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Analysis of Volatile Compounds in Roasted Liberica Coffee in the Philippines by Gas Chromatography Mass Spectrometry

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Abstract

In the Philippines, not much research has been accessible for the volatile compounds of roasted Liberica coffee. Thus, these findings might contribute to the addition of preliminary data for the said coffee variety. The research sought to provide information regarding the volatile compounds of roasted Liberica coffee (*Coffea liberica*) collected from Lipa Batangas in the Philippines. Sample analysis was performed using Static Headspace Gas Chromatography. The roasting process generated furans, pyridines, aldehydes, and pyrazines potent volatile compounds in Liberica beans including unique volatile compounds including terpinene 4-acetate (0.65%) and trans-β-Ocimene (0.47%). Furthermore, the presence of the above-mentioned compounds revealed the essential marker as Liberica coffee beans.

Keywords: Kapeng barako, volatile compounds, SH/GC-MS

INTRODUCTION

The Philippines is one of the few countries in the world where coffee varieties such as Arabica, Robusta, Excelsa and Liberica can be grown (Santos *et al.,* 2018). Due to the popularity of coffee as a routine and social beverage, the study of coffee and its composition has piqued the interest of many industries around the world.

The most prevalent coffee variety in the Philippines is Robusta, which accounted for 76.5% of total production or 41,807 tons dried cherries (10,904 tons green coffee beans) in the year 2020 and it is generally used for instant coffee. Next is Arabica, cultivated on high elevation areas (1000 meters above sea level) which is marketed at a premium price and constitutes 16.70% or 14,657 tons of dried berries. In addition, it is utilized for brewing or blending. The remaining varieties are Excelsa with 5.7% or 3,712 tons dried cherries total production (1,856 tons green coffee beans) and Liberica or *Kapeng Barako* at 1.1% or 462.53 tons (231.26 tons green coffee beans) (DA, 2022).

Robusta was also the main type planted at 76.26% (86,376 ha) of all areas in the year 2020, followed by Arabica with 16.02% (18,156 ha), Excelsa with 6.56% (7,430 ha), and Liberica with 1.16% (1,303 ha) (DA, 2022).

Liberica is commonly known as *Kapeng Barako*, which has a powerful flavor and scent (DA-DTI, 2017). Liberica is a third coffee bean variety that is less well recognized. Liberica coffee accounts for about two percent of all coffee drinks worldwide, with most of this consumption taking place in the Philippines, where Liberica coffee is quite popular since it has a distinct flavor. People who enjoy Liberica coffee adore the smoky and chocolaty flavor, which is enhanced by flowery and spicy overtones. Liberica coffee is referred to in the Philippines as *barako*, which means "manly," due to its powerful and bold flavor. The peculiar smell that emerges from the beans when they are being roasted is another reason why Liberica is said to be an acquired taste. Liberica beans have a distinct durian aroma when roasted or brewed (PCB, 2020).

Liberica beans are usually darkly roasted and finely crushed. A cup of *barako* coffee is considered a breakfast staple in the Philippines. All of this is being done to benefit local coffee producers, notably in Batangas and Cavite provinces, where the majority of Liberica coffee is grown (PCB, 2020).

Volatile compounds are involved in differentiation of roasted coffee based on their geographical origins or authenticity purposes related to species (Caporaso *et al.,* 2018). However, little research in the Philippine was available for the volatile compounds of Liberica coffee.

Apart from helping fill the research literature gap, this study generally aimed to characterize the volatile compounds of Liberica from Lipa Batangas, Philippines. Specifically, it aimed to tentatively identify the volatile compounds of Liberica variety by Gas Chromatography Mass Spectrometry; to compare the volatile compounds of Liberica as opposed to Arabica, Robusta and Excelsa coffee; to quantify the concentration of the volatile compounds expressed in percent peak area; and to determine the dominant chemical group of the Liberica coffee.

MATERIALS AND METHODS

Liberica coffee beans were obtained from Cailles Coffee House. The coffee supplier is in Lipa Batangas, Philippines with an altitude of 300-500 m asl. The beans were roasted at 207 ^{0}C for 12 minutes.

Extraction of coffee volatiles

Roasted Liberica coffee beans were ground by using Krups 100-g capacity home grinder, until average coffee fineness. Ground sample (2 g) was transferred into a 20 mL-sized glass vial which was sealed with a silicone rubber teflon cap. The vial was equilibrated at 70 ^{0}C for 30 minutes in the static headspace sampler and 1 mL of the coffee headspace sample was injected to the HP-5MS column (30 m x 0.250 mm, 0.25-micron film thickness). The volatile compounds were separated with HP-5MS capillary column showed a good compromise between resolution and speed of volatile compound separation. The method was also based on the previous studies of Sarghini *et al.* (2019) with appropriate modification.

Analysis of the Volatile Compound Profile

The injector temperature was set at 220 ^{0}C with split injection mode and the follow-on of the helium carrier gas was 1 mL min^{-1}. The oven temperature was set at an initial 40 ^{0}C, followed by an increase of 2 ^{0}C min^{-1} to 80 ^{0}C, and 20 ^{0}C min^{1} to 220 ^{0}C (held for five minutes). Mass spectrometry was carried out using the 5977B Mass Selective Detector (MSD) coupled to the GC system. The mass spectrometer operated in the electron impact ionization mode of 70 eV, with a scan range of 27 to 400 amu. Moreover, Table 1 shows the summary of the SH/GC-MS parameter conditions.

Data Interpretation

The following data produced from Gas Chromatography - Mass Spectrometry (GC-MS) analysis was obtained and tabu-

Table 1. SH/GC-MS parameters

Column	Incubation temperature	Incubation time	Injection volume	Split less injection	Carrier gas flow	Oven temperature	Electron ionization	Mass range
HP5-MS	70 ^{0}C	30 min	1 mL	1:10	1 mL m^{-1}	220 ^{0}C for 5 minutes	70 eV	27 to 400 amu

lated. The tentative identified compound was compared to the peaks from the library's mass spectra in the National Institute of Standards and Technology (NIST). The Agilent Mass Hunter Qualitative Analysis 10.00. was utilized to process the data, while the NIST MS Search 2.3 database was utilized for the identification of the peaks present in the chromatogram. An 85% mass spectral profile match percentage was considered as the main criteria. Furthermore, the relative percentages of individual compounds were calculated from the total contents of volatiles on the chromatograms.

% Relative peak area =

$$\frac{Area\ of\ an\ individual\ compound}{Total\ area}\ x\ 100$$

RESULTS AND DISCUSSIONS

The relative peak area percentages (RPA%) in the present study was vastly different from the reported by Saw *et al.* (2015) in green coffee and roasted coffee bean (Marquez & Mojica, 2020). In connection to this, identified volatile compounds were shown to obtain many derivatives from chemical groups such as furans, pyridines, aldehydes, and pyrazines.

Furans detected includes tentatively identified furfuryl alcohol (14.61%), 2-methylfuran (9.79%), furfural (3.02%) furfuryl acetate (0.43%). The first three furan derivatives were significantly higher in relative peak area (RPA%) except for furfuryl acetate with 0.43%. Sensory descriptors range from burnt, cooked-sugar, and rubber-like odor, pungent, fruity, sweet, woody, almond, and floral notes according to the findings of Caporaso *et al.* (2018) and Swasti & Murkovic (2012). The presence of dihydro-2-methyl-3(2H)-furanone (2.92%) in the present study is considered as a frequently reported key aromatic compound in literatures (Herawati *et al.,* 2022) The formation of furans, furan rings, and furanones are through the decomposition of serine, threonine, and sucrose (Caporaso *et al.,* 2018)

Pyridine (19.60%) were quite lower than the obtained value of 22.7% from the study of Marquez & Mojica (2020). This may be due to the specific medium roasting temperature utilized by the researchers. This compound also imparts various notes such as sour, putrid, fishy, amine, bitter, roasted, burnt/ smoky according to Caporaso *et al.* (2018), Amanpour & Selli (2015).

Aldehydes includes 2-methylbutanal (9.15%), pyruvaldehyde (6.93%), hexanal (0.80%) and 5-methylfurfural (0.79%) which corresponds to the study of Caporaso *et al.* (2018) which has a distinct malty, fermented/ buttery–oily, green, grassy, fruity, and spice, caramel, and maple like notes. Buffo & Cardelli-Frei (2004) explained that aldehydes can be formed through Strecker degradation, and this chemical group can be utilized as an indicator of freshness in coffee. Moreover, Cheong *et al.* (2013) concluded that ketones were characterized to be less sharp compared to aldehydes. Ketones in the present study include 2,3-butanedione (2.29%) and acetylpropionyl (2.28%) which gives a buttery, oily, caramel-like notes stated in the findings of Caporaso *et al*. (2018).

Pyrazines in this study includes 2-methylpyrazine (7.63%), 2,6-dimethylpyrazine (3.69%), pyrazines (2.15%), 2,6-dimethyl-pyrazine (1.04%), ethylpyrazine (0.82%), 2 ethyl-5-methylpyrazine (0.35%), and 2,3-dimethylpyrazine (0.20%). In connection to this, pyrazines are solely responsible for the roasted and nutty flavors (Halim-Lim *et al.,* 2022).

1-(acetyloxy)-2-propanone (4.14%) is under the keto ester chemical group which gives a peculiar fruit buttery with a tinge of sour odor according to the data of Flament (2002).

Acetic acid (1.82%) under carboxyl group in the present study was lower compared to the reported values of Saw *et al.* (2015) with 27.2% and 9.4% in the findings of Marquez & Mojica (2020). Based on the study of Caporaso *et al.* (2018), acetic acid has pungent, vinegar notes.

Monoterpenes in the study includes γ-terpinene (2.06%), D-limonene (1.42%) and β-terpinene (0.72%) are directly in line with previous findings of Romano *et al.* (2022) and Del Terra *et al.* (2013) that monoterpenes

Table 2. Tentatively identified volatile compounds of Liberica roasted coffee

Peak number	Retention time (min)	Tentatively identified volatile compounds	Peak area, %
		Furans	
13	7.185	Furfuryl alcohol	14.61
2	2.276	2-Methylfuran	9.79
12	6.381	Furfural	3.02
23	14.308	Furfuryl acetate	0.43
		Pyridines	
8	3.979	Pyridine	19.60
		Aldehydes	
4	2.787	2-Methylbutanal	9.15
3	2.739	Pyruvaldehyde	6.93
9	5.35	Hexanal	0.80
21	12.343	5-Methylfurfural	0.79
		Pyrazines	
11	6.027	2-Methylpyrazine	7.63
17	9.626	2,6-Dimethylpyrazine	3.69
7	3.800	Pyrazine	2.15
16	9.578	2,5-Dimethylpyrazine	1.04
18	9.805	Ethylpyrazine	0.82
24	14.360	2-Ethyl-5-methylpyrazine	0.35
19	9.984	2,3-Dimethylpyrazine	0.20
		Ketones	
6	3.346	2,3-Butanedione	2.29
5	3.193	Acetylpropionyl	2.28
		Monoterpenes	
26	14.932	γ-terpinene	2.06
27	16.090	D-Limonene	1.42
22	12.923	β-Terpinene	0.72
		Keto ester	
14	7.792	1-(acetyloxy)-2-propanone	4.14
		Furanones	
10	5.543	Dihydro-2-methyl-3(2H)-furanone	2.92
		Carboxyl	
1	2.197	Acetic acid	1.82
		Menthane Monoterpenoids	
25	14.587	Terpinene 4-acetate	0.65
		Acyclic Monoterpenoids	
20	10.648	Trans-β-Ocimene	0.47
		Esters	
15	9.412	Furfuryl formate	0.23

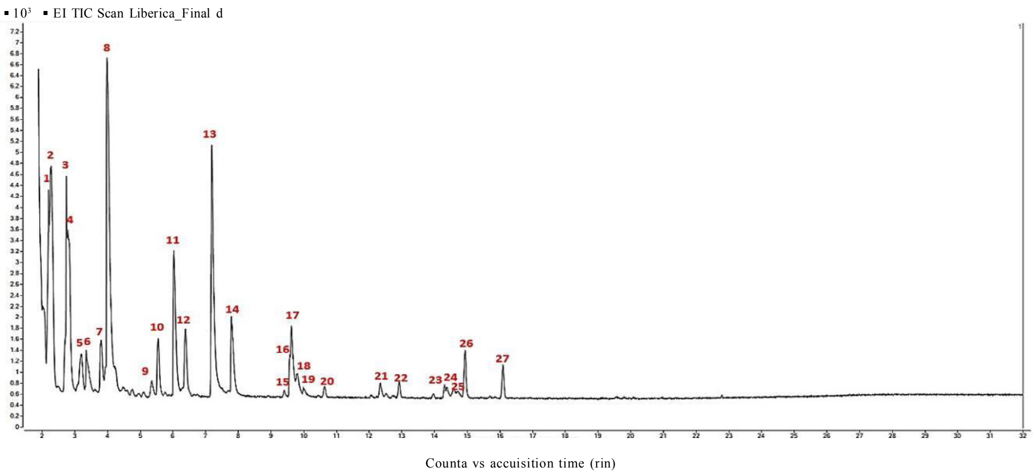

Figure 1. GC-MS total ion chromatogram of Liberica coffee from Batangas

are responsible for fruity and citrus notes. In addition, unique compounds were also observed in roasted Liberica coffee such as terpinene 4-acetate (0.65%) and trans-β-ocimene (0.47%) which were not found in roasted Arabica, Excelsa and Robusta coffee beans.

Terpinene 4-acetate (0.65%) is classified in the NIST Chemistry WebBook, SRD 69 as menthane monoterpenoids and considered as a natural terpene alcohol isolated from essential oils. In the study of Pereira *et al.* (2012), essential oils of cinnamon, citronella, lemongrass, clove, tea, thyme, neem, and eucalyptus were alternatively used for integrated management of diseases in coffee. The toxicity of oils on pathogens is mainly attributed to the antimicrobial compounds of terpinen-4-ol or also known as terpinene 4-acetate. In addition, it gives an earthy-green note with a slightly pepperywoody undernote.

Trans-β-Ocimene (0.47%) is classified in the NIST Chemistry WebBook, SRD 69 as a volatile aroma compound under acyclic monoterpenoids. In the study of Luo *et al.* (2017), this gives a flowery note and is considered a significant contributor to the overall flavor of paocai baby ginger. On the other hand, the presence of this compound was detected in the findings of Nebesny *et al.* (2006) where Robusta green coffee beans obtained a peak area of 0.20% which is slightly lower than the value in this study. The difference between the concentration of volatile compounds of green coffee and roasted coffee beans was primarily because of roasting. The volatile compounds increase 50-fold during roasting but do not exceed in parts per million (ppm) concentration. Despite the several reviews in the literature that address the importance of trans-β-ocimene, recent published article by De la Rosa-Cancino *et al.* (2021) have comprehensively discussed that trans-β-ocimene were emitted from medium infestation of coffee berry borer.

Furfuryl formate (0.23%) is classified under the chemical group of esters and was lower than the obtained value of 9.9% from the study of Saw *et al.* (2015). In addition, this compound is responsible for giving floral notes (Seninde & Chambers, 2020).

CONCLUSIONS

Analysis of roasted Liberica coffee beans is feasible through Static Headspace Gas Chromatography Mass Spectrometry (SH/GC-MS). The study revealed a total of 27 tentatively identified in Liberica coffee from Lipa Batangas. Notable compounds such as terpinene 4-acetate (0.65%) and trans-β-ocimene (0.47%) were unique to this variety. Thus, this study provided preliminary data regarding the generation of volatile compounds, however, internal standards for confirmation are needed for the tentatively identified volatile compounds.

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