The numbers of pyrazines at15, 20 and 25 minutes roasting were 10, 12 and 9 respectively. Between 15 to 20 minutes, pyrazines were increased as its formation demands great activation energy, longer roasting time followed cocoa liquor temperature increase led to higher number of pyrazine in the presence of tetramethylpyrazines precursors i.e diacetyl and acetoin (Hashim *et al.*, 1999). However, the majority of pyrazines were originated from the strecker degradation during Maillard reactions.

Our study showed that 2-acetyl-3-methylpirazine and pyrazine,2-ethyl-5-methyl responsible for nutty flavor were found only at 20 minutes, during which highest compounds number and unit area were also obtained, and not detected at 15 and 25 minutes. The highest unit area was found on 2.5-dymethyl-pyrazine generated nutty, peanut, musty, earthy, powdery, and slighty roasted cocoa powder nuance odor. These findings were in agreement with Jinap *et al.* (1998) reported that 2.5 dimethyl pyrazine had relatively high unit area.

Esters

Esters were the second largest group of volatile compounds after pyrazines (Afoakwa *et al.*, 2009; Jinap *et al.*, 1998). Most esters characteristically produce fruity/flowery and honey flavor notes (Aculey *et al.*, 2010; Owusu *et al.*, 2012). Jinap *et al.* (1998) previously reported that unit area of esters will increase on all of roasting time even at low temperatures, but the result of this study showed that the esters can only be identified at 20 minutes in form of acetic acid, 2-phenylethyl ester. Jinap *et al.* (1998) also mentioned that2-Phenylethylacetate is responsible for Asia cocoa liquor characteristic aroma with flowery and honey notes. Rodriguez-Campos *et al.* (2012) mentioned that 2-phenylethyl acetate and ethylphenyl acetate in high concentrations were advantageous on cocoa aroma characteristics correlated to them.

The highest concentration of these compounds was found at 6 and 8 fermentation days. A study by Frauendorfer&Schieberle (2008) mentioned that yeast metabolism can result in esters during fermentation. Whereas in this study, ester in roasted cocoa liquor was obtained from unfermented cocoa beans.

Aldehydes

Aldehyde is one of flavor compounds commonly found various products and often used as food flavoring. Resulted from degradation of unsaturated fatty acids in cocoa fat during roasting process, aldehyde has bitter and almond-like characteristic (Belitz *et al.*, 2001). The results showed that the highest area was obtained by 3-methyl butanal responsible for ethereal aldehydic, chocolate, peach, and fatty flavor notes. The compound is an important flavor of cocoa similar to pyrazine formed by strecker degradation of amino acids (Frauendorfer & Schieberle, 2006). Jinap (1994) also mentioned that 3-methyl-butanal could be produced from precursors such as isoleucine and leucine, by lactic acid bacteria during fermentation. In unroasted and roasted cocoa, the compound yield smalty and chocolate flavor notes (Frauendorfer & Schieberle, 2008; Schnermann & Schieberle, 1997). At 15 and 20 minutes roasting, other aldehyde with caramel flavor notes, such as furfural, was also identified. In general, there were 9, 12 and 6 aldehyde compounds found at 15, 20 and 25 minutes roasting, respectively. The highest number of compounds was identified at 20 minutes. These compounds affected roasted cocoa liquor flavor by producing fruity and flowery notes.

Alcohols

Alcohol fermentation generated compound attached in dry cocoa beans and cocoa fat. Alcohol produces sweet, fruity, alcoholic, balsamic, and green flavor notes depending on the molecular structure. High alcohol content generates desirable flowery and candy flavor notes (Aculey *et al.*, 2010; Frauendorfer & Schieberle, 2008), and also responsible for the fruity, floral, caramel-like, sweet, and honey flavor notes (Afoakwa *et al.*, 2009). During roasting, alcohol would be reduced due to volatilization or destruction. The result showed that the highest area was in 15-minutes-roasting, while the highest compound was 2,3-butanediol. It produced fruity, creamy, and buttery flavor notes. Several compounds with fruity flavor, such as phenylethyl alcohol, were also found in all roasting time. However, the highest unit area was in 20 minutes. Jinap *et al.* (1998) mentioned that benzylalcohol responsible for flowery flavor notes was identified at 20 and 25 minutes roasting. Generally, at 15, 20 and 25 minutes roasting generated 16, 13, and 16 compounds, respectively.

Acids

The results showed that the numbers of acids found at 15, 20 and 25 minutes roasting were 8, 10, and 10 respectively (Table 2). Acetic acid had the highest area at 15 minutes roasting, a compound causing acidity in chocolate, produced desirable sharp pungent odor of vinegar sour flavor notes. Frauendorfer&Schieberle, (2008) reported that 70% of acetic acid was removed during roasting. It was indicated that longer roasting time led to lower area unit, represented decreasing concentration of the compound. Organic acids increasing concentration was the result of cocoa pulp sugar metabolisms (Bonvehí, 2005). Other compound, such as 3-methyl butanoic acid, predominantly found at 20 and 25 minutes roasting. Those two were part of 35 most active flavor compounds cocoa. The presence of the compounds proved that carboxylic acid groups had an impact on cocoa flavor formation (Frauendorfer & Schieberle, 2006).

Hydrocarbons

Unsaturated hydrocarbons were important compounds played major role in foods flavor formation. This study found 5, 7, and 6 hydrocarbon compound at 15, 20 and 25 minutes roasting, respectively, with β-myrcene to have the highest area at 15 and 25 minutes. Other compound which only found at 20 minutes, β-pinene, responsible for cooling, woody, pine, terpenic, fresh, minty, eucalyptus, camphoreous, spicy, peppery and nutmeg flavor notes, was identified to have high unit area. In addition, there were also several other compounds found only in 20 minutes i.e. eicosane, nonane, 2-methyl-5-propyl-, and cis-β-Ocimene. Generally, the highest area and most of hydrocarbons were identified at 20-minutes-roasting.

Ketones

Ketones were responsible for buttery flavor notes, with the highest area obtained by 2-heptanone at 25-minutes-roasting. It produced cheesy, fruity, coconut, waxy and green flavor notes. The compounds were identified to have higher area with longer roasting time, indicated higher produced compound concentration. Several other compounds responsible for sweet and almond flavor notes were acetophenone, while2-Nonanone produced buttery flavor notes. Overall, the longer the roasting times the higher the number of produced compounds.

Others

During the roasting, from the seven compound group classifications, there were several other produced compounds affected roasted unfermented cocoa liquor flavor. Some caramel producing compounds from maltol and 2-Acetyl-1H-Pyrrole were identified only in 20 minutes roasting time. The later was produced from proline by streker degradation during the Maillard reaction as mentioned in previous research (Afoakwa *et al*., 2009). At 25 minutes, phenol-2-methyl produced during drying was also identified. This compound was associated with undesirable smoky and roasted cocoa flavor notes (Jinap *et al*., 1998; Serra Bonvehí & Ventura Coll, 1998).

CONCLUSIONS

The roasting times affects the physicochemical characteristics (temperature, pH and color) of unfermented cocoa liquor roasted. The results showed that the longer the roasting time, the higher the temperature, °Hue and ΔE value, but the lower of pH and L value of cocoa liquor roasting. Identified flavor compounds profile was strongly influenced by roasting time. The highest area and number of compound such as pirazine and aldehydes were obtained at 20 minutes. Even, the esters were only identified on this time. These result also confirmed the sensory analysis from the panelists, which showed that a very strong flavor was produced at 20-minutes-roasting. Therefore, unfermented cocoa liquor using oil bath method needs to consider the roasting time to produce high-flavor compounds.

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CONFLICT OF INTEREST

Authors declare no conflict of interest.

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