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Effect of roasting time on quality, acceptability, and volatile aroma components of roasted defective coffee beans

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Abstract

This study aimed to evaluate the effect of roasting time of defective coffee beans on the quality, acceptability, and volatile aroma components. Green defective coffee beans were roasted for 9, 11, 13, 15, or 17 min at 200°C. Water activity, moisture content, and color parameters decreased with increasing roasting time. In addition, the beans that were roasted for 13 minutes at 200°C received the highest mean liking score from 60 panelists (7.22 ± 1.34). Volatile aroma compounds were extracted from the roasted beans using headspace solid-phase microextraction (HS-SPME) and analyzed using gas chromatograph-mass spectrometry/olfactometry (GC-MS/O). Furans (68.54%) were the most abundant volatile aroma compound in roasted defective beans, followed by pyrazines (16.45%), phenols (5.17%), pyrroles (5.07%), pyridines (3.53%), and ketones and lactones (1.24%). Furthermore, 3-ethyl-2,5-dimethylpyrazine had the highest odor activity value (OAV) in roasted defective beans, which contribute to its burnt and sweet notes.

Keywords: Defective coffee beans, Roasting time, Coffee quality, Consumer acceptance, Volatile aroma components, SPME

1. Introduction

Coffee is one of the most consumed beverages around the world. Total coffee production has increased globally to 3.04 million tons in 2020 [1]. However, defective beans accounts for about 20 percent of total coffee production, which amounts to 0.61 million tons annually [2]. These defective beans are generally rejected from the market because of their negative impact on the sensory qualities of coffee products [2]. Common reported defects include black, sour, brown, broken, and immature beans. These could result from impaired bean formation inside coffee cherries or inadequate processing methods (strip-picking harvesting and processing practices) [2,3]. A previous study showed that off-aroma or flavor can result from black, sour, and brown beans, but not broken and immature beans [4]. Oliveira et al. [2] reported that the proximate compositions of defective and non-defective Arabica green coffee beans were similar, except for the ash content. These suggest that the volatile aroma compounds in broken and immature beans might be similar to in non-defective coffee beans [5].

The roasting process can modify the chemical composition of the beans, resulting in a unique coffee color, aroma, and flavor. During roasting, moisture content and density of the beans decrease, while the porosity increase. Chemical reactions that occur are the Maillard reaction, caramelization, lipid oxidation, decomposition of phenolic compounds, and pyrolytic reactions, which contribute to the characteristic coffee flavor and aroma [6-9]. The extent of reactions and thermal decomposition determines the amount of small, volatile molecules that cause aroma [10].

Adequate control of roasting time and temperature is essential to allow chemical reactions to proceed as desired. Conventional roasting is typically done at temperatures from 200 to 230°C for periods of 12 to 20 min [11]. These settings can be varied depending on the degree of roasting intended, type of roasting machine, and characteristics of the coffee beans. The degree of roasting can be monitored using multiple parameters, such as the color of the beans, loss of mass or moisture, development of flavor and aroma, or chemical changes for certain

components [11,12]. A combination of these parameters is recommended for accurately determining the degree of roasting [11,13]. Furthermore, evaluation of coffee quality in the Brazilian coffee sector still relies on expert classification and sensory characteristics [14]. However, there is a need to develop evaluation methods that consider consumer preferences.

To the best of our knowledge, there are only a few studies on the quality and acceptance of coffee aroma from defective coffee beans and the effect of roasting time on these outcomes. Moreover, there is a lack of reports that determined the volatile aroma components of roasted defective coffee beans. Thus, the objectives of this study were to investigate the effect of roasting time on the properties of defective coffee beans and to identify volatile aroma compounds in selected defective beans.

2. Materials and methods

2.1 Materials

Broken and immature green Arabica coffee beans (Coffea Arabica) were purchased from MTT Organic Coffee Farm in Chiang Mai province, Thailand. Bean samples were stored in sealed HDPE-laminated jute bag and kept in a dry area at ambient temperature. All chemicals, reagents, and solvents were analytical grade.

2.2 Sample preparation

Roasted coffee beans were prepared according to the method reported by Franca et al. [11] with some modifications. Green defective beans (20 g) were placed in a metal tray lined with parchment paper baking sheet and placed in preheated oven (SO6102TS, Smeg, Italy) at 200°C. After specific roasting times (9, 11, 13, 15, or 17 min), the roasted beans were placed into another metal tray and cooled at room temperature for 15 min. After cooling, the coffee silver skin was removed by sieving. The beans were divided and placed in odorless laminated bags (MOPP/VMPET/PE) equipped with CO_2 degassing valves. The beans were kept in a dark place at 25 ± 2°C for not more than 14 days before further analyses.

2.3 Determination of moisture, ash, lipid, protein, and carbohydrate contents

The proximate composition of the beans, including moisture, ash, lipid, protein (using nitrogen factor of 6.25), and carbohydrate contents, were determined using established AOAC techniques [15].

2.4 pH measurement and determination of total acidity

Coffee bean sample (3 g) was blended in 50 mL of hot water at 80°C and cooled to room temperature. The pH was measured using a pH meter (Seven Compact S220, Mettler Toledo, Switzerland) [16]. Titratable acidity was determined following a previously published method [15]. Briefly, green coffee powder (10 g) was mixed with 75 mL of 80% ethanol and stirred for 16 h. The mixture was filtered, and 25 mL of filtrate was diluted in 100 mL distilled water. The resulting solution was titrated against 0.1 N NaOH with phenolphthalein as the indicator. Titratable acidity was calculated as the volume of 0.1 N NaOH required to neutralize a gram of sample (wet matter) and expressed as mL 0.1 N NaOH/g [16].

2.5 Determination of water activity (Aw)

Water activity of the coffee bean samples was determined using the Aqua Lab (4TE, Meter, USA) analyzer.

2.6 Color measurement

The color of the coffee beans was determined using a colorimeter (CR-400, Konica Minolta, Japan). The color parameters were expressed using the CIE Lab scale: L^* (lightness), a^* (redness), and b^* (yellowness). The total color difference (ΔE^*), chroma (C^*), and hue angle (H^o) were calculated using previously published formulae [17,18]. Browning index (BI) was calculated using the method described by Maskan [17].

2.7 Sensory evaluation

Sixty panelists (20-37 years old, 17 males and 43 females) who regularly drink at least 5 cups of coffee per week were invited to participate. The evaluation was conducted in booths illuminated with red light to minimize interference with visual perception. The coffee beans were ground to particle sizes between 250 to 500 μm. Ground samples were presented in 30-g portions contained in 75-mL amber glass sample vials with plastic-lined

caps. The samples were labeled with a 3-digit code and randomly served to the panelists who gave liking scores to each coffee aroma using a 9-point hedonic scale [19].

2.8 HS-SPME, GC-MS/O analysis

Headspace solid-phase microextraction (HS-SPME) was performed using a modification of the method described by Agresti et al. [4]. Briefly, 500 mg of ground roasted coffee was placed in a 20-mL vial, sealed with a PTFE-coated silicone septum (Agilent, California, USA). A volume of 10 µL of 100.047 µg/mL 2,4,6-trimethylpyridine was spiked into the vial with the sample. A Supelco 50/30 µm Divinylbenzene/Carboxen/Polydimethylsiloxane (CAR/DVB/PDMS) SPME fiber (Pennsylvania, USA) was used to extract volatile compounds at 60°C for 20 min with agitation at 250 rpm.

The SPME fiber was introduced to the GC system using thermal desorption unit (TDU, Gerstel, Germany). It was programmed to maintain temperature at 40°C for 5 min and then heated at a rate of 5°C/min to a final temperature of 220°C, which was maintained for another 5 min. Volatile compounds were transferred for analysis using splitless mode and were eluted in an Agilent 7890B gas chromatograph (GC) equipped with a mass spectrometer (MS) and olfactometer (sniffing port, O). Compounds were separated on an Agilent DB-Wax column (30 m × 0.25mm × 0.25 µm) (Woodbridge, USA). Helium gas was used as carrier gas at a constant flow rate of 2.0 mL/min. The oven temperature was programmed at an initial temperature of 40°C maintained for 5 min, then increased at a rate of 5°C/min to 220°C, which was held for another 5 min.

At the end of column, fractions were split into MS and sniffing port. The MS conditions were set as follows: transfer line temperature, 250°C; ionization voltage, 70 eV; mass range (scan mode), 35 to 350 amu. The temperature of the olfactometer was maintained at 150°C. To obtain the retention index (RI) of each compound, retention times of alkane standards from C10 to C40 (Sigma-Aldrich, St. Louis, USA) were used in the calculation method described by Kulapichitr et al. [20]. Volatile compounds were identified by comparing their mass spectra, RI, and odor description to available libraries (NIST 14.0 library) and other references. Quantities of analytes was calculated using the ratio of the peak area of each compound to the peak area of the internal standard (2,4,6-trimethylpyridine). In addition, the odor activity value (OAV) of each compound was also calculated following a previously published method [21]. Triplicate experiments were performed, and the mean values and standard deviations were reported.

3. Results and discussion

We first determined the proximate composition of defective green coffee beans, which are shown in Table 1. The moisture, ash, protein, lipid, and carbohydrate contents of the beans were 8.53, 3.85, 12.85, 10.17, and 64.59 percent, respectively. These results are comparable to previously reported ranges of 8.64-9.99 for moisture, 3.00-4.50 for ash, 11.56-15.27 for protein, 9.00-15.66 for lipid, and 60.00-63.99 for carbohydrate [3,8,13,22].

Table 1 Proximate composition, titratable acidity, and pH of defective green coffee beans.

Composition (%, wb)					Titratable acidity	pH
Moisture	Ash	Protein	Lipid	Carbohydrate	(mL 0.1N NaOH/g)	
8.53 ± 0.14	3.85 ± 0.05	12.85 ± 0.36	10.17 ± 0.58	64.59 ± 0.81	2.35 ± 0.10	5.98 ± 0.02

Means (± standard deviation) of triplicate analysis.

We next determined the titratable acidity and pH of the defective coffee beans. As shown in Table 1, defective green beans had a titratable acidity of 2.35 ± 0.10 mL 0.1N NaOH/g and pH of 5.98 ± 0.02, suggesting slight acidity that may have caused its sour taste. Coffee acidity plays a significant role in shaping its flavor [23]. The overall sensorial profile of coffee results from the effects of various factors, such as sourness, bitterness, savory, coffee flavor, and sweetness [3].

We measured the moisture content and Aw of the green coffee beans for different roasting times, as seen in Table 2. Initial moisture content (MC) is a crucial factor in aroma formation in roasted beans. At lower MC, water mobility is restricted, resulting in underdeveloped roasted beans. On the other hand, a higher MC can retard evaporation and promote case hardening on the bean surface.

Across increasing roasting times in green coffee beans (Table 2), MC decreased from 8.53% to 0.80%. The Aw of the defective green coffee bean was 0.532 (data not shown), which significantly dropped to 0.227 after 17 minutes of roasting. During the early stage of roasting, water in green coffee bean matrix evaporated, which decreased the MC [2,13,25]. At the same time, water vapor increases the pressure within the bean, resulting in bean expansion [24,25], increasing the risk for degradation of the cellular and intercellular matrices of coffee beans. At the same time, pyrolysis and other degradation reactions caused by heating could produce CO_2, which creates pores in the beans and facilitate water evaporation. These results are consistent with data reported by Fadai

et al. [25] which found decreasing MC as a result of water evaporation during roasting from an initial value of 12 % (wb) to approximately 2% (wb).

Table 2 Water activity (A_w) and moisture content (MC) of roasted coffee beans affected by roasting time.

Roasting time (min)	A_w	MC (% by wt)
9	$0.322^{a} \pm 0.003$	$2.29^{a} \pm 0.17$
11	$0.276^{b} \pm 0.003$	$1.37^{b} \pm 0.17$
13	$0.258^{c} \pm 0.002$	$1.46^{b} \pm 0.20$
15	$0.238^{d} \pm 0.001$	$0.87^{c} \pm 0.03$
17	$0.227^{e} \pm 0.003$	$0.80^{c} \pm 0.02$

Means ± standard deviation (n=3). Different letters within a column are significantly different ($p \leq 0.05$).

The impact of roasting time on coffee bean color is shown in Table 3. The L^*, a^*, and b^* of coffee beans decreased progressively with increasing roasting times. The total color difference (ΔE^*) values were significantly different ($p \leq 0.05$), with the highest ΔE^* value of 14.7 after 17 min of roasting. This high ΔE^* value indicates a marked change in the color from the original green beans. In addition, chroma (C^*), hue angle (H^o), and browning (BI) decreased over increasing roasting time. These suggest that thermal processing affected chemical transformations in the beans. Additionally, the change in hue angle indicates that green coffee beans transition from a yellowish tint (90) to a reddish-orange shade (45) after roasting.

Table 3 Color values, ΔE^*, C^*, H^o, and BI values of roasted coffee beans affected by roasting time.

Roasting time (min)	Color values			ΔE^*	C^*	H^o	BI
	L^*	a^*	b^*				
9	$33.28^{a} \pm 0.04$	$7.83^{a} \pm 0.03$	$18.43^{a} \pm 0.03$	$8.98^{d} \pm 0.03$	$20.02^{a} \pm 0.04$	$66.98^{a} \pm 0.05$	$94.92^{a} \pm 0.11$
11	$31.31^{b} \pm 0.10$	$7.40^{b} \pm 0.02$	$16.74^{b} \pm 0.06$	$8.61^{e} \pm 0.03$	$18.3^{b} \pm 0.06$	$66.14^{b} \pm 0.08$	$91.22^{b} \pm 0.24$
13	$28.31^{c} \pm 0.03$	$6.90^{c} \pm 0.01$	$15.06^{c} \pm 0.11$	$9.77^{c} \pm 0.00$	$16.57^{c} \pm 0.10$	$65.39^{c} \pm 0.16$	$91.27^{b} \pm 0.65$
15	$23.49^{d} \pm 0.09$	$6.13^{d} \pm 0.05$	$10.99^{d} \pm 0.05$	$13.58^{b} \pm 0.08$	$12.58^{d} \pm 0.06$	$60.83^{d} \pm 0.16$	$80.68^{c} \pm 0.17$
17	$22.33^{e} \pm 0.03$	$5.60^{e} \pm 0.02$	$9.78^{e} \pm 0.01$	$14.70^{a} \pm 0.04$	$11.27^{e} \pm 0.02$	$60.23^{e} \pm 0.09$	$74.81^{d} \pm 0.17$

Means ± standard deviation (n=3). Different letters within a column are significantly different ($p \leq 0.05$).

The brown color could have resulted from different possible pathways, including Maillard reactions, thermal oxidation, Strecker degradation, polymerization of polyphenols, and caramelization [7,9]. Previous research has reported that the L^*, a^*, and b^* values of coffee beans was negatively correlated with roasting temperature, suggesting that the brown color enhanced with longer roasting times [9,28]. Mendonça, Franca, and Oliveira [9] also observed that defective coffee beans underwent a significant change in color after roasting, with C^* decreasing from 19 to 9 and H^o values from 91 to 79. In a related study, Bicho et al. [28] reported a reduction in the hue angle with an increase in the degree of roasting, with the lowest value observed at 30.

Table 4 Average liking scores of roasted coffee beans affected by roasting time.

Roasting time (min)	Liking score
9	$5.29^{d} \pm 1.70$
11	$6.52^{b} \pm 1.35$
13	$7.22^{a} \pm 1.34$
15	$5.89^{c} \pm 1.65$
17	$3.55^{e} \pm 1.35$

Means ± standard deviation (n=60) with different letters within a column are significantly different ($p \leq 0.05$).

To determine the effect of roasting time on the acceptability of, we asked frequent coffee drinkers to evaluate the aroma of the coffee beans using a 9-point hedonic scale. The sensory liking scores of all samples are shown in Table 4. Beans roasted at 200°C for 13 min showed the highest liking score (7.22, $p \leq 0.05$), indicating the strongest preference for this sample. Based on the comments from the panelists, beans that were roasted the longest (17 min) had an unpleasant burnt aroma, while the sample roasted for 9 min had a green and beany aroma. During roasting, coffee beans turn dark brown and become brittle and swollen [10]. Moreover, oils are released and various volatiles compounds are formed [3]. These chemical reactions include Maillard reactions, caramelization, degradation reactions (phenolic acid, carotenoid, sulfur amino acids, trigonelline, chlorogenic acids, quinic acid,

and lipids), Strecker degradation, and other intermediate reactions [6,7]. Because beans roasted for 13 min showed the highest liking score, it was selected for further characterization of volatile aroma compounds.

We used GC-MS/O to identify a total of 31 volatile compounds in the beans roasted for 13 min, as enumerated in Table 5. The most abundant compounds were furans (68.54%), pyrazines (16.45%), phenols (5.17%), pyrroles (5.07%), pyridines (3.53%), and ketones and lactones (1.24%). Among these 31 compounds, 7 were marked "unknown," indicating that these molecules can be perceived by the human nose while sniffing but did not correspond to a peak in the chromatogram. It could be that these compounds contributed to the aroma of the beans even at concentrations below the machine limit of detection.

To identify compounds that actively contribute to the aroma, we analyzed the odor activity values (OAVs) of the compounds. In this scale, humans cannot perceive any aroma from compounds with OAV less than 1. We found that the aroma active compounds found in the sample were 2,3-pentanedione, 1-methylpyrrole, pyridine, furfuryl methyl ether, 2-methylpyrazine, furfural, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine, 2-acetylfuran, furfuryl acetate, 3-ethyl-2,5-dimethylpyrazine, 5-methylfurfural, 2-propionylfuran, γ-butyrolactone, furfuryl alcohol, 6-methyl-2-acetylpyrazine, guaiacol, 2-phenylethanol, 2-acetylpyrrole, 2-pyrrolecarboxaldehyde, 4-ethylguaiacol, 4-vinylguaiacol, and indole. These compounds can be classified into six groups, which represent different odor qualities; pyrazines (burnt, nutty, and potato-like), phenols (phenolic and spicy), furans (fruity, bready, and sweet), pyrroles (musty, animalic, and woody), pyridine (burnt), and ketones and lactones (buttery).

Table 5 Volatile compounds in roasted defective coffee beans.

No.	RI[A]	Ref. RI[B]	Compound	Relative concentration (μg/kg, ppb)	Odor threshold[C] (μg/kg, ppb)	OAV	Odor description	Identification[D]
1	1071	1069	2,3-Pentanedione	82.27 ± 11.23	20[a]	4	buttery, milky	MS,RI,O
2	1198	1195	1-Methylpyrrole	125.06 ± 0.39	40[c]	3	woody	MS,RI
3	1226	1227	Pyridine	748.07 ± 194.82	79[a]	9	burnt	MS,RI,O
4	1245	n.a.	unknown	n.d.	n.a.	n.a.	meaty	O
5	1281	1260	Furfuryl methyl ether	110.57 ± 6.03	n.a.	n.a.	coffee	MS,RI
6	1303	1305	2-Methylpyrazine	1198.99 ± 52.75	60[a]	20	hazelnut, roasted nut	MS,RI,O
7	1419	1410	Furfural	1978.76 ± 377.86	282[a]	7	roasted, bready	MS,RI,O
8	1447	1420	2-Ethyl-6-methylpyrazine	821.63 ± 20.29	40[a]	21	potato, meaty	MS,RI,O
9	1451	1419	2-Ethyl-5-methylpyrazine	690.55 ± 13.53	16[a]	43	nutty, roasted	MS,RI,O
10	1462	1437	2,3,5-Trimethylpyrazine	690.17 ± 9.88	23[a]	30	roasted nut	MS,RI,O
11	1466	1467	2-Acetylfuran	716.99 ± 54.81	10000[a]	<1	balsamic	MS,RI
12	1491	n.a.	unknown	n.d.	n.a.	n.a.	fermented	O
13	1504	1512	Furfuryl acetate	2429.25 ± 141.10	100[b]	24	acidic, fruity	MS,RI,O
14	1510	1499	unknown	n.d.	n.a.	n.a.	meaty	O
15	1517	1480	3-Ethyl-2,5-dimethylpyrazine	842.95 ± 26.48	0.4[a]	2107	burnt, sweet	MS,RI,O
16	1525	1523	5-Methylfurfural	2525.35 ± 365.41	500[a]	5	bready	MS,RI
17	1542	1551	2-Propionylfuran	171.05 ± 20.10	n.a.	n.a.	fruity	MS,RI
18	1549	1592	γ-Butyrolactone	179.71 ± 17.70	1000[a]	<1	fatty	MS,RI
19	1560	1613	Furfuryl alcohol	5502.22 ± 475.46	1900[a]	3	chemical, pungent	MS,RI,O
20	1662	1676	6-Methyl-2-acetylpyrazine	242.60 ± 24.79	300[a]	<1	roasted	MS,RI
21	1769	1815	Guaiacol	373.19 ± 32.11	1.6[a]	233	herbal, spicy	MS,RI,O
22	1836	1857	2-Phenylethanol	238.78 ± 46.81	390[a]	<1	floral	MS,RI
23	1845	n.a.	unknown	n.d.	n.a.	n.a.	nutty	O
24	1914	1927	2-Acetylpyrrole	440.70 ± 45.72	160[a]	3	musty	MS,RI
25	1867	n.a.	unknown	n.d.	n.a.	n.a.	cereal, popcorn	O
26	1941	1978	2-Pyrrolecarboxaldehyde	364.59 ± 50.23	37[a]	10	musty, fermented	MS,RI,O
27	2002	2010	4-ethylguaiacol	173.47 ± 24.52	16[a]	11	musty, spicy	MS,RI,O
28	2118	2146	4-vinylguaiacol	309.10 ± 54.93	19[a]	16	spicy	MS,RI,O
29	2120	n.a.	unknown	n.d.	n.a.	n.a.	pungent	O
30	2196	n.a.	unknown	n.d.	n.a.	n.a.	sweet	O
31	2372	2403	Indole	145.67 ± 19.73	40[a]	4	animalic, pungent	MS,RI,O

[A]RI (wax): Experimental retention index on an DB-Wax column relative to C10-C40 alkane standards.
[B] Ref RI: Reference retention index values from NIST library version 14.0.
[C] Odor threshold values in water (μg/kg, ppb) from literatures: [a]Van Gemert [21], [b]Puvipirom and Chaiseri [29], [C]Czerny and Grosch [30].
[D] Identification methods: MS=mass spectra; RI=retention index; O=odor description.
n.d. is not detected, n.a. is not available.

Volatile compounds in coffee span a wide range of functional classes, including hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, esters, pyrazines, pyrroles, pyridines, sulfur compounds, furans, furanones, phenols, and oxazoles. Among these, furans and pyrazines have been reported to be the most abundant in coffee and most significant contributors to coffee flavor [6]. The large variations in the concentrations of these compounds produces complexity in coffee flavor, resulting in a diversity of unique flavors [7].

Our analysis of volatile compounds using HS-SPME and GC-MS/O techniques revealed that 3-ethyl-2,5-dimethylpyrazine had the highest OAV at 2,107, followed by guaiacol with OAV of 233. Interestingly, these

compounds were not the most abundant in the sample. In contrast, furfuryl alcohol was approximately 5,500 μg/kg in the sample but exhibited only an OAV of 3. Eight other compounds showed OAVs above 10, including 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine, furfuryl acetate, 2-ethyl-6-methylpyrazine, 2-methylpyrazine, 4-vinylguaiacol, 4-ethylguaiacol, and 2-pyrrolecarboxaldehyde. Ten of the compounds had OAVs more than 1, including pyridine, furfural, 5-methylfurfural, 2,3-pentanedione, indole, 1-methylpyrrole, 2-acetylpyrrole, furfuryl alcohol, 6-methyl-2-acetylpyrazine, and 2-phenylethanol.

These molecules could be formed during roasting from the Maillard reaction, which then leads to the formation of Amadori products, and cause sugar fragmentation products through dehydration, fragmentation, cyclization, and polymerization reactions. These reactions could produce many compounds that contribute to coffee flavor [7,31]. In addition, furfural, which was reported as one of the most important compounds in coffee, was generated from the rearrangement of Amadori products, particularly deoxyosones [7]. Furfural can also be produced by the oxidation of furfuryl alcohol, which is a product of the reaction between sugars (deoxyribose or sucrose) and amino acids (cysteine or methionine) [6]. Furans was the most abundant class in the sample (Table 5). We found that 7 furans, including furfuryl alcohol, 5-methylfurfural, furfuryl acetate, furfural, furfuryl methyl ether, 2-acetylfuran, and 2-propionylfuran were were presnt in significant concentrations. Moreover, furfuryl acetate showed the highest OAV (28) among furans and gives off a fruity-like aroma.

Pyrazines were second most abundant chemical class in the sample. These molecules are derived from self-condensation and oxidation of α-aminoketones, which, in turn, are formed from dicarbonyl compounds and amino acids during Strecker degradation [6,31]. Alkyl-substituted pyrazines, such as 2,3,5-trimethylpyrazine and 2-ethyl-6-methylpyrazine, are formed during coffee roasting via the Maillard and Strecker pathways and determined coffee flavor [6,7]. In this class of compounds, 3-ethyl-2,5-dimethylpyrazine was the predominant pyrazine, with the highest OAV in roasted defective coffee beans. Previous work has identified this compound in roasted non-defective beans [4,32,33]. Additionally, various pyrazines, such as 2-methylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine, could contribute to a roasted, nutty, sweet, and potato-like aroma.

Among phenolic compounds, guaiacol exhibited the highest OAV at 233, followed by 4-vinylguaiacol and 4-ethylguaiacol with OAVs 16 and 11, respectively. In addition, 2-phenylethanol was also found in the sample, but with OAV was less than 1. Specifically, guaiacol, 4-ethylguaiacol, and 4-vinylguaiacol had been reported as spicy phenolics [32,33]. These phenolic compounds are thermal degradation products of chlorogenic acids, ferulic, caffeic, and quinic acids. Their concentrations in roasted coffee beans are directly related to the amount of organic acids present [18].

Pyrroles can be produced from deoxyosone fragmentation during the Maillard reaction and Strecker degradation. These compounds are closely related to furans and impact coffee aroma both positively and negatively [6,31]. While some pyrroles, such as 1-ethyl-1H-pyrrole-2-carbaldehyde, contribute to a pleasant roasted aroma, other compounds, such as alkyl and acetylpyrroles, have been found to have musty and fermented odors [6]. In particular, 2-pyrrolecarboxaldehyde had the highest OAV (10) among pyrroles and contributed a musty-like aroma. Moreover, 1-methylpyrrol (OAV = 3) was also detected in the sample, which was associated to a woody-like aroma. This compound was considered as an undesirable compound in defective coffee beans [34].

During roasting, trigonelline degradation may lead to the formation of pyridine and nicotinic acid [7]. Pyridine is commonly associated with the aroma of aged roasted coffee. Moreover, some pyridines derivatives, such as 2-methylpyridine, were reported to confer astringency in coffee [32,33]. In the present study, we found that the pyridine level was around 750 μg/kg and the OAV was 9, which may have contributed to burnt aroma.

Ketones and lactones, such as 2,3-butanedione and 2,3-pentanedione, are the main compounds responsible for buttery and oily properties [33]. Caporaso et al. reported that Arabica coffee beans contain higher concentrations of 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione than Robusta coffee [35]. In our study, only 2,3-pentanedione and γ-butyrolactone were detected in defective green coffee. However, the OAV of γ-butyrolactone was lower than 1, suggesting that it was no a significant contributor to the aroma.

Toci and Farah [5] investigated the chemical composition of green, immature coffee beans and found two key compounds, 2-methylpyrazine and furfuryl acetate, which our present study corroborates (Table 5). Additionally, While the relative abundance of 2-methylpyrazine and furfuryl acetate was 7.3% and 3.9% in their study [5], we found that the relative concentration of furfuryl acetate (~2400 μg/kg) was greater than that of 2-methylpyrazine (~1200 μg/kg).

4. Conclusion

We found that the major components of defective green coffee, in descending order, were carbohydrates, proteins, lipids, moisture, and ash. Its titratable acidity and pH were in the range of previously reported values and indicated slight acidity. Roasting at 200°C for 9–17 min significantly affected water activity, moisture content, and color parameters in the samples. The roasting of defective green coffee beans at 200°C for 13 min showed the

highest liking score. The aroma volatile compounds identified were 3-ethyl-2,5-dimethylpyrazine, guaiacol, 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine, furfuryl acetate, 2-ethyl-6-methylpyrazine, 2-methylpyrazine, 4-vinylguaiacol, 4-ethylguaiacol, 2-pyrrolecarboxaldehyde, pyridine, furfural, 5-methylfurfural, 2,3-pentanedione, indole, 1-methylpyrrole, 2-acetylpyrrole, furfuryl alcohol, 6-methyl-2-acetylpyrazine, and 2-phenylethanol were aroma compounds in the roasted defective coffee beans. Our findings suggest that defective coffee beans can serve as potential raw materials for extracting coffee oil, which can be used as a flavoring.

5. Ethical approval

An acceptance test was conducted in this study, which was approved by the Research Ethics Review Committee for Research Involving Human Research Participants, Health Sciences Group, Chulalongkorn University (COA No. 037/66).

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