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Research Article

Discriminating Green Beans of Puntang Arabica Coffees with ^{1}H NMR Based-Metabolomics

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Abstract

Puntang Arabica Coffee is one of the famous Indonesian coffees from West Java. This coffee is cultivated in the area of Mount Puntang, Bandung Regency. This study evaluated green beans of Puntang Arabica coffee obtained from different cultivating locations, including Cimulek, Cimenong, Ganda Paraja, and Nameur, with 1H NMR-based metabolomics. The green coffee bean samples were ground, extracted with D_2O, and then measured with NMR spectroscopy. The obtained ^{1}H NMR spectra were processed and evaluated by multivariate data analysis techniques using Orthogonal Partial Least Square Discriminant Analysis (OPLSDA) as the main model. In total, 20 metabolites were successfully identified in the ^{1}H NMR spectra of Puntang coffees. Based on multivariate analysis, Cimulek and Cimenong coffee regions possessed similar metabolite profiles possibly due to being in proximity. Trigonelline, 5-chlorogenic acid, and citric acid were detected as the discriminant compounds for Cimulek and Cimenong coffees, whereas lactic acid, lipids, and stearic acid were associated with Ganda Paraja coffee. Meanwhile, GABA was detected constantly as the characteristic compound of Nameur coffee. This report revealed the metabolite profile of Puntang Arabica coffees for the first time and provided scientific information for the development of coffee plantations.

Keywords: Green coffee beans, metabolomics, multivariate data analysis, NMR, Puntang Arabica coffee

1. INTRODUCTION

Coffee is the second most consumed beverage globally, following mineral water [1] and is the main source of caffeine for humans [2]. In 2022, global coffee consumption reached around 178 million bags (60 kg per bag)[3]. Indonesia is one of the largest coffee producers in the world [3]. West Java is one of Indonesia's central coffee-producing provinces known to have high-quality coffee beans. According to data from the BPS-statistics Indonesia, in 2021, West Java produced 24,333 tons of coffee [4]. Puntang Arabica coffee is one of the West Java coffees with a distinctive taste and has been recognized by the domestic and global markets. This coffee is cultivated in the Mount Puntang area, Bandung Regency, West Java. However, the chemical information of Puntang coffee is very limited in the literature.

^{1}H NMR-based metabolomics is widely used to analyze the chemical composition of biological samples. This technique eliminates time-consuming sample preparation and quickly provides a large amount of information about the material's composition, making it a reliable analytical method for investigating complex chemical information [5]. ^{1}H NMR-based metabolomics approaches have also been carried out on several coffee samples, including Arabica coffee quality analysis [6], coffee classification based on varieties and geography [7–11], diagnosis of defective coffee beans [12], and the exploration of metabolite profiles of coffee beans with various postharvest methods [13].

In this study, metabolite profiles of green beans of Puntang Arabica coffees were evaluated using ^{1}H NMR-based metabolomics approach. The OPLSDA model was employed to classify the coffees based on their plantation origins. The characteristic metabolites for each coffee sample were investigated with the S-plot of the two-class OPLSDA models. This report

illustrated the effectiveness of ^{1}H NMR-based metabolomics in evaluating the green beans of Arabica coffees cultivated in four plantations around Mount Puntang, offering valuable insights into one of Indonesia's most popular coffees.

2. RESEARCH METHODS

Coffee sample preparation

This work obtained Arabica green coffee bean samples from coffee plantations around Mount Puntang, including Cimulek, Cimenong, Ganda Paraja, and Nameur. Cimulek and Cimenong coffee plantations are situated in Warjabakti Village (1300-1400 m above sea level). Ganda Paraja coffee plantation is located in Mekarsari village which has an altitude of around 1000 m above sea level. Meanwhile, Nameur coffee plantation is in Campakamulya village, situated at an altitude of 1100-1300 m above sea level. The location of the villages is pointed in **Figure 1**. A total of 50 grams of Puntang Arabica coffee bean sample was pulverized with a 600 N coffee grinder (Yang Chia Machine Work, Taiwan) using a fineness level of 8-4-1 (stepwise grinding). Then, the resulting coffee powder is filtered to obtain a fine and uniform particle size. The coffee powder was then closely packed and stored in the freezer. For each coffee sample, 5 biological replicates were prepared.

Figure 1. The location of the coffee plantations is are located around Puntang Mountain, Cimaung District, Bandung Regency, West Java, Indonesia. Cimulek and Cimenong coffee plantations are located in Warjabakti village; the Ganda Paraja coffee plantation is located in Mekarsari village; and the Nameur coffee plantation is in Campakamulya village

Extraction

The coffee samples were extracted using the published method [7] with slight modifications. 400 mg of coffee powder was put in a 4 mL plastic tube and mixed with 2 mL ~~of~~ D_2O solution containing 1.0 mM TSP and phosphate buffer pH 6.0. The sample was then homogenized for 1 min with a Digital Vortex Genie2 (Scientific Industries Inc., New York, USA) and then sonicated for 20 min with a Mujigae Ultrasonic Cleaner LUC-250H (Sungdong Ultrasonic Co., Seoul, South Korea). Next, the samples were incubated in a Memmert WNB 14 water bath (Memmert, Buchenbach, Germany) containing hot water at 95 °C for 30 min. Afterward, the samples were cooled at room temperature for 10 min. The samples were centrifuged for 6 min at 12,000 rpm with a Benchmark MC-12 Microcentrifuge (Benchmark Scientific Inc, New Jersey, USA). 500 µL of supernatant was placed in a 5 mm Wilmad NMR tube (Wilmad LabGlass, USA) for further NMR measurement.

^{1}H-NMR Spectra Measurement and Metabolite Identification

^{1}H-NMR spectra measurements of Puntang coffee samples were carried out with a Varian Unity INOVA-500 NMR spectrophotometer (Agilent Technologies, California, USA) at a frequency of 500 MHz. The samples were measured using the presaturation pulse method to suppress the water signal, with an acquisition time of 2.72 seconds, a rest time of 2 seconds, a spectral width of 8012 Hz, data points of 64K, and scan numbers of 128. The raw FID 1H NMR data were processed with ACD/Labs 12 software (Advance Chemistry Development, Inc., Toronto, Canada). Chemical shifts of each spectrum were calibrated with TSP. Some characteristic signals of the detected metabolites were further validated using 2D NMR ^{1}H-^{1}H Correlation Spectroscopy (COSY) with 4 scans and 512 enhancements.

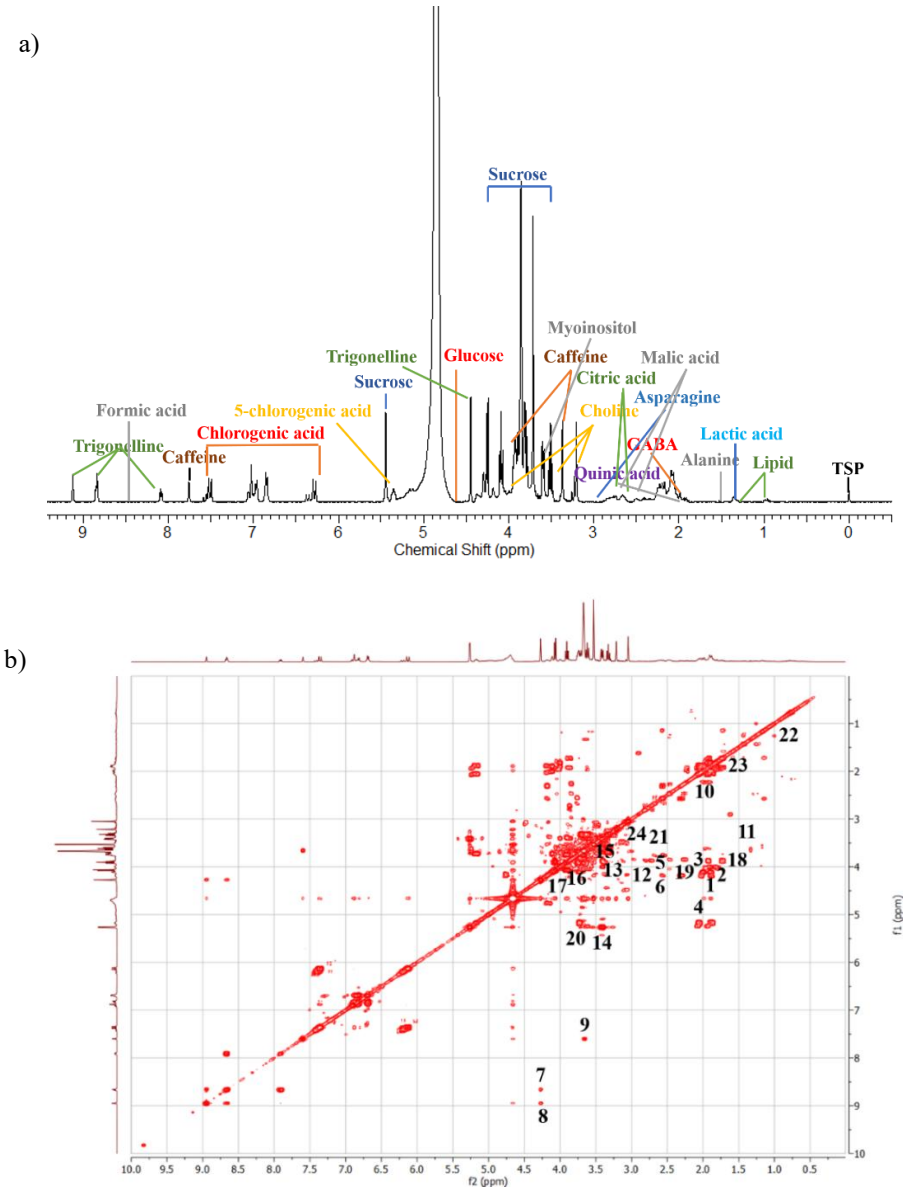


Figure 2. (a) Fingerprint signals of detected metabolites in the ^{1}H NMR spectrum of Puntang Arabica green coffee beans. (b) the correlation signals of identified metabolites in the COSY spectrum of the coffee samples. 1. H2e/H3 quinic acid, 2. H2a/H3 quinic acid, 3. H6a/H5 quinic acid, 4. H6e/H5 quinic acid, 5. H3/H2 malic acid, 6. H3/H2 malic acid, 7. H6/NCH3 trigonelin, 8. H2/NCH3 trigonelin, 9. H8/NCH3 trigonelin, 10. H2/H3 GABA, 11. H2/H3 alanine, 12. H3/H2 asparagine, 13. H3/H2 asparagine, 14. H1/H2 sucrose, 15. H3/H4 sucrose, 16. H2/H3 sucrose, 17. H3'/H4' sucrose, 18. H13/H10 5-chlorogenic acid, 19. H15/H10 5-chlorogenic acid, 20. H11/H10 5-chlorogenic acid, 21. H4/H5 myoinositol, 22. CH3/CH2- lipids, 23. stearic acid, 24. choline

Multivariate Statistical Analysis

^{1}H-NMR spectra were treated with alignment and bucketing using ACD/Labs 12.0 software. Bucketing was performed by integrating the chemical shift region with a width of 0.04 ppm within the chemical shift range of 0.50-10.00 ppm. To eliminate interference during the analysis process, the residual water signal was removed at a chemical shift of 4.71-5.23 ppm. Given that caffeine can form complexes with chlorogenic acid, resulting in different chemical shift values in each spectrum, these signals were excluded from the analysis. The resulting buckets were normalized to the total bucket area in each spectrum using Microsoft Excel 2019 software. Subsequently, the cleaned data underwent further analysis using SIMCA-P software version 12 (Umetrics in Umea, Sweden). The data was scaled using the Pareto method. The Orthogonal Projection to Latent Structure Discriminant Analysis (OPLSDA) model was used as the main model to evaluate the metabolite profile of Puntang Arabica green coffee bean samples. In the OPLSDA model, variable X (predictor) represents NMR spectrum data, while variable Y (response) represents test group data. Model validation was conducted using a permutation test with 200 iterations, evaluating the R^2Y value for model accuracy and the Q^2 value for prediction accuracy. S-plots generated from the two-class

OPLSDA model were analyzed to identify distinguishing metabolites for each coffee sample.

3. RESULTS AND DISCUSSION

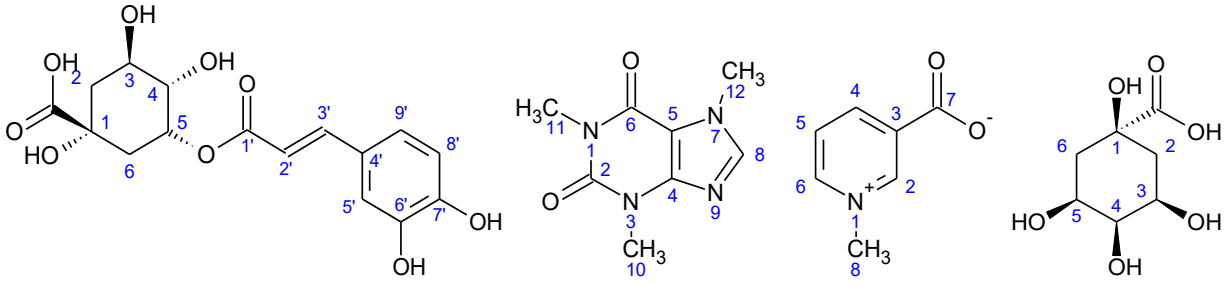
Metabolite Identification

Identification of metabolites in Puntang Arabica coffee samples was performed by detecting their characteristic signals in the ^{1}H NMR spectra (**Figure 2a**). The identified signals were verified with the corresponding ^{1}H NMR reference spectrum obtained from www.hmdb.ca and literature[7,14]. Furthermore, some of these signals were confirmed through 2D NMR spectra analysis, particularly COSY (**Figure 2b**). A total of 20 metabolites were identified successfully in the ^{1}H NMR spectra of Puntang coffee samples, with sucrose, caffeine, trigonelline, and chlorogenic acids detected as the major metabolites. These results are in accordance with metabolites identified in Arabica coffee from various regions of Indonesia [11] and other countries [6].

In Puntang Arabica green coffee beans, 3 metabolites belonging to the carbohydrate group were identified as sucrose, glucose, and myoinositol (sugar alcohols commonly found in fruits and nuts). Sucrose, a major metabolite, was identified at δ 5.45, 3.60, 3.80, 3.51, 3.89, and 3.85 ppm as glucose moiety signals, and at δ 3.71, 4.25, 4.09, 3.91, and 3.85 ppm as fructose moiety signals. Furthermore, Puntang coffees contained metabolites from the amino acid group, including alanine, asparagine, and GABA. Alanine signals were detected at δ 1.52 ppm as a methyl group and δ 3.82 ppm as a C-tertiary proton. Asparagine signals were identified at δ 2.87, 2.97, and 4.04 ppm. Meanwhile GABA signals with triplet multiplicity were detected at δ 2.35 and 3.05 ppm.

Table 1. Characteristic signals of the identified metabolites in the ^{1}H-NMR spectra of Puntang Arabica green coffee beans. 1: Cimulek, 2: Cimenong, 3: Ganda Paraja, 4: Nameur

No.	Compounds	Chemical shifts (ppm)	1	2	3	4
1.	Sucrose	3.51 (H-4, t), 3.60 (H-2, dd), 3.71 (H-1′, s), 3.80 (H-3, t), 3.85 (H-6′/H-6, m), 3.89 (H-5, m), 3.91 (H-5′, m), 4.09 (H-4′, t), 4.25 (H-3′, d), 5.45 (H-1, d)	+	+	+	+
2.	Glucose	4.68 (d)	+	+	+	+
3.	Myoinositol	3.28 (H-5, t), 3.56 (H-2, m), 3.64 (H-4, H-6, m)	+	+	+	+
4.	Alanine	1.52 (H-3, d), 3.82 (H-2, d)	+	+	+	+
5.	Asparagine	2.90 (H-3b, dd), 2.99 (H-3a, dd), 4.04 (H-2, m)	+	+	+	+
6.	GABA	1.91 (H-2, t), 2.35 (2H-3, t), 3.01 (2H-4, t)	+	+	+	+
7.	5-chlorogenic acid	2.08 (H-13, m), 2.20 (H-15, m), 3.92 (H-12, dd), 4.19 (H-10, d), 6.36 (H-1, d), 6.85 (H-4, d), 6.96 (H-2, d), 7.51 (H-8, d), 7.57 (H-2, d)	+	+	+	+
8.	4-chlorogenic acid	2.08 (H-13, m), 2.20 (H-15, m), 4.35 (H-10, m), 4.38 (H-12, m), 6.36 (H-1, d), 6.85 (H-5, d), 6.96 (H-4, d), 7.51 (H-8, d), 7.57 (H-2, d)	+	+	+	+
9.	3-chlorogenic acid	2.08 (H-13, m), 2.20 (H-15, m), 3.92 (H-12, dd), 4.25 (H-10, d), 5.35 (H-12, m), 6.28 (H-1, d), 6.85 (H-5, d), 6.96 (H-4, d), 7.51 (H-8, d), 7.57 (H-2, d)	+	+	+	+
10.	Caffeine	3.20 (N1CH_3, s), 3.37 (N3CH_3, s), 3.86 (N7CH_3, s), 7.76 (H-8, s)	+	+	+	+
11.	Trigonelline	4.45 (NCH_3, s), 8.09 (H-5, t), 8.84 (H-4/H-6, m), 9.12 (H-2, s)	+	+	+	+
12.	Quinic acid	1.92 (H-2a, d), 2.02 (H-2e, m), 2.08 (H-6e, d), 3.60 (H-4, dd), 4.04 (H-3, d), 4.19 (H-5, d), 1.98 (H-6a, s)	+	+	+	+
13.	Citric acid	2.65 (H-3, d), 2.76 (H-3, d)	+	+	+	+
14.	Malic acid	2.50 (H-3, m), 2.74 (H-3, m), 4.37 (H-2, m)	+	+	+	+
15.	Lactic acid	1.35 (3H-3, d), 4.13 (H-2, m)	+	+	+	+
16.	Formic acid	8,49 (H-1, s)	+	+	+	+
17.	Acetic acid	1.99 (3H-2, s)	+	+	+	+
18.	Stearic acid	1.03 (t), 1,43 (m), 1.74 (d), 2.48 (m)	+	+	+	+
19.	Lipid	0.94 (–CH_2-CH_3, brs), 1.33 ((–CH_2-)n, brs)	+	+	+	+
20.	Choline	3.23 (N(CH_3)$_3$, s), 3.51 (H-1, t), 4.09 (H-2, t)	+	+	+	+



5-chlorogenic acid Caffeine Trigonelline Quinic acid

Figure 3. Some molecular structures of identified metabolites in the green beans of Puntang Arabica coffees.

Puntang Arabica coffees contained secondary metabolites, including 5-chlorogenic acid, 4-chlorogenic acid, 3-chlorogenic acid, caffeine, and trigonelline. These secondary metabolites were identified as major components. The caffeine signals were identified at δ 3.20, 3.37, and 3.86 ppm as three signals of the N-methyl caffeine group, and at δ 7.76 ppm as a singlet signal of the methyl group on the aromatic caffeine. Caffeine, a coffee metabolite, is known for its various health benefits [15,16] when consumed appropriately. Trigonelline signals were identified at δ 4.45 ppm as the singlet signal of the methyl group and δ 8.09, 8.84, and 9.12 ppm as the proton signals of the pyridine ring of trigonelline. Chlorogenic acids were major secondary metabolites identified in the spectra. These compounds were reported to possess antioxidant properties [17]. Additionally, organic acid compounds such as citric acid, malic acid, lactic acid, formic acid, and acetic acid were identified successfully. Organic acids are common metabolites found in coffee [17]. Beyond these compounds, choline and lipids were also identified in the spectra, in which lipids were detected at δ 0.94 and 1.33 ppm as methyl and methylene groups. Stearic acid (fatty acid) was also detected in the ^{1}H NMR spectra of the coffee samples. A comprehensive summary of the signals of the identified metabolites in the ^{1}H NMR spectra of Puntang Arabica coffee was presented in **Table 1**. The molecular structures of some identified metabolites are described in **Figure 3**.

Multivariate Statistical Analysis

Multivariate data analysis evaluated the metabolite profiles of Puntang Arabica green coffee bean samples. Initially, we applied the PCA model (unsupervised approach) to discriminate the coffee samples based on the plantation origins. However, those could not be separated (data not shown). We also employed the PLSDA and OPLSDA models (supervised approach) by labeling each coffee sample with its origins. Unfortunately, these models could not distinguish Cimulek coffee from the Cimenong sample (data not shown), indicating similar metabolite profiles. Cimenong and Cimulek coffee plantations are located in the same village: Warjabakti Village, Cimaung District, Bandung Regency. Thus, both coffee plantations have similar environmental conditions, including soil conditions, microclimate (temperature, humidity, light intensity, rainfall), and altitude (around 1300-1400 m above sea level). Besides that, coffee farmers living in the same village usually use the same agricultural techniques. Therefore, it is reasonable to suggest that the same environmental conditions and agricultural techniques may lead to Cimenong and Cimulek coffees having similar metabolite profiles.

Given this similarity, we treated Cimenong and Cimulek as a single group in the subsequent OPLSDA model to reveal their metabolite profiles of Puntang Arabica coffees in more detail. OPLSDA is an extension of PLSDA that incorporates orthogonal signal correction and eliminates systematic variance in the dataset unrelated to the sample class, enhancing the interpretability of predictive components [18]. This approach facilitates the identification of the most crucial variables for distinguishing between sample groups [18]. The obtained OPLSDA model explained total variances of 95.4% (R2X) and 99.4% (R2Y), and cross-validation (Q2) value of 83.4 % (**Figure 4a**). The validation of the OPLSDA model was conducted through a permutation test comprising 200 iterations, resulting in the Q2 regression line intersecting the Y-axis below zero [Q2= (0.000, -1.43); R2= (0.000, 0.877)] as seen in **Figure 4b**. This confirmed the statistical validity of the model.

The score plot of the OPLSDA model derived from combining component 1 (18.6%) and component 2 (12.9%) successfully classified the green bean samples of Puntang Arabica coffee based on their origin coffee plantations. The loading plot illustrated that the buckets contributed to the sample clustering. The loading plot analysis derived from the combination of component 1 and component 2 (**Figure 4c**) revealed the most influential buckets in this classification. These buckets represented the signals of 8 identified compounds, including citric acid (δ 2.62-2.68 ppm), trigonelline (δ 4.42-4.48; 8.06-8.12; and 8.81-8.87 ppm), 5-chlorogenic acid (δ 2.04-2.10; and 2.14-2.20 ppm), lactic acid (δ 1.32-1.38 ppm), lipids (δ 0.92-0.98; and 1.58-1.64 ppm), stearic acid (δ 1.40-1.46 ppm), GABA (δ 2.31-2.37 ppm), and sucrose (δ 3.47-3.53; 3.57-3.62; 3.69-3.75; 4.23-4.28; and 5.41-5.47 ppm). Differences in the metabolite profiles in Puntang coffee samples were possibly attributed to the variations in their geographical locations [19,20]. The farther the bucket position from the axis intersection point (0,0), the greater its contribution to the classification. Given that the buckets corresponding to sucrose trigonelline, lactic acid, and lipids were situated furthest from the axis crossing point, these compounds possibly played the most significant role in classifying the metabolite profiles of Puntang Arabica green coffee beans based on their geographic origin. This observation aligned with the VIP plot of the OPLSDA model (**Figure 4d**), where sucrose (δ 3.47-3.53 ppm) emerged as the most contributing metabolite in the grouping of the metabolite profiles of Puntang Arabica green coffee beans.

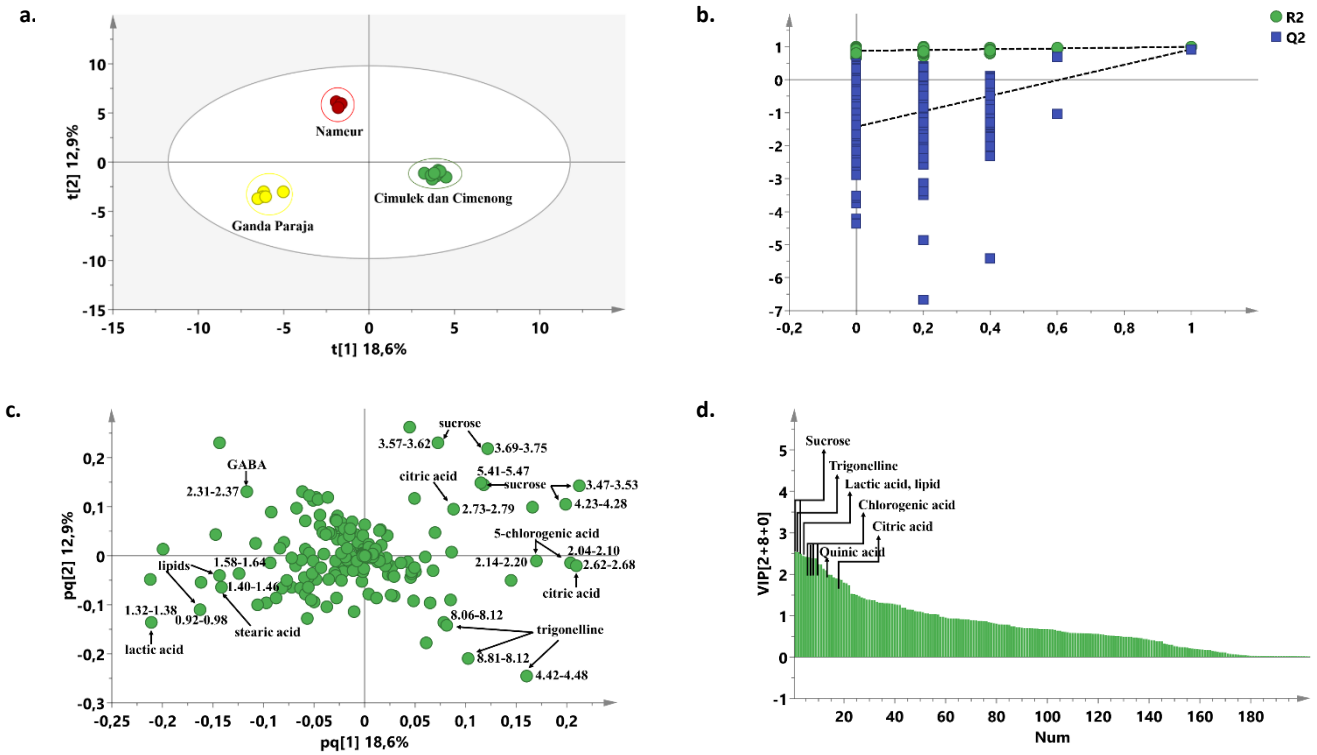


Figure 4.OPLSDA model of green beans of Puntang Arabica coffee. Score plot (a) explained how well the model can separate each sample; permutation test (b) confirmed the validity of the model; loading plot (c) showed the metabolites contributing in the clustering of the samples; VIP plot (d) exhibited the most important metabolites in the coffee sample classification

S-plot of two-class OPLSDA models were investigated to reveal the discriminant compounds for each coffee sample. The parameters of these two-class OPLSDA models are depicted in **Table 2**. The high Q2 values (> 50.0%) indicated good OPLSDA models. The S-plot in **Figure 5a** shows the compounds that contributing to the discrimination of Cimulek-Cimenong and Ganda Paraja coffees. Sucrose (δ 3.47-3.53; 3.57-3.62; 3.69-3.75; 4.06-4.12; 4.23-4.28; and 5.41-5.47 ppm), citric acid (δ 2.62-2.68; and 2.73-2.79 ppm), trigonelline (δ 4.42-4.48 ppm), and 5-chlorogenic acid (δ 2.04-2.10; 2.14-2.20; and 6.77-6.89 ppm) were typical compounds for Cimulek-Cimenong coffee in this discrimination. Meanwhile, lactic acid (δ 1.32-1.38 ppm), stearic acid (δ 1.40-1.46 ppm), and lipids (δ 0.92-0.98; 1.38-1.40; and 1.58-1.64 ppm) were the discriminant compounds for Ganda Paraja coffee. The distinguishing compounds in the discrimination of Cimulek-Cimenong and Nameur coffee were depicted in the s-plot **Figure 5b**. Cimulek-Cimenong coffee was characterized by trigonelline (δ 4.42-4.48; 8.81-8.87; and 9.08-9.14 ppm), citric acid (δ 2.62-2.68 ppm), malic acid (δ 2.68-2.71 ppm), and 5-chlorogenic acid (δ 2.04-2.10; and 2.14-2.20 ppm). Meanwhile, the discriminant compound for Nameur coffee in this differentiation was GABA (δ 2.31-2.37; and 3.02-3.06 ppm). **Figure 5c** shows the S-plot discriminating the green coffee beans obtained from the Ganda Paraja and Nameur regions. As seen in the figure, the distinguishing compounds of Ganda Paraja coffee were lactic acid (δ 1.32-1.38 ppm), stearic acid (δ 1.40-1.46 ppm), lipid (δ 0.92-0.98; and 0.98-1.03 ppm), and trigonelline (δ 4.42-4.48; and 8.81-8.87 ppm). Meanwhile, in this classification, Nameur coffee was characterized with sucrose (δ 3.47-3.53; 3.57-3.62; 3.69-3.75; 4.06-4.12; 4.23-4.28; and 5.41-5.47 ppm), GABA (δ 2.31-2.37; and 3.02-3.06 ppm), and citric acid (δ 2.62-2.68; and 2.73-2.79 ppm). We also created an S-plot of two-class OPLSDA models for discriminating Cimulek coffee from the Cimenong sample. As illustrated in **Figure 5d**, the discriminating compounds for Cimulek coffee were asparagine (δ 2.85-2.91; 2.91-2.95; and 2.95-2.99 ppm) and malic acid (δ 2.48-2.54; and 2.68-2.71 ppm). This finding indicated that Cimulek coffee had higher concentrations of asparagine and malic acid than Cimenong. Conversely, the distinguishing compounds for Cimenong coffee were sucrose (δ 4.23-4.28; and 5.41-5.47 ppm) and 5-chlorogenic acid (δ 2.04-2.10; and 5.33-5.38 ppm). It indicated both compounds were more abundant in Cimenong than in Cimulek coffee.

Table 2. The parameters of the two-class OPLSDA models computed for Puntang Arabica coffees

No.	Comparison of coffee samples	Component numbers	R2X (%)	R2Y (%)	Q2 (%)
1.	Cimulek-Cimenong vs Ganda Paraja	4	86.1	95.6	84.2
2.	Cimulek-Cimenong vs Nameur	3	57.2	99.1	96.3
3.	Ganda Paraja vs Nameur	4	85.3	99.1	80.5
4.	Cimulek-Cimenong	8	99.0	100.0	88.7

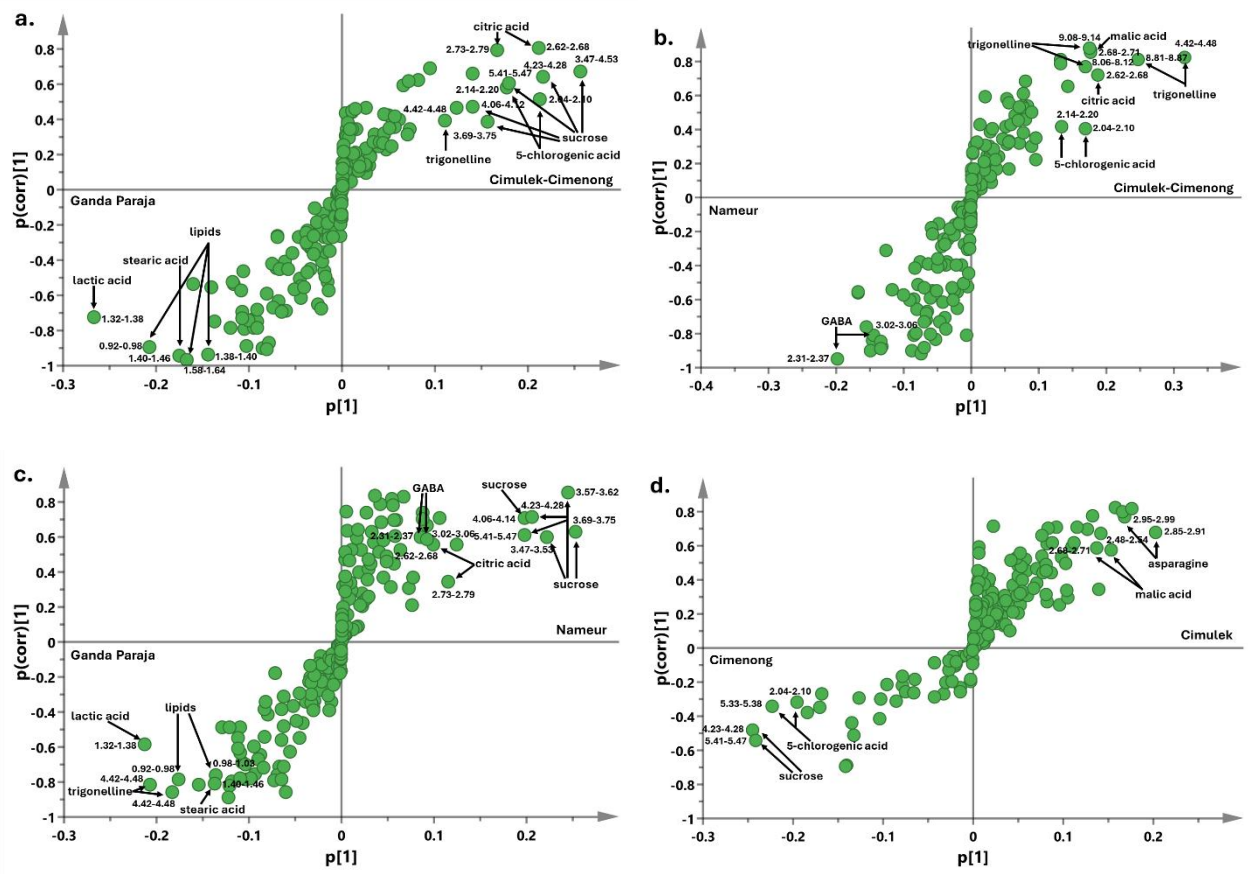


Figure 5. S-plot of two-class OPLSDA models. (a) Cimulek-Cimenong vs Ganda Paraja, (b) Cimulek-Cimenong vs Nameur, (c) Ganda Paraja vs Nameur, (d) Cimulek vs Cimenong

Based on the results of the comparison of the two-class OPLSDA models, 5-chlorogenic acid, trigonelline, and citric acid constantly emerged as crucial distinguishing compounds for Cimulek and Cimenong coffees. Lactic acid, lipids, and stearic acid consistently appeared as the discriminant compounds of Ganda Paraja coffee in the corresponding S-plot of two-class OPLSDA models. Meanwhile, GABA was always identified as the discriminant metabolite of Nameur coffee in the correlating S-plots, underscoring its significance as the most important characteristic compound in differentiating this coffee from the others.

4. CONCLUSIONS

This reports the OPLSDA model to evaluate Arabica green coffee beans obtained from 4 coffee plantations around Mount Puntang, including Cimulek, Cimenong, Ganda Paraja, and Nameur. In total, 20 metabolites were successfully detected in the ^{1}H-NMR spectra of the coffee samples. Multivariate data analysis indicated that the metabolite profiles of Cimulek and Cimenong regions were similar, possibly due to their close geographical locations (originating from the same village). Thus, our results suggested that coffees from neighboring plantations tend to exhibit comparable metabolite profiles.

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