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Investigation of volatile compounds of Liberica coffee beans fermented at varying degrees of roasting

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Abstract

Liberica coffee (*Coffea liberica* Bull ex Hiern) has gained worldwide popularity, because it has a unique taste and aroma, and it is able to adapt to peatlands and is more tolerant of disease. Previous studies suggested that fermentation with hydrolytic bacteria could improve flavors, mostly determined by volatile compounds by the roasting process. However, studies about the volatile compounds and their roles in the taste and aroma of this coffee are still limited. This study aimed to investigate volatile compounds from fermented Liberica coffee beans roasted at light roast (150-160°C, 2.2 Mbar, 12 mins); medium roast (175-185°C, 2.2 Mbar, 7.30 mins); and dark roast (200-220°C, 2.2 Mbar, 10 mins). Samples were collected from various fermentation times 0, 4, 8, and 12 hrs and dried. Green beans with a moisture content of 12% were roasted in 3 roast stages. In this work, the extraction of volatile coffee compounds was performed using solid phase microextraction (SPME) and subsequently analyzed by gas chromatography-mass spectrometry (GC-MS). To determine the significance of fermentation time and degree of coffee roasting in the area, a two-way univariate analysis of variance (ANOVA) test was used, followed by a Tukey's honest significant difference (HSD) test with a statistical significance level of $p<0.05$. The results showed that a total of 59 of the 130 volatile compounds had a significant difference at different roasting degrees to the area of compounds with a statistical significance level of $p<0.05$. Those compounds consisted of 5 aldehydes, 18 furans, 4 ketones, 9 phenols, 13 pyrazines, 5 pyridines and 5 pyrroles.

1. Introduction

An agricultural commodity that is most traded as a food product in the world is coffee. Coffee is an increasingly popular product due to its characteristic properties such as flavor, aroma and stimulating effect on humans (Maksimowski *et al.*, 2022). Liberica coffee (*Coffea liberica* Bull ex Hiern) is also called jackfruit coffee due to its unique flavor and aroma of jackfruit. Liberica coffee has acquired an interest in the last few years. This coffee was introduced to replace Arabica coffee due to its adaptability to peatlands and tolerance to disease (Kyaw *et al.*, 2020; Wibowo *et al.*, 2021).

Coffee requires a number of processes before it can be consumed, starting with harvesting, fermenting, drying, roasting, and brewing. The wet fermentation process using a bacterial consortium can increase coffee aroma and flavor diversity. There exists a very extensive literature on the topic of wet fermentation for the removal of mucilage. Demucilization involves the production of metabolic products by bacteria, such as free sugars and free amino acids, which contribute to the formation of volatile chemicals during coffee roasting (Haile and Kang, 2019; Aditiawati *et al.*, 2020). These metabolic products diffuse into the coffee seeds and affect the coffee quality.

Volatile compounds act as fundamental components

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that determine the sensory properties of coffee (Dippong *et al.*, 2022). Volatile components are important to the flavor and aroma characteristics of coffee. Variations in concentration and different sensory potentials of each compound give a unique and diverse aroma, so it is necessary to investigate volatile compounds (Angeloni *et al.*, 2021).

The volatile compound groups commonly found in coffee fermentation are pyrazines and pyridines, which have a beneficial aroma that is desirable in coffee beverages (Ribeiro *et al.*, 2020). In addition, other compounds such as acids, alcohols, aldehydes, ketones, and esters also associated with contribute to the citric, herbaceous, caramel-like, musty, mushroom-like, or fruity flavors desired in coffee beverages (Ribeiro *et al.*, 2020).

The tastes of Liberica coffee were improved after 8 to 12 hrs of fermentation and were categorized as specialty coffee (Wibowo *et al.*, 2021). Specialty coffee has high demands on the quality of sensory factors. Specialty coffee detects volatile compounds that significantly affect the aroma and flavor composition such as 2-ethyl-3,5-dimethylpyrazine (hazelnut), 3-methylbutanal (chocolate), 2,3-dimethyl-5-ethylpyrazine (hazelnut, cacao), linalool (floral, fruity) and others (Piccino *et al.*, 2014; Laukalēja and Krūma, 2018).

Coffee bean types, coffee origin and processing can have an impact on volatile composition (Somporn *et al.*, 2011; Wu *et al.*, 2022). Roasting is the most important step in coffee processing as it determines the taste of the coffee (Maksimowski *et al.*, 2022). Metabolic products in green coffee beans serve as precursors for the compounds responsible for flavor and aroma after roasting. In order to improve the taste of coffee, investigators currently must consider the time and temperature of roasting due to their effects on coffee volatile compounds, which directly affect the aroma of the roasted coffee. The physicochemical changes such as color and aroma in the coffee beans that occur during coffee roasting involve heating (Halim-Lim *et al.*, 2022). These results agree well with existing studies by Wu *et al.* (2022) that showed that the aroma of volatile compounds such as pyrroles, pyridines and phenols were detected to have an increased tendency associated with the increasing roasting level caused by some chemical reactions. Meanwhile, the green coffee beans begin to change color during the roasting process from grey, greenish to brown, dark brown or black.

Previous research only examined the volatile chemicals in green Liberica coffee beans. The compounds found, such as phenols, aldehydes, alcohols, pyrroles, esters, ketones, furans, hydrocarbons and others (Saw *et al.*, 2015). This work is limited to volatile compounds in green beans without roasting. It should be noted here that according to Chindapan *et al.* (2021), complex chemical processes such as the Maillard reaction, Strecker reactions and caramelization take place during roasting, causing the change in volatile compounds. (Herawati *et al.*, 2022) revealed that volatile compounds in roasted Excelca coffee obtained from different postharvest processing, such as 2-ethylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,5-dimethyl-3-ethylpyrazine, guaiacol, 4-vinyl-guaiacol, and isovaleric acid.

The production of Liberica coffee is only 2% in the world (Halim-Lim *et al.*, 2022). The study of the volatile compounds in roasted Liberica coffee beans under various fermentation times and at different roasting degrees is limited. Therefore, the main aim of this work is to investigate volatile compounds in Liberica coffee beans fermented at different roast degrees, divided into 3 degrees: light, medium and dark, using SPME-GC-MS methods.

2. Materials and methods

2.1 Materials

The liberica coffee bean (*Coffea liberica* Bull ex Hiern) cultivars LiM were sourced for this research from the Pakuwon experimental garden of the Indonesian Industrial and Beverages Crops Research Institute (IIBCRI), Sukabumi, West Java, Indonesia. In the polypropylene bags, 10 kg of peeled coffee fruit were fermented at various times using bacterial consortium (*Lysinibacillus fusiformis*, *Bacillus cereus* and *B. subtilis*). Coffee beans were taken in different batches during the fermentation for 0, 4, 8 and 12 hrs. Then the beans were dried until they had a moisture content of 12% (Figure 1).

Figure 1. Liberica coffee green bean.

2.2 Coffee roasting

The green coffee beans were roasted using a roaster (Probat 2 Barrel Roaster-BRZ, Emmerich am Rhein, Germany) following the method described previously by Wibowo *et al*. (2021). The roast degree was set up at 150 - 160°C, 2.2 Mbar, for 12 mins (light), 175 - 190°C, 2.2 Mbar, for 7.30 mins (medium), and 200 - 220°C, 2.2

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Mbar, for 10 mins (dark) (Figure 2). Subsequently, the coffee beans were ground using a coffee grinder and screened through a sieve size of 100 mesh for further analysis.

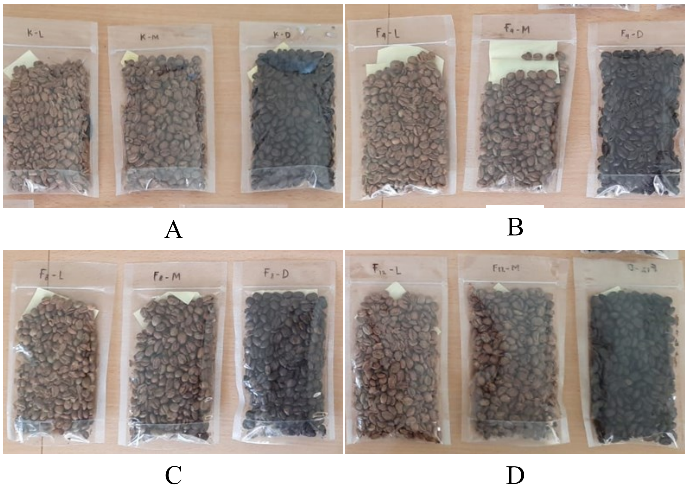

Figure 2. Liberica roasted coffee beans: (A) no fermentation (0 hr), (B) fermented for 4 hrs, (C) fermented for 8 hrs and (D) fermented for 12 hrs.

2.3 Analysis of volatile compounds

Volatile compounds of Liberica roasted coffees were analyzed by solid phase microextraction - gas chromatography-mass spectrometry (SPME-GC-MS) as described by Marek *et al.* (2020) with some modifications. The extraction of volatile compounds was performed with the Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber (2 cm). In a 22 mL SPME vial, 500 mg of ground roasted coffee and 9 mL boiling Milli-Q water were extracted at 80°C for 45 mins. GC-MS analysis to identify volatile compounds was performed using an Agilent 7890A gas chromatograph (GC) system with a 5975C XL electron ionization/ chemical ionization (EI/CI) mass spectrometer (Agilent Technologies, USA). The volatile components extracted from SPME fiber were desorbed in the GC injection port in the splitless mode at 250°C. The volatile compounds were transported by helium carrier gas, which was set at 1 mL/min through the column. A DB-WAX column 30 m × 250 µm × 0.25 µm was used in the analysis. The oven program was set at an initial temperature of 40°C for 1 min, followed by 4°C/min to 150°C for 10 min. Furthermore, a temperature gradient of 30°C/min to 230°C was maintained for 15 minutes. The interface MS condition was set at 250°C. The MS quadrupole temperature was 150°C. The MS ion source temperature was 230°C. In addition, mass scans have been performed with a range of 29 - 550. The identification of volatile compounds was based on a comparison of the mass spectra with the National Institute of Standards and Technology (NIST) 14 database mass spectra until the volatile compounds were identified.

2.4 Statistical analysis

All data were analyzed with IBM SPSS Statistics 26 (IBM, Armonk, NY, USA) using two-way univariate analysis of variance (ANOVA) to look at the main effect between each variable (fermentation time and roasting degrees) on volatile compounds and using the Tukey's HSD tests to test for significant differences in volatile chemicals. P = 0.05 was chosen as the criterion of significance.

3. Results and discussion

The volatile compounds are produced by the metabolism of the beans after harvest, fermentation, and roasting, as well as from the original components of the beans (Elhalis *et al.*, 2021). Among the 130 volatile compounds detected, about 59 compounds were significantly different depending on the degree of roasting. Meanwhile, the effect of fermentation time on volatile compounds in the groups aldehydes (Table 1), furans (Table 2), ketones (Table 3), phenols (Table 4), pyrazine (Table 5), pyridine (Table 6), and pyrrole (Table 7) was similar, there was no significant difference between the four fermentation times.

The presence of microorganisms in the fermentation process contributes to coffee flavor, aroma and other sensory attributes. Bacteria can produce secondary metabolites such as alcohols, esters, ketones and aldehydes, which can diffuse into the beans and enhance the coffee flavor (Elhalis *et al.*, 2021). However, during fermentation, microbes did not significantly affect the volatile compounds. This has been studied by (Galarza

Table 1. Volatile compounds of aldehyde.

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	1.4671	Acetaldehyde	37468487.50^{b}	48854391.75^{a}	47921101.50^{ab}
2	21.5765	Benzene acetaldehyde	3141355.50^{b}	4958661.50^{b}	10163871.50^{a}
3	21.7434	4-methyl-Benzaldehyde	2906457.75^{c}	6167776.75^{b}	14526480.75^{a}
4	2.7566	2-methyl-Butanal	36568638.75a	38001452.00^{a}	27961519.50^{b}
5	32.6793	2-(2-Furyl) pentanal	456780.75b	1610656.50^{b}	14460340.75^{a}

Values with different superscripts are statistically significantly different between different roasting degrees.

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Table 2. Volatile compounds of furan.

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	2.3352	Furan, 2-methyl-	20357632.00[b]	22551782.75[ab]	32218149.50[a]
2	5.1756	Vinylfuran	784018.25[b]	1447883.00[b]	4859735.00[a]
3	16.3292	Furfural	15420552.50[b]	41746526.50[a]	30144138.50[a]
4	17.5833	2-Acetylfuran	3769169.25[b]	12759772.50[a]	14882479.25[a]
5	19.3716	3-Furan	1180462.00[b]	1466725.00[b]	3845598.75[a]
6	20.1692	2-Methylbenzofuran	1361978.25[b]	1499791.75[b]	4038155.00[a]
7	20.7668	2-Furfurylfuran	1322978.50[c]	4361917.50[b]	52712883.75[a]
8	22.4246	2-Furanmethanol	20186997.00[c]	29416743.00[b]	53671253.50[a]
9	22.8025	2-Furfuryl-5-methylfuran	3960683.25[c]	8923492.75[b]	64804559.50[a]
10	23.6644	2-hexyl-Furan	2185380.00[c]	3469472.25[b]	8866728.75[a]
11	25.4929	2-heptyl-Furan	890233.75[b]	2981808.00[b]	9876625.00[a]
12	30.1988	2-Furan, 2'-vinylenedi-	2928284.75[b]	4362006.00[b]	16036432.00[a]
13	31.8704	2-Methylselenomethylfuran	3741346.00[c]	10730289.75[b]	72882907.00[a]
14	32.237	5-furfuryl-5-methyl-	1514981.00[b]	2315739.50[b]	10458327.50[a]
15	18.6707	2-Furfuryl acetate	3776807.00[c]	12966884.75[b]	48124810.00[a]
16	19.6245	5-Methylfurfural	9533116.25[b]	34673661.25[a]	43250512.00[a]
17	25.9993	2-Furfuryl methyl disulphide	578271.25[b]	1659944.75[b]	18695742.50[a]
18	29.9296	Furfuryl ether	1978184.50[b]	3584241.50[b]	77407084.50[a]
19	31.6801	Furfuryl sulfide	1306501.25[b]	1457442.00[b]	27388611.00[a]

Values with different superscripts are statistically significantly different between different roasting degrees.

Table 3. Volatile compounds of ketones

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	4.8812	3-Hexanone	1867796.75[b]	5782475.00[a]	2908954.00[ab]
2	18.5559	1-Acetoxy-2-butanone	12184746.25[a]	7455573.75[ab]	6499511.00[b]
3	25.644	β-Isophorone	959852.50[c]	3085572.25[b]	13211918.75[a]
4	31.453	3-methyl-2-(2-pentenyl)	2514119.50[b]	3178155.25[b]	9954209.25[a]

Values with different superscripts are statistically significantly different between different roasting degrees.

Table 4. Volatile compounds of phenol

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	6.9435	2-methyl phenol	1147878.75[c]	2992228.00[b]	6466939.50[a]
2	27.6486	2-methoxyphenyl,	8933051.50[b]	7521396.75[b]	36789501.75[a]
3	28.9102	2,6-dimethylPhenol, -	1074458.25[b]	1737279.25[b]	8775935.50[a]
4	30.699	4-tert-amylphenol	2404782.00[b]	3955201.50[b]	7857740.50[a]
5	30.829	3-methyl-Phenol	3552553.50[b]	6877757.50[b]	16739660.25[a]
6	31.3314	3-Allyl-6-methoxy phenol	3833799.25[b]	5819140.50[b]	15295215.75[a]
7	30.3671	4-Ethylguaiacol	8314877.75[b]	4974143.50[b]	103026386.75[a]
8	31.5139	4-Vinylguaiacol	139753494.25[b]	137901068.50[b]	206696806.50[a]
9	34.1797	Vanillin	2503972.750[b]	2022393.000[b]	6662116.500[a]

Values with different superscripts are statistically significantly different between different roasting degrees.

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Table 5. Volatile compounds of pyrazine.

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	5.2834	3-Methylpyridazine	3129095.75[ab]	3874601.75[a]	2396523.50[b]
2	10.3353	methyl-pyrazine	6309865.50[b]	11792478.00[ab]	13550193.75[a]
3	12.0688	2,5-dimethyl-pyrazine	4245331.75[b]	12199847.75[a]	9205461.00[ab]
4	14.6373	2-ethyl-3-methyl-pyrazine	7373091.00[b]	12870817.00[a]	8815971.75[ab]
5	17.1601	2-methyl-6-vinyl-pyrazine	5515172.00[a]	3198738.25[b]	3212064.25[b]
6	17.2371	2-methyl-3-pyrazine,	14818106.25[a]	1548282.50[b]	1670711.00[b]
7	17.917	2,5-dimethyl-3-propyl- pyrazine	525805.75[a]	526510.75[a]	2618129.75[b]
8	18.341	2-methoxy, 3-isobutyl pyrazine	5096344.00[b]	52116331.25[a]	3132740.75[b]
9	20.274	1-methyl ethenyl-pyrazine,	1720723.25[b]	4160437.75[a]	5472164.75[a]
10	21.0731	6,7-dihydrocyclopentapyrazine	2481427.75[b]	4568567.25[ab]	6639919.75[a]
11	21.2328	2-Isoamyl-6-methyl pyrazine	3972436.75[b]	8614572.50[a]	11430360.25[a]
12	22.0373	2-methyl-6- pyrazine	2438597.75[b]	3903244.00[b]	10642246.50[a]
13	23.7578	2-methyl-6-propenyl-pyrazine,	3073871.50[b]	2661269.75[b]	12171010.00[a]

Values with different superscripts are statistically significantly different between different roasting degrees.

Table 6. Volatile compounds of pyridine.

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	8.0328	Pyridine	2315694.00[c]	10697026.50[b]	21182432.00[a]
2	11.2046	Pyridine, 3-methyl-	1057528.2[b]	4021397.00[a]	6141880.25[a]
3	16.8	Pyridine, 3-ethenyl-	3091923.00[b]	7624261.00[a]	4011936.50[b]
4	30.923	3-Pyridinemethanol	3088027.25[b]	4958084.25[b]	28778023.25[a]
5	32.1441	3-Pyridinol, 2-methyl-	1671928.50[b]	1650441.50[b]	19467731.25[a]

Values with different superscripts are statistically significantly different between different roasting degrees.

Table 7. Volatile compounds of pyrrole

No	RT (min)	Compound	Roasting degree		
			Light	Medium	Dark
1	6.6379	1-Methylpyrrole	1281344.75[b]	969377.75[b]	2520917.75[a]
2	20.6299	1-Ethyl-2-formylpyrrole	4037956.00[c]	6723022.00[b]	10167852.75[a]
3	20.9516	1-Methyl-2-formylpyrrole	2433206.25[b]	4523635.50[b]	7935301.25[a]
4	29.7831	2-Acetyl pyrrole	5115854.00[b]	7570482.50[b]	22264158.75[a]
5	30.305	2-Formylpyrrole	4212409.75[b]	5332445.00[b]	20185354.50[a]

Values with different superscripts are statistically significantly different between different roasting degrees.

and Figueroa, 2022), that some volatile compounds such as pyrazine and furan, did not increase during the fermentation process due to microorganisms did not have a significant impact in terms of content during the fermentation process. This indicates a need to take thermal reactions like the Maillard reaction and other reactions in order to synthesise some volatile compounds.

Previous work by Saw *et al.* (2015) reported volatile components identified in Liberica coffee green beans such as phenolic compounds, aldehydes, alcohol, pyrroles, esters, ketones, furans, hydrocarbons and miscellaneous compounds. Volatile compounds detected only some furans and pyrroles. Meanwhile, the volatiles identified in roasted coffee beans have a large number of pyrroles, furans, pyrazines, thiazole, oxazole, thiophene and imidazoles (Saw *et al.*, 2015). In this study, volatile compounds in Liberica roasted coffee beans at different degrees of roast are identified in Figure 3 and Figures 4a, 4b, and 4c show a GC–MS chromatogram of the volatiles.

Roasting degrees are controlled by roasting time and temperature, which cause chemical changes in the green beans (Somporn *et al.*, 2011). During roasting, several chemical reactions such as Maillard reaction, caramelization and Strecker degradation, polyphenol degradation, polymerization of carbohydrates, and pyrolysis affect the color, flavor, and aroma of coffee (Dippong *et al.*, 2022).

Pyrazine compounds were significantly different

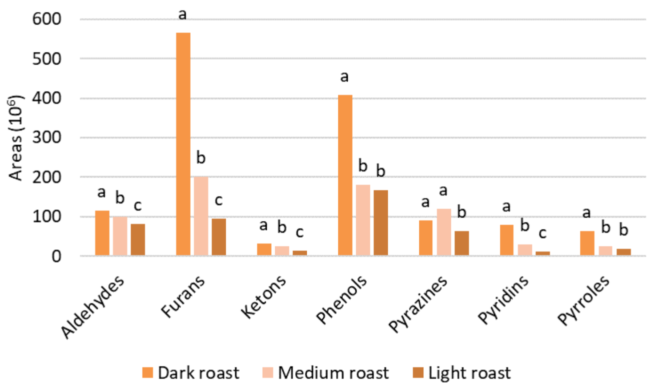

Figure 3. Volatile compounds in Liberica coffee of different roast degrees. Bars with different notations are statistically significantly different between different roasting degrees.

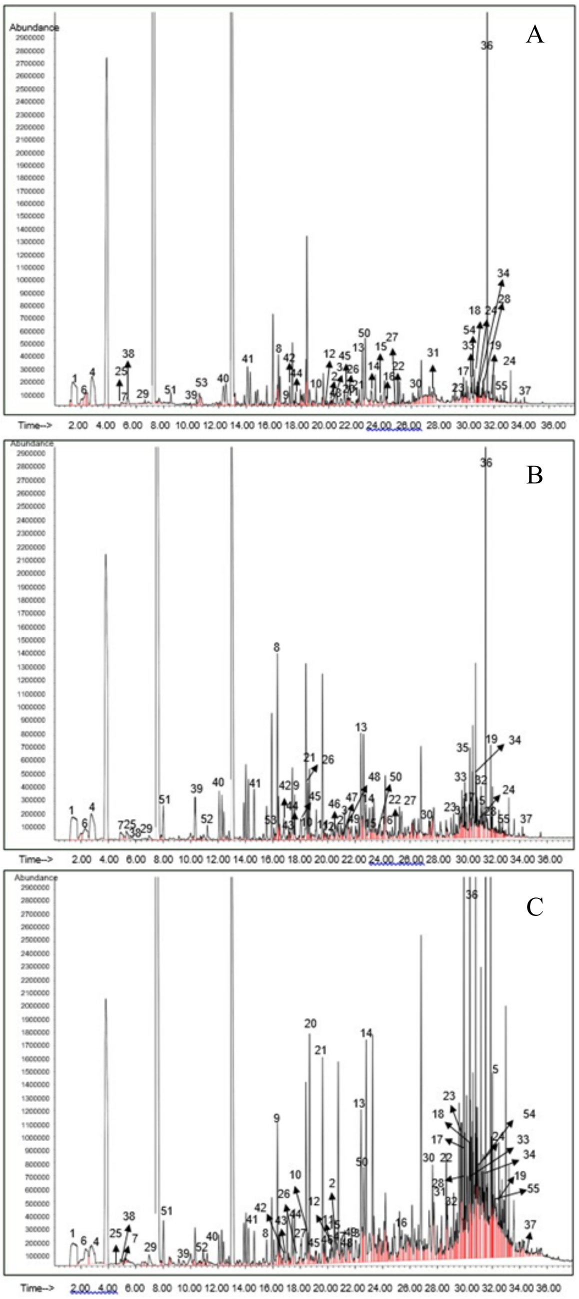

Figure 4. GC-MS chromatogram of the volatile compounds from Liberica coffee roasted: (A) light roast, (B) medium roast and (C) dark roast. The numbers presented are based on the distribution of each compound, aldehydes (Table 1), furans (Table 2), ketones (Table 3), phenols (Table 4), pyrazine (Table 5), pyridine (Table 6), and pyrrole (Table 7).

under medium roasting conditions of 175 - 190°C. At this temperature, the Maillard reaction will occur (Gancarz *et al.*, 2022). Meanwhile, aldehydes, furans, ketones, phenols, pyridines, and pyrroles compounds were detected to have the highest area in the dark roast coffee with a temperature of 200 - 220°C. When the temperature rises range 200-250°C, the beans undergo a pyrolysis reaction, which is principally the volatile compounds (Pantaleo *et al.*, 2017).

Latief *et al.* (2022) explained that the levels of polysaccharides change when beans are roasted. In addition, the protein content would reduce while the concentration of free fatty acids would increase (Latief *et al.*, 2022). Several factors influence the chemical composition of coffee beans, including types of coffee beans, variety, fruit ripeness, harvesting methods, geographic location, soil conditions, storage of coffee and roasting procedures (Marek *et al.*, 2020). The major volatile compounds of roasted Liberica coffee beans consisted of 5 aldehydes, 18 furans, 4 ketones, 9 phenols, 13 pyrazines, 5 pyridines and 5 pyrroles.

3.1 Aldehydes

Aldehydes compounds are presented in Table 1. Acetaldehyde increased in medium-roast coffee and then decreased at dark roast with no significant difference. Acetaldehyde compounds give a fruity, pungent, fresh and musty aroma (Yeretzian *et al.*, 2019). Butanal, 2-methyl-, shows an increase at the medium roast but was not significantly different in the comparison between light and medium-roast coffee beans. For dark roast, the area of these compounds was detected lower than the light and medium roast with a significant difference. These compounds contributed to rancid, almond-like, toasty aromas (Yeretzian *et al.*, 2019). The unit area of Benzeneacetaldehyde and 2-(2-Furyl)pentanal was increased slightly at medium roast. However, there was no significant difference compared to light roasting. After that, the unit area of both compounds increased significantly in dark roast. Benzeneacetaldehyde gives sweet-fruity aromas (Zou *et al.*, 2022).

Aldehydes compounds are formed by lipid oxidation degradation and Maillard reaction (Maksimowski *et al.*, 2022). In addition, this study found that benzaldehyde, 4-methyl- area increased significantly in medium and dark roast compared to light roast.

3.2 Furans

In this study, furans were found most frequently compared to other compounds. The results are given in Table 2 and show that all furan compounds were significantly improved by roasting degrees. The main components of green coffee beans are carbohydrates and amino acids (Chaichi *et al.*, 2015; Wu *et al.*, 2022). The existence of 2-furanmentanol is formed by the Maillard reaction and thermal processes that degrade carbohydrates and sugars (Galarza and Figueroa, 2022). Some other compounds that were identified are furfural and 5-methylfurfural. Furfural has significantly increased in medium-roast coffee at 175°C. Herawati *et al.* (2022) reported that furfural and 5-methylfurfural are potent compounds that contribute to sweet, woody, almond aromas and spice, caramel, and maple, respectively.

The reaction of amino acids and reducing sugars to produce furanic compounds has been explained by Caporaso *et al.* (2018). The reaction undergoes rearrangement into Amadori products in the Maillard reaction and through complex reaction pathways such as dehydration, cyclization, and polymerization to lead to the production of flavor component. Furthermore, one of the formation pathways of furanic compounds such as furfuryl alcohol (2-furanmetanol) is the thermal oxidation of polyunsaturated fatty acids (PUFAs) and ascorbic acid (Caporaso *et al.*, 2018; Wu *et al.*, 2022). The synthesis of these compounds requires a thermal reaction. For this reason, furfuryl alcohol significantly increased between roasting degrees from light to dark roast generating an increase of furfural and 5 methylfurfural. Wu *et al.* (2022) reported similar observations in their experiments. Furans usually play a role in floral, nut, cereal, roast, spicy, and vegetable (Sarghini *et al.*, 2019).

3.3 Ketones

The results of the ketone compounds are given in Table 3. Light-roast coffee beans contained the highest area of 1-Acetoxy-2-butanone, then decreased when the roasting degree was increased. The results agreed with a previous study by Cotter and Hopfer (2018) that 1-acetoxy-2-butanone obtained a higher area in the light roast of coffee beans. This is possible because ketones have the ability to interact with amino acids, peptides, proteins, and other compounds to decrease their amount (Xie *et al.*, 2022). While 3-Hexanone, β-Isophorone and 3-methyl-2-(2-pentenyl)-Cyclopentanone were increased when the roasting degree was increased. However, the highest unit area of 3-hexanones is at medium roast and decreases at dark roast Increased Maillard reactions and lipid degradation generate increased volatiles in darker roast samples (Laukalēja *et al.*, 2022). Ketones are associated with the buttery flavor notes of coffee (Li, 2022).

3.4 Phenols

Table 4 shows that all phenol compounds increased when the roasting degree was enhanced. All compounds, including Guaiacol (2-methoxy-phenol) and 4-Vinylguaiacol (2-methoxy-4-vinylphenol) in dark roast, were significantly different compared to the medium and light roast ($p<0.05$). Guaiacol contributes to phenolic, burnt, smoke, spice, vanilla, and woody aromas. While 4-ethyl guaiacol contributes to spicy, smoky, bacon, phenolic, and clove aromas (Yeretzian *et al.*, 2019). Yu *et al.* (2021) reported similar observations in their experiments. Increased levels of Guaiacol and 4-ethylguaiacol compounds are associated with an increase in roasting temperature and time. Laukalēja *et al.* (2022), found a positive association between dark roast coffee with 2-methoxy-4-vinylphenol and 2-methoxy-phenol. Guaiacol and 4-ethylguaiacol were produced by bacteria used as starters. According to Martinez *et al.* (2019), Guaiacol is a precursor marker in green beans that is produced by microbes used as starters, one of them is *B. subtilis*. *B. subtilis* was also used in this study. This is attributed to the non-oxidative decarboxylation of vanillic acid by bacteria, such as *B. megaterium* and *B. subtilis*, as reported in the literature (Martinez *et al.*, 2019).

Ferulic acid in roasted coffee beans could be converted by enzymatic decarboxylation. Ferulic acid undergoes a biotransformation process into 4-vinyl-guaiacol using microorganisms such as *B. coagulans* and *B. cereus.* These findings compounds demonstrate that *B. cereus* as starter culture in this study, acts as a biotransformation agent in the formation of these compounds. Bacteria play a role in the coffee fermentation process and would convert ferulic acid in coffee to 4-vinylguaiacol (Mishra *et al.*, 2014). These findings reinforce the general belief that the presence of bacteria in the fermentation process would increase the concentration of those compounds (Afriliana *et al.*, 2019). The use of the bacterial consortium in this study is believed to have an effect on forming both components (Table 4). 4-Vinylguaiacol and Guaiacol were also found in both green and roasted coffee reported elsewhere (Toci and Farah, 2014; Amanpour and Selli, 2016; Yu *et al.,* 2021).

3.5 Pyrazines

The distribution of 13 pyrazines in the Liberica beans is shown in Table 5. Pyrazines were identified as a significant value ($p<0.05$). Several studies have explored the effects of the heating process associated with the formation of pyrazine compounds. There are mechanisms for the formation of pyrazine, i.e. when they are heated during the roasting process, reducing sugars and amino acids in coffee undergo Maillard reactions. Pyrazine compounds give a coffee-nutty, roasted, corn, hazelnut, potato or earthy, depending on the substituents of the pyrazine ring (Dippong *et al.*, 2022). The pyrazine compound in this study, i.e. 2-Methyl-6-vinyl-pyrazine, 2-methyl-3-(2-methylpropyl)-pyrazine, 2,5-dimethyl-3-propyl-pyrazine, clearly has the highest unit area in light roast coffee ($p<0.05$). Thereafter, these compounds were reduced as roasting degrees were increased. When the temperature was increased, the pyrazines in these compounds would be incorporated into melanoidins (Wu *et al.*, 2022).

3-methylpyridazine, 2,5-dimethylpyrazine, 2-ethyl-3 -methylpyrazine, 2-methoxy, 3-isobutyl pyrazine achieved the highest area in the medium roast. Meanwhile, the area of methylpyrazine, 1-methylethenyl -pyrazine, 5-methyl-6,7-dihydrocyclopentapyrazine, 2-Isoamyl-6-methylpyrazine, 2-methyl-6-(1-propenyl)-, (Z)-pyrazine, and 2-methyl-6-propenyl-(E)-pyrazine was increased after the roast degree were enhanced to dark roast. In a previous study, the content of pyrazines was detected in higher amounts when the roasting temperature was around 250°C (Wu *et al.*, 2022). Methylpyrazine and 2,5-dimethylpyrazine were reported by Herawati *et al*. (2022) that give a potent aroma in roasted Excelca coffee. Methylpyrazine contributes to the nutty aroma. On the other hand, 2,5-dimethylpyrazine imparts hazelnut and roasted aromas (Herawati *et al*., 2022).

3.6 Pyridines

Table 6 shows that with increased roasting degrees, pyridine, 3-methyl-pyridine, 3-pyridine methanol and 2-methyl-3-pyridinol all significantly increased ($p<0.05$). This may cause as the heating rate increases, trigonelline decomposition and Maillard reactions occur then forming pyridines (Maksimowski *et al.*, 2022). 3-ethenyl -pyridine showed the highest unit in medium roast, then decreased in dark roast coffee. The reduction of that compound could be caused by over-roasting (Wu *et al.*, 2022). Pyridine is related to bitter, fishy or burnt aromas (Dippong *et al.*, 2022). Pyridine gives potent aromas in roasted Excelca coffee (*C. liberica* var. dewevrei) (Herawati *et al*., 2022).

3.7 Pyrrole

Results illustrated in Table 7 show that all compounds of pyrrole show an increase in the area when the roasting degree is enhanced. All compounds of pyrroles in this study show an increasing trend with significant differences in dark roast. These findings are different to the data reported by Amanpour and Selli (2016). 2-acetyl pyrrole in city-roasted beans shows important compounds in medium-roasted beans (Amanpour and Selli, 2016). 1-methylpyrrole and 2-formyl-1-methyl-pyrrole are also found in roasted ground Arabica coffee (Amanpour and Selli, 2016). Furthermore, 2-Formylpyrrole was found to be significantly higher in dark roast (200°C) in this study. As stated by Arkadaş and Avşar (2018), the formation of 2-Formylpyrrole occurs between 140°C and 200°C. Green coffee beans consist of carbohydrates and proteins and can lead to the formation of pyrroles through the Maillard reaction when roasted (Maksimowski *et al.*, 2022). These pyrroles were associated with nutty, sweet, and burnt aromas (Afriliana *et al.*, 2019). The main flavor chemicals found in coffee are Pyrazine, pyridines, and pyrroles (Lee *et al.*, 2016) because it contributes to the desired aromas of coffee.

4. Conclusion

The investigation revealed the volatile compounds in Liberica coffee roast beans with different roast degrees were detected 59 compounds were significantly different ($p<0.05$) among the 130 volatile compounds. However, there were no significant differences between the four fermentation times. Microbes during fermentation did not significantly affect the volatile compound content. During roasting, thermal reactions such as the Maillard reaction and other reactions produce volatile substances. The volatile compounds were detected to fall into 7 major groups that consisted of 5 aldehydes, 18 furans, 4 ketones, 9 phenols, 13 pyrazines, 5 pyridines and 5 pyrroles. Pyrazines were found at the highest in the medium roast, while aldehydes, furans, ketones, phenols, pyridine, and pyrroles compounds were found at the highest in the dark roast. Among all the volatile compounds, pyrazine was found to be the most abundant group which contributes to coffee-nutty, roasted, corn, hazelnut, potato or earthy aromas of the coffee. Finally, the volatile compound chosen which is potent to aromas in Liberica roast beans is pyridine which contributes to sour, fishy, amine, bitter and roasted aromas. Methylpyrazine contributes to the nutty aroma, 2,5-Dimethylpyrazine contributes to hazelnut and roasted aromas, and furfural contributes to sweet, woody and almond aromas. 5-Methylfurfural contributes to spice, caramel and maple aromas. Furthermore, comparative volatile compounds in Liberica coffee prepared by different brewing have not been reported, therefore, this is something that can be investigated in the future.

Conflict of interest

The authors declare no conflict of interest.

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