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Doctoral Dissertation

Metabolomics-based study for the quality related metabolites and factors during the production of specialty Arabica green coffee beans

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Table of contents

List of Abbreviations

(*in alphabetical order*)

FAO	Food and Agriculture Organization
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
ICCRI	Indonesia Coffee and Cacao Research Institute
LC	Liquid Chromatography
LC-MS	Liquid Chromatography-Mass Spectrometry
MS	Mass Spectrometry
MSTFA	N-Trimethylsilyl-N-methyl trifluoroacetamide
OPLS	Orthogonal Projection to Latent Square
OPLS-DA	Orthogonal Projection to Latent Square – Discrimination Analysis
PC	Principal Component
PCA	Principal Component Analysis
QC	Quality Control
RMSEE	Root-Mean-Square-Error of Estimation
RMSEP	Root-Mean-Square-Error of Prediction
RSD	Relative Standard Deviation
SCAA	Specialty Coffee Association of America
SCAI	Specialty Coffee Association of Indonesia
VIP	Variable Importance in Projection

Chapter 1

General Introduction

1.1 The Specialty Coffee Arabica

Coffee is a popular beverage in the world with approximately 2.25 billion cups of coffee are consumed everyday (Cordoba et al. 2019). Hence, coffee become an important commodity with increasing consumption and production trend for the last five decades (FAO 2015). There are two commercially predominant coffee species, Robusta (*Coffea canephora*) and Arabica (*Coffea arabica*). The two species have different characteristic, including the taste of the coffee. Robusta has hint of woody, brunt rubber, heavy body and mouthfeel cup quality while Arabica has hint of fruity, berry, and high acidity (Hoffmann 2014). Although the consumer preference is diverse, the taste of Arabica coffee is more appreciated than Robusta. Moreover, the term of "specialty coffee" was introduced back in the 1990's specifically for coffee from microclimates with distinctive flavor and aroma (Samoggia and Riedel 2018). The increasing number of the coffee chains in 1990's also contributed the popularity of specialty coffee Arabica by provided the product to fulfil the consumer needs (Samoggia and Riedel 2018). Therefore, Specialty Coffee Association of America (SCAA) develop the standard protocol to evaluate coffee quality in terms of flavor in numerical value to grade the coffee quality. If the coffee has score more than 80, it will be graded as specialty coffee Arabica. This grade will further influence the coffee price in the market (Tolessa et al. 2017). The sensory evaluation protocol called "cupping test" is widely used in the coffee industry to grade the Arabica coffee.

SCAA cupping test protocol. The coffee sensory evaluation or cupping test is conducted by trained panelist called Q-grader. Before conducting the cupping test, the brewed coffee needs to be prepared based on the established protocol. The raw, green coffee beans is roasted until the color of the beans reach the Agtron "Gourmet" color metric number 63. The roasting process is not less than 8 minutes and not more than 12 minutes. The roasted coffee then rested and air cooled (water quenching are prohibited). The roasted coffee beans need to be used for the cupping test within 24 hours after roasting process. 8.25 g of roasted coffee beans (whole beans) are used for 150 ml of water. The roasted coffee beans then grinded with particle size slightly coarser than for filter drip brewing. The coffee powder then placed into ceramic cup and closed with a lid prior to brewing. The water for brewing the coffee should be clean and odor free with total dissolve solids around 125-175 ppm. The water is boiled and prepared with temperature 93°C. The hot water then poured directly to wet all the coffee powder in the cup and left it for 3-5 minutes before evaluation. Five cups of coffee are prepared for each kind of coffee beans samples. Two or three trained panelists will taste all five cups of the same kind of coffee prepared by established standard protocol. The panelists will evaluate the taste attributes including, fragrance/aroma, flavor, aftertaste, acidity, body, balance, uniformity, clean cup, sweetness, defects, and overall. In theory, the score ranged from 0 to 10. However, the evaluation form provides 16-point scale of quality in quarter point increments to describe the intensity of the taste attributes. The final score is the sum of all taste attributes except for defects. The score of defects will be subtracted from the final score of all the taste attributes. Based on this protocol, coffee with the final score more than 80 will be graded as "specialty coffee" with three different classes. If the final score has 80 until 84.99, it will be classified as "very good", 85-89.99 as "excellent", and 90-100 as "outstanding" (**Table 1.1-1**) (Specialty Coffee Association/SCAA 2015).

The SCAA cupping test protocol to grade the coffee quality is a detailed process that require the expertise of the panelists. Although the protocol is a golden standard and widely used for coffee quality assessment, the determination of coffee quality based on the flavor still faces some challenges. The detailed step and the training of the panelist make the cupping test are costly and time consuming and skipping some steps might sacrifice the quality of assessment itself. Moreover, it is previously reported that the panelist is prone to subjectivity and sensory fatigue due to large number of samples. Nevertheless, the cupping test score still the main parameter for coffee quality in the industry. Hence, the investigation of coffee quality by means of chemical composition using analytical approach are suggested to assist the sensory evaluation (Pereira et al. 2017).

Table 1.1-1 The classification of the coffee quality based on the final cup score in the cupping test based on SCAA

Total Score Quality Classification		
90-100	Outstanding	Specialty
85-89.99	Excellent	
80-84.99	Very Good	
<80	Below Specialty Quality	Not Specialty

1.2 The production of Arabica coffee

The coffee graded as specialty coffee based on the SCAA cupping test protocol will determine the coffee price in the market. It is reported that, the specialty coffee might have 20-50% higher price compared to the regular coffee (Tolessa et al. 2017). Therefore, the coffee farmer and producer are keen to improve their own products based on this standard. However, the production of Arabica coffee requires long steps from cherry to cup (**Fig. 1.2-1**). The production starts from the harvesting of the coffee cherry, sorting the coffee cherry, the postharvest process method in which has its own steps and produced the raw, green coffee beans. Furthermore, the green coffee beans are roasted, grind and brewed to obtain the cup of coffee that evaluated based on its sensory properties to get the specialty grade. The green coffee beans, seems to be the intermediate product that connects the production process and the sensory evaluation. During the production process of the green coffee beans, various of factors influence the coffee quality including the genetical factor, geographical origins, and postharvest process methods. All of these factors need to be considered to achieve the good quality of coffee and the trial-and-error effort will costly and required long period of time.

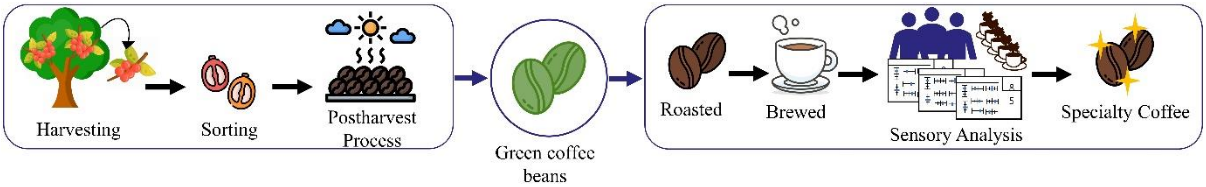

Figure 1.2-1 The production process of Arabica coffee from cherry to cup. In specialty coffee Arabica production, the sensory analysis is conducted to determine the coffee beans grade.

1.2.1 The factors related to Arabica coffee quality during production

Genetical traits

Arabica coffee has various varieties such as typica, bourbon, mundo novo, caturra, gesha, and other varieties comes with its own local name depending on the production countries. Among these varieties, Typica is the original variety comes from Ethiopia that has excellent cup quality and unfortunately low yield of production. Hence, the development of Arabica coffee variety was started from Typica to fulfil the production needs in which happen naturally, or human made. This development influenced the production yield, dwarfism, bean size, and resistance to plant diseases of Arabica coffee variant Typica (Hoffmann 2014). Although it is possible that each variety might have different notes to each other, the overall cup quality and the biochemical composition of the coffee beans were reported to be not significantly different (Leroy et al. 2006).

Geographical origin

Geographical origin become important aspect of Arabica coffee since more of specialty coffee Arabica is from a single origin of place where Arabica coffee is produced. Arabica coffee is mostly produced by country located in the tropical belt in which could provide suitable condition of coffee tree growth. Interestingly, the taste of Arabica coffee from different countries are distinct to each other. It is also reported that different location of Arabica coffee production within the same country also poses different flavor and biochemical compositions (Wei et al. 2012; Da Silva Taveira et al. 2014; Putri et al. 2019). The differences of Arabica coffee flavor might cause by the underlaying environmental factors within the geographical origin. Among all environmental factors, altitude is considered as the most important factor that influence coffee quality (Joët et al. 2010; Tolessa et al. 2017; Worku et al. 2018).

Altitude. The Arabica coffee tree is commonly cultivated at medium to high altitude. In equatorial region, it is 1000 – 2100 m above sea level, or at 400 – 1200 m above sea level in the place further from equatorial regions (9 – 24° to the North and South latitudes) (Illy and Viani 2005). At this altitude, it could provide the optimum temperature (18 - 21°C) for the Arabica coffee tree growth and coffee cherry ripening process (Illy and Viani 2005; DaMatta et al. 2008; Poltronieri and Rossi 2016). Moreover, it is generally believed that coffee grown in higher altitudes has better sensory quality than coffee grown at lower altitudes. (Avelino et al. 2007; Bertrand et al. 2012; Davis et al. 2012; Schroth et al. 2015)

Postharvest process method

The postharvest process method is a series of steps to remove the fruit part of coffee cherry including pulp, mucilage, and silverskin, to obtain the coffee beans (**Fig. 1.2.1-1**). The harvested coffee cherry will be subjected to particular postharvest process method depending on the natural resources available at the production place to reduce the production cost. There are several postharvest process methods that classified into three different categories: dry process (natural process), washed process (full-washed process), and hybrid methods (Hoffmann 2014) (**Fig. 1.2.1-2**). Since each of the postharvest process has different step to produce the green coffee beans, it is reported that the biochemical composition of green coffee beans as well as coffee taste were affected.

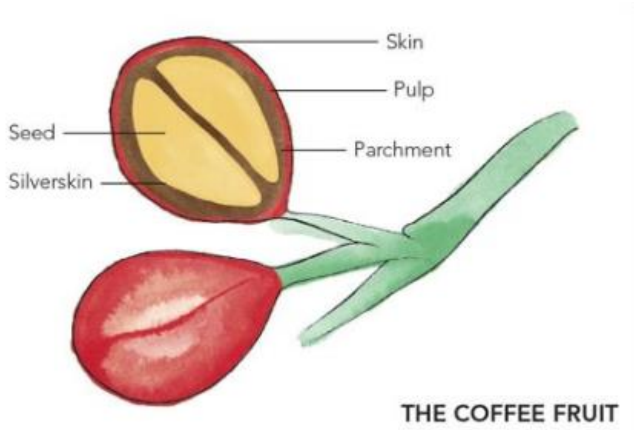

Figure 1.2.1-1 The morphology of coffee cherry (Hoffmann 2014)

Drying process (natural process). The drying process or commonly known as natural process is the oldest and cheapest method that used for obtaining the green coffee beans from the coffee cherry. The harvested coffee cherries are dried under the sun by spreading out the coffee cherry on the brick patio or drying table for 10 until 25 days. During the drying process, the coffee cherries are turned periodically to avoid unwanted microbial growth such as mold. The coffee beans are yield after the fruit part of coffee cherry are dried and removed mechanically. This postharvest method is commonly applied in Ethiopia and Brazil where the access of the water is limited.

Washed process (full-washed process / wet process). The washed process is a method that aiming to remove the fruit part of coffee cherry to obtain the coffee beans before conducting the drying process to reduce the risk of flavor defect during drying process. The removal of the coffee pericarp and flesh is performed mechanically, leaving the coffee beans with the thin layer of mucilage. Subsequently, the mucilage layer is removed by breaking down the pectin by fermentation for 24 – 48 hours. The duration of fermentation is depending on the ambient temperature of the fermentation place. The control checking might be necessary to avoid over-fermentation in which caused undesired flavor in the coffee brew. Afterwards, the coffee beans are cleaned by water and dried under the sun until the water content in the coffee beans reach 11-13%.

Hybrid process. The hybrid process is a combination of dry and washed process method. This method performed by de-pulping the coffee cherry to remove the pericarp and fruit part of coffee cherry, followed by the sun-drying of the coffee beans with the mucilage layer still intact. Hence, the hybrid process required less water compared to washed process. The pulped natural process and honey process are two common postharvest processes that classified into this category. **The pulped natural process** method conducted by de-pulp the coffee cherries and then carefully dry on the brick patios or drying table. **The honey process** method is slightly different from the pulped natural process. In the honey process the remaining flesh after de-pulping process were controlled into specific amount (approximately 20-80% mucilage). The amount of mucilage before drying will be mentioned in the final product of the coffee beans produced by honey process method.

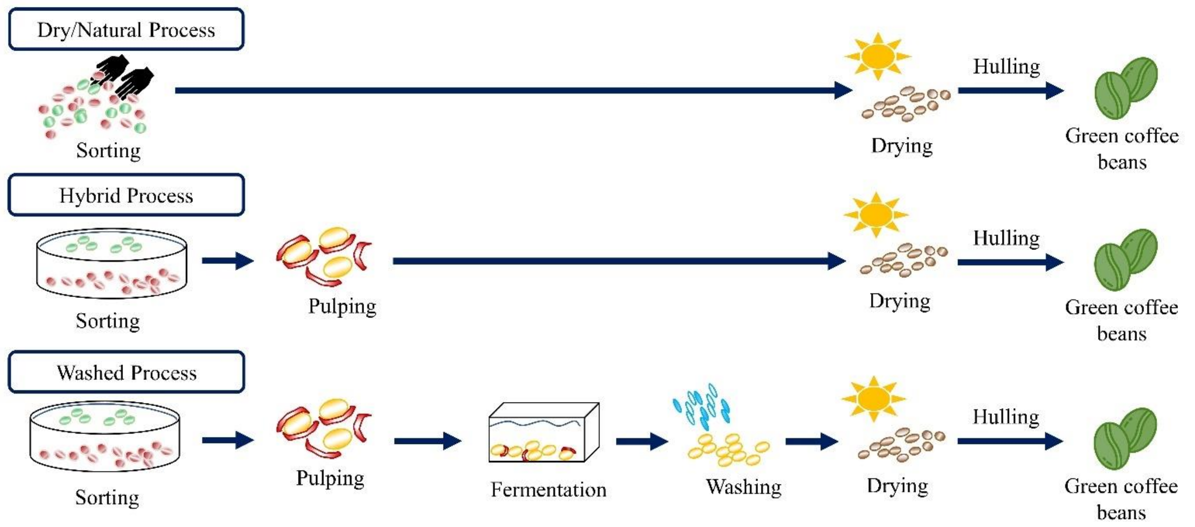

Figure 1.2.1-2 The three different postharvest process methods : dry/natural process, hybrid process, and washed process. Each of postharvest process method has different step of process to obtain green coffee beans from the coffee cherry (Hoffmann 2014).

1.3 Metabolomics

Metabolomics is an omics study for assessing as many metabolites as possible in a living system, offering a systematic and comprehensive approach to describe the complex phenotypes based on the variation of metabolome profile (Cevallos-Cevallos and Reyes-De-Corcuera 2012; Putri and Fukusaki 2015). Metabolomics approach become a powerful tool and has been applied in human (Jobu et al. 2012; Sakanaka et al. 2021; Taya et al. 2021), plant (Cevallos-Cevallos et al. 2012; Uthe et al. 2021), and animal (Selvarasu et al. 2012; Yao et al. 2021)studies. In recent years, metabolomics approach is also adopted for food science (Wishart 2008; Cevallos-Cevallos and Reyes-De-Corcuera 2012; Kim et al. 2016; Putri et al. 2022).

The metabolomics analysis is categorized into two different approaches based on the metabolite recovery and identification: untargeted approach and targeted approach. The untargeted metabolomics approach aims to obtained patterns or metabolite fingerprinting by detecting the broadest range of the metabolites present in the sample's extract without any prior knowledge of the sample's metabolome (Cevallos-Cevallos et al. 2009; Johnson et al. 2016). Hence, the untargeted approach will result in complex dataset and the require suitable statistical and computational tools to find the correlation between the metabolome and the phenotype (Johnson et al. 2016). Targeted metabolomics approach focused on specific group of metabolites based on the previous knowledge or theory. Therefore, the targeted analysis requires higher sensitivity and selectivity to aim quantification of a metabolome of interest. Targeted approach might be an expansion of the untargeted approach to validate the findings based on the later approach (Johnson et al. 2016).

The analysis of metabolome, regardless of the study approach, require the selection of the suitable analytical instrument. There are various analytical techniques that could be employed for metabolomics study to detect the metabolites such as mass spectrometry (MS) and nuclear magnetic resonance (NMR) (Wishart 2008; Fukusaki 2015). In mass spectrometry, it is often coupled with the separation techniques such as gas chromatography, liquid chromatography, capillary electrophoresis (Wishart 2008; Cifuentes 2013; Fukusaki 2015). Each of the analytical instruments has its own advantages and disadvantages regarding the metabolite coverage or the target metabolites of the study. Therefore, the selection of the separation and detection technologies become a crucial step to achieve the aim of the study.

The chromatography-mass spectrometry-based metabolomics analysis resulting a complex data matrix. Therefore, the statistical tool is essential to interpret the result of analysis (Johnson et al. 2016). In metabolomics study, multivariate analysis such as principal component analysis (PCA) and orthogonal projection of latent structures (OPLS) are often employed to observe the metabolome variance between the samples. Therefore, the data interpretation and hypothesis generation could be conducted (Putri & Fukusaki 2015).

1.3.1 Metabolomics application in coffee

The application of metabolomics in food science are more common in recent years due to the complex nature of the food chemical components that easily transformed and affected by various factors in which further influence the final attributes of the food product such as sensory perception and shelf life (Cevallos-Cevallos and Reyes-De-Corcuera 2012). The metabolomics approach is applied to observe the resource, process, and safety of the food by the variance of the food metabolome profile (Kim et al. 2016). Fruit, fermented food, shrimp, cacao and coffee are some of food that subjected to the metabolomics analysis (Putri et al. 2022).

Coffee is also a subject of the metabolomics studies. The variance of coffee could be observed by its sensory properties in which also reflected on its chemical components. The metabolomics study shown promising results for discrimination and authentication of coffee based on species (El-Abassy et al. 2011; Defernez et al. 2017), cultivars and varieties (Garrett et al. 2013; Zhang et al. 2016), origin (Da Silva Taveira et al. 2014; Putri et al. 2019) and process (Jumhawan et al. 2013). Metabolomics approach also employed to observe the coffee quality based on the cupping test score on the roasted coffee or powdered coffee (Sittipod et al. 2019; Sittipod et al. 2020; Rocchetti et al. 2020). This study also employed the GC/MS-based metabolomics approach to discover the low molecular metabolite correlated with the coffee quality based on the cupping test score in the green coffee beans. Moreover, this study also investigates the most influential factors that influence the coffee quality by means of metabolome profile obtained from green coffee beans. The results from this study might be contributed to assist the cupping test sensory evaluation and also the coffee producer to reduce the time required for coffee quality assessment and coffee production optimization.

1.4 Research objectives

Therefore, the objective of this study is to perform metabolomic-based study for the quality-related investigation during the production of green coffee beans of specialty coffee Arabica. The green coffee beans are used since it connects the sensory evaluation and the production process. Therefore, this study pursues the understanding coffee quality and its related factors during the green coffee beans production observed in the metabolome profile. To achieve this, the first strategy is to investigates the metabolite correlated between sensory evaluation result and green beans metabolome profile by GC/MS-based metabolite profiling combined with multivariate analysis. The second strategy is to determine the predominant factor during the green coffee beans process as seen through the metabolome profile. Lastly, the validation study is conducted by using the samples from specific farm in Indonesia.

1.5 Thesis outline

This thesis is contained five chapters providing the metabolomics-based study to investigate the quality-related metabolite and factors in Arabica green coffee beans production. In the chapter one, general introduction regarding the specialty coffee Arabica and its production and how metabolomics could be employed to achieve the aims of this study. The chapter two describe the metabolomics-based approach for the quality-related metabolite investigation in specialty coffee Arabica green coffee beans. In the chapter three are moving back to the production process on the specialty Arabica green coffee beans by investigating the predominant factor that influence the metabolome profile and the coffee quality. The chapter four describe the study using green coffee beans from one location in Indonesia to validate the findings in chapter two and three. Finally, the chapter 5 describe the conclusion and the future perspective of this study.

Chapter 2

The metabolomics-based approach to investigate the quality related metabolites in the green beans of specialty coffee Arabica

2.1 Introduction

The flavor of coffee is the main parameter to describe the coffee quality and the determinant factor for the coffee price (Tolessa et al. 2017; Fernandez-Alduenda 2018). The assessment of coffee quality based on coffee flavor conducted using the widely used protocol developed by Specialty Coffee Association of America. The protocol described in detail on the preparation and how to conduct the sensory evaluation of the coffee. The sensory evaluation, as known as cupping test, will evaluate ten flavor attributes in which the score ranged from 0 to 10 and will be summed up as final score. If there is some defect, the score of defects is subtracted from the final score (Specialty Coffee Association/SCAA 2015). If the final score more than 80 out of 100, the coffee graded as specialty coffee and sold 20-50% higher price than regular coffee (Tolessa et al. 2017). However, the sensory evaluation, as known as cupping test, could only be performed by certified panelist called Q-grader that should be periodically trained. Moreover, the cupping test is time consuming process and prone to subjectivity of the panelist (Worku et al. 2016; Pereira et al. 2017). If there is a lot of samples that needs to be assessed, the panelist also prone to exhaustion and sensory fatigue (Carpenter et al. 2000). Regardless of the shortcomings in the cupping test, the test still the golden standard for coffee quality in the coffee industry. Therefore, to assist the sensory test, the analytical-based quality assessment developed from the analysis of the biochemical composition of coffee beans might be necessary (Pereira et al. 2017).

Green coffee beans have various compounds that act as flavor precursor in which influence the coffee quality in the cup of coffee (Montavon et al. 2003; Joët and Dussert 2018). Hence, previous study investigated the correlation of biochemical compound in green coffee beans to the sensory quality of coffee with analytical approach. Near-infrared spectroscopy (NIRS) is often used to investigate the correlation between the composition of green coffee beans with the coffee quality (Barbin et al. 2014; Santos et al. 2012; Tolessa et al. 2016; Barbosa et al. 2019). Raman spectroscopy also employed to investigate the coffee quality during storage in green coffee beans (Abreu et al. 2019). However, these study approach produced the spectra rather than the actual compound or have limited metabolite coverage. Hence, metabolomic approach was applied to investigate the metabolite correlated with the coffee quality, described as cup score, using green coffee beans of specialty Arabica from Indonesia. Gas chromatography/mass spectrometry (GC/MS) analysis was employed to obtain the metabolite profile of the green coffee beans. Subsequently, orthogonal projection to latent structure (OPLS) analysis was used to construct a prediction model of cupping scores. The correlated metabolites with the cupping score could be suggested based on the variable importance in projection (VIP) scores in which showed the important contribution to the model. The quality-related metabolites find in this study could be proposed as marker that could provide early and rapid screening methods of coffee quality by analyzing the quality-related marker(s) in green coffee beans to assist the sensory evaluation.

2.2 Materials and methods

2.2.1 Chemicals

All chemicals used in this study were of analytical grade and described in previous publication (Jumhawan et al. 2013; Putri et al. 2019). Methanol (99.8%), infinity pure pyridine, and ribitol were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Chloroform (99%) was purchased from Kishida Chemical (Osaka, Japan). Methoxyamine hydrochloride was purchased from Sigma Aldrich (Milwaukee, WI, USA). N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) and a standard alkane mixture (C10–C40) were purchased from GL Science Inc. (Tokyo, Japan).

2.2.2 Coffee beans sample collection

All coffee beans were collected and provided by Indonesian Coffee and Cocoa Research Institute (ICCRI), Jember, Indonesia during Indonesian Specialty Coffee Competition (Kontes Kopi Spesialti Indonesia). All the samples were coded in number and ten kinds of green (raw, not roasted) were used as training set for constructing the model while thirty-five of green Arabica coffee beans were used as the test set in this study (**Table 2.2.2-1**). These ten kinds of green coffee beans were stored at −30°C prior to metabolite profiling.

2.2.3 Sensory analysis

The sensory analysis was conducted at ICCRI for all the samples used in this study. The sensory analysis was performed within 24 hours after roasting process and was done according to the standardized protocol published by Specialty Coffee Association of America (SCAA) by certified panelist (Q-Grader). Ten parameters which rated from 0-10, with 0 indicating the least strong and ten for the strongest taste. The total cup score was obtained by accumulating the scores of all parameters and determined the coffee grade (3).

Table 2.2.2-1 List of Specialty Coffee Arabica Samples

Rank	Code	Fragrance /Aroma	Flavor	Aftertaste	Acidity	Body	Uniformity	Balance	Clean cup	Sweetness	Overall	Final score[a]
Training set												
1	A/008	8.50	8.00	7.75	8.00	8.50	10.00	8.00	10.00	10.00	8.00	86.75
2	A/034	7.75	7.75	7.75	7.75	8.00	10.00	7.75	10.00	10.00	7.75	84.50
3	A/009	8.00	8.00	7.75	7.50	8.00	10.00	7.50	10.00	10.00	7.50	84.25
4	A/001	7.75	7.75	7.50	7.50	7.50	10.00	7.50	10.00	10.00	7.50	83.00
5	A/018	8.50	8.25	8.00	8.50	8.00	10.00	3.00	10.00	10.00	8.50	82.75
6	A/026	7.75	7.50	7.50	7.50	7.50	10.00	7.50	10.00	10.00	7.50	82.75
7	A/067	7.75	7.25	7.25	7.50	8.00	10.00	7.50	10.00	10.00	7.50	82.75
8	A/025	7.50	7.00	7.00	7.00	8.00	10.00	7.50	10.00	10.00	7.50	81.50
9	A/063	8.00	7.25	7.00	7.00	7.25	10.00	7.00	10.00	10.00	7.00	80.50
10	A/039	7.5	7.00	7.00	7.00	7.75	10.00	7.00	10.00	10.00	7.00	80.25
Validation set												
1	A/097	8.00	8.06	8.00	8.13	8.06	10.00	8.06	10.00	10.00	8.13	86.44
2	A/037	7.88	8.19	8.00	8.06	8.00	10.00	8.00	10.00	10.00	8.19	86.31
3	A/100	7.88	8.13	8.06	8.06	8.00	10.00	8.06	10.00	10.00	8.06	86.25
4	A/013	8.00	8.13	8.00	8.19	7.94	10.00	7.88	10.00	10.00	8.13	86.25
5	A/023	7.88	7.88	7.81	7.94	8.44	10.00	8.44	10.00	10.00	7.88	86.25
6	A/060	8.00	7.94	8.00	7.88	7.94	10.00	8.44	10.00	10.00	7.94	86.13
7	A/038	7.94	8.00	7.94	8.19	7.94	10.00	8.00	10.00	10.00	8.06	86.06
8	A/062	8.00	7.94	8.00	8.00	7.94	10.00	7.94	10.00	10.00	8.00	85.81
9	A/113	8.00	8.00	7.94	8.06	7.81	10.00	7.94	10.00	10.00	8.00	85.75
10	A/110	7.81	7.88	7.94	8.13	8.06	10.00	7.94	10.00	10.00	8.00	85.75
11	A/102	8.00	7.94	8.00	8.00	7.81	10.00	7.88	10.00	10.00	8.00	85.63
12	A/011	8.06	7.94	7.94	7.94	7.94	10.00	7.81	10.00	10.00	7.88	85.50
13	A/065	7.94	8.06	7.88	7.94	7.81	10.00	7.81	10.00	10.00	7.88	85.31
14	A/078	7.81	8.00	7.88	7.94	7.88	10.00	7.88	10.00	10.00	7.81	85.19
15	A/107	7.94	7.81	7.75	8.00	7.81	10.00	7.81	10.00	10.00	8.00	85.13
16	A/061	7.88	7.94	7.75	7.94	7.75	10.00	7.81	10.00	10.00	7.88	84.94
17	A/059	8.00	7.94	7.81	7.88	7.81	10.00	7.69	10.00	10.00	7.75	84.88
18	A/043	7.94	7.81	7.88	7.81	7.75	10.00	7.81	10.00	10.00	7.88	84.88
19	A/112	7.88	7.81	7.75	7.94	7.88	10.00	7.75	10.00	10.00	7.75	84.75
20	A/106	7.94	7.69	7.69	7.75	7.81	10.00	7.69	10.00	10.00	7.69	84.25
21	A/088	8.00	7.69	7.75	7.75	7.56	10.00	7.69	10.00	10.00	7.75	84.19
22	A/091	7.81	7.75	7.75	7.75	7.81	10.00	7.63	10.00	10.00	7.69	84.19
23	A/064	7.75	7.81	7.69	7.81	7.63	10.00	7.75	10.00	10.00	7.75	84.19
24	A/074	8.00	7.75	7.56	7.88	7.63	10.00	7.56	10.00	10.00	7.69	84.06
25	A/056	7.75	7.81	7.63	7.75	7.69	10.00	7.63	10.00	10.00	7.63	83.88
26	A/115	7.75	7.75	7.56	7.69	7.63	10.00	7.69	10.00	10.00	7.69	83.75
27	A/109	7.63	7.63	7.63	7.63	7.81	10.00	7.69	10.00	10.00	7.69	83.69
28	A/044	7.63	7.56	7.75	7.56	7.75	10.00	7.63	10.00	10.00	7.63	83.50
29	A/058	7.88	7.63	7.69	7.56	7.50	10.00	7.56	10.00	10.00	7.56	83.38
30	A/095	7.75	7.69	7.38	7.63	7.56	10.00	7.44	10.00	10.00	7.44	82.88
31	A/024	7.56	7.50	7.56	7.50	7.69	10.00	7.50	10.00	10.00	7.50	82.81
32	A/105	7.75	7.50	7.56	7.38	7.69	10.00	7.50	10.00	10.00	7.44	82.81
33	A/093	7.50	7.56	7.63	7.56	7.50	10.00	7.50	10.00	10.00	7.50	82.75
34	A/017	7.56	7.50	7.50	7.25	7.69	10.00	7.44	10.00	10.00	7.44	82.38
35	A/103	7.50	7.25	7.31	7.25	7.63	10.00	7.31	10.00	10.00	7.13	81.38

[a] Final scores were calculated by summing scores of all attributes. (The attribute of defects was not recorded in this study.)

2.2.4 Metabolite extraction and derivatization

Extraction was performed following the protocol as described previously with some modifications (Jumhawan et al. 2013; Putri et al. 2019). Green coffee beans were put into 50 ml tube (Yasui Kikai Co., Osaka, Japan) with metal cone (Yasui Kikai Co., Osaka, Japan) and was quenched using liquid nitrogen. The beans were ground at 2000 rpm for 30 seconds using multi-beads shocker (Yasui Kikai Co., Osaka, Japan), and this step was repeated three times to produce a fine coffee powder. The powdered coffee beans (15 mg) were transferred into a 2 ml Eppendorf tube and three technical replicate was prepared (n=3) for each sample. At this time, a blank was prepared and followed all steps together with other samples. The powdered coffee beans were extracted using a single-phase solvent mixture of methanol, ultrapure water, and chloroform in a ratio of 5/2/2 (v/v/v) containing ribitol (12 µg/ml) as an internal standard. The samples were incubated at 37°C and 1200 rpm for 30 minutes, and then centrifuged at 4°C and 13100 rpm for 3 minutes. The supernatant (900 µl) was transferred into a 1.5 ml tube, and 400 µl of ultrapure water was added to the tube. The mixture was then vortexed and centrifuged at 4°C and 13100 rpm for 3 minutes. A 200 µl of the aqueous phase was transferred into a new 1.5 ml tube with a pierced cap. The solvent was evaporated by vacuum centrifugation for 50 minutes, followed by lyophilizing overnight.

The derivatization process consists of two steps, oximation and trimethylsilylation, as described in the published procedure (Jumhawan et al. 2013; Putri et al. 2019). The lyophilized green coffee beans extract was subjected to oximation by adding 100 µl methoxyamine hydrochloride (20 mg/ml in pyridine), then vortexed and incubated at 1200 rpm and 30℃ for 90 minutes. Subsequently, 50 µl MSTFA was added, and the mixture was re-vortexed and incubated at 1200 rpm and 37℃ for 30 minutes. Sample mixture (100 µl) was transferred into a GC/MS vial prior to GC/MS analysis.

2.2.5 Gas chromatography-mass spectrometry analysis

The protocol of GC/MS analysis has been described in previous publications with some modifications (Jumhawan et al. 2013; Putri et al. 2019). Derivatized samples were subjected to GC/MS analysis immediately after derivatization process. GC/MS analysis were performed using a GCMSQP2010 Ultra (Shimadzu, Kyoto, Japan). The instrument was equipped with a 30 m × 0.25 mm i.d. fused silica capillary column coated with 0.25 μm InertCap 5MS/NP (GL Science, Inc., Tokyo, Japan) and an AOC-20i/s (Shimadzu, Kyoto, Japan) as an autosampler. System control and data acquisition were conducted using the GCMS solutions software (Shimadzu, Kyoto, Japan). The mass spectrometer was tuned and calibrated prior to analysis. The standard alkane mixture (C10−C40) was injected at the beginning of the retention index calculation. The derivatized green coffee beans extracts samples (1 μl) were injected in split mode (12:1 (v/v)) at an injection temperature of 230°C. All samples were injected in random order with QC injections (1 μl) every four or five injections. Helium was used as carrier gas with a flow rate of 1.12 ml/min and a linear velocity of 39 cm/s. The column temperature was held at 80°C for 2 minutes, increased by 15°C per minute to 330°C, and finally kept at 330°C for 6 minutes. The transfer line temperatures were 250°C. The ion source temperature was 200°C and the ions were generated by electron ionization (EI) at 70 eV. EI mass spectra were recorded at 6.67 scans per second over the mass range of *m/z* 85-500 (13,14).

2.2.6 Data processing

The chromatogram data obtained by GC/MS analysis were converted to a netCDF format using the GCMS Solution software package (Shimadzu, Kyoto, Japan). The netCDF files were further converted into ABF format using Reifycs Abf Converter (https://www.reifycs.com/AbfConverter/). Peak detection, deconvolution analysis, identification, and alignment were performed using MS-DIAL version 4.18 (Tsugawa et al.

2015; Lai et al. 2018; Tsugawa et al. 2019), which is a free software (http://prime.psc.riken.jp/Metabolomics_Software/MS-DIAL/). The minimum height for peak detection was set as 1,000 amplitudes with a linear weight moving average smoothing method. Smoothing level began at 5 scans and average peak width of 20 scans. In deconvolution analysis the sigma window value was set as 1, and the EI spectra cut-off was 200 amplitudes. Peak identification used the retention index (RI) based on the retention time of the standard alkane mixture (C10-C40) and GL-Science DB library (InertCap 5MS-NP, Kovats RI, 494 records; http://prime.psc.riken.jp/Metabolomics_Software/MS-DIAL/GCMS%20DB_InertCap%205MS-NP_GLscience.msp). The parameters for peak identification and alignment were; RI tolerance 10, RT tolerance 0.5 minute, *m/z* tolerance 0.5 Da, EI similarity cut-off 70%, and identification score was cut-off at 70%. Metabolite identification was conducted by comparing the mass spectra and RI with the GL-Science DB library. After peak detection, the height of the detected peaks was normalized by the height of the internal standard peaks. The data matrix was constructed consisting of the raw height and normalized height of peaks. Filtering was then performed to exclude peaks that were not of biological origin by referring to the blank chromatogram from the data matrix (Putri et al. 2019). Moreover, peaks with a relative standard deviation of more than 30% in QC and with a raw height less than 10,000 were also removed. The final data matrix with filtered and assigned peaks was constructed and used for further analysis.

2.2.7 Multivariate analysis

The relative intensities data metabolites were used as explanatory variables, and the cupping score data was used as response variable. Orthogonal projection to latent structure (OPLS) regression analysis was performed using the commercially available SIMCA-P+ version 13.0.3 (Umetrics, Umeå, Sweden). The data matrix was subjected to PCA and OPLS with auto-scale and without transformation, to analyze all the obtained metabolites equally (van den Berg et al. 2006).

2.2.8 Quantitation of marker candidate

The quality marker candidate was quantitated in the sample using the calibration curve of the galactinol standard prepared at various concentrations. The concentrations of the standard were 0.04, 0.4, 0.8, 1.6 and 2.4 µg/ml in ultrapure water. The samples extracts were prepared by using green coffee beans. Both standard solution and samples extracts were lyophilized overnight. After derivatization, the standard and extract of samples was analyzed using GC/MS with the same parameter as described previously except ion monitoring mode was set at *m/z* 204. After data processing, the construction of the standard calibration curve, sample quantitation, and student *t*-test were performed using Microsoft Excel.

2.3 Result and discussion

2.3.1 GC/MS metabolite profiling analysis of specialty Arabica green coffee beans

The metabolic profiling of ten different kind of green coffee beans focusing on low molecular hydrophilic compound was conducted by gas chromatography/mass spectrometry (GC/MS) in which employed in previous studies (Jumhawan et al. 2013; Putri et al. 2019). The chromatogram obtained by GC/MS were undergo data pretreatment and filtering. Thus, 124 metabolite peaks were detected and consisted of 68 annotated metabolites while the rest are unknowns. The annotated peaks were classified as amino acid, sugar, sugar alcohol, organic acid, and other compounds (Table S1). The data matrix contained the metabolites' relative intensity were further used as explanatory variable in multivariate analysis for data mining and visualization of the sample variance.

2.3.2 The selection of quality-related metabolite in specialty Arabica green coffee beans by multivariate analysis

The principal component analysis (PCA) and orthogonal projection to latent structure (OPLS) regression analysis were employed for data mining. The unsupervised data analysis was performed using PCA to observe the data structure of the samples' data matrix. The PCA result showed that the samples were not separated based on the tendency of the cupping score (**Fig. 2.3.2-1**). However, the replicates from same samples still clustered together and the variance between samples were higher than within the samples. Hence, the supervised analysis by OPLS were conducted to obtain more information about metabolites in green coffee beans that correlates with the coffee quality.

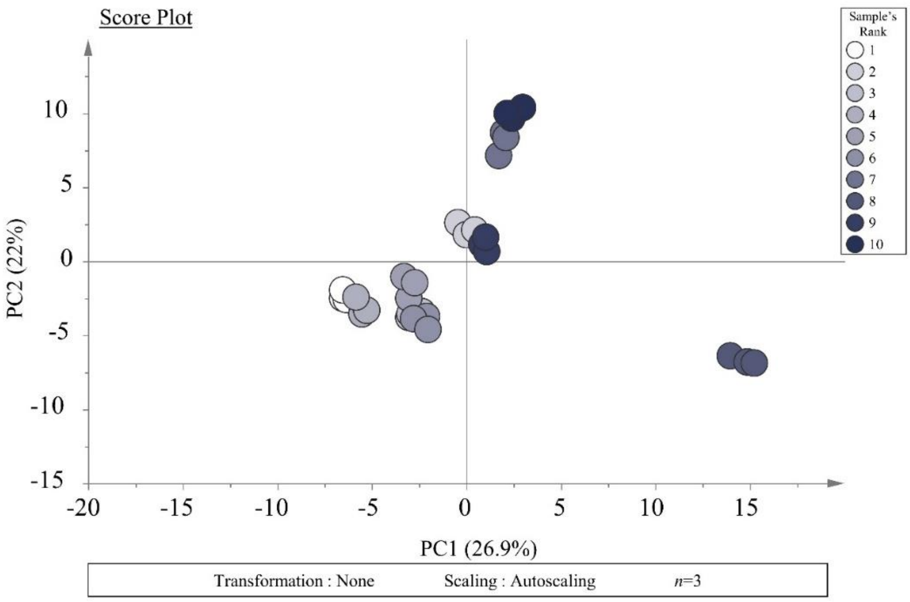

Figure 2.3.2-1 The PCA result of ten kinds of green coffee beans with the cup score ranged from 80.25 – 86.75. The samples were represented as circle and the gradient blue color represent the sample rank based on the score. The tendency based on cup score could not be observed in the PCA score plot.

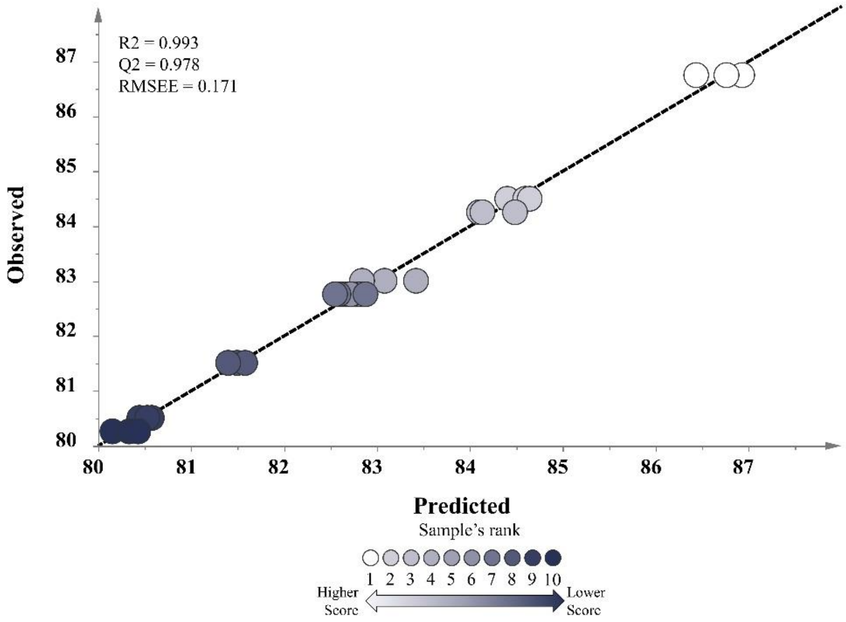

Figure 2.3.2-2 The OPLS model of final score of cupping test (scale : autoscale ; *n*=3). The circles represent the samples with cup score ranged from 80.25 – 86.75. The gradient blue color represents the sample rank based on the score. The model has high value of R2 and Q2 value indicating the good correlation between the variables.

The coffee quality is described by its final score of cupping test, which a sum of ten different taste attributes score. Hence, the OPLS analysis was conducted for the final score as the response variable and the green coffee beans metabolite profile as explanatory variable. The result of OPLS regression model using the final score of the cupping test as the response variable (score range 80.25 – 86.75) was shown in **Fig. 2.3.2-2**. The constructed OPLS model showed good correlation between the final score of the cupping test and the metabolites as the R2 and Q2 values were more than 0.9 (R2=0.993 and Q2=0.978 respectively) (Varmuza and Filzmoser 2009; Worley and Powers 2013; Alexander et al. 2015). The correlated metabolites to the OPLS model were sorted based on the variable importance in projection (VIP) score and those with VIP score more than 1 were considered as important metabolites to the model (Galindo-Prieto et al. 2014; Ikram et al. 2020). In this study, the metabolites with VIP score more than 1.5 were selected. There are 12 metabolites found to be positively or negatively correlated with the final cup score (Table S2). Galactinol, glutamic acid, caffeine, trehalose, and unknown compounds number 2, 16, 18, and 45 are the metabolites that have positive correlation with the cup score. Meanwhile, shikimic acid, alanine, and unknown compounds number 15 and 34 have negative correlation with the cup score. The relative intensity of these metabolites confirmed the positive and negative correlation with the final score of cupping test (**Fig. 2.3.2-3**). Further annotation was conducted for the unknown compounds. The mass spectrums of the important unknown compounds were compared to various databases (FoodB, MoNA, HMDB, and NIST). The result found that apigenin (unknown 2), 2,5-dimethylpyrazine (unknown 16), galactopyranoside (unknown 18), and D-lactitol (unknown 45) were correlated positively with cup score while gentistic acid (unknown 15) and alpha-1,2-mannobiose (unknown 34) were negatively correlated with cup score. However, these metabolites' identity needs to be further validated in future study using different analytical approach method(s).

Since the final score of the cupping test is the sum of the ten different taste attributes, the OPLS analysis also conducted to each taste attribute to observe if the VIP metabolites in the final score model showed strong correlation with the score of the taste attributes. However, the OPLS model for uniformity, clean cup, and sweetness cannot be constructed since these characteristics have same scores for all samples. The OPLS result of the seven taste attributes is shown in **Fig. 2.3.2-4**. The OPLS models of each taste attribute have good correlation between each variable based on their R2 and Q2 value (Varmuza and Filzmoser 2009; Worley and Powers 2013; Alexander et al. 2015). The VIP metabolites of the final score model also found to be important in the model of each attribute based on the VIP score more than 1.5 except for trehalose (**Table 2.3.2-1**). Galactinol found to be important with the highest number of taste attribute models with consistent tendency with final score, followed by galactopyranoside, and alpha-1,2-mannobiose. Galactinol have positive correlation with fragrance/aroma, flavor, aftertaste, acidity, and overall attributes while galactopyranoside have positive correlation with fragrance/aroma, flavor, acidity, and overall attributes. Alpha-1,2-

mannobiose found to has negative correlation with fragrance/aroma, flavor, acidity, and body taste attributes. Since galactinol, galactopyranoside, and alpha-1,2-mannobiose were correlated to the final score and the taste attribute(s), further observation was conducted to ensure the robustness of these metabolites as quality-related marker.

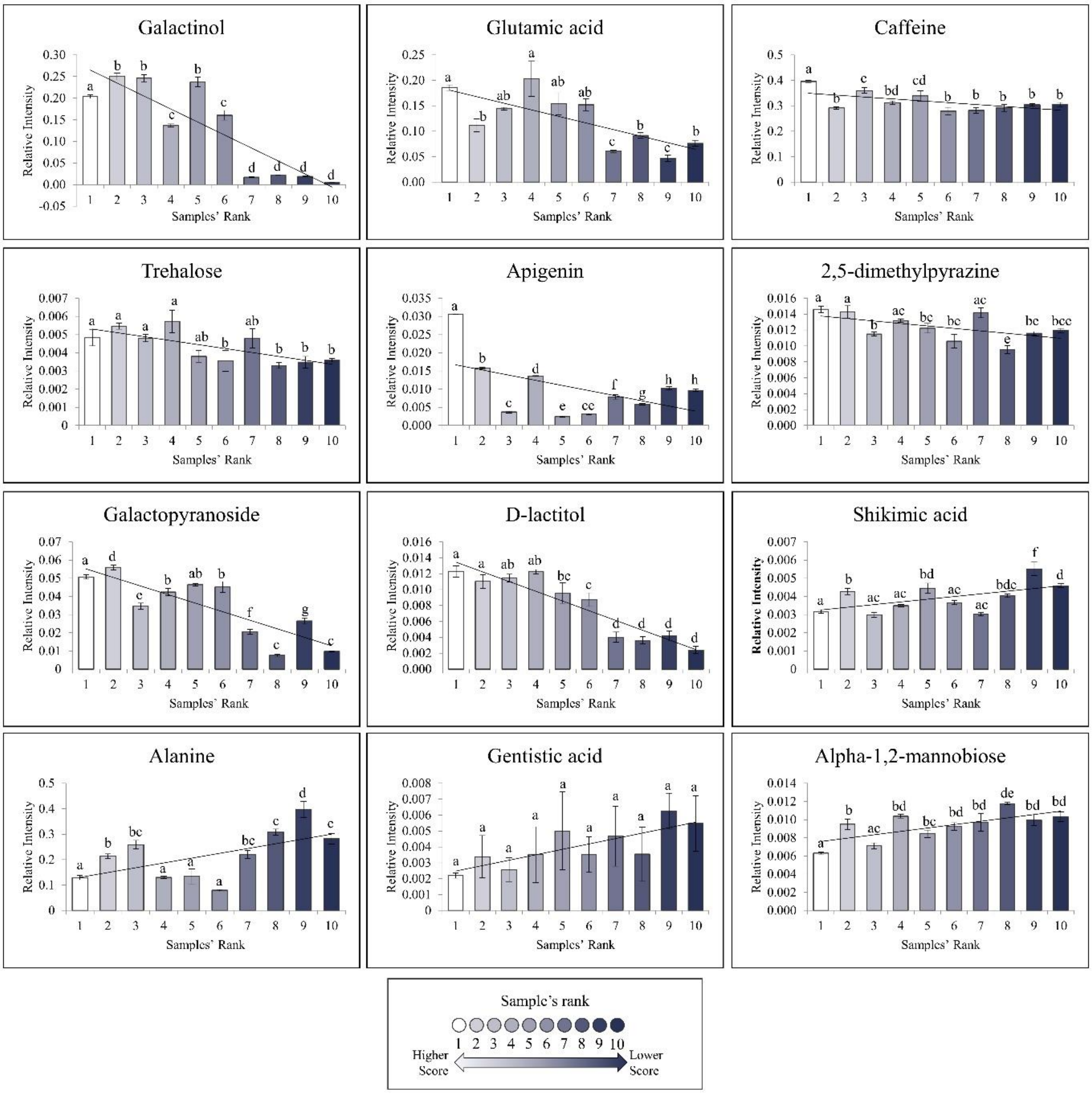

Figure 2.3.2-3 The relative intensity of the important metabolites to OPLS model of final score. The error bar showed the standard deviation. The same letter showed no significant different based on Tukey's post-hoc multiple comparisons with p values <0.05.

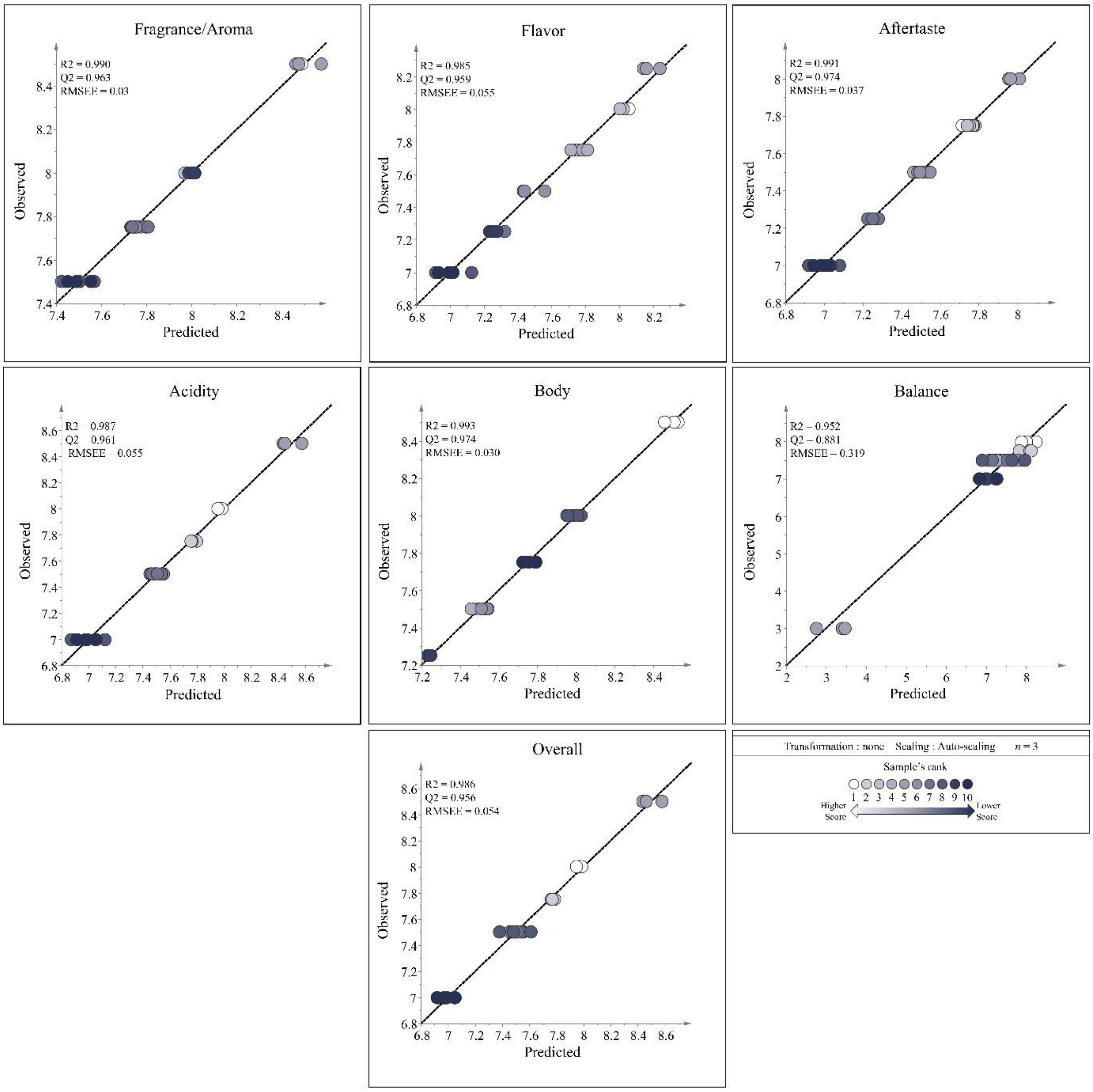

Figure 2.3.2-4 The OPLS model of the seven attributes score (scale : autoscale ; *n*=3). The circles represent the samples, and the gradient blue color represents the sample rank based on the final score. The seven model has high value of R2 and Q2 value indicating the good correlation between the variables.

Table 2.3.2-1 The VIP score of important metabolites in final score model to each respective taste attributes

VIP metabolites in "Final Score" model	Fragrance/Aroma		Flavor		Aftertaste		Acidity		Body	
	VIP score	Coefficient	VIP score	Coefficient	VIP score	Coefficient	VIP score	Coefficient	VIP score	Coefficient
Unknown_45 (D-lactitol)	1.413	0.005	**1.940**	**0.046**	0.629	0.053	**1.753**	**0.033**	1.121	0.030
Galactinol	**1.546**	**0.036**	**2.041**	**0.062**	**2.248**	**0.075**	**2.044**	**0.064**	1.484	0.052
Unknown_34 (alpha-1,2-mannobiose)	**2.038**	**-0.066**	**1.654**	**-0.030**	0.169	-0.031	**1.618**	**-0.037**	**1.957**	**-0.082**
Unknown_18 (galactopyranoside)	**1.583**	**0.039**	**1.841**	**0.045**	0.046	0.060	**1.993**	**0.063**	0.698	0.041
Shikimic acid	0.191	0.065	0.699	0.014	0.887	0.010	0.706	0.047	**1.976**	**-0.034**
Glutamic acid	1.160	0.010	**1.607**	**0.029**	**1.636**	**0.031**	**1.542**	**0.030**	0.964	0.012
Caffeine	**1.990**	**0.094**	1.458	0.046	1.244	0.038	1.269	0.057	**2.162**	**0.081**
Unknown_2 (apigenin)	0.882	0.054	0.424	0.010	0.013	0.016	0.459	0.034	**1.710**	**0.101**
Trehalose	0.273	-0.064	1.003	0.024	1.088	0.027	0.851	-0.017	0.941	-0.014
Unknown_15 (gentistic acid)	0.299	0.029	0.727	-0.001	0.360	-0.005	0.564	0.021	**1.553**	**-0.020**
Unknown_16 (2,5-dimethylpyrazine)	0.940	0.027	0.854	0.030	1.285	0.037	1.237	0.044	**1.535**	**0.068**
Alanine	0.904	-0.022	1.297	-0.015	**1.589**	**-0.032**	**1.826**	**-0.050**	0.998	-0.045

Note: The bold text show the VIP metabolites is more than 1.5 in each respective taste attributes model

Table 2.3.2-1 The VIP score of important metabolites in final score model to each respective taste attributes (cont.)

VIP metabolites in "Final Score" model	Balance		Overall	
	VIP score	Coefficient	VIP score	Coefficient
Unknown_45 (D-lactitol)	0.026	0.018	**1.786**	**0.032**
Galactinol	0.998	-0.018	**2.171**	**0.066**
Unknown_34 (alpha-1,2-mannobiose)	0.312	-0.013	1.453	-0.036
Unknown_18 (galactopyranoside)	0.537	-0.001	**1.909**	**0.063**
Shikimic acid	**1.618**	**-0.115**	0.834	0.051
Glutamic acid	0.324	-0.014	**1.720**	**0.032**
Caffeine	0.524	-0.040	1.355	0.061
Unknown_2 (apigenin)	**1.964**	**0.063**	0.372	0.039
Trehalose	1.377	0.072	0.645	-0.025
Unknown_15 (gentistic acid)	1.394	-0.081	0.808	0.021
Unknown_16 (2,5-dimethylpyrazine)	0.563	0.027	0.922	0.044
Alanine	0.696	0.008	**1.934**	**-0.054**

Note: The bold text show the VIP metabolites is more than 1.5 in each respective taste attributes model

The correlated metabolites to coffee quality found in the training set consist of 10 different green coffee beans were further validated. The OPLS analysis was conducted using metabolite profiles of 35 green coffee beans samples (**Table 2.2.2-1**) independent with the training set to observe if the same metabolites found to be correlated to the final score of the cupping test. The result showed that the model has high accuracy and prediction model as the model has R^2 = 0.96 and Q^2 = 0.865 (**Fig. 2.3.2-5**). In this model, only galactinol found to be consistently have positive correlation to the final score of cupping test with VIP value more than 1.5 (Table S3). Based on this result, galactinol could be proposed as a quality-related marker for the rapid screening methods in green coffee beans and complementing cupping test by skilled panelists.

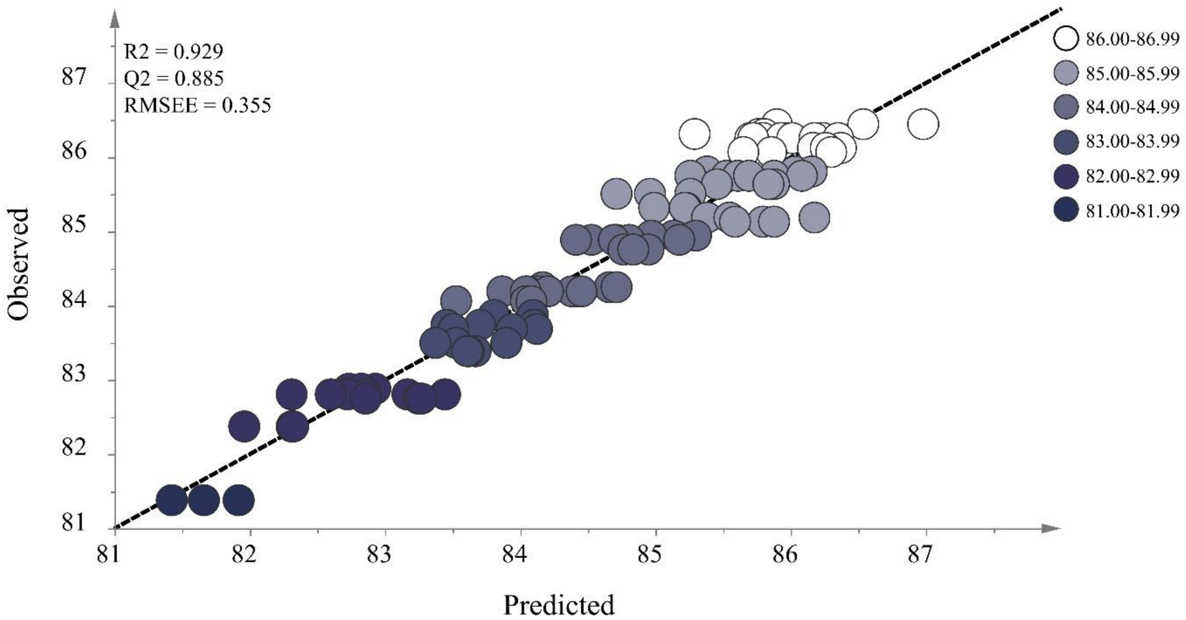

Figure **2.3.2-5** The OPLS model of final score of cupping test of 35 green coffee beans samples (scale : autoscale ; *n*=3). The circles represent the samples with cup score ranged from 81.38 – 86.44. The gradient blue color represents the score category. The model has high value of R2 and Q2 value indicating the good correlation between the variables.

2.3.3 The galactinol quantitation in green coffee beans

Determining coffee quality from metabolome information of green beans could be an efficient screening method for coffee quality. Based on supervised multivariate analysis, galactinol has strong correlation with coffee quality in green coffee beans. Therefore, further analysis was conducted to obtain the information about the galactinol content in green coffee beans. This analysis will compare the galactinol concentration found in the green coffee beans of highest score and the lowest score in the training set (**Table 2.2.2-1**). The quantitation result is show that the highest score sample has 7.02 μg/mL, and the lowest score sample has 0.32 μg/mL galactinol in the green bean samples (**Fig. 2.3.3-1**). The highest has 22 times higher galactinol content compared to the lowest score samples.

This study described galactinol as the potential quality-related marker in green coffee beans of specialty coffee from Indonesia. Galactinol is often detected in recent metabolomics-based coffee studies (Da Silva Taveira et al. 2014; Putri et al. 2019; Aditiawati et al. 2020). However, there is no further discussion or literature found related the role of galactinol in coffee. The only known galactinol role in plant system is as the substrate for larger soluble oligosaccharide during seed development (Sengupta et al. 2015). Nevertheless, in parallel with

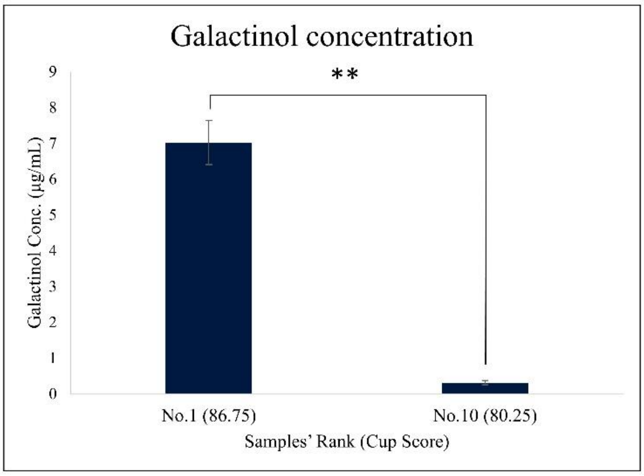

Figure 2.3.3-1 The quantification of galactinol concentration between the sample with high cup score and the sample with lower cup score in green coffee beans. The asterisk show that concentration difference is statistically significant according to Student *t*-test method with *p*-value <0.01.

this study, GC/MS analysis using the roasted beans and brew coffee of the same training set samples also found galactinol as the quality-related marker indicating the galactinol versatility to be used in different coffee sample matrix (Irifune 2019; Takegami 2021).

2.4 Conclusion

GC/MS-based metabolomics approach was performed to investigate correlation between the metabolite profile of the specialty Arabica green coffee beans and the coffee quality as describe in cupping score. This study found galactinol has robust correlation with the final score of the cupping test and its taste attributes by multivariate analysis of ten different kinds of green coffee beans samples. Furthermore, the correlation of galactinol with the final score was validated using different data set consisted of 35 green coffee beans samples. Hence, this study proposed galactinol as the potential quality-related marker in green coffee beans that could be used as a parameter to provide a rapid screening method that complement cupping test by skilled panelists.

Chapter 3

The GC/MS-based metabolomics approach to investigate the most influential factors in coffee quality in green coffee beans production

3.1 Introduction

The production of Arabica coffee requires a long chain from cherry to cup. Green coffee beans (raw beans) are obtained from the coffee cherry during the production (De Bruyn et al. 2017). The green coffee beans contained the non-volatile compounds that could act as flavor and aroma precursor of coffee taste and quality (Fisk et al. 2012; Joët and Dussert 2018). The non-volatile composition of green coffee beans is influenced by various factors including species, geographical origin, and postharvest process (Joët and Dussert 2018; Putri et al. 2019; Sunarharum et al. 2014).

Arabica coffee beans is produced by various of country, mostly located at tropical belt. Arabica coffee from each producing country poses different taste to each other. Hence, the information of geographical origin, including the information of country and location within the country, in Arabica coffee product become important. Recently, the high-grade Arabica coffee product is often marketed as single-origin coffee (Purnomo et al. 2019). Since the coffee taste from different geographical origin has different taste, the studies to investigate the influence of geographical origin on coffee quality have been conducted. The previous studies reported that geographical origin has influence on chemical composition of coffee beans such as sugars, amino acids, and organic acids compounds (Wei et al. 2012; Da Silva Taveira et al. 2014; Putri et al. 2019). There are several factors surrounding within the geographical origin that responsible in the distinctiveness of each single-origin coffee; among these factors, altitude and place of cultivation are generally believed to affect the flavor of Arabica coffee (Joët et al.

2010). It is generally believed that coffee grown at high altitudes (1,000-1,200 m above sea level) has better sensory quality with good aroma, acidity, and fruitiness than that grown at lower altitudes featuring earthy and green taste notes (Avelino et al. 2007; Bertrand et al. 2012; Davis et al. 2012; Schroth et al. 2015). Previous studies describe the correlation between altitude and the biochemical composition of coffee beans focusing on sugar, chlorogenic acid, and caffeine with various of observations (Avelino et al. 2005; Joët et al. 2010; Tolessa et al. 2017). Joët et al. (2010) found that the caffeine content in coffee beans was not affected by altitude. However, more recent study reported that the caffeine content is decreased as the altitude increased (Tolessa et al. 2017). The variety of result also found in chlorogenic acid content in relation with altitude. Chlorogenic acid found to be increased (Avelino et al. 2005) or decreased (Tolessa et al. 2017) as the altitude increase. Based on these studies, it is important to increase the metabolite coverage of the analysis to better clarify the relationship between altitude and biochemical composition of coffee beans.

The postharvest process is a series of steps to obtain the dried coffee beans or green coffee beans by the removing the pericarp, flesh and mucilage of the coffee cherry. There are at least three types of postharvest process methods: dry, hybrid, and washed method. Each of postharvest method has different step in order to obtain the green coffee beans. Hence, the postharvest process affected the biochemical compounds of green coffee beans and the final taste of the coffee (Hoffmann 2014; Lee et al. 2015; De Bruyn et al. 2017; de Melo Pereira et al. 2019). The previous studies compared the differences the biochemical composition of green coffee beans obtained from dry process and washed process. The green coffee beans obtained from dry process have a higher content of sugar compounds, caffeic acid, caffeine, trigonelline, and several caffeoylquinic acid isomers, whereas green coffee beans obtained from the washed process are high in citric acid, erythritol, glutamic acid, and aspartic acid (Bytof et al. 2005; Knopp et al. 2006; De Bruyn et al. 2017). The microbial activity in fermentation step at washed process yields of reducing sugars, amino acids, organic acids aldehydes, esters, alcohols, and ketones that contribute to the aroma and flavor of the roasted beans and coffee brew (Seninde and Chambers 2020; Ruta and Farcasanu 2021). Hence, the coffee taste obtained by washed process has fruity and acidic attributes and less bitterness (Lee et al. 2015). Based on these reports, postharvest process has contribution for the biochemical composition of green coffee beans and coffee quality, along with the geographical origin and the altitude.

The previous studies investigated the influence of each factor, geographical origin, altitude, and postharvest process method, separately and independently to each other to the biochemical composition of green coffee beans. Moreover, the metabolite coverage is more limited and targeted for the coffee-related compounds such as caffeine and chlorogenic acids. Hence, in this study, we aimed to investigate the factor that has the dominant influence on coffee quality. GC/MS-based metabolomics analysis was performed on green coffee beans from various geographical origin, altitude, and postharvest processes simultaneously to achieve this aim. The GC/MS analysis workflow allow wider range of low molecular hydrophilic class compound through extraction and derivatization that might complement with previous study focusing on non-polar factions, volatile compounds, and coffee-related compounds to describe the effects of the factors mentioned on coffee quality (Joët et al. 2010; Bertrand et al. 2012; De Bruyn et al. 2017; Zhang et al. 2019; Putri et al. 2019; Tsegay et al. 2020). The multivariate analysis was also employed to provide the unsupervised analysis of the dominant factors that influenced the green coffee bean metabolite profile, leading to descriptive analysis of the profile. The results described by this study could be used by coffee industry stakeholders to decide the most crucial factors impacting coffee production.

3.2 Materials and methods

3.2.1 Chemicals

All chemicals used in this study were of analytical grade and described previously in previous publications (Jumhawan et al. 2013; Putri et al. 2019). Methanol (99.8%), infinity pure pyridine, and ribitol were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Chloroform (99%) was purchased from Kishida Chemical (Osaka, Japan). Methoxyamine hydrochloride was purchased from Sigma Aldrich (Milwaukee, WI, USA). N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) and a standard alkane mixture (C9–C40) were purchased from GL Science Inc. (Tokyo, Japan).

3.2.2 Green coffee beans sample collection

Green coffee bean samples were collected from the Indonesian Coffee and Cocoa Research Institute (ICCRI) coffee collection which was collected and purchased from producers. The green coffee beans were stored in a vacuum-sealed pack and during the sample transportation, the direct sun exposure was prevented. Samples were stored at -30°C upon arrival in Japan until extraction and analysis. A total of 17 specialty grade samples of Arabica green coffee beans were obtained from coffee fruit harvested from coffee plantations at various altitudes across Indonesia. The altitude ranged from 400 to 1,600 m above sea level. Coffee fruit harvested from trees planted at 400 m and 800 m above sea level were processed by three different processes: dry, honey, and washed process method. Since Arabica coffee is usually cultivated in higher altitude (1,000 m above sea level), one sample each from lower altitude (400 m and 800 m) were used in this study. Coffee fruit harvested from trees planted at more than 1,000 m above sea level were processed by washed process. Detailed information on the samples used, including their cup scores, is shown in **Table 3.2.2-1**.

3.2.3 Sensory analysis

The green coffee beans used in this study were subjected to sensory analysis at the Indonesian Coffee and Cocoa Research Institute (ICCRI) facility in Jember, Indonesia. The roasting process of the beans and the sensory analysis of the roasted beans, and coffee brew, was conducted according to a standardized protocol which was published by the Specialty Coffee Association of America (SCAA). The sensory analysis was performed by a certified panelist (Q-grader) on ten parameters which were rated from to 6-10, with zero indicating the least strong and ten for the strongest taste. The score from each parameter was accumulated and the total cup score was obtained. The cup score was used to determine coffee bean grade (Specialty Coffee Association/SCAA 2015).

3.2.4 Metabolite extraction and derivatization

Metabolite extraction and derivatization were performed using a published protocol with minor modifications (Jumhawan et al. 2013; Putri et al. 2019). The metabolite extraction of each sample was performed in a technical replicate (n = 3). Prior to extraction, green coffee bean powder was prepared by grinding. Green coffee beans were added to a 50 ml grinding tube (Yasui Kikai Co., Osaka, Japan) along with a metal cone (Yasui Kikai Co., Osaka, Japan). The tube was closed tightly and quenched by dipping in liquid nitrogen. The closed tube was then immediately put into a multi-beads shocker (Yasui Kikai Co., Osaka, Japan), shaken at 2000 rpm for 30 seconds, repeated for 2-3 times to produce a fine powder of green coffee beans. Ten milligrams of green coffee powder were transferred to a 2 ml Eppendorf tube and extracted using 1 ml of a mixed solvent (methanol, ultrapure water, and chloroform with 5/2/2 (v/v/v) ratio) containing an internal standard (ribitol 12 µg/ml). The samples and blank (mixed solvent only) were vortexed and incubated at 1200 rpm at 37°C for 30 minutes. Afterwards, the samples and blank were centrifuged at 13100 rpm for 3 minutes at 4°C. The supernatant (900 µl) was transferred to a 1.5 ml Eppendorf tube and 400 µl ultrapure water was added before the samples were vortexed and re-centrifuged. Subsequently, 100 µl of the aqueous layer was transferred to a new tube with a pierced cap. For quality control (QC) purposes, 100 µl of the aqueous layer obtained from samples were collected in one pool by transferring it into a 15 ml Eppendorf tube. The collection of sample extracts in the QC pool was homogenized and 100 µl extract was transferred into a 1.5 ml Eppendorf tube with a pierced cap. The sample, QC, and blank extracts were concentrated by vacuum centrifugation for 20 minutes and lyophilized overnight.

The derivatization process consists of two steps, oximation and trimethylsilylation, as described previously in the published procedure (Jumhawan et al. 2013; Putri et al. 2019). The dried extract was subjected to oximation by adding 100 µl methoxyamine hydrochloride (20 mg/ml in pyridine), then vortexed and incubated at 1200 rpm and 30°C for 90 minutes. Subsequently, 50 µl MSTFA was added, and the mixture was re-vortexed and incubated at 1200 rpm and 37°C for 30 minutes. Sample mixture (100 µl) was transferred into a GC/MS vial prior to GC/MS analysis.

Table 3.2.2-1 List of sample sets

Sample Name/Code	Coffee Processing Method	Altitude (m above sea level)	Origin	Total Cupping Score
Sample set I				
400-DB	Dry Process	400	Bajulmati	83.42
400-HB	Honey Process	400	Bajulmati	82.58
400-WB	Washed Process	400	Bajulmati	81.33
800-DK	Dry Process	800	Kalibendo	81.92
800-HK	Honey Process	800	Kalibendo	81.50
800-WK	Washed Process	800	Kalibendo	82.83
Sample set II				
400-BM	Washed Process	400	Bajulmati	81.33
800-KB	Washed Process	800	Kalibendo	82.83
1000-B	Washed Process	1000	Bondowoso	84.92
1000-AG	Washed Process	1000	Aceh Gayo	85.19
1200-B	Washed Process	1200	Bondowoso	83.42
1200-AS	Washed Process	1200	Andungsari	84.06
1200-F	Washed Process	1200	Flores	86.44
1400-B	Washed Process	1400	Bondowoso	84.08
1400-M1	Washed Process	1400	Manglayang	85.08
1400-M2	Washed Process	1400	Manglayang	80.08
1600-B	Washed Process	1600	Bondowoso	83.58
1600-M1	Washed Proess	1600	Manglayang	84.25
1600-M2	Washed Process	1600	Manglayang	82.92
Sample set III				
1000-B	Washed Process	1000	Bondowoso	84.92
1200-B	Washed Process	1200	Bondowoso	83.42
1400-B	Washed Process	1400	Bondowoso	84.08
1600-B	Washed Process	1600	Bondowoso	83.58

3.2.5 Gas chromatography-mass spectrometry (GC/MS) analysis

The workflow for gas chromatography-mass spectrometry (GC/MS) analysis of coffee bean extract has been developed and published elsewhere with several modifications (Jumhawan et al. 2013; Putri et al. 2019). GC/MS analysis was performed on a GCMSQP 2010 Ultra (Shimadzu, Kyoto, Japan) equipped with a 30 m × 0.25 mm i.d. fused silica capillary column coated with 0.25 µm InertCap 5MS/NP (GL Science, Inc., Tokyo, Japan) and an AOC-20i/s (Shimadzu, Kyoto, Japan) as an autosampler. System control and data acquisition were conducted using GC/MS solution software (Shimadzu, Kyoto, Japan). The mass spectrometer was tuned and calibrated prior to analysis. The standard alkane mixture (C10−C40) was injected at the beginning of the retention index calculation. The derivatized sample and blank (1 µl) were injected in random order with QC injections (1 µl) every four injections. The injections were conducted in split mode, 25:1 (v/v), and at an injection temperature of 270°C. Helium was used as the carrier gas with a flow rate of 1.12 ml/min and a linear velocity of 39 cm/s. The column and transfer line temperature settings were adjusted to those previously published (Jumhawan et al. 2013; Putri et al. 2019). The ion source temperature was 280°C and ions were generated by electron ionization at 70 eV. The mass spectra were recorded at 20 scans per second over the mass range 85−500 *m/z*.

3.2.6 Data processing

The chromatogram data obtained by GC/MS analysis were converted to a netCDF format using the GCMS Solution software package (Shimadzu, Kyoto, Japan). The netCDF files were further converted into ABF format using Reifycs Abf Converter (https://www.reifycs.com/AbfConverter/). Peak detection, deconvolution analysis, identification, and alignment were performed using MS-DIAL version 4.18 (Tsugawa et al. 2015; Lai et al. 2018; Tsugawa et al. 2019), which is a free software (http://prime.psc.riken.jp/Metabolomics_Software/MS-DIAL/). The minimum height for peak detection was set as 1,000 amplitudes with a linear weight moving average smoothing method. Smoothing level began at 5 scans and average peak width of 20 scans. In deconvolution analysis the sigma window value was set as 1, and the EI spectra cut-off was 200 amplitudes. Peak identification used the retention index (RI) based on the retention time of the standard alkane mixture (C10-C40) and GL-Science DB library (InertCap 5MS-NP, Kovats RI, 494 records; http://prime.psc.riken.jp/Metabolomics_Software/MS-DIAL/GCMS%20DB_InertCap%205MS-NP_GLscience.msp). The parameters for peak identification and alignment were RI tolerance 10, RT tolerance 0.5 minute, *m/z* tolerance 0.5 Da, EI similarity cut-off 70%, and identification score was cut-off at 70%. Metabolite identification was conducted by comparing the mass spectra and RI with the GL-Science DB library. After peak detection, the height of the detected peaks was normalized by the height of the internal standard peaks. The data matrix was constructed consisting of the raw height and normalized height of peaks. Filtering was then performed to exclude peaks that were not of biological origin by referring to the blank chromatogram from the data matrix (Putri et al. 2019). Moreover, peaks with a relative standard deviation of more than 30% in QC and with a raw height less than 3,000 were also removed. The final data matrix with filtered and assigned peaks was constructed and used for further analysis.

3.2.7 Multivariate analysis

Principal component analysis (PCA) and orthogonal projection to latent structure (OPLS) regression analyses were performed using the commercially available SIMCA-P+ version 13.0.3 (Umetrics, Umeå, Sweden). The data matrix was subjected to PCA and OPLS with auto-scale and without transformation, to analyze all the obtained metabolites equally (van den Berg et al. 2006). The relative intensity differences between samples on selected metabolites were evaluated using one-way analysis of variance and post hoc multiple comparison tests using JASP version 0.13.1 (JASP Team, 2020), which is a freely available software (https://jasp-stats.org).

3.3 Result and discussion

3.3.1 GC/MS metabolite profiling analysis of green coffee beans obtained from various geographical origin, altitude, and postharvest process methods

Gas chromatography-mass spectrometry (GC/MS)-based analysis was performed to obtain the low molecular hydrophilic class compound in the aqueous phase of the green coffee beans extract. This approach was employed in previous studies on coffee beans (Jumhawan et al. 2013; Putri et al. 2019). There were 142 metabolites detected in GC/MS analysis. After data filtering, 79 detected metabolites were selected, consisted of 50 annotated metabolites and 29 unknown metabolites. The annotated metabolites were categorized as amino acids, sugar compounds, sugar alcohol compounds, organic acids, and other class compounds (Table S11). The unknown metabolites found in this study were numbered based on their retention times. The data matrix of normalized peaks was constructed and subjected to multivariate analysis for data exploration and visualization of information based on sample variance.

3.3.2 Principal component analysis of green coffee beans obtained from various geographical origin, altitude, and postharvest process methods

The metabolome profile of nine kinds of coffee beans obtained from two altitude, two geographical origin, and three different postharvest process methods (**Table 3.2.2-1** sample set 1) was subjected to principal component analysis to observe the unsupervised overview of the metabolome profile. The PCA result showed in **Fig. 3.3.2-1**. The PCA score plot (**Fig. 3.3.2-1.A**) showed the sample clustering based on postharvest process methods in the first principal component (41%) and geographical origin and altitude on the second principal component (23.4%). In the first principal component, coffee metabolome profiles were separated into two groups, the green coffee beans obtained from the dry process method on the positive quadrant and green coffee beans obtained from honey and washed process on the negative quadrant.

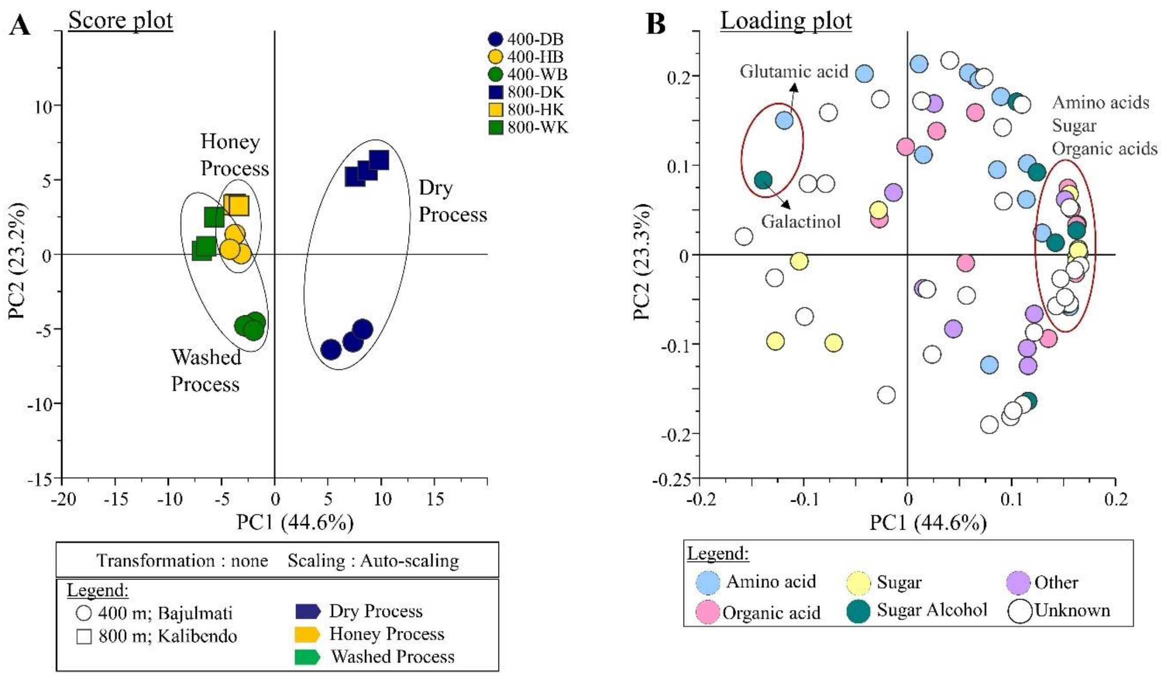

Figure 3.3.2-1 The PCA result of green coffee beans with various altitude, geographical origin, and postharvest process methods. (A) PCA score plot cluster the samples based on the postharvest methods. The different colors represent the different postharvest methods, and the different shapes represent altitude and geographical origin. (B) PCA loading plot showed the correlated metabolites for each cluster. The different colors represent the class of the compounds. The metabolites within the red circle are correlated metabolites with the sample clustering in the PCA score plot.

The PCA loading plot (**Fig. 3.3.2-1.B**) also showed that most of metabolites located at the positive quadrant of the plot than the negative quadrant, suggesting that green coffee beans obtained by dry process method contained a greater number of metabolites compare to green coffee beans obtained by honey and washed process. Amino acids, organic acid, and sugar compounds are the metabolites that commonly correlated in the green coffee beans obtained from the dry process method while galactinol and glutamic acid are correlated with green coffee beans obtained from the honey and washed process methods. The sample clustering and the differences in number of metabolites correlated with each group might be due to the existence or absence of the de-pulping step in the coffee process methods. The de-pulping step is required in honey and washed process, which causes injuries and leads to the loss of sugar compounds (Hoffmann 2014; Selmar et al. 2014; De Bruyn et al. 2017).

The metabolites correlated with green coffee beans, which were obtained from coffee fruit after the dry process method, were glycine, lysine, sorbose, fructose, glyceric acid, and glycolic acid (**Fig. 3.3.2-2**). This finding is corroborated with the previous study in which describe that the green coffee beans obtained from dry process methods have a higher glucose and fructose content (De Bruyn et al. 2017). Glycine and lysine were found in higher content in green coffee beans produced by dry process method which consistent with previous study (Bytof et al. 2005). However, the previous study did not mention and discuss this phenomenon further since both of glycine and lysine were not found as dominant amino acids in green Arabica coffee beans with low concentration (Bytof et al. 2005; Murkovic and Derler 2006). The limited discussion regarding glycine and lysine in previous study might be due to the differences of the statistical approach. In the present study by metabolomics approach employed an auto scale for data pretreatment and gave all the obtained metabolites equal importance and elimination the importance of concentration (van den Berg et al. 2006; Sumner et al. 2007). Therefore, it would be interesting to closely observe the amino acid profile in future coffee studies using different and more advanced analytical and statistical methods. Organic acids that found correlated with green coffee beans obtained by dry process method are glyceric acid and glycolic acid. The study about both of organic acids in relation with postharvest process methods are scarce. However, the previous study reported the accumulation of organic acids such as lactic acid, gluconic acid, and glucuronic acid in green coffee beans obtained by dry process methods (De Bruyn et al. 2017). Hence, the finding in present study might complement the previous study. The findings of more organic acid class compounds in green coffee beans such as glyceric acid, glycolic acid, lactic acid glucuronic

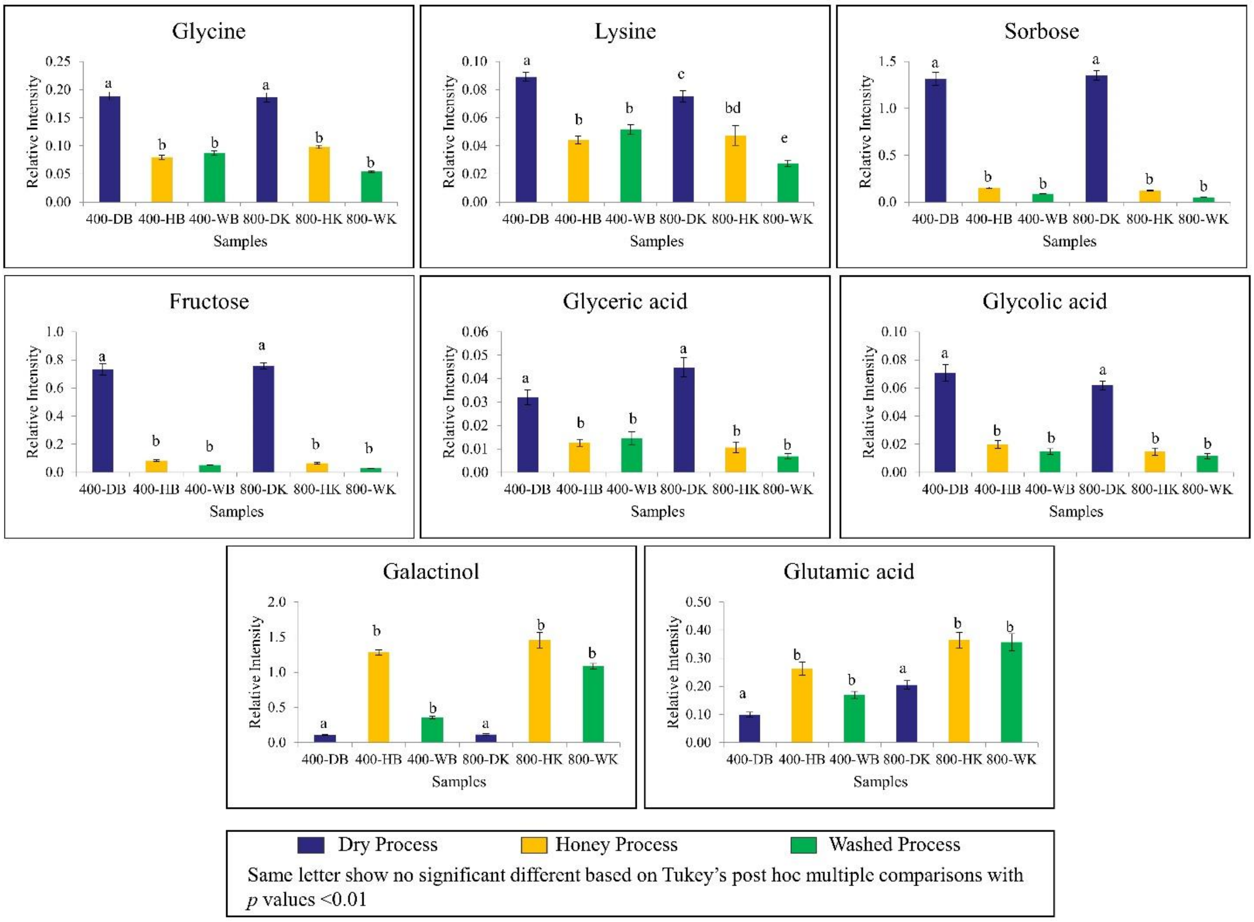

Figure 3.3.2-2 The relative intensity correlated metabolites to the sample clustering based on the postharvest process methods. The error bar showed the standard deviation. The same letter showed no significant different based on Tukey's post-hoc multiple comparisons with p values <0.01

acid, succinic acid, and the known coffee-related organic acids such as citric acid, malic acid, chlorogenic acid, and quinic acid might be useful for future investigation of flavor development in roasting process models.

The metabolites correlated with green coffee beans obtained by honey and washed process methods were galactinol and glutamic acid. Recent coffee studies employed metabolomics approach reporting galactinol in the coffee beans. Galactinol reported as potential metabolite marker for coffee beans produced in specific area in Brazil and correlated with the coffee beans produced from the western and middle part of Indonesia (Da Silva Taveira et al. 2014; Putri et al. 2019). Galactinol also reported to be correlated with the coffee fermentation process (Aditiawati et al. 2020). In addition to those reports, galactinol reported for the first time in relation with the postharvest process, especially honey and washed process methods. However, there is no further report nor discussion about the role of galactinol in coffee beans. The only proven function of galactinol is as substrate for larger soluble oligosaccharides in plant systems, including during seeds development (Sengupta et al. 2015). Glutamic acid content was found to be higher in green coffee beans produced by honey and washed processed methods (**Fig. 3.3.2-2**). The finding is consistent with previous reports comparing the content of glutamic acid and GABA in green coffee beans obtained by dry process method and washed process method (Bytof et al. 2005; Selmar et al. 2014). In those reports, glutamic acid concentration is increase in green coffee beans obtained by washed process method while the GABA concentration is increase in green coffee beans obtained by dry process method (Bytof et al. 2005).

3.3.3 Principal component analysis of green coffee beans obtained from various geographical origin and altitude with the same postharvest process method

The analysis result of sample from two altitude and geographical origin with three different postharvest process methods in **Fig. 3.3.2-1** showed the clustering based on postharvest process methods. Therefore, further investigation was conducted to observe the influence the geographical origin and altitude to green coffee beans metabolome profile. In this investigation, thirteen green coffee beans samples were obtained from washed process method to eliminate the influence of postharvest process method (**Table 3.2.2-1** sample set II). The sample set consisted of six different altitudes and seven different geographical origins, and they were subjected to GC/MS analysis.

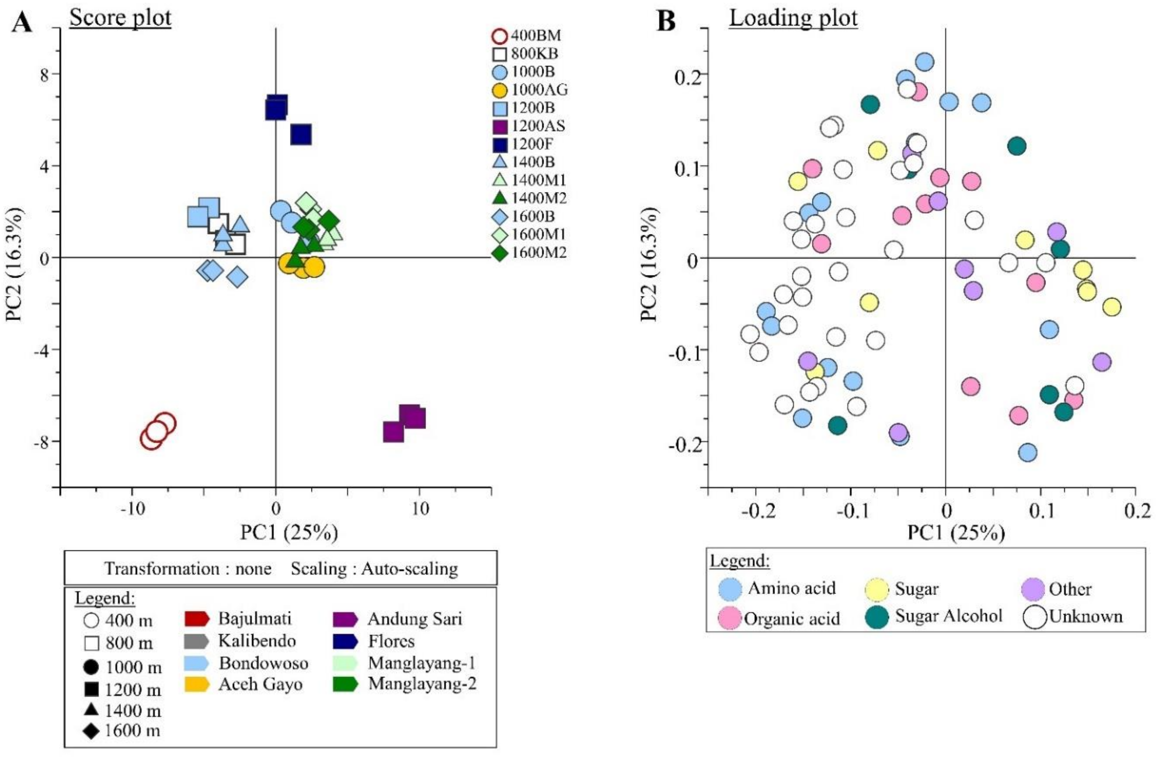

Figure 3.3.3-1 The PCA result of green coffee beans obtained from various altitude and geographical origin with the same postharvest process method. (A) The different shape of symbol (open and closed symbol) described the altitude while the colors represent each geographical origin in the PCA score plot. The samples were clustered based on their own respective geographical origin. (B) PCA loading plot showed the metabolites were evenly distributed along the axis, showing that each geographical origin has their own unique correlated metabolites. The different colors represent the class of the compounds.

The PCA result of thirteen green coffee beans is showed in **Fig. 3.3.3-1**. The result showed that the samples were clustered based on their own respective geographical origin (**Fig. 3.3.3-1A**) in which is similar with previous study focusing on Indonesia's specialty coffee based on geographical origin (Putri et al. 2019). Moreover, the metabolites in the loading plot were evenly distributed and describe different correlated metabolites for each geographical origin (**Fig. 3.3.3-1B**). The samples obtained from the same origin such as sample from Bondowoso and Manglayang are clustered together in the PCA score plot despite that the samples were obtained from different altitudes. Based on this observation, geographical origin might be influenced the sample clustering more than the altitude. Therefore, the geographical origin has greater influence on the green coffee beans metabolome profile compared to altitude.

3.3.4 The further observation on the influence of altitude in coffee metabolome profile

The influence of postharvest process and geographical origin are greater than the influence of altitude in green coffee beans metabolome profile in previous PCA results. However, the coffee industry stake holder still considered the altitude as relevant factors to the Arabica coffee quality. Hence, the further observation was conducted by analyzing the green coffee beans samples from different altitude with the same geographical origin and postharvest process method (**Table 3.2.2-1** sample set III).

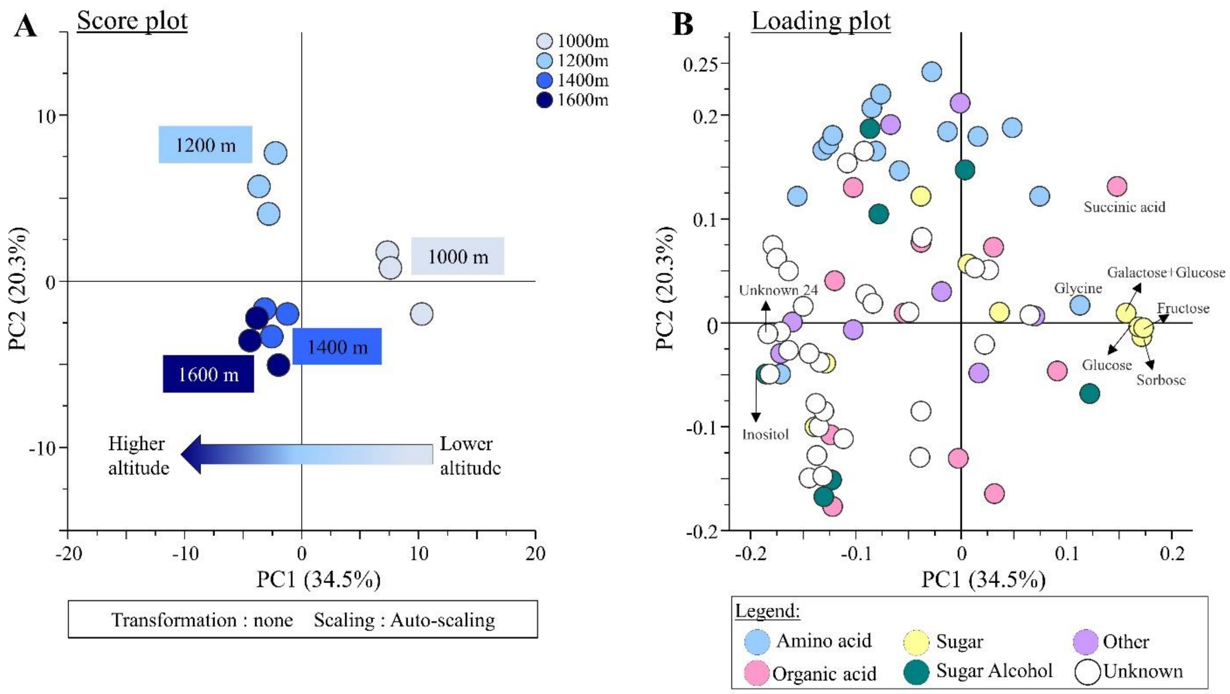

Figure 3.3.4-1 The PCA result of green coffee beans obtained from various altitude with same geographical origin and postharvest process method. (A) The PCA score plot showed sample were clustered based on the respective altitude. (B) PCA loading plot showed the metabolites were correlated with the sample clustering.

The PCA result of the green coffee beans samples obtained from different altitude with the same geographical origin and postharvest process method is showed in **Fig. 3.3.4-1**. Based on the PCA score plot (**Fig. 3.3.4-1A**), the samples were clustered based on the respective altitude with samples from the lower altitude (1000 m above sea level) is located at positive axis of the first principal component and from higher altitudes (1200 m, 1400 m, and 1600 m above sea level) are located at the negative axis of the first principal component. The metabolites correlated with this clustering were visualized in the PCA loading plot (**Fig. 3.3.4-1B**). Fructose, sorbose, glucose, galactose+glucose, glycine, and succinic acid are the metabolites that correlated with the green coffee beans obtained from the lower altitude. The relative intensity of these metabolites was decrease as the altitude increase (**Fig. 3.3.4-2**). Inositol and unknown compound number 24 are the metabolites that correlated with the green coffee beans from the higher altitude. These metabolites found in higher relative intensity in samples from higher altitude (1200 m, 1400 m, and 1600 m above sea level) (**Fig. 3.3.4-2**).

The previous studies were describing the influence of altitude to biochemical composition of coffee beans limited into several targeted compounds such as caffeine, chlorogenic acids, and sugar compounds (Joët et al. 2010; Tolessa et al. 2017; Worku et al. 2018). This study also found sugar compounds, such as fructose, sorbose, glucose, galactose+glucose, and inositol, as correlated metabolites with altitude. The accumulation of these metabolites in green coffee beans obtained from different altitude might contribute to different taste to the coffee beverage. Fructose and glucose in green coffee beans as the flavor

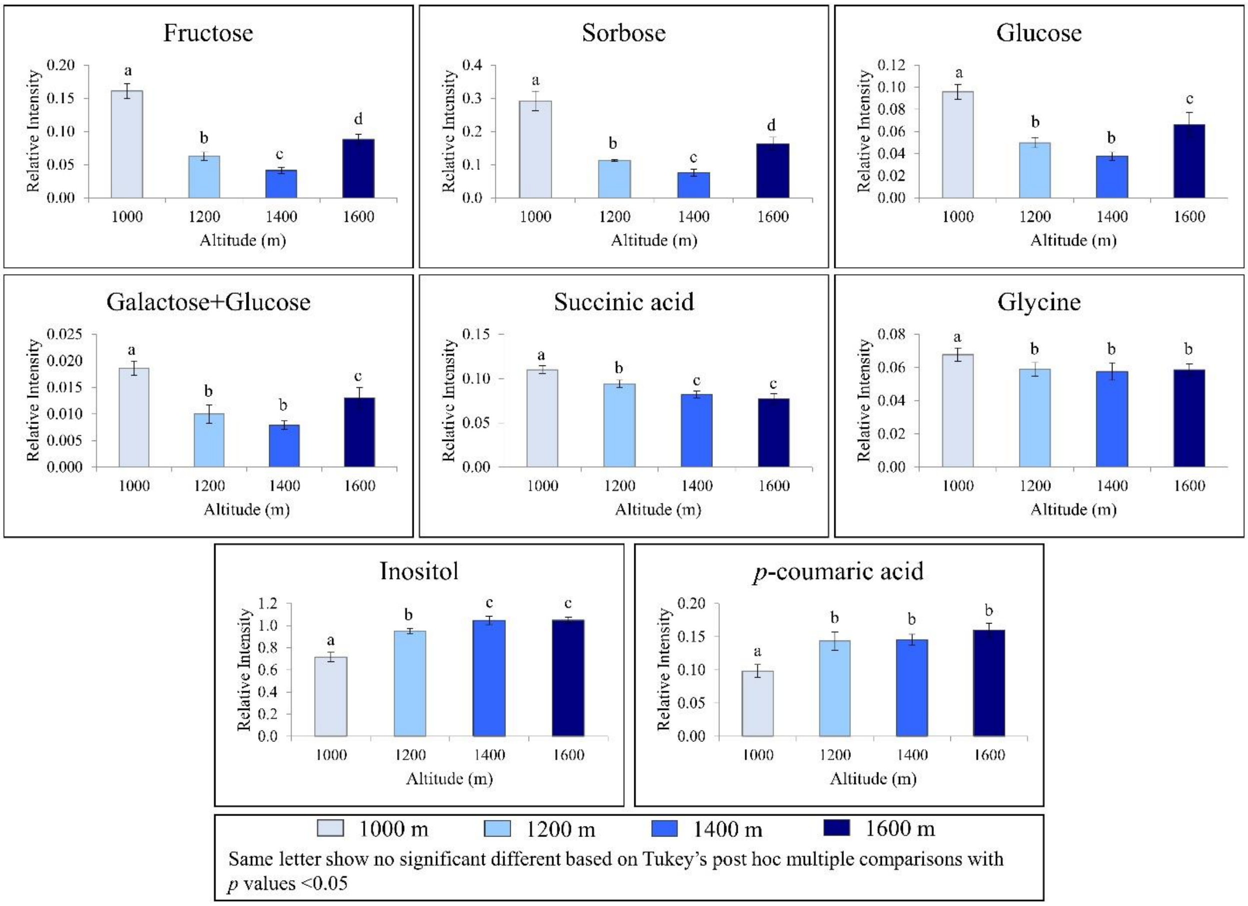

Figure 3.3.4-2 The relative intensity correlated metabolites to the sample clustering based on altitude. The error bar showed the standard deviation. The same letter showed no significant different based on Tukey's post-hoc multiple comparisons with p values <0.01

precursor will be degraded into aliphatic acids during roasting process (Ginz et al. 2000). This might influence the acidity aspects in the coffee beverage using the beans from the lower altitude. In contrast, inositol is relatively thermostable and have the sweet taste properties in which could influence the taste of coffee beverage using the beans from the higher altitude (Wei et al. 2012). In addition to previous studies, this study found glycine, succinic acid, and unknown compound number 24 as correlated metabolites with altitude. The literature about glycine and succinic acid in relation with altitude are scarce and this study might be described these metabolites in relation with altitude for the first time. The unknown compound number 24 had lower than 80% of the total similarity score with the metabolites that available in the library. The closest similarity of unknown compound number 24 was with *p*-coumaric acid and chlorogenic acid, with total similarity scores of 23% and 25.8%, respectively. *p*-Coumaric acid belong to the hydroxycinnamic acid and hydroxycinnamate family compounds that are commonly found in coffee (Matei et al. 2019). Hydroxycinnamic acid and hydroxycinnamates are conjugate compounds in chlorogenic acids, the most abundant metabolites in coffee (Matei et al. 2019). However, further study is needed to confirm the identity of unknown compound number 24 and might be relevant to describe the coffee beans obtained from higher altitude.

The influence of altitude could be observed after the elimination of geographical origin and postharvest process factors through unsupervised multivariate analysis. Therefore, further data analysis was conducted using supervised multivariate analysis, OPLS In this data analysis, the samples obtained from various altitude and geographical origin with the same postharvest process method (**Table 3.2.2-1** sample set II) were divided into training set and prediction set. This analysis was conducted to further investigate the correlated metabolites with altitude. The constructed OPLS models (**Fig. 3.3.4-3A**, **B**) has good correlation between variables since the R2 and Q2 value were more than 0.6 and 0.5 respectively (R2 = 0.997 Q2 = 0.974) (Varmuza and Filzmoser 2009; Worley and Powers 2013; Alexander et al. 2015). Furthermore, the models have a low root mean squared error of estimation (RMSEE) and root mean square error of prediction (RMSEP) values, which indicate model accuracy and robustness (Putri and Fukusaki 2015). The metabolites correlated with altitude extracted from this model were sorted based on their variable importance in the projection (VIP) scores (Table S12). In this study there are 29 metabolites were considered important since these metabolites have VIP score more than 1 (Galindo-Prieto et al. 2014; Ikram et al. 2020). Within these metabolites, there are four metabolites with VIP score more than two namely inositol, tyrosine , serine, and serotonin. Inositol and serine have positive correlation while tyrosine and serotonin have negative correlation with altitude. The relative intensity of these metabolites shown in **Fig. 3.3.4-4**. Based on the bar graph, only inositol, tyrosine, and serotonin that have linear tendency in relation of altitude. Based on these results, inositol consistently showing correlation with altitude in both supervised and unsupervised multivariate analysis. This finding might be different with previous study describing the correlation between inositol and altitude is not significant by univariate analysis (Joët et al. 2010). However, the multivariate statistical analysis employed in this study could conclusively find the underlying correlation between inositol and altitude.

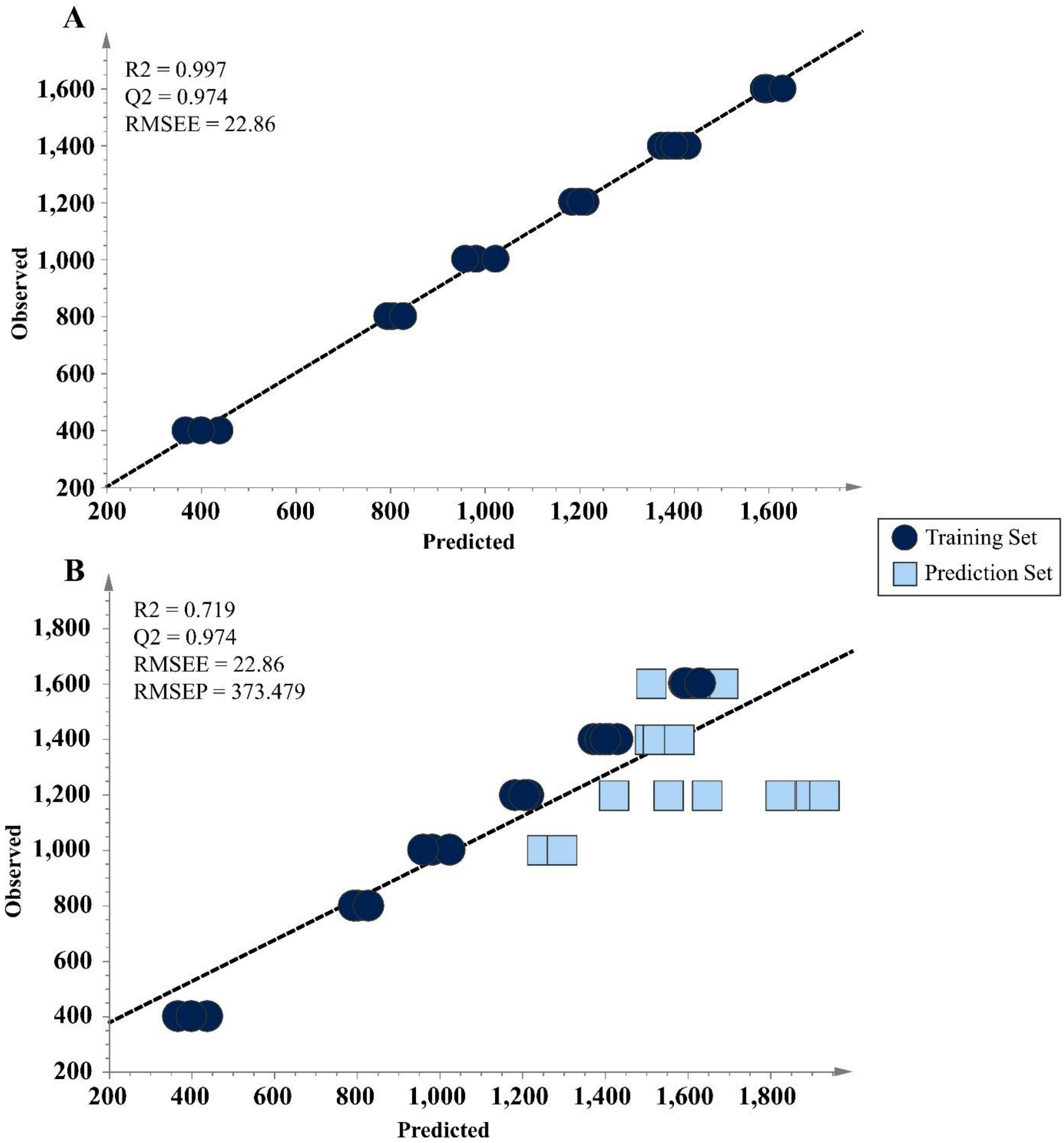

Figure 3.3.4-3 The OPLS regression model of thirteen different green coffee samples with six different altitudes from various geographical origin and same postharvest process method (scale: autoscale; n=3). (A) The OPLS model constructed from training set (dark blue circle) has R^2 = 0.997 and Q^2 = 0.974 (B) The OPLS model constructed from both training set (dark blue circle) and prediction set (light blue box) has R^2 = 0.719, Q^2 = 0.974, root mean squared error of estimation (RMSEE) = 22.86, and root mean square error of prediction (RMSEP) = 373.479.

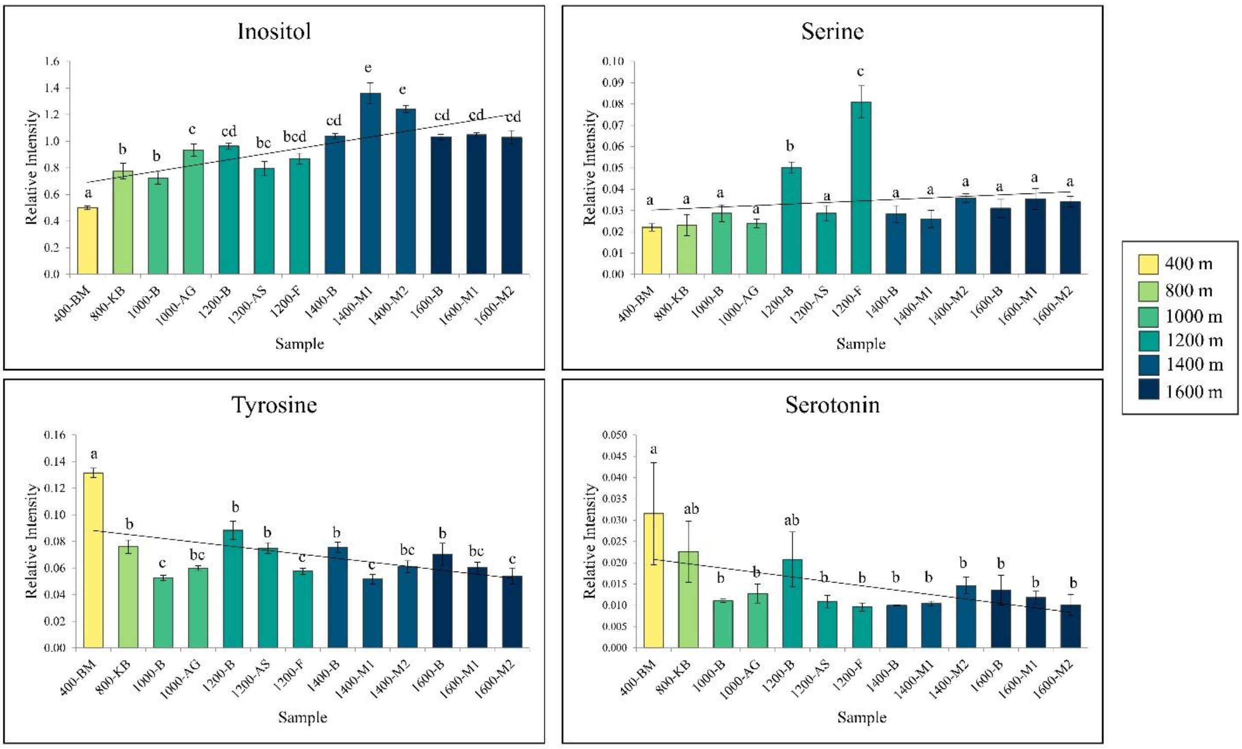

Figure 3.3.4-4 The relative intensity of metabolites with the highest VIP score. The error bar showed the standard deviation. The same letter showed no significant different based on Tukey's post-hoc multiple comparisons with p values <0.01

3.4 Conclusion

GC/MS-based metabolite profiling focusing on low molecular hydrophilic metabolites was conducted on green coffee beans obtained from different altitude, geographical origin, and postharvest process methods simultaneously. This study found that the postharvest process had the greatest influence on the green coffee beans metabolome profile, followed by geographical origin and altitude. Moreover, several metabolites found to be correlated to each factor in addition with coffee related compounds such as caffeine and chlorogenic acid that describe in previous reports. The finding of the postharvest process methods as the dominant factor could be useful for coffee producer to be more focused on optimizing or maintaining the postharvest process methods to produce specialty coffee Arabica.

Chapter 4

The predominant factor and quality-related metabolite validation in green bean production at Dombu, Sigi, Central Sulawesi

4.1 Introduction

The previous chapters describe that galactinol is the metabolite correlated with quality and the postharvest process methods is the predominant factor for coffee metabolome profile. These findings need to be validated further to observe the robustness of the findings.

Indonesia is one of the largest coffee producing countries. Within Indonesia, there are enormous coffee production location distributed from Sumatra until Papua Island. Sulawesi Island is one of the biggest islands in Indonesia. The well-known Toraja coffee is the specialty coffee Arabica that produced from this island. However, Toraja, located in South Sulawesi is not the only place that produce coffee in Sulawesi Island. Dombu is a small village located in Sigi, Central Sulawesi that also have coffee farm and produced coffee. The coffee farm is located at 1250 until 1600 m above sea level. Unfortunately, coffee from this place is less known and the producers still developing the best practice to produce the coffee from Dombu, Sigi, Central Sulawesi. Hence, the sensory quality of the coffee from Dombu is underexplored. Moreover, there are various of green coffee beans with various of postharvest process methods are available. There are green coffee beans produced by dry/natural process, honey process, and washed process. Within washed process, there are two different drying and hulling process called wet hulling (*giling basah*) and dry hulling.

In this chapter, the green beans from Dombu, Sigi, Central Sulawesi is subjected to GC/MS-based metabolite profiling. In this dataset, the variable of different drying and hulling process are added to observe if the postharvest process method still become the predominant factor for the coffee metabolome profile. Since the sensory quality of coffee from Dombu still underexplored, this experiment subjected the green coffee beans with various of postharvest method to cupping test and correlate it to the metabolome profile. This experiment intended to observe if galactinol still relevant to the coffee quality in terms of final score. Moreover, the finding of this study could also be used a recommendation to the development of the green coffee bean production process in Dombu, Sigi, Central Sulawesi.

4.2 Materials and methods

4.2.1 Chemicals

All chemicals used in this study were of analytical grade (Jumhawan et al. 2013; Putri et al. 2019). Methanol (99.8%), infinity pure pyridine, and ribitol were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Chloroform (99%) was purchased from Kishida Chemical (Osaka, Japan). Methoxyamine hydrochloride was purchased from Sigma Aldrich (Milwaukee, WI, USA). N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) and a standard alkane mixture (C9–C40) were purchased from GL Science Inc. (Tokyo, Japan).

4.2.2 Green coffee beans sample collection

Green coffee bean samples were collected from the farmer in Dombu, Sigi, Central Sulawesi. The farm is located at 1250 until 1600 m above sea level and processed with four different postharvest process method; dry/natural process, honey process, washed – wet hulled process, and washed – dry hulled process. The green coffee beans were stored in a vacuum-sealed pack and during the sample transportation, the direct sun exposure was prevented. Samples were subjected into sensory analysis in Indonesia and transported to Japan for metabolite profiling. Upon arrival in Japan, samples are stored at -30°C upon arrival in Japan until extraction and GC/MS analysis. Detailed information on the samples used, including their cup scores, is shown in **Table 4.2.2-1**.

4.2.3 Sensory analysis

The green coffee beans used in this study were subjected to sensory analysis certified Q-grader at the Specialty Coffee Association of Indonesia facility in Jakarta, Indonesia. The roasting process of the beans and the sensory analysis of the roasted beans, and coffee brew, was conducted according to a standardized protocol which was published by the Specialty Coffee Association of America (SCAA). The sensory analysis was performed by a certified panelist (Q-grader) on ten parameters which were rated from to 6-10, with zero indicating the least strong and ten for the strongest taste. The score from each parameter was accumulated and the total cup score was obtained. The cup score was used to determine coffee bean grade (Specialty Coffee Association/SCAA 2015)

Table 4.2.2-1 The sample list from Dombu, Sigi, Central Sulawesi

Sample Code	Postharvest Process	Altitude (m)	Geographical origin	Cup Score
Nat	Dry/Natural Process	1250-1600	Dombu, Sigi, Central Sulawesi	80.57
Hon	Honey Process			82.7
WH	Washed Process – Wet Hulled			80.75
DH	Washed Process – Dry Hulled			80.4

4.2.4 Metabolite extraction and derivatization

Metabolite extraction and derivatization were performed using a published protocol with minor modifications (Jumhawan et al. 2013; Putri et al. 2019). The metabolite extraction of each sample was performed in a technical replicate (n = 3). Prior to extraction, green coffee bean powder was prepared by grinding. Green coffee beans were added to a 50 ml grinding tube (Yasui Kikai Co., Osaka, Japan) along with a metal cone (Yasui Kikai Co., Osaka, Japan). The tube was closed tightly and quenched by dipping in liquid nitrogen. The closed tube was then immediately put into a multi-beads shocker (Yasui Kikai Co., Osaka, Japan), shaken at 2000 rpm for 30 seconds, repeated for 2-3 times to produce a fine powder of green coffee beans. Fifteen milligrams of green coffee powder were transferred to a 2 ml Eppendorf tube and extracted using 1 ml of a mixed solvent (methanol, ultrapure water, and chloroform with 5/2/2 (v/v/v) ratio) containing an internal standard (ribitol 12 µg/ml). The samples and blank (mixed solvent only) were vortexed and incubated at 1200 rpm at 37°C for 30 minutes. Afterwards, the samples and blank were centrifuged at 13100 rpm for 3 minutes at 4°C. The supernatant (900 µl) was transferred to a 1.5 ml Eppendorf tube and 400 µl ultrapure water was added before the samples were vortexed and re-centrifuged. Subsequently, 200 µl of the aqueous layer was transferred to a new tube with a pierced cap. For quality control (QC) purposes, 200 µl of the aqueous layer obtained from samples were collected in one pool by transferring it into a 15 ml Eppendorf tube. The collection of sample extracts in the QC pool was homogenized and 200 µl extract was transferred into a 1.5 ml Eppendorf tube with a pierced cap. The sample, QC, and blank extracts were concentrated by vacuum centrifugation for 20 minutes and lyophilized overnight.

The derivatization process consists of two steps, oximation and trimethylsilylation, as described previously in the published procedure (Jumhawan et al. 2013; Putri et al. 2019). The dried extract was subjected to oximation by adding 100 µl methoxyamine hydrochloride (20 mg/ml in pyridine), then vortexed and incubated at 1200 rpm and 30°C for 90 minutes. Subsequently, 50 µl MSTFA was added, and the mixture was re-vortexed and incubated at 1200 rpm and 37°C for 30 minutes. Sample mixture (100 µl) was transferred into a GC/MS vial prior to GC/MS analysis.

4.2.5 Gas chromatography-mass spectrometry (GC/MS) analysis

The workflow for gas chromatography-mass spectrometry (GC/MS) analysis of coffee bean extract has been developed and published elsewhere with several modifications (Jumhawan et al. 2013; Putri et al. 2019). GC/MS analysis was performed on a GCMSQP 2010 Ultra (Shimadzu, Kyoto, Japan) equipped with a 30 m × 0.25 mm i.d. fused silica capillary column coated with 0.25 μm InertCap 5MS/NP (GL Science, Inc., Tokyo, Japan) and an AOC-20i/s (Shimadzu, Kyoto, Japan) as an autosampler. System control and data acquisition were conducted using GC/MS solution software (Shimadzu, Kyoto, Japan). The mass spectrometer was tuned and calibrated prior to analysis. The standard alkane mixture (C10−C40) was injected at the beginning of the retention index calculation. The derivatized sample and blank (1 μl) were injected in random order with QC injections (1 μl) every four injections. The injections were conducted in split mode, 25:1 (v/v), and at an injection temperature of 270°C. Helium was used as the carrier gas with a flow rate of 1.12 ml/min and a linear velocity of 39 cm/s. The column and transfer line temperature settings were adjusted to those previously published (Jumhawan et al. 2013; Putri et al. 2019). The ion source temperature was 280°C and ions were generated by electron ionization at 70 eV. The mass spectra were recorded at 20 scans per second over the mass range 85−500 *m/z*.

4.2.6 Data processing

The chromatogram data obtained by GC/MS analysis were converted to a netCDF format using the GCMS Solution software package (Shimadzu, Kyoto, Japan). The netCDF files were further converted into ABF format using Reifycs Abf Converter (https://www.reifycs.com/AbfConverter/). Peak detection, deconvolution analysis, identification, and alignment were performed using MS-DIAL version 4.18 (Tsugawa et al. 2015; Lai et al. 2018; Tsugawa et al. 2019), which is a free software (http://prime.psc.riken.jp/Metabolomics_Software/MS-DIAL/). The minimum height for peak detection was set as 1,000 amplitudes with a linear weight moving average smoothing method. Smoothing level began at 5 scans and average peak width of 20 scans. In deconvolution analysis the sigma window value was set as 1, and the EI spectra cut-off was 200 amplitudes. Peak identification used the retention index (RI) based on the retention time of the standard alkane mixture (C10-C40) and GL-Science DB library (InertCap 5MS-NP, Kovats RI, 494 records; http://prime.psc.riken.jp/Metabolomics_Software/MS-DIAL/GCMS%20DB_InertCap%205MS-NP_GLscience.msp). The parameters for peak identification and alignment were RI tolerance 10, RT tolerance 0.5 minute, *m/z* tolerance 0.5 Da, EI similarity cut-off 70%, and identification score was cut-off at 70%. Metabolite identification was conducted by comparing the mass spectra and RI with the GL-Science DB library. After peak detection, the height of the detected peaks was normalized by the height of the internal standard peaks. The data matrix was constructed consisting of the raw height and normalized height of peaks. Filtering was then performed to exclude peaks that were not of biological origin by referring to the blank chromatogram from the data matrix (Putri et al. 2019). Moreover, peaks with a relative standard deviation of more than 30% in QC and with a raw height less than 5,000 were also removed. The final data matrix with filtered and assigned peaks was constructed and used for further analysis.

3.2.7 Multivariate analysis

Principal component analysis (PCA) and orthogonal projection to latent structure (OPLS) discrimination analyses were performed using the commercially available SIMCA-P+ version 13.0.3 (Umetrics, Umeå, Sweden). The data matrix was subjected to PCA and OPLS with auto-scale and without transformation, to analyze all the obtained metabolites equally (van den Berg et al. 2006). The relative intensity differences between samples on selected metabolites were evaluated using one-way analysis of variance and post hoc multiple comparison tests using JASP version 0.13.1 (JASP Team, 2020), which is a freely available software (https://jasp-stats.org).

4.3 Result and discussion

4.3.1 GC/MS metabolite profiling analysis of green coffee beans obtained from Dombu, Sigi, Central Sulawesi with various of postharvest process methods

GC/MS-based analysis of the green coffee beans extract has been described in previous studies (Jumhawan et al. 2013; Putri et al. 2019). The workflow of the analysis started by extracting and derivatizing the low molecular hydrophilic class compound in the green coffee beans prior to GC/MS analysis. Based on this workflow, 222 metabolites were detected. After data preprocessing and filtering, 79 detected metabolites were selected, consisted of 47 annotated metabolites and 32 unknown metabolites. The annotated metabolites were categorized as amino acids, sugar compounds, sugar alcohol compounds, organic acids, and other class compounds (Table S16). The unknown metabolites found in this study were numbered based on their retention times. The data matrix of normalized peaks was constructed and subjected to multivariate analysis for data exploration and visualization of information based on sample variance.

4.3.2 Principal component analysis of green coffee beans obtained from Dombu, Sigi, Central Sulawesi with various of postharvest process methods

The metabolome profile of green coffee beans with same altitude and geographical origin and four different postharvest process methods was subjected to principal component analysis to observe the sample clustering in unsupervised manner. The result showed in **Fig. 4.3.2-1**. The score plot of PCA (**Fig. 4.3.2-1A**) showed the sample clustering based on the postharvest process methods in which corroborated with the previous findings using different set of samples consisting of samples obtained from various altitude, geographical origin, and postharvest process methods in the previous chapter. This figure also showed that, although applied different drying and hulling method in the washed process method, the samples still clustered together as washed process method. The PCA loading plot (**Fig. 4.3.2-1B**) showed

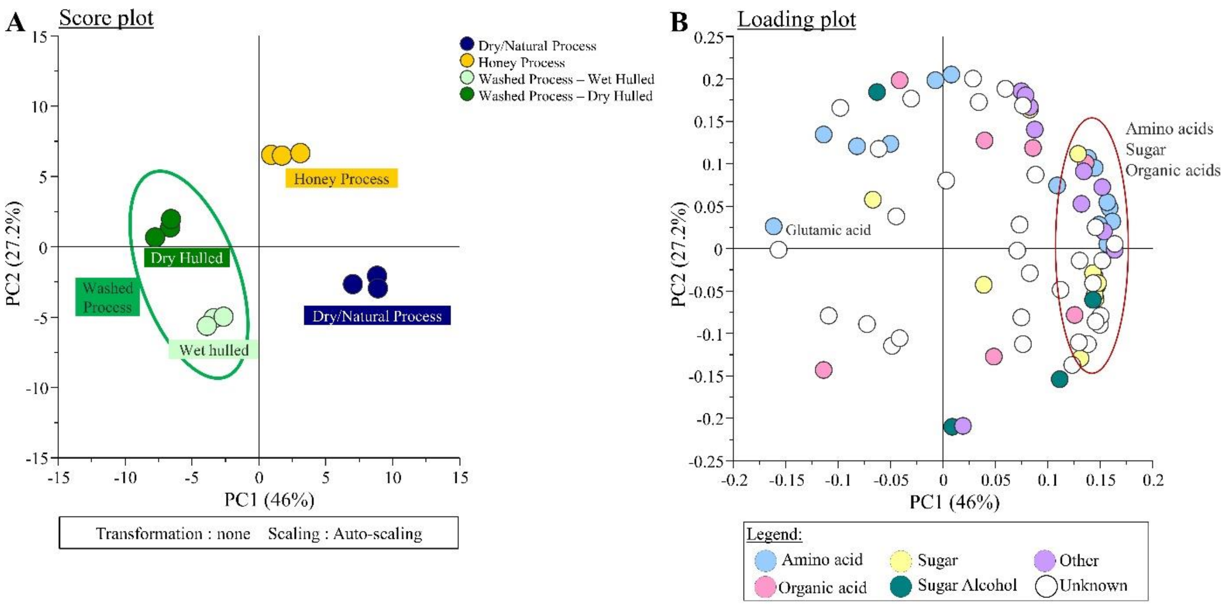

Figure 4.3.2-1 The PCA result of green coffee beans obtained from Dombu, Sigi, Central Sulawesi with various of postharvest process methods. (A) PCA score plot cluster the samples based on the postharvest methods. The different colors represent the different postharvest methods. (B) PCA loading plot showed the correlated metabolites for each cluster. The different colors represent the class of the compounds. The metabolites within the red circle are correlated metabolites with the sample clustering in the PCA score plot. The PCA result showed the same tendency with the previous experiment using various altitude, geographical origin, and postharvest process methods.

the metabolite correlated with the sample clustering. The result show that most of metabolites correlated with the dry/natural process than the washed process method, in which in line with the result in the previous experiment. Metabolites consisted amino acids, organic acids, and sugar compounds were correlated with dry/natural process methods. Glutamic acid consistently correlated with green coffee beans obtained from the washed process method and supported the previous report about the glutamic acid correlation with washed process method (Bytof et al. 2005; Selmar et al. 2014). This result validated the postharvest process methods as the predominant factor during the production of green coffee beans of Arabica. Therefore, the producer could focus more on the production cost and resource to optimize the postharvest process method to produce good quality of Arabica coffee.

4.3.3 Orthogonal projection latent structures discriminant analysis (OPLS-DA) of green coffee beans obtained from Dombu, Sigi, Central Sulawesi with various of postharvest process methods

The green beans samples obtained from Dombu, Sigi, Central Sulawesi with various postharvest methods were subjected to sensory analysis, cupping test. The final score of the cupping test is shown in the Table 4.2.2-1. The green coffee beans obtained from the honey process method has the highest final score with 82.7 while the green coffee beans from other postharvest process methods have final score around 80. The OPLS discriminant analysis was conducted to observe the difference of the metabolome profile of the green coffee beans with the score 82.7 and the green coffee beans with the score 80.4 – 80.75. The OPLS model is shown in **Fig. 4.3.3-1**. The model shows the good correlation between variables based on its

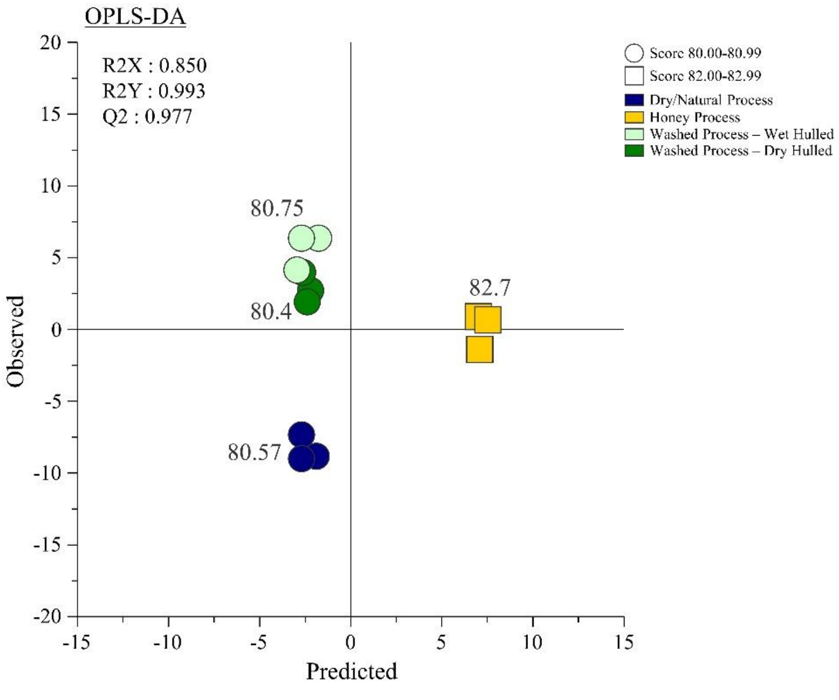

Figure 4.3.3-1 The OPLS-DA result of green coffee beans obtained from Dombu, Sigi, Central Sulawesi with various of postharvest process methods. The different colors represent the different postharvest methods and the different shape represent different group of final score. The model has R2X = 0.850, R2Y = 0.993, and Q2 = 0.977 in which showed good correlation between variables in the OPLS-DA model.

R2 and Q2 values (Varmuza and Filzmoser 2009; Worley and Powers 2013; Alexander et al. 2015). The correlated metabolites were sorted based on its VIP values (Table S17). The metabolites were considered as important if the VIP value more than 1 (Galindo-Prieto et al. 2014; Ikram et al. 2020). This study selected metabolites with VIP value more than 1.5 and resulted in 13 metabolites considered important to the model. Among thirteen metabolites, galactinol is included and correlated with the green coffee beans with higher final score. To confirm the positive correlation of galactinol to the final score, the relative intensity between the samples with score 80.4 – 80.75 and 82.7 were observed (**Fig. 4.3.3-2**). The relative intensity of galactinol found to be higher in coffee beans with higher final cup score. This result is validated the previous experiment about the quality-related metabolites that also found galactinol has positive correlated metabolite to the coffee quality as describe as final score. It is interesting thing to note that, the sensory analysis was conducted by two different institutes, ICCRI and SCAI. Despite of this, the correlation between galactinol and the final score is still consistent. Therefore, galactinol could be used as additional parameter for quality of specialty Arabica coffee in raw, green bean state.

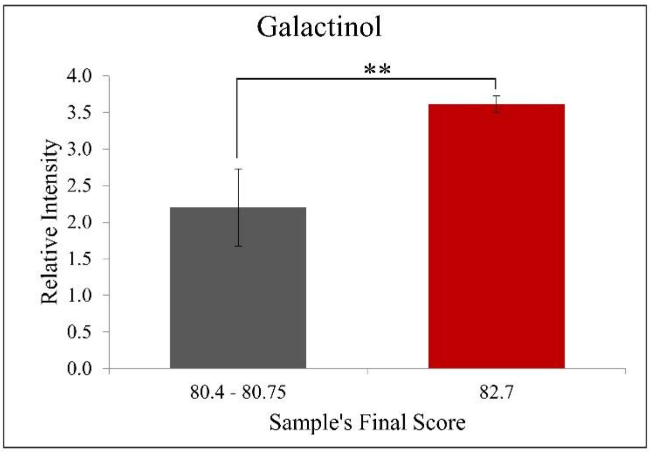

Figure 4.3.3-2 The relative intensity of galactinol between the samples with score 80.4 – 80.75 and 82.7. The error bar showed the standard deviation. The asterisk show that concentration difference is statistically significant according to Student *t*-test method with p-value <0.01.

4.4 Conclusion

The metabolite profiling of green coffee beans from Dombu, Sigi, Central Sulawesi validated that the postharvest process method is the main factor that clustered the sample. In this study found the honey postharvest process method is suitable for green coffee bean production using coffee cherry from Dombu as the green coffee beans obtained from honey process has the highest cupping score. However, there is also possibility that the suitable postharvest process method is depend on the geographical origin of the coffee producing location. Moreover, the content of galactinol is also higher in honey processed green coffee beans in which validated the correlation between the galactinol and the final score of the cupping test.

Chapter 5

Conclusion and Future Perspective

5.1 Conclusion

In this thesis, the metabolomics approach accumulated the knowledge about the correlation between green coffee beans metabolome profile with coffee sensory quality and the factors correlated with the green coffee beans production in Arabica coffee species produced in Indonesia. Green coffee bean was used as it connects between the production process and the sensory quality in which the metabolome profile was influenced by the production-related factors and act as the flavor precursor for the flavor of the cup of coffee brew. Throughout this study, it is found that galactinol is correlated with the coffee quality and the postharvest process method is the predominant factor that influence the green coffee beans metabolome profile.

Galactinol as quality-related metabolite is validated in various green coffee beans sample set from Indonesia, showing consistent importance and positive correlation with the sensory quality of coffee as describe in final score of the cupping test. Furthermore, galactinol is found not only in green bean state, but also in roasted bean and coffee brew. It is also found that although the sensory evaluation was done by different institutes, galactinol still have correlation with the final score of the cupping test.

The postharvest process found as the predominant factor to the green coffee bean metabolome profile, followed by geographical origin and altitude factor. The finding is validated when the metabolome of green coffee beans produced from specific location and altitude with various postharvest process method showing the same tendency with the earlier experiment with various locations, altitudes, and postharvest process methods. Although there are some varieties of drying process in the validation set samples, the differences of postharvest process methods still apparent.

5.2 Future perspective

As previously mentioned in the first chapter, coffee is popular beverage and consumed worldwide. As the coffee consumption increasing, the various coffee product concerning quality and traceability also introduced. Specialty coffee Arabica is one of the Arabica coffee products that promote the distinctiveness of coffee taste by evaluating the coffee through standardized sensory test and grading system. Hence, the coffee producers are keen to improve their product to meet the standard. As more and more Arabica product were produced and subjected to sensory evaluation, the overwhelmed time-consuming process might need additional parameter to assist the sensory evaluation itself. The time-consuming and costly optimization process of coffee product improvement also might need a clue on which factors that influence the coffee quality the most. Therefore, the exploration of the chemical compounds contains in the green beans that correlates with the coffee quality and production process could help the coffee industry. The metabolomics approach workflow could facilitate this study to found the connections between the chemical compounds and coffee quality and production.

The suggestion from this research could be applicable in coffee industry especially to the coffee sensory assessment and the coffee production. This study suggested galactinol to be used as the early-screening or additional parameter to assist the sensory evaluation for coffee quality grading. The present study also suggests the coffee producers to more focus on the postharvest process methods optimization. Moreover, the application of galactinol as parameter could be monitored during the optimization of postharvest process methods to predict the sensory quality of the coffee. Further research might be necessary to explore the role of galactinol in terms of coffee taste to have better understanding about the correlation of galactinol with the coffee quality

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List of publications

Original Paper

Amalia F, Aditiawati P, Yusianto, Putri SP, Fukusaki E. Gas chromatography/mass spectrometry-based metabolite profiling of coffee beans obtained from different altitudes and origins with various postharvest processing. *Metabolomics*. 2021 Jul 12;17(7):69. doi: 10.1007/s11306-021-01817-z. PMID: 34254180.

Conference

1. Fitri Amalia, Pingkan Aditiawati, Sastia Prama Putri, Eiichiro Fukusaki. Untargeted metabolomic approach of coffee beans obtained from different altitude. Japan-Indonesia International Scientific Conference (2018) – Poster and oral presentation
2. Fitri Amalia, Pingkan Aditiawati, Yusianto, Sastia Prama Putri, Eiichiro Fukusaki. The metabolic profiling of coffee obtained from various altitude, geographical origin, and postharvest processes in Indonesia. SBJ Annual Meeting (2021) – Poster presentation

Appendices

Table S1 List of detected metabolites in green beans

No	Metabolite name	Class	RT[a] (min)	RI[b]	Quant mass (*m/z*)	MSI Level[c]
1	Alanine	Amino Acid	5.46	1108.46	116	1
2	Asparagine	Amino Acid	10.74	1682.93	116	1
3	Aspartic acid	Amino Acid	9.54	1531.00	232	1
4	beta-Glutamic acid	Amino Acid	10.28	1622.94	232	1
5	Glutamic acid	Amino Acid	10.33	1629.43	246	1
6	Glutamine	Amino Acid	11.50	1785.39	156	1
7	Glycine	Amino Acid	7.63	1316.70	174	1
8	Isoleucine	Amino Acid	7.49	1301.96	158	1
9	Leucine	Amino Acid	7.27	1280.04	158	1
10	Lysine	Amino Acid	12.56	1939.63	156	1
11	Phenylalanine	Amino Acid	10.42	1641.18	218	1
12	Proline	Amino Acid	7.52	1305.89	142	1
13	Pyroglutamic acid	Amino Acid	9.55	1532.71	156	1
14	Serine	Amino Acid	7.10	1263.26	116	1
15	Threonine	Amino Acid	8.39	1398.21	219	1
16	Tryptophan	Amino Acid	14.48	2247.64	202	1
17	Tyrosine	Amino Acid	12.68	1957.34	218	1
18	Valine	Amino Acid	6.70	1224.12	144	1
19	Chlorogenic acid	Organic Acid	19.05	3173.71	345	1
20	Ferulic acid	Organic Acid	13.61	2102.45	338	1
21	Fumaric acid	Organic Acid	7.93	1348.54	245	1
22	Galacturonic acid	Organic Acid	13.03	2010.30	333	1
23	Glucarate	Organic Acid	13.34	2059.50	333	1
24	Gluconic acid	Organic Acid	13.24	2043.65	333	1
25	Glyceric acid	Organic Acid	7.85	1340.76	147	1
26	Glycolic acid	Organic Acid	5.14	1079.44	147	1
27	Citric acid	Organic Acid	11.89	1840.38	273	1
28	Lactic acid	Organic Acid	4.98	1065.83	117	1
29	Malic acid	Organic Acid	9.26	1498.03	147	1
30	Methyl succinic acid	Organic Acid	7.84	1339.28	147	1
31	Nicotinic acid	Organic Acid	7.43	1296.35	180	1
32	Quinic acid	Organic Acid	12.24	1891.72	345	1
33	Shikimic acid	Organic Acid	11.76	1821.61	204	1
34	Succinic acid	Organic Acid	7.62	1316.32	147	1
35	Xylonic acid	Organic Acid	11.57	1794.54	217	1
36	Fructose	Sugar	12.40	1915.13	103	1
37	Galactose	Sugar	12.48	1927.23	319	1
38	Gentiobiose	Sugar	17.91	2917.30	204	1
39	Glucose	Sugar	12.52	1933.14	319	1
40	Mannose	Sugar	12.44	1920.38	319	1
41	Melezitose	Sugar	21.36	3587.18	361	1
42	Panose	Sugar	22.88	3774.93	204	1
43	Psicose+Tagatose	Sugar	12.34	1905.03	103	1
44	Raffinose	Sugar	20.80	3503.65	361	1
45	Sorbose	Sugar	12.34	1905.04	103	1
46	Sucrose	Sugar	16.94	2710.17	361	1
47	Trehalose	Sugar	17.46	2818.68	361	1
48	Galactose+Glucose	Sugar	12.65	1953.06	319	1

49	Galactinol	Sugar Alcohol	18.62	3077.84	204	1
50	Galactitol	Sugar Alcohol	12.86	1983.59	281	1
51	Inositol	Sugar Alcohol	13.80	2132.87	217	1
52	Mannitol	Sugar Alcohol	12.76	1968.83	319	1
53	Meso erythritol	Sugar Alcohol	9.49	1525.01	147	1
54	Sorbitol	Sugar Alcohol	12.81	1976.58	319	1
55	Threitol	Sugar Alcohol	9.41	1516.34	147	1
56	Xylitol	Sugar Alcohol	11.13	1735.04	217	1
57	2-Dehydro gluconate	Sugar Derivatives	12.47	1924.57	349	1
58	2-Aminoethanol	Other	7.23	1276.25	174	1
59	4-Aminobutyric acid	Other	9.62	1541.52	174	1
60	Adenosine	Other	16.73	2667.59	230	1
61	Caffeine	Other	12.05	1863.08	194	1
62	Glucono-1,5-lactone	Other	12.37	1910.85	129	1
63	Glycerol	Other	7.30	1283.10	147	1
64	N-Methylnicotinate	Other	9.39	1513.55	210	1
65	Paeoniflorin	Other	20.87	3513.86	361	1
66	Phosphate	Other	7.29	1282.14	299	1
67	Putrescine	Other	11.29	1757.53	174	1
68	Serotonin	Other	15.82	2489.52	174	1
69	Unknown_1	Unknown	4.68	1039.10	117	4
70	Unknown_2 (apigenin)	Flavone	4.78	1048.10	117	2
71	Unknown_3	Unknown	6.29	1184.33	281	4
72	Unknown_4	Unknown	6.97	1251.14	147	4
73	Unknown_5	Unknown	7.11	1264.60	98	4
74	Unknown_6	Organic Acid	8.43	1402.61	147	3
75	Unknown_7	Organic Acid	8.66	1428.30	160	3
76	Unknown_8	Unknown	9.10	1479.61	210	4
77	Unknown_9	Unknown	9.57	1535.39	174	4
78	Unknown_10	Unknown	9.63	1543.07	304	4
79	Unknown_11	Unknown	9.74	1555.93	120	4
80	Unknown_12	Organic Acid	9.97	1583.51	129	3
81	Unknown_13	Unknown	10.04	1592.21	210	4
82	Unknown_14	Unknown	10.12	1602.09	159	4
83	Unknown_15 (gentistic acid)	Organic Acid	10.63	1668.62	355	4
84	Unknown_16 (2,5-methylpyrazine)	Pyrazines	11.45	1778.43	217	4
85	Unknown_17	Unknown	11.67	1809.02	292	4
86	Unknown_18 (galactopyranoside)	Sugar	11.95	1848.95	204	4
87	Unknown_19	Unknown	12.72	1963.69	204	4
88	Unknown_20	Organic Acid	12.99	2003.92	217	3
89	Unknown_21	Organic Acid	13.02	2009.13	319	3
90	Unknown_22	Organic Acid	13.21	2039.22	217	3
91	Unknown_23	Organic Acid	13.51	2086.76	333	3
92	Unknown_24	Organic Acid	13.60	2100.89	218	3
93	Unknown_25	Sugar	13.81	2135.70	355	3
94	Unknown_26	Unknown	13.96	2160.34	290	4
95	Unknown_27	Unknown	14.28	2212.92	204	4
96	Unknown_28	Unknown	15.39	2409.60	217	4
97	Unknown_29	Unknown	15.57	2443.17	204	4
98	Unknown_30	Unknown	16.09	2541.39	204	4
99	Unknown_31	Unknown	16.76	2674.24	259	4

100	Unknown_32	Unknown	17.02	2725.71	191	4
101	Unknown_33	Unknown	17.35	2795.82	191	4
102	Unknown_34 (alpha-1,2-mannobiose)	Sugar	17.83	2899.14	191	4
103	Unknown_35	Unknown	18.25	2991.30	355	4
104	Unknown_36	Unknown	18.30	3002.06	355	4
105	Unknown_37	Unknown	18.36	3016.01	355	4
106	Unknown_38	Unknown	18.39	3024.43	345	4
107	Unknown_39	Unknown	18.45	3037.82	355	4
108	Unknown_40	Unknown	18.74	3104.34	219	4
109	Unknown_41	Unknown	18.78	3113.19	204	4
110	Unknown_42	Unknown	18.82	3121.59	204	4
111	Unknown_43	Unknown	18.92	3145.18	345	4
112	Unknown_44	Unknown	19.01	3163.63	207	4
113	Unknown_45 (D-lactitol)	Sugar	19.16	3198.69	204	2
114	Unknown_46	Unknown	19.18	3201.05	249	4
115	Unknown_47	Unknown	19.27	3219.91	307	4
116	Unknown_48	Unknown	19.30	3227.10	249	4
117	Unknown_49	Unknown	19.33	3233.57	207	4
118	Unknown_50	Unknown	19.38	3242.47	307	4
119	Unknown_51	Unknown	20.67	3482.95	255	4
120	Unknown_52	Unknown	20.73	3491.92	255	4
121	Unknown_53	Unknown	21.09	3546.40	361	4
122	Unknown_54	Unknown	21.56	3615.61	362	4
123	Unknown_55	Sugar	21.57	3615.75	361	3
124	Unknown_56	Unknown	21.64	3625.13	361	4

There are 124 metabolites detected in all green bean samples

a Retention time in minute(s)

b Retention indices (RI) are calculated using a standard alkane mixture (C10–C40).

c Mass spectra of metabolite peaks that are compared only with the in-house library are considered Metabolic Standards Initiative (MSI) level 1 identification. Mass spectra of metabolite peaks that compared to external library (NIST, FoodB, HMDB, MoNA) are considered as MSI level 2. Several unknown compounds are considered MSI level 3 based on similarity to known compounds of a chemical class in library and MSI level 4 if there are no similarities with any chemical class compound in library.

Table S2 VIP value of the final score OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Unknown_45 (D-lactitol)	2.15584	0.0530035
Galactinol	2.00792	0.0532871
Unknown_34 (alpha-1,2-mannobiose)	1.97846	-0.0648565
Unknown_18 (galactopyranoside)	1.94286	0.0561994
Shikimic acid	1.71275	-0.065621
Glutamic acid	1.70144	0.0203317
Caffeine	1.65976	0.0407852
Unknown_2 (apigenin)	1.61316	0.0917506
Trehalose	1.61262	0.0415493
Unknown_15 (gentistic acid)	1.54368	-0.0513991
Unknown_16 (2,5-dimethylpyrazines)	1.53754	0.0694761
Alanine	1.51482	-0.0390176
Ferulic acid	1.47228	-0.0361815
Unknown_13	1.45132	-0.0129047
Unknown_8	1.44623	-0.0102604
N-Methylnicotinate	1.44305	-0.0144679
Glycerol	1.43487	-0.0376557
Unknown_9	1.42794	0.0270916
Unknown_1	1.42436	0.0906582
Threitol	1.42056	-0.0497443
Melezitose	1.39462	0.0277498
Unknown_55	1.37495	0.03856
beta-Glutamic acid	1.37163	-0.0218956
Unknown_56	1.35297	-0.024074
Unknown_3	1.35115	-0.036267
Unknown_54	1.30418	0.0358293
Glutamine	1.29839	0.0175611
Unknown_32	1.29669	-0.000443373
Mannose	1.29494	-0.0130563
Unknown_43	1.25767	0.0219314
Unknown_49	1.25755	-0.0357673
Glycolic acid	1.23405	0.0427446
Sorbitol	1.20802	-0.026873
Inositol	1.20667	-0.000914343
Unknown_35	1.19498	0.00573727
Unknown_36	1.18884	-0.00248397
Gentiobiose	1.17734	-0.0186304
2-Dehydro gluconate	1.16971	0.0229788
Phenylalanine	1.15942	0.0516498
Unknown_17	1.15509	-0.00795777
Paeoniflorin	1.15084	-0.0571618
Glycine	1.1456	-0.0172038
Unknown_20	1.13022	-0.0182547
Galacturonic acid	1.12777	-0.0124666
Unknown_23	1.12643	-0.0283422
Phosphate	1.12511	-0.009649
Sucrose	1.10512	0.0410844

Unknown_21	1.0965	-0.0108354
Tryptophan	1.08954	0.00190973
Unknown_50	1.08933	-0.0132361
Unknown_47	1.06432	-0.0136034
Xylitol	1.05599	-0.00184296
Meso erythritol	1.05378	-0.0132324
Unknown_12	1.05311	-0.00867443
Glyceric acid	1.04626	0.00330828
Fumaric acid	1.03487	-0.00665873
Unknown_52	0.954007	0.0443139
Galactose	0.909022	-0.00640079
Succinic acid	0.905832	-0.0241105
Methyl succinic acid	0.87385	-0.0387764
Unknown_39	0.870519	-0.00380447
Unknown_7	0.868187	-0.0114199
Lactic acid	0.834655	0.000196397
Unknown_30	0.831905	-0.024296
Unknown_40	0.813334	-0.0139657
Unknown_37	0.786522	-0.000340221
Unknown_48	0.775572	-0.00341188
Unknown_19	0.769465	-0.01859
Unknown_53	0.769288	-0.0068355
Unknown_27	0.751143	-0.00200948
Unknown_10	0.74874	0.0494994
Xylonic acid	0.699394	0.00632183
Proline	0.685163	-0.0105655
Unknown_5	0.657895	0.0186611
Unknown_11	0.655636	0.047721
Unknown_29	0.645882	0.0213868
Raffinose	0.634853	0.00243659
Aspartic acid	0.62461	-0.00807526
Putrescine	0.622769	0.0442388
Mannitol	0.589787	-0.0467659
Nicotinic acid	0.588326	0.00368913
Galactose+Glucose	0.584612	-0.0245792
Glucose	0.573358	-0.0228029
Glucarate	0.572382	0.0104978
Unknown_46	0.551752	0.00552144
Unknown_31	0.527607	-0.0039432
Serine	0.516249	-0.0305532
Unknown_41	0.505278	0.000157449
Valine	0.494075	0.00538587
Glucono-1,5-lactone	0.480173	-0.00116074
Threonine	0.475417	-0.00155854
2-Aminoethanol	0.474763	0.0248763
Gluconic acid	0.411684	0.00170539
Unknown_33	0.400826	0.0100461
Unknown_26	0.378141	-0.00110658
Unknown_24	0.360342	0.0476624
Pyroglutamic acid	0.359511	-0.0356336

Unknown_28	0.340305	0.0297842
Tyrosine	0.316538	0.0173693
Lysine	0.299313	0.0153053
Unknown_4	0.282971	-2.18E-05
Citric acid	0.253817	0.0289369
Unknown_22	0.243489	0.0376479
Isoleucine	0.22712	0.017301
Galactitol	0.197914	-0.0213646
Malic acid	0.181443	-0.0422881
Quinic acid	0.153534	0.0012144
Chlorogenic acid	0.146111	0.00618824
4-Aminobutyric acid	0.136952	0.03791
Unknown_38	0.126596	-0.0328954
Fructose	0.107141	6.20E-05
Unknown_14	0.103562	-0.0122599
Psicose+Tagatose	0.091679	0.000135519
Sorbose	0.090646	6.85E-05
Unknown_6	0.084612	-0.0103886
Unknown_42	0.084286	-0.0105056
Leucine	0.080499	0.0254171
Unknown_51	0.073441	0.00123923
Panose	0.039065	0.0229473
Asparagine	0.024262	-0.00744769
Unknown_44	0.021305	-0.0346056
Serotonin	0.01666	-0.00863516
Unknown_25	0.015463	-0.0128496
Adenosine	0.012148	0.018157

Table S3 VIP value of the final score OPLS model in 35 different green coffee bean samples

Metabolite	VIP Score	Coefficient
Unknown_68	2.0138	-0.050494
Alanine	2.00748	-0.122828
Sucrose	1.94555	0.106378
Xylonic acid	1.85889	-0.0467556
Glycerol	1.84591	-0.0353
Unknown_50	1.83712	0.103058
Propyleneglycol	1.79702	-0.0374822
Xylitol	1.76215	-0.0415846
Adenine	1.7463	-0.0276063
Unknown_37	1.69115	-0.0372734
Unknown_27	1.68189	-0.073675
Unknown_79	1.68003	-0.0036683
Unknown_77	1.66566	0.00111516
Unknown_35	1.62959	-0.0736667
Glyceric acid	1.61697	-0.0076745
Valine	1.59459	-0.0272082
Unknown_81	1.52486	-0.0012878
Unknown_47	1.51458	-0.0227094
Galactinol	1.50251	0.045065
Unknown_80	1.49611	0.00173155
Unknown_78	1.48731	0.00241995
Inositol	1.47474	-0.0112267
Unknown_34	1.4585	-0.0656462
Unknown_5	1.44735	-0.058715
2-Aminoethanol	1.443	-0.0356055
Unknown_61	1.42538	-0.0219272
Tyrosine	1.41668	-0.0290268
Unknown_24	1.41586	-0.0399368
Unknown_36	1.41163	-0.061597
Unknown_22	1.40255	-0.0556507
Unknown_54	1.40104	-0.0509704
Phosphate	1.35405	-0.003513
Unknown_58	1.32553	-0.0105948
Isoleucine	1.32443	-0.0151152
Unknown_26	1.31894	-0.0189628
Unknown_20	1.29045	-0.0400039
Caffeine	1.25672	-0.0774961
Unknown_11	1.23925	-0.0110936
Unknown_1	1.20202	-0.0437373
Unknown_16	1.20127	0.0101786
Phenylalanine	1.19445	-0.043698
Chlorogenic acid	1.18771	0.0303139
Unknown_87	1.17659	-0.0411424
Unknown_4	1.17171	-0.0039499
Unknown_59	1.16742	-0.0259275
Unknown_46	1.16441	-0.0008025
Threitol	1.15921	-0.0059346

Raffinose	1.15819	-0.0369361
Unknown_8	1.15797	-0.0435239
N-Methylnicotinate	1.15448	0.00641645
Unknown_40	1.15226	-0.0290194
Unknown_86	1.13666	-0.0343611
Gentiobiose	1.13234	-0.0452012
Unknown_15	1.11299	0.00019155
Unknown_7	1.09462	0.00056923
Succinic acid	1.08382	-0.0332419
Glycine	1.08325	-0.0332291
Arabionose	1.07793	-0.0157509
Unknown_66	1.07144	0.00430148
Glucono-1,5-lactone	1.06375	-0.0032888
Tryptophan	1.06269	-0.049412
Quinic acid	1.04792	-0.0279008
Gluconic acid	1.04496	0.00089522
Unknown_48	1.04272	-0.0320482
Mannose	1.02586	0.0111807
Glutamic acid	1.02025	0.0291226
Unknown_62	1.01567	-0.0545341
Leucine	1.01084	-0.0051736
Methionine	1.00215	0.0125444
Unknown_90	1.00035	-0.0297926
Proline	0.981326	-0.0043361
Unknown_9	0.951758	-0.0168612
Galacturonic acid	0.942092	0.00370926
Unknown_23	0.93031	0.0238322
Unknown_97	0.907009	-0.0211928
Unknown_33	0.903623	0.00613103
Unknown_10	0.898711	0.0185413
Unknown_75	0.894441	0.0195091
Meso erythritol	0.886079	0.00158173
beta-Glutamic acid	0.884249	-0.0265784
Unknown_12	0.873111	-0.0418743
Threonine	0.869872	0.00838093
Unknown_18	0.861253	0.0272173
Unknown_43	0.82118	-0.0439889
Unknown_44	0.816692	0.0469155
Unknown_13	0.815968	0.00066426
4-Aminobutyric acid	0.81542	0.0139775
Glycolic acid	0.811605	-0.0100454
Unknown_98	0.762731	-0.0137915
Unknown_55	0.760714	-0.014695
Glucarate	0.732633	0.0321083
2-Aminoadipic acid	0.706752	-0.0429157
Unknown_38	0.705599	0.0799343
Galactose+Glucose	0.700014	0.0181918
Unknown_30	0.69255	-0.0085909
Unknown_2	0.69019	0.0130831
Unknown_21	0.686287	-0.0093543

Unknown_6	0.666357	0.0527266
Unknown_25	0.664844	0.0585552
Unknown_17	0.662825	0.00384431
Unknown_19	0.662692	0.0113864
Unknown_71	0.658474	-0.0085472
Unknown_32	0.636566	-0.0102599
Aspartic acid	0.622846	0.00224405
Melezitose	0.616874	-0.0441149
Glucose_1	0.608818	0.0280619
Sorbose_2	0.597496	0.0185882
Fructose_2	0.590507	0.0183227
Putrescine	0.586249	0.0419222
Unknown_91	0.572466	-0.0133856
Lysine	0.565525	0.0145088
Tryptamine	0.543304	0.00356857
Icosanoic acid	0.529253	0.0113987
Serotonin	0.518311	0.0323045
Urea	0.5073	0.0014029
Shikimic acid	0.500749	0.0201402
Unknown_3	0.500326	0.017999
Unknown_31	0.48274	0.0189467
Unknown_53	0.474027	-0.0229272
Maltose	0.463745	0.00846569
Unknown_51	0.452438	0.0151423
Unknown_85	0.43392	-0.0086261
Myristic acid	0.418948	-0.0404127
Unknown_28	0.414067	0.00598816
Unknown_56	0.411373	0.0551527
Unknown_49	0.409943	0.00149511
Unknown_99	0.398216	-0.0201378
Unknown_52	0.389123	0.00767934
Unknown_70	0.378333	-0.0020569
Unknown_57	0.356393	0.0470792
Trehalose	0.34483	0.0382884
Unknown_42	0.341967	0.0404576
Citric acid	0.335007	0.0219069
Unknown_67	0.333055	0.00485846
Unknown_74	0.326811	-0.0045175
Unknown_93	0.322607	-0.0101961
Unknown_73	0.315542	-0.0006595
Unknown_63	0.30539	0.00253745
Sorbitol	0.289293	0.0200614
Unknown_89	0.284077	-0.0099818
Adenosine	0.27182	0.0450529
Unknown_39	0.259575	0.0213406
Unknown_69	0.258827	-0.0361344
Unknown_65	0.21271	0.010912
Unknown_14	0.198193	0.021128
Unknown_76	0.19424	0.002474
Unknown_96	0.166018	0.00802859

Unknown_84	0.15689	0.0396847
Malic acid	0.143244	0.00715869
Unknown_29	0.121063	-0.0175561
Unknown_82	0.113599	0.0190832
Unknown_45	0.108456	-0.0103488
Unknown_72	0.103257	-0.0102266
Unknown_64	0.0966723	0.0153514
Unknown_83	0.0894726	0.0081057
Unknown_60	0.0704623	0.0228471
Unknown_95	0.0608834	-0.0053251
Unknown_92	0.0489605	0.0453112
Unknown_94	0.0481105	0.00542433
Unknown_88	0.0462713	0.0452442
Mannitol	0.0294796	0.00165403
Serine	0.0183022	-0.0013815
Unknown_41	0.00714314	0.0194141

Table S4 VIP value of the fragrance/aroma OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Unknown_34 (alpha-1,2-mannobiose)	2.03829	-0.0658972
Caffeine	1.98954	0.0936543
Unknown_28	1.75245	-0.0818232
Inositol	1.71183	-0.0382405
Mannose	1.69568	-0.0206505
Unknown_43	1.6348	0.062379
Unknown_17	1.6183	-0.0337872
Unknown_18 (galactopyranoside)	1.58344	0.0393262
beta-Glutamic acid	1.57043	-0.0613441
Phosphate	1.57017	-0.0159735
Galactinol	1.54649	0.0355366
Unknown_8	1.52151	-0.0259378
Unknown_29	1.48339	-0.0462429
Unknown_5	1.47026	-0.0727993
Unknown_13	1.46412	-0.0241754
N-Methylnicotinate	1.44622	-0.0286484
Galacturonic acid	1.42282	-0.0329429
Unknown_21	1.41654	-0.0329648
Unknown_3	1.41643	-0.0279996
Unknown_45 (D-lactitol)	1.41345	0.00532347
Unknown_20	1.39703	-0.0243494
Glyceric acid	1.37439	-0.0174015
Malic acid	1.3661	0.0439918
Xylitol	1.33754	-0.00992944
Glucarate	1.33406	-0.0289012
Unknown_23	1.31999	-0.033724
Glycerol	1.30701	-0.0205882
Tryptophan	1.28735	0.0011149
Unknown_32	1.27074	-0.00253035
Threitol	1.2386	-0.0570497
Sorbitol	1.22481	-0.0238859
Unknown_35	1.22435	0.0116096
Melezitose	1.22137	0.0105354
Unknown_54	1.21025	0.0214565
Gentiobiose	1.19835	0.00608037
Unknown_55	1.19126	0.0172266
Glutamic acid	1.16024	0.0101407
Proline	1.14512	-0.0292789
Unknown_36	1.12738	0.012016
Unknown_30	1.12007	-0.0197513
Unknown_40	1.11651	-0.0216619
Unknown_50	1.11494	0.0060858
2-Aminoethanol	1.09826	-0.0591218
Unknown_49	1.09425	-0.016189
Fumaric acid	1.09058	-0.0393458
Unknown_7	1.0898	-0.00440227

Unknown_9	1.07343	0.0174341
Sucrose	1.04481	0.0276834
Valine	1.04052	-0.0213062
Unknown_47	1.0372	0.0131234
Unknown_56	1.00843	-0.013137
Unknown_12	0.985623	-0.0243999
Citric acid	0.971251	-0.0321026
Xylonic acid	0.943442	-0.0209443
Isoleucine	0.940199	-0.0222425
Unknown_16 (2,5-dimethylpyrazines)	0.940161	0.0273397
Unknown_22	0.933707	-0.0151775
Threonine	0.925375	-0.0104531
Galactose+Glucose	0.912872	-0.0419382
Galactitol	0.909985	0.00709961
Alanine	0.903543	-0.0219955
Aspartic acid	0.9006	-0.00134923
Ferulic acid	0.885583	0.012679
Unknown_2 (apigenin)	0.882273	0.0538145
Raffinose	0.875832	-0.0197289
Chlorogenic acid	0.870937	0.0638961
Lysine	0.865464	-0.00956558
Gluconic acid	0.860556	-0.0203197
Glucono-1,5-lactone	0.852191	-0.0177764
Lactic acid	0.832762	-0.0264216
Unknown_39	0.824676	0.019359
Unknown_48	0.824463	0.0278415
Glucose_1	0.809868	-0.0343589
Unknown_37	0.809537	0.0145505
Unknown_51	0.80945	0.0480749
Meso erythritol	0.797159	-0.0157421
2-Dehydro gluconate	0.73672	0.00585949
Adenosine	0.717719	-0.028009
Unknown_46	0.71621	0.0327772
Unknown_53	0.708629	-0.00974461
Unknown_44	0.70703	0.0243688
Mannitol	0.702365	0.0148748
Glycolic acid	0.700359	0.0215051
Unknown_26	0.699336	-0.0276942
Nicotinic acid	0.669668	-0.0239617
Galactose	0.609387	-0.0354753
Unknown_10	0.60511	0.0392956
Unknown_42	0.57359	-0.0530884
Unknown_52	0.541583	0.0131907
Unknown_33	0.516852	-0.0168515
Putrescine	0.514896	0.0634861
Leucine	0.49631	-0.0153162
Unknown_38	0.482267	-0.0318642
Glutamine	0.467457	-0.0505282
Asparagine	0.459378	-0.0253854
Unknown_6	0.452078	-0.0658216

Unknown_1	0.418139	0.0332802
Panose	0.396073	0.0481664
Methyl succinic acid	0.391971	-0.00932614
Unknown_41	0.381944	-0.0225588
Unknown_25	0.326802	-0.00925328
Unknown_31	0.307957	0.0226832
Unknown_19	0.300047	0.0213718
Unknown_15 (genistic acid)	0.299381	0.0290458
Pyroglutamic acid	0.285065	-0.0278971
Serotonin_1	0.282923	-0.0323019
Trehalose	0.273219	-0.0641049
Glycine	0.26792	0.0174202
Succinic acid	0.260374	0.0270276
Phenylalanine	0.192545	-0.0312116
Shikimic acid	0.190771	0.0649015
Fructose	0.163854	-0.000271437
Unknown_14	0.159057	-0.0163582
Quinic acid	0.148918	-0.0469939
Unknown_24	0.147387	0.0359081
Unknown_4	0.147077	0.0160265
Psicose+Tagatose	0.146269	0.00130736
Sorbose	0.14575	0.00130481
Paeoniflorin	0.135854	0.0358969
Unknown_27	0.105944	-0.0489105
Unknown_11	0.0922845	-0.0362506
Serine	0.0896961	-0.0788588
Tyrosine	0.0681141	-0.0436867
4-Aminobutyric acid	0.0642574	0.0339942

Table S5 VIP value of the flavor OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Galactinol	2.04092	0.0622235
Unknown_45 (D-lactitol)	1.93953	0.0459288
Unknown_18 (galactopyranoside)	1.84086	0.0451769
Glyceric acid	1.73417	-0.0360792
Unknown_34 (alpha-1,2-mannobiose)	1.6536	-0.0304048
Mannose	1.62482	-0.019908
Glutamic acid	1.60665	0.0287362
Inositol	1.52697	-0.0230996
Unknown_8	1.52212	-0.0421998
Xylitol	1.50885	-0.0237524
Unknown_32	1.49184	-0.0103228
Unknown_13	1.48757	-0.0399153
Unknown_56	1.47924	-0.035509
Phosphate	1.47291	-0.0188154
Unknown_35	1.46234	-0.0189145
Caffeine	1.45762	0.0462198
Unknown_43	1.45496	0.0422521
N-Methylnicotinate	1.43981	-0.0420181
Unknown_17	1.40802	-0.0161461
Glycerol	1.39186	-0.0296639
Unknown_20	1.35139	-0.0245159
beta-Glutamic acid	1.31453	-0.0530175
Galacturonic acid	1.30877	-0.0226829
Unknown_9	1.29965	0.00982425
Unknown_21	1.297	-0.0224978
Alanine	1.29684	-0.0152251
Unknown_36	1.29435	-0.0139459
Fumaric acid	1.28294	-0.0342205
Lactic acid	1.2513	-0.0358731
Unknown_50	1.24449	-0.0171987
Unknown_12	1.23861	-0.0307332
Unknown_47	1.23328	-0.0156547
Unknown_49	1.23126	-0.029046
Meso erythritol	1.22081	-0.0268233
Unknown_23	1.18859	-0.0280709
Unknown_28	1.18742	-0.0119602
Glycine	1.18149	-0.0269972
Threitol	1.15048	-0.0333678
Sorbitol	1.13604	-0.0186989
Melezitose	1.12397	0.00469613
Unknown_3	1.11053	-0.0303602
Gentiobiose	1.10868	0.0117848
Tryptophan	1.10671	0.0062231
Unknown_29	1.09249	-0.00306185
Ferulic acid	1.08699	-0.0105601
Unknown_7	1.07439	-0.0122652
Xylonic acid	1.06748	-0.0190029

Unknown_39	1.06378	-0.0139389
Malic acid	1.05863	0.0206292
Unknown_40	1.05433	-0.0292917
Unknown_37	1.03665	-0.0142102
Glucarate	1.01642	-0.00898128
Unknown_48	1.0155	-0.0059897
Trehalose	1.00302	0.0241847
Proline	1.00266	-0.00952797
Unknown_5	1.00228	-0.0515465
Glutamine	0.981309	0.0138035
Galactose+Glucose	0.938968	-0.0182217
Glucose_1	0.928611	-0.0177294
Unknown_53	0.911858	-0.0214177
Unknown_46	0.906892	-0.00200691
Unknown_30	0.901787	-0.0141869
Unknown_55	0.89368	-0.00279915
Sucrose	0.887124	0.0252669
Valine	0.879538	-0.0122305
Unknown_54	0.877727	-0.0018193
Glucono-1,5-lactone	0.875647	-0.0209636
Unknown_16 (2,5-dimethylpyrazines)	0.853802	0.0303322
Galactose	0.841862	-0.0143442
Gluconic acid	0.84019	-0.0181833
2-Aminoethanol	0.834301	-0.00811482
Unknown_52	0.819238	0.0148824
Aspartic acid	0.816997	-0.00293282
Unknown_26	0.803879	-0.0204691
Galactitol	0.785438	0.0060623
Lysine	0.781546	-0.00174341
Serine	0.766633	-0.00328731
Raffinose	0.747836	-0.00372227
Unknown_22	0.735952	-0.0223266
Unknown_15 (genistic acid)	0.726819	-0.000526415
Threonine	0.720314	0.00772483
Succinic acid	0.710206	-0.0191605
Shikimic acid	0.699097	0.0144064
Isoleucine	0.677962	-0.0054374
2-Dehydro gluconate	0.636219	0.00192035
Unknown_19	0.610758	-0.0225297
Unknown_27	0.597811	0.0111417
Methyl succinic acid	0.58396	-0.00906418
Panose	0.583803	-0.0183471
4-Aminobutyric acid	0.576641	0.00298211
Nicotinic acid	0.532289	-0.0122276
Phenylalanine	0.526561	-0.00655679
Unknown_38	0.521756	-0.0295631
Citric acid	0.509981	-0.0149633
Glycolic acid	0.494432	-0.00374229
Unknown_44	0.46609	0.00256258
Unknown_2 (apigenin)	0.424058	0.00959612

Paeoniflorin	0.397121	0.023984
Psicose+Tagatose	0.361997	-0.0113375
Sorbose_2	0.361822	-0.0113407
Fructose_2	0.351003	-0.0113393
Unknown_51	0.350349	0.0139632
Unknown_25	0.338981	0.0044065
Chlorogenic acid	0.332833	0.0225501
Unknown_31	0.330002	-0.00340849
Leucine	0.321816	0.00866447
Serotonin	0.290296	0.00986362
Unknown_42	0.275741	-0.0198574
Unknown_41	0.2446	-0.0209175
Unknown_14	0.243116	0.00440298
Unknown_33	0.23168	0.00528063
Asparagine	0.214254	0.00823024
Unknown_1	0.179634	0.00669254
Unknown_24	0.166595	0.0367158
Mannitol	0.163691	0.00544248
Unknown_6	0.152001	-0.025707
Quinic acid	0.133865	-0.0302571
Putrescine	0.102202	0.0274874
Unknown_10	0.0912267	0.0247991
Unknown_4	0.0837917	0.0134994
Pyroglutamic acid	0.0778974	-0.00167591
Unknown_11	0.023237	-0.0455758
Adenosine	0.0146305	0.0330329
Tyrosine	0.00817168	-0.0183516

Table S6 VIP value of the aftertaste OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Galactinol	2.24786	0.0751531
Unknown_40	2.00894	-0.0315824
Unknown_10	2.0056	0.016747
Glyceric acid	1.80912	-0.0416175
Unknown_28	1.64297	-0.00366437
Glutamic acid	1.63607	0.0313053
Mannose	1.6018	-0.0188588
Alanine	1.58853	-0.0317219
Glycine	1.53412	-0.0431276
Unknown_52	1.52071	0.0352618
Xylitol	1.47268	-0.0253267
Unknown_55	1.44773	-0.00577631
Unknown_5	1.44206	-0.0274133
Phosphate	1.42651	-0.0164287
Unknown_26	1.40772	-0.0238185
Unknown_38	1.40681	-0.039063
N-Methylnicotinate	1.38255	-0.0296947
Glycerol	1.37633	-0.030345
Unknown_56	1.33626	-0.0417102
Unknown_29	1.31639	0.0125873
Unknown_44	1.31055	-0.00376306
Unknown_42	1.31017	-0.0241876
Unknown_46	1.30907	-0.00139087
Inositol	1.28646	-0.0149676
Unknown_16 (2,5-dimethylpyrazines)	1.28463	0.0373119
Lactic acid	1.24794	-0.0400686
Unknown_48	1.24515	-0.00585342
Caffeine	1.24356	0.0376429
Unknown_13	1.22758	-0.027875
Glucose	1.21679	-0.0326818
Meso erythritol	1.20472	-0.0317725
Galactose+Glucose	1.19219	-0.0321405
Fumaric acid	1.18617	-0.0349148
Unknown_9	1.18195	0.0162713
Unknown_30	1.17801	-0.0151423
Threitol	1.15804	-0.0333524
Succinic acid	1.15607	-0.0384723
Unknown_4	1.14779	0.0141118
Unknown_35	1.13408	-0.0113106
beta-Glutamic acid	1.13331	-0.0407055
Unknown_33	1.1272	0.0224984
Galacturonic acid	1.11515	-0.0160784
Unknown_54	1.10862	-0.00540113
Unknown_14	1.10247	-0.0104659
Unknown_31	1.10203	-0.0101913
Unknown_43	1.10014	0.043321
Trehalose	1.08816	0.0267517

Ferulic acid	1.0826	-0.00992391
Unknown_11	1.0491	-0.0401313
Unknown_23	1.02207	-0.0255848
Proline	1.02149	-0.0148525
Unknown_21	1.01232	-0.0156105
Sorbitol	1.00688	-0.0141616
Unknown_41	0.9977	-0.0291699
Unknown_19	0.974503	-0.0398712
Malic acid	0.970829	0.0131157
Panose	0.969254	-0.0301542
Glucarate	0.955209	0.00171792
Unknown_8	0.947334	-0.0285273
Galactose	0.938705	-0.0179244
Melezitose	0.933547	0.00198103
Unknown_24	0.903582	0.0444381
Sucrose	0.903274	0.0303213
Valine	0.901738	-0.0133196
Gentiobiose	0.899591	0.018196
Shikimic acid	0.887384	0.0103409
Xylonic acid	0.869806	-0.0150205
Unknown_7	0.866748	-0.0142924
Glutamine	0.863125	0.00394221
Methyl succinic acid	0.857505	-0.0175043
Aspartic acid	0.842673	-0.00536048
Glucono-1,5-lactone	0.823024	-0.0185979
Lysine	0.814589	-0.00375804
Unknown_49	0.799268	-0.0339696
Unknown_22	0.78631	0.00452368
Gluconic acid	0.77454	-0.0153111
Threonine	0.750018	0.00527056
Unknown_51	0.709591	0.0157691
Tryptophan	0.706195	-0.0100323
Unknown_50	0.681021	-0.0171541
Unknown_20	0.659374	-0.0189629
Isoleucine	0.657323	-0.00320926
4-Aminobutyric acid	0.656112	-0.00571977
2-Aminoethanol	0.644586	-0.00167585
Unknown_45 (D-lactitol)	0.629007	0.0527675
Serine	0.598936	-0.0139782
Phenylalanine	0.574792	-0.00247962
Sorbose	0.569394	-0.0193042
Psicose+Tagatose	0.569144	-0.0192858
Unknown_6	0.55789	-0.0125945
Fructose	0.549916	-0.018934
Galactitol	0.528405	-0.00557488
Nicotinic acid	0.51731	-0.00679043
Raffinose	0.510569	-0.0104538
Unknown_47	0.501346	-0.0170419
Unknown_39	0.454245	-0.014127
Unknown_25	0.45066	-0.00641497

Citric acid	0.433372	-0.00468127
Adenosine	0.425014	0.0503042
Paeoniflorin	0.420073	0.0165739
Unknown_32	0.382218	-0.00604929
2-Dehydro gluconate	0.381297	-0.00632348
Asparagine	0.37144	-0.000402587
Leucine	0.369726	0.00723522
Unknown_37	0.366469	-0.0159325
Unknown_15 (genistic acid)	0.359721	-0.00495761
Unknown_53	0.34668	-0.0197207
Unknown_12	0.341831	-0.0290066
Pyroglutamic acid	0.341793	-0.0130488
Quinic acid	0.318903	-0.0337801
Glycolic acid	0.314209	-0.00476338
Tyrosine	0.276432	-0.0295177
Mannitol	0.27347	-0.0136714
Chlorogenic acid	0.213645	0.0163292
Unknown_1	0.211082	0.0177771
Unknown_34 (alpha-1,2-mannobiose)	0.169434	-0.030857
Putrescine	0.169277	0.0273365
Serotonin	0.0911968	0.0032802
Unknown_27	0.0638602	0.0153098
Unknown_3	0.0471274	-0.0207576
Unknown_18 (galactopyranoside)	0.0461935	0.0596914
Unknown_36	0.0138111	-0.00851676
Unknown_2	0.0126972	0.0159341
Unknown_17	0.00696344	-0.00663059

Table S7 VIP value of the acidity OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Galactinol	2.04356	0.0638177
Unknown_18 (galactopyranoside)	1.99276	0.0625755
Alanine	1.82599	-0.0496724
Unknown_45 (D-lactitol)	1.7533	0.0325745
Mannose	1.65912	-0.018979
Unknown_34 (alpha-1,2-mannobiose)	1.61848	-0.0370521
Glyceric acid	1.59172	-0.0318008
Glycine	1.55205	-0.0396623
Glutamic acid	1.54236	0.030455
Unknown_8	1.54104	-0.0283956
Unknown_13	1.52938	-0.0279732
Unknown_43	1.52296	0.0571692
N-Methylnicotinate	1.49696	-0.0320079
Phosphate	1.46329	-0.0129622
Unknown_52	1.44603	0.0404531
beta-Glutamic acid	1.43184	-0.0632119
Malic acid	1.43011	0.0426218
Unknown_9	1.34783	0.0223627
Unknown_49	1.32147	-0.0284284
Inositol	1.31189	-0.0270337
Unknown_23	1.31114	-0.0214437
Unknown_50	1.29387	-0.00216523
Unknown_40	1.28918	-0.0311047
Xylitol	1.27368	-0.0138605
Caffeine	1.26895	0.0566669
Glycerol	1.24043	-0.0242574
Unknown_16 (2,5-dimethylpyrazines)	1.23676	0.0441894
Unknown_47	1.22507	0.00284624
Unknown_28	1.21317	-0.0417725
Valine	1.20924	-0.0262561
Unknown_56	1.20542	-0.0317319
Unknown_3	1.19007	-0.0215503
Unknown_32	1.18811	0.0033836
Glucose	1.18538	-0.038553
Galactose+Glucose	1.17787	-0.0411543
Unknown_7	1.17206	-0.00933531
Succinic acid	1.14961	-0.0303669
Galactose	1.14513	-0.0446704
Unknown_19	1.13028	-0.036187
Unknown_51	1.11245	0.0471853
Lysine	1.10385	-0.0174122
Unknown_39	1.10189	0.00326779
Unknown_37	1.09994	-0.00177567
Unknown_48	1.08639	0.0153553
Unknown_20	1.06848	-0.0145976
Sucrose	1.06477	0.0328192
Threitol	1.06102	-0.041666

Tyrosine	1.0501	-0.0835369
Unknown_26	1.04598	-0.029246
Isoleucine	1.04451	-0.0215375
Glucarate	1.04393	-0.00121005
Unknown_17	1.03247	-0.00981111
Ferulic acid	1.03076	0.000146039
Unknown_35	1.02348	0.00936007
Proline	1.01287	-0.0167741
Methyl succinic acid	1.00575	-0.0236814
2-Aminoethanol	1.00309	-0.0466387
Unknown_46	0.995222	0.0196287
Panose	0.977609	-0.0171251
Threonine	0.977202	-0.0032092
Galacturonic acid	0.974858	-0.0195632
Unknown_21	0.967387	-0.0195194
Unknown_36	0.942419	0.0112878
Fumaric acid	0.940696	-0.040119
Sorbitol	0.937317	-0.0164761
Melezitose	0.936048	0.00553769
Aspartic acid	0.916178	-0.000773557
Lactic acid	0.893187	-0.0362876
Leucine	0.888649	-0.0217387
Unknown_30	0.873899	-0.00710676
Unknown_12	0.871627	-0.0266333
Trehalose	0.850528	-0.0171583
Unknown_5	0.834652	-0.0506543
Unknown_55	0.826861	0.0020052
Unknown_54	0.797808	0.00413054
Meso erythritol	0.776558	-0.0213698
Nicotinic acid	0.763835	-0.022496
Unknown_44	0.758872	0.0174106
Unknown_27	0.755046	0.00698927
Unknown_14	0.745565	-0.0239306
Unknown_29	0.719597	-0.00289149
Shikimic acid	0.70558	0.0465654
Quinic acid	0.665109	-0.0620107
Putrescine	0.662374	0.0612674
Citric acid	0.64245	-0.0128465
Glucono-1,5-lactone	0.634357	-0.0139136
Asparagine	0.621342	-0.0152908
Pyroglutamic acid	0.575265	-0.0280815
Gluconic acid	0.572347	-0.011678
Unknown_15 (genistic acid)	0.564499	0.0210547
Chlorogenic acid	0.553954	0.0413069
Unknown_53	0.548401	-0.0169403
Unknown_2 (apigenin)	0.45906	0.0335409
Mannitol	0.447918	-0.0188742
Gentiobiose	0.438061	0.0404446
2-Dehydro gluconate	0.431866	0.000196585
Sorbose	0.413156	-0.00833259

Psicose+Tagatose	0.412794	-0.00831023
Xylonic acid	0.408847	-0.00546948
Fructose	0.397755	-0.00839173
Tryptophan	0.394635	-0.0248899
Raffinose	0.378468	-0.0257266
4-Aminobutyric acid	0.378065	0.00556288
Glycolic acid	0.373649	0.008014
Unknown_11	0.362295	-0.070973
Adenosine	0.33837	0.025292
Unknown_1	0.323844	0.0283792
Unknown_22	0.321267	0.00326028
Galactitol	0.316804	-0.00791327
Unknown_25	0.30797	-0.0189202
Unknown_38	0.278042	-0.0498923
Glutamine	0.277328	-0.0445758
Unknown_10	0.210914	0.0229249
Serotonin	0.204873	-0.02785
Unknown_42	0.167665	-0.0234977
Unknown_33	0.166596	0.0136398
Unknown_31	0.159281	0.00351644
Paeoniflorin	0.149161	0.0475983
Unknown_6	0.146681	-0.0349014
Unknown_4	0.12365	0.0168614
Unknown_41	0.0967612	-0.0254988
Serine	0.0640353	-0.0643243
Phenylalanine	0.0182443	-0.0372543
Unknown_24	0.00232116	0.0448177

Table S8 VIP value of the body OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Unknown_24	2.35241	0.0865086
Caffeine	2.16211	0.080558
N-Methylnicotinate	2.09751	-0.0269242
Mannitol	2.096	-0.0713848
4-Aminobutyric acid	2.06424	0.071478
Unknown_6	2.03436	-0.0674736
Putrescine	2.01908	0.0780315
Unknown_10	1.98589	0.0634588
Shikimic acid	1.9761	-0.0337704
Unknown_8	1.95975	-0.0200851
Unknown_34 (alpha-1,2-mannobiose)	1.95714	-0.0819646
Unknown_13	1.93098	-0.0203872
Threitol	1.91893	-0.0759112
Unknown_23	1.846	-0.0521005
Unknown_1	1.79145	0.0972157
Unknown_2 (apigenin)	1.70975	0.100632
Unknown_19	1.65704	-0.0337577
Serotonin	1.65225	-0.0621027
Raffinose	1.60326	-0.0529924
Unknown_15 (genistic acid)	1.55272	-0.0203504
Unknown_16 (2,5-dimethylpirazines)	1.53514	0.068128
Galactinol	1.48377	0.051905
Succinic acid	1.47467	-0.0310773
Unknown_3	1.40843	-0.0360296
Unknown_5	1.40467	-0.0257781
Galactose_1	1.40158	-0.0442216
beta-Glutamic acid	1.3636	-0.0334735
Methyl succinic acid	1.29448	-0.0433487
Nicotinic acid	1.16903	-0.0128212
Unknown_41	1.14924	-0.0394699
Lysine	1.12778	0.0315793
Unknown_31	1.12732	-0.0191763
Unknown_45 (D-lactitol)	1.12144	0.0299599
Unknown_38	1.11054	-0.0509965
Adenosine	1.09075	0.0236366
Glutamine	1.08745	-0.0154248
Alanine	0.997678	-0.0454154
Galactitol	0.991838	-0.0269044
Phenylalanine	0.965887	0.0230141
Glutamic acid	0.964014	0.0117845
Unknown_26	0.963237	-0.0370624
Malic acid	0.956779	-0.0385546
Leucine	0.942496	0.021321
Trehalose	0.940914	-0.0140122
Unknown_25	0.914262	-0.0198336
Unknown_52	0.800128	0.0410289
Glycine	0.794131	-0.0110204

Unknown_49	0.789197	-0.0360416
Unknown_43	0.763925	0.0404788
Unknown_28	0.762886	0.00524403
Quinic acid	0.759913	-0.0320302
Unknown_33	0.73148	0.000393072
Pyroglutamic acid	0.729094	-0.037089
Glycolic acid	0.702624	0.0411701
Unknown_18 (galactopyranoside)	0.697777	0.0405498
Isoleucine	0.689994	0.0178112
Unknown_42	0.685496	-0.0447097
Threonine	0.684521	0.00760586
Glucarate	0.652735	-0.00911875
Gluconic acid	0.597785	0.017118
Unknown_9	0.597521	0.0330957
Citric acid	0.549097	0.021504
Inositol	0.542094	0.0129356
Xylitol	0.535026	0.0187238
Glucono-1,5-lactone	0.52599	0.01665
Ferulic acid	0.52541	-0.00128436
Valine	0.513147	0.0108885
Tryptophan	0.512578	-0.0290331
Aspartic acid	0.490292	0.010519
Fructose	0.482135	0.0120041
Psicose+Tagatose	0.468776	0.0124647
Sorbose	0.465398	0.0123699
2-Dehydro gluconate	0.457029	0.0114154
Unknown_46	0.451186	0.0367173
Serine	0.434709	-0.0639416
Proline	0.414223	-0.0108677
Unknown_50	0.405144	0.00370493
Xylonic acid	0.402055	0.0101716
2-Aminoethanol	0.395	0.00074466
Sucrose	0.389837	0.0289419
Glyceric acid	0.388052	0.0159613
Phosphate	0.379416	0.0129307
Unknown_32	0.3585	0.00615683
Unknown_40	0.354318	-0.00885578
Glycerol	0.335245	-0.0136248
Unknown_53	0.327199	0.010696
Melezitose	0.323829	-0.00269356
Unknown_51	0.316169	0.0179675
Unknown_47	0.314774	0.00564774
Panose	0.310036	0.0431478
Unknown_7	0.297223	0.0104981
Paeoniflorin	0.295157	-0.0192797
Unknown_12	0.288846	-0.00584688
Unknown_56	0.28668	-0.00928196
Unknown_21	0.284817	0.00564336
Mannose	0.277883	0.0086647
Asparagine	0.277572	-0.0224594

Unknown_30	0.27601	-0.0178898
Unknown_36	0.272134	0.0186346
Unknown_27	0.263286	-0.0381712
Galacturonic acid	0.262797	0.00438777
Unknown_17	0.254056	0.00522172
Chlorogenic acid	0.24891	0.0353038
Gentiobiose	0.236851	0.00819146
Unknown_14	0.221941	-0.029047
Meso erythritol	0.219639	-0.0109286
Unknown_29	0.184614	0.00680248
Unknown_4	0.158834	0.00781456
Fumaric acid	0.157001	-0.00972862
Lactic acid	0.145895	-0.00690863
Unknown_39	0.142266	0.0166344
Unknown_20	0.136623	0.000363701
Unknown_48	0.123916	0.024765
Unknown_35	0.11091	0.0268144
Sorbitol	0.0709803	-0.00595473
Glucose	0.0664688	-0.0263481
Unknown_54	0.0497265	0.0160299
Unknown_11	0.0475801	0.0218384
Unknown_55	0.0374094	0.0171476
Galactose+Glucose	0.0277096	-0.0299485
Unknown_22	0.0276532	0.0356996
Unknown_37	0.00990526	0.0172051
Tyrosine	0.00347777	-0.0141243
Unknown_44	0.00214146	-0.0210719

Table S9 VIP value of the balance OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Malic acid	2.24261	-0.0892732
Unknown_28	2.17892	0.0850582
Paeoniflorin	2.08965	-0.118254
Unknown_1	2.08936	0.0705106
Tyrosine	2.04892	0.101207
Unknown_2 (apigenin)	1.96446	0.0626823
Quinic acid	1.93655	0.0783725
Unknown_11	1.83966	0.130544
Unknown_51	1.78684	-0.0496194
Citric acid	1.73478	0.0533628
Unknown_26	1.62308	0.0490979
Panose	1.62156	0.0389203
Shikimic acid	1.61817	-0.114574
Unknown_44	1.61772	-0.0603483
Glycolic acid	1.57222	0.0392658
Glucose	1.53546	0.0157057
Galactose+Glucose	1.52711	0.0171316
Glyceric acid	1.49682	0.0378532
Phenylalanine	1.45687	0.0924284
Glucarate	1.40539	0.0313838
Unknown_15 (genistic acid)	1.39442	-0.0809861
Trehalose	1.37719	0.0715258
Unknown_5	1.35561	0.105291
2-Dehydro gluconate	1.26855	0.023938
Unknown_41	1.24716	0.0406616
Fructose	1.2113	0.00729953
Psicose+Tagatose	1.20933	0.00707839
Sorbose	1.20845	0.00703036
Unknown_8	1.18131	0.0458573
Leucine	1.17987	0.0419583
Isoleucine	1.15745	0.0374353
2-Aminoethanol	1.12977	0.0788919
Unknown_23	1.12121	0.0139918
Unknown_42	1.11145	0.0270987
Unknown_13	1.11071	0.0405255
Unknown_55	1.10262	0.0458907
N-Methylnicotinate	1.08538	0.0443982
Valine	1.04653	0.028551
Lysine	1.03283	0.024391
Unknown_54	1.02454	0.0404598
Unknown_22	1.00503	0.0598081
Glutamine	0.99886	0.055982
Galactinol	0.998292	-0.0183822
beta-Glutamic acid	0.984748	0.0605802
Glycine	0.973818	0.0218389
Unknown_4	0.972611	-0.0265517
Galactose	0.953753	0.0525745

Unknown_52	0.95329	0.0120126
Lactic acid	0.947351	0.0463692
Unknown_43	0.93824	-0.045357
Unknown_40	0.929138	0.0193822
Unknown_29	0.917323	0.0408152
Mannose	0.915867	0.00533629
Gluconic acid	0.909718	0.0166235
Glucono-1,5-lactone	0.887735	0.0154068
Unknown_14	0.869082	0.00949609
Unknown_19	0.85804	0.0223123
Chlorogenic acid	0.855927	-0.0484979
Gentiobiose	0.844664	-0.060142
Asparagine	0.802429	0.00682377
Melezitose	0.798056	0.0316504
Tryptophan	0.796301	0.0253717
Phosphate	0.779907	0.00292171
Nicotinic acid	0.731387	0.0357031
Raffinose	0.721867	0.0438808
Alanine	0.695818	0.00768726
Galactitol	0.682358	-0.025172
4-Aminobutyric acid	0.681506	0.0176228
Xylitol	0.658747	0.0104802
Fumaric acid	0.656103	0.0406943
Succinic acid	0.641513	0.00742713
Methyl succinic acid	0.639933	-0.0110946
Unknown_46	0.623791	-0.0177453
Unknown_20	0.61371	0.00311396
Proline	0.609088	0.00458192
Serotonin	0.600323	0.0321709
Inositol	0.590342	0.0292259
Serine	0.569365	0.0298073
Threonine	0.568263	-0.0046728
Putrescine	0.567614	-0.0305537
Unknown_16 (2,5-dimethylpyrazines)	0.562975	0.0270092
Unknown_12	0.543341	0.0270998
Unknown_18 (galactopyranoside)	0.537295	-0.0008319
Adenosine	0.530007	-0.0082292
Threitol	0.529783	0.0120977
Unknown_17	0.528514	0.00911409
Caffeine	0.523963	-0.0404985
Unknown_50	0.50965	-0.0089288
Unknown_37	0.494407	-0.0005084
Unknown_56	0.480493	0.0101037
Unknown_10	0.472074	0.0142211
Unknown_48	0.467737	-0.0210891
Unknown_21	0.461067	0.0130495
Pyroglutamic acid	0.445411	-0.0152487
Unknown_7	0.431364	-0.0073484
Unknown_47	0.424051	-0.0152138
Unknown_27	0.419889	0.00395185

Galacturonic acid	0.417045	0.0111743
Ferulic acid	0.416686	-0.0418657
Unknown_39	0.38889	-0.00732
Unknown_32	0.381604	0.00424708
Unknown_31	0.351704	-0.0009784
Glycerol	0.336715	-0.012039
Unknown_49	0.333728	-0.0015042
Glutamic acid	0.324472	-0.013514
Unknown_34 (alpha-1,2-mannobiose)	0.311546	-0.0133963
Unknown_33	0.309784	0.0121774
Mannitol	0.297379	-0.027528
Aspartic acid	0.270703	-0.0143361
Meso erythritol	0.26039	0.0133108
Unknown_6	0.24302	0.0525713
Xylonic acid	0.220727	0.0189269
Unknown_25	0.217746	-0.0034393
Unknown_38	0.190689	0.017461
Unknown_35	0.186035	0.00214243
Unknown_30	0.181882	-0.016182
Unknown_24	0.177299	-0.0101475
Unknown_53	0.16475	0.0108674
Sucrose	0.164266	0.0143035
Unknown_9	0.153546	0.00223507
Unknown_3	0.13572	-0.0019843
Sorbitol	0.109448	-0.0087744
Unknown_36	0.088325	-0.0108043
Unknown_45 (D-lactitol)	0.026063	0.0183525

Table S10 VIP value of the balance OPLS model in 10 different green coffee bean samples

Metabolite	VIP score	Coefficient
Galactinol	2.17058	0.0659363
Glycine	1.96224	-0.0450476
beta-Glutamic acid	1.94423	-0.0735734
Alanine	1.93386	-0.0542195
Unknown_18 (galactopyranoside)	1.90879	0.062691
Threitol	1.79381	-0.053207
Unknown_45 (D-lactitol)	1.78558	0.0321799
Glutamic acid	1.72027	0.0317971
Unknown_13	1.65375	-0.0307806
Unknown_8	1.64276	-0.0306899
Methyl succinic acid	1.63973	-0.0317133
N-Methylnicotinate	1.63354	-0.0350857
Unknown_52	1.62831	0.0414041
Glycerol	1.62772	-0.0271757
Galactose	1.61938	-0.0551652
Succinic acid	1.61745	-0.0365893
Unknown_56	1.60674	-0.0360402
Unknown_19	1.5969	-0.0431965
Quinic acid	1.49664	-0.0761401
Unknown_34 (alpha-1,2-mannobiose)	1.45281	-0.0359317
Putrescine	1.45248	0.0762276
Ferulic acid	1.42365	-0.000680696
Glucose	1.42025	-0.0407646
Galactose+Glucose	1.41018	-0.0435663
Unknown_12	1.39663	-0.0332956
Tyrosine	1.36084	-0.0949496
Sorbitol	1.35794	-0.0206751
Caffeine	1.35512	0.0614347
Fumaric acid	1.35251	-0.0465017
Unknown_20	1.35145	-0.0164378
Panose	1.27653	-0.0189391
Unknown_9	1.26766	0.0242393
Lactic acid	1.26237	-0.0418341
Galacturonic acid	1.26199	-0.0223314
Unknown_21	1.26013	-0.0223387
Glyceric acid	1.24653	-0.0253129
Unknown_17	1.17651	-0.00995241
Unknown_28	1.15478	-0.0432219
Mannose	1.14513	-0.0102858
Meso erythritol	1.07737	-0.0252271
Unknown_23	1.07118	-0.0177941
Glucono-1,5-lactone	1.05896	-0.0165039
Inositol	1.05003	-0.024232
2-Aminoethanol	1.03871	-0.0526371
Unknown_53	1.0175	-0.0222284
Unknown_43	0.9895	0.0538438
Mannitol	0.98122	-0.0284336

Gluconic acid	0.978134	-0.0141772
Nicotinic acid	0.956289	-0.023455
Unknown_51	0.935491	0.0460788
Unknown_32	0.934353	0.00882659
Malic acid	0.927659	0.0366986
Unknown_5	0.926565	-0.0568949
Unknown_16 (2,5-dimethylpyrazines)	0.921767	0.0438691
Pyroglutamic acid	0.865008	-0.0301272
Shikimic acid	0.833994	0.0507674
Serotonin	0.828392	-0.0406266
Phosphate	0.810458	-0.00254322
Unknown_15 (genistic acid)	0.808399	0.0210294
Unknown_49	0.806968	-0.0244319
Unknown_29	0.783929	-0.00345783
Unknown_3	0.779382	-0.0171336
Unknown_22	0.761241	-0.00116693
Sorbose	0.747004	-0.00885117
Psicose+Tagatose	0.74593	-0.00882158
Unknown_26	0.739955	-0.0282273
Fructose	0.718914	-0.00877986
Unknown_44	0.71803	0.0149283
Unknown_27	0.678129	0.00544142
Melezitose	0.661257	0.00203235
Xylitol	0.649189	-0.00388648
Trehalose	0.645472	-0.0250682
Unknown_40	0.607102	-0.0220901
Glutamine	0.598771	-0.0478488
Unknown_50	0.592458	0.00967058
Glucarate	0.588153	0.00626053
Unknown_35	0.537445	0.0194694
Unknown_47	0.508891	0.0154127
Unknown_10	0.508841	0.0281554
Xylonic acid	0.497572	-0.00581579
Phenylalanine	0.482611	-0.0371952
Valine	0.482197	-0.0176206
Unknown_11	0.481272	-0.0766793
Sucrose	0.48041	0.0276707
Leucine	0.398645	-0.0186635
Lysine	0.393937	-0.00799338
Unknown_7	0.388094	0.0026395
Unknown_55	0.374526	-0.00288887
Unknown_2 (apigenin)	0.37229	0.038783
Unknown_36	0.367163	0.0223493
Unknown_33	0.346123	0.00597086
Unknown_39	0.345642	0.0157928
Unknown_37	0.333836	0.0108766
Isoleucine	0.331021	-0.0137304
Unknown_48	0.328818	0.0295357
2-Dehydro gluconate	0.319489	0.000913277
Unknown_54	0.316456	-0.000871471

Unknown_31	0.303203	0.00136702
Adenosine	0.276576	0.0247422
Unknown_14	0.274989	-0.0197946
Chlorogenic acid	0.270072	0.0448608
Proline	0.268867	-0.00852834
Galactitol	0.264902	-0.0117679
Unknown_24	0.256833	0.0524357
4-Aminobutyric acid	0.253253	0.0101699
Unknown_25	0.235594	-0.0204382
Unknown_46	0.22878	0.0344638
Unknown_41	0.228415	-0.0303808
Threonine	0.226095	0.0060224
Unknown_4	0.223955	0.0192985
Serine	0.21969	-0.0732589
Raffinose	0.188237	-0.0367523
Glycolic acid	0.187913	0.00954209
Unknown_1	0.164622	0.0322203
Unknown_38	0.135754	-0.0596193
Tryptophan	0.125563	-0.0312919
Gentiobiose	0.0978442	0.0498064
Paeoniflorin	0.0926718	0.048624
Unknown_30	0.0785738	0.00410014
Asparagine	0.0752738	-0.00931778
Aspartic acid	0.0634613	0.0114618
Unknown_42	0.0482748	-0.0223428
Unknown_6	0.0306422	-0.0427467
Citric acid	0.0178777	-0.00453581

Table S11. List of detected metabolites

No	Metabolite name	Class	RT[a] (min)	RI[b]	Quant. *m/z*	MSI Level[c]
1	Alanine	Amino Acid	4.99	1108	116	1
2	Asparagine	Amino Acid	10.29	1685	116	1
3	Aspartic acid	Amino Acid	9.09	1533	232	1
4	Glutamic acid	Amino Acid	9.88	1631	246	1
5	Glycine	Amino Acid	7.16	1317	174	1
6	Isoleucine	Amino Acid	7.03	1302	158	1
7	Leucine	Amino Acid	6.81	1280	158	1
8	Lysine	Amino Acid	12.11	1940	174	1
9	Phenylalanine	Amino Acid	9.96	1641	218	1
10	Proline	Amino Acid	7.06	1306	142	1
11	Pyroglutamic acid	Amino Acid	9.09	1533	156	1
12	Serine	Amino Acid	7.68	1372	204	1
13	Tryptophan	Amino Acid	14.03	2248	202	1
14	Tyrosine	Amino Acid	12.23	1958	218	1
15	Valine	Amino Acid	6.24	1224	144	1
16	Chlorogenic acid	Organic Acid	18.59	3173	345	1
17	Fumaric acid	Organic Acid	7.47	1350	245	1
18	Glucarate	Organic Acid	12.88	2059	333	1
19	Gluconic acid	Organic Acid	12.78	2043	333	1
20	Glyceric acid	Organic Acid	7.4	1342	147	1
21	Glycolic acid	Organic Acid	4.67	1079	147	1
22	Citric acid	Organic Acid	11.44	1842	273	1
23	Lactic acid	Organic Acid	4.51	1065	147	1
24	Malic acid	Organic Acid	8.81	1499	147	1
25	Quinic acid	Organic Acid	11.79	1892	345	1
26	Succinic acid	Organic Acid	7.17	1317	147	1
27	Fructose	Sugar	11.95	1916	103	1
28	Galactose	Sugar	12.03	1928	205	1
29	Galactose+Glucose	Sugar	12.2	1953	205	1
30	Glucose	Sugar	12.07	1934	205	1
31	Maltose	Sugar	16.99	2814	204	1
32	Melezitose	Sugar	20.67	3585	361	1
33	Raffinose	Sugar	20.17	3502	361	1
34	Sorbose	Sugar	11.88	1906	103	1
35	Sucrose	Sugar	16.48	2707	361	1
36	Galactinol	Sugar Alcohol	18.17	3076	204	1
37	Inositol	Sugar Alcohol	13.34	2132	217	1
38	Mannitol	Sugar Alcohol	12.3	1969	205	1
39	Meso-erythritol	Sugar Alcohol	9.03	1526	217	1
40	Sorbitol	Sugar Alcohol	12.35	1976	205	1
41	Threitol	Sugar Alcohol	8.97	1518	147	1
42	Xylitol	Sugar Alcohol	10.67	1736	217	1
43	2-Aminoethanol	Other	6.76	1276	174	1

44	4-Aminobutyric acid	Other	9.16	1542	174	1
45	Caffeine	Other	11.58	1862	194	1
46	Glycerol	Other	6.85	1284	147	1
47	N-Methylnicotinate	Other	8.94	1514	210	1
48	Phosphate	Other	6.83	1283	299	1
49	Putrescine	Other	10.82	1756	174	1
50	Serotonin	Other	15.37	2490	174	1
51	Unknown 1	Unknown	4.20	1037	117	4
52	Unknown 2	Organic Acid	4.31	1047	117	3
53	Unknown 3	Unknown	5.83	1184	147	4
54	Unknown 4	Unknown	6.65	1264	98	4
55	Unknown 5	Unknown	7.71	1375	156	4
56	Unknown 6	Unknown	7.99	1404	147	4
57	Unknown 7	Unknown	8.21	1430	160	4
58	Unknown 8	Unknown	9.13	1537	174	4
59	Unknown 9	Unknown	9.28	1556	120	4
60	Unknown 10	Organic Acid	9.52	1585	129	3
61	Unknown 11	Unknown	9.59	1593	210	4
62	Unknown 12	Unknown	11.01	1781	217	4
63	Unknown 13	Unknown	11.07	1789	217	4
64	Unknown 14	Unknown	12.40	1983	147	4
65	Unknown 15	Organic Acid	12.76	2039	217	3
66	Unknown 16	Organic Acid	12.90	2061	204	3
67	Unknown 17	Organic Acid	13.06	2087	333	3
68	Unknown 18	Unknown	13.85	2216	204	4
69	Unknown 19	Unknown	13.93	2231	204	4
70	Unknown 20	Organic Acid	17.96	3026	345	3
71	Unknown 21	Sugar	18.39	3126	204	3
72	Unknown 22	Organic Acid	18.49	3148	345	3
73	Unknown 23	Sugar	18.71	3200	204	3
74	Unknown 24	Unknown	18.72	3204	249	4
75	Unknown 25	Unknown	18.80	3222	307	4
76	Unknown 26	Organic Acid	18.83	3229	249	3
77	Unknown 27	Organic Acid	18.90	3244	307	3
78	Unknown 28	Organic Acid	19.17	3305	324	3
79	Unknown 29	Unknown	22.04	3776	204	4

There are 79 metabolites detected in all samples

a Retention time in minute(s)

b Retention indices (RI) are calculated using a standard alkane mixture (C9–C40).

c Mass spectra of metabolite peaks that are compared only with the in-house library are considered Metabolic Standards Initiative (MSI) level 1 identification. Several unknown compounds are considered MSI level 3 based on similarity to known compounds of a chemical class in library and MSI level 4 if there are no similarities with any chemical class compound in library.

Table S12. List of metabolites sorted based on VIP value

Metabolite	VIP	Coefficient
Inositol	2.3028	0.103256
Tyrosine	2.09735	-0.0706747
Serine	2.03512	0.114529
Serotonin	2.01535	-0.0661732
Tryptophan	1.84303	-0.0558109
Unknown 2	1.68935	-0.0667527
Unknown 26	1.68592	-0.038523
Leucine	1.67076	-0.0452749
Unknown 1	1.65779	-0.055465
Valine	1.62957	-0.0437052
Lysine	1.6215	-0.0569174
Unknown 27	1.50931	-0.0322694
Isoleucine	1.5079	-0.0427985
Unknown 24	1.44793	-0.0312407
Unknown 25	1.43718	-0.0284523
Unknown 16	1.41569	0.0794785
Melezitose	1.35889	-0.0711967
Glutamic acid	1.24873	0.0256198
Chlorogenic acid	1.20923	0.0477504
2-Aminoethanol	1.17631	0.0308364
Galactose+Glucose	1.12433	0.0426751
Glucose	1.11729	0.0433287
Unknown 8	1.10155	-0.0151577
Maltose	1.09117	-0.0237914
Citric acid	1.0666	-0.0436519
Asparagine	1.04405	0.00630859
Sorbose	1.02462	0.0397916
Fructose	1.01608	0.0394254
4-Aminobutyric acid	1.01455	0.00426298
Unknown 15	0.977759	0.0889678
Succinic acid	0.961636	-0.0493505
Unknown 19	0.94918	-0.0291571
Unknown 3	0.934071	-0.010462
Unknown 13	0.909244	-0.0284779
Quinic acid	0.880498	-0.0564018
Galactose	0.822901	0.0350426
Unknown 12	0.804255	0.0461621
Gluconic acid	0.723257	-0.00198133
Sorbitol	0.719986	-0.0183619
Glycine	0.708984	-0.0248831
Proline	0.682042	-0.0292702
Glucarate	0.670633	0.0514676

Unknown 4	0.649054	0.000856223
Unknown 22	0.633566	0.0349796
Caffeine	0.616295	-0.045223
Glyceric acid	0.556716	-0.0137275
Unknown 20	0.545224	0.0376733
Aspartic acid	0.533978	-0.00321751
Unknown 17	0.512243	0.0487359
Unknown 21	0.500783	0.0206962
Mannitol	0.481804	0.032392
Phenylalanine	0.458176	0.0847116
Unknown 11	0.457388	-0.0251981
Galactinol	0.379535	0.0191434
Glycerol	0.376731	0.00940554
Unknown 7	0.361338	-0.032803
Xylitol	0.35312	0.0372025
N-Methylnicotinate	0.325726	-0.0193914
Fumaric acid	0.315467	0.00892215
Unknown 23	0.313901	-0.010591
Unknown 6	0.304348	0.0894609
Unknown 5	0.28901	-0.00257925
Unknown 18	0.279609	0.048798
Pyroglutamic acid	0.264187	-0.0191659
Threitol	0.260674	-0.00990163
Unknown 28	0.237126	-0.0254546
Sucrose	0.235525	-0.0087589
Unknown 9	0.228038	0.0346508
Unknown 14	0.219284	-0.0325646
Unknown 29	0.198357	-0.00195892
Alanine	0.183306	-0.0180161
Unknown 10	0.163949	0.00321003
Putrescine	0.16286	0.0420075
Malic acid	0.159746	0.0426592
Glycolic acid	0.157956	0.0249943
Phosphate	0.108682	0.02381
Raffinose	0.089464	0.0148455
Lactic acid	0.086177	0.0539822
Meso-erythritol	0.008641	0.00451688

Table S13. List of metabolites based on principal component loading coefficient in **Fig. 3.3.2-1**

PC1		PC2	
Metabolite	Coefficient	Metabolite	Coefficient
Unknown 23	-0.157413	Unknown 22	-0.190806
Galactinol	-0.138069	Unknown 24	-0.182421
Unknown 21	-0.127597	Unknown 26	-0.175262
Sucrose	-0.126976	Unknown 6	-0.168237
Glutamic acid	-0.118066	Mannitol	-0.163856
Melezitose	-0.103976	Unknown 19	-0.157583
Unknown 12	-0.0986498	4-Aminobutyric acid	-0.124526
Unknown 3	-0.0949585	Tryptophan	-0.124283
Unknown 14	-0.0779539	Unknown 18	-0.111737
Unknown 10	-0.0759288	Glycerol	-0.104957
Maltose	-0.0707973	Maltose	-0.0990554
Aspartic acid	-0.0409498	Sucrose	-0.0971915
Raffinose	-0.0274839	Gluconic acid	-0.0943909
Chlorogenic acid	-0.0268388	Unknown 8	-0.0872751
Unknown 7	-0.0261441	Serotonin	-0.0838053
Unknown 19	-0.0195807	Unknown 12	-0.0696327
2-Aminoethanol	-0.0133424	Caffeine	-0.0667114
Malic acid	-0.00118704	Lysine	-0.058809
Alanine	0.0111154	Unknown 25	-0.0581962
Unknown 11	0.0143571	Sorbitol	-0.0563098
Phenylalanine	0.0157487	Unknown 1	-0.0546393
Putrescine	0.016039	Unknown 27	-0.0477905
Unknown 13	0.019041	Unknown 9	-0.0463763
Unknown 18	0.0238002	Unknown 13	-0.0395707
N-Methylnicotinate	0.0255227	Putrescine	-0.0378797
Citric acid	0.0281519	Unknown 29	-0.0274991
Unknown 5	0.0409303	Unknown 21	-0.0261299
Serotonin	0.0447481	Glycolic acid	-0.0219268
Lactic acid	0.0565377	Unknown 16	-0.0177384
Unknown 9	0.0573991	Unknown 2	-0.0122835
Proline	0.058512	Lactic acid	-0.00947073
Quinic acid	0.0655481	Glucose	-0.00876303
Asparagine	0.0660153	Melezitose	-0.00761581
Serine	0.0689109	Galactose+Glucose	-0.00241389
Unknown 4	0.0744566	Glycine	0.00072424
Unknown 22	0.0787929	Sorbose	0.00451078
Tryptophan	0.0794794	Fructose	0.00592305
Isoleucine	0.0870081	Xylitol	0.0124414
Pyroglutamic acid	0.0905238	Unknown 23	0.0199557
Unknown 20	0.0914978	Leucine	0.0236497
Unknown 28	0.0924431	Threitol	0.0271185
Unknown 24	0.0995495	Succinic acid	0.0327544
Unknown 26	0.101852	Glyceric acid	0.0335194

Inositol	0.10552	Chlorogenic acid	0.0395174
Unknown 17	0.110315	Raffinose	0.0495871
Unknown 6	0.111441	Glucarate	0.0499654
Tyrosine	0.114394	Unknown 15	0.0519923
Valine	0.115524	Unknown 28	0.0592104
Glycerol	0.115936	Tyrosine	0.0609459
Mannitol	0.116561	Phosphate	0.0611056
4-Aminobutyric acid	0.116709	Galactose	0.0673
Caffeine	0.122331	2-Aminoethanol	0.0688598
Unknown 8	0.122451	Fumaric acid	0.0734826
Meso-erythritol	0.125057	Unknown 14	0.0784141
Leucine	0.129772	Unknown 3	0.0784574
Gluconic acid	0.136348	Galactinol	0.0830139
Xylitol	0.142516	Meso-erythritol	0.0913654
Unknown 25	0.143848	Isoleucine	0.0949719
Unknown 29	0.147506	Valine	0.100944
Unknown 27	0.151629	Phenylalanine	0.11124
Phosphate	0.151692	Malic acid	0.119859
Sorbitol	0.154262	Citric acid	0.138277
Fumaric acid	0.154637	Unknown 20	0.141326
Unknown 1	0.156116	Glutamic acid	0.149783
Galactose	0.156268	Quinic acid	0.158817
Lysine	0.156426	Unknown 10	0.158845
Unknown 15	0.156673	Unknown 17	0.167597
Glucarate	0.157974	N-Methylnicotinate	0.168619
Unknown 16	0.160961	Inositol	0.169999
Glycolic acid	0.162009	Unknown 11	0.171301
Threitol	0.162656	Unknown 7	0.17312
Galactose+Glucose	0.162882	Pyroglutamic acid	0.17586
Succinic acid	0.163326	Serine	0.194733
Glucose	0.163326	Unknown 4	0.197571
Glyceric acid	0.164	Asparagine	0.197656
Sorbose	0.164303	Aspartic acid	0.201754
Fructose	0.164375	Proline	0.202795
Glycine	0.165781	Alanine	0.212779
Unknown 2	0.166752	Unknown 5	0.216305

Table S14. List of metabolites based on principal component loading coefficient in **Fig. 3.3.3-1**

PC1		PC2	
Metabolites	Coefficient	Metabolites	Coefficient
Unknown 25	-0.206937	Glycine	-0.215552
Unknown 27	-0.197776	Tryptophan	-0.195751
Isoleucine	-0.188816	4-Aminobutyric acid	-0.191211
Valine	-0.18186	Mannitol	-0.17931
Unknown 4	-0.174	Tyrosine	-0.176141
Unknown 26	-0.171349	Glyceric acid	-0.173074
Unknown 19	-0.165823	Meso-erythritol	-0.170757
Unknown 18	-0.158272	Fumaric acid	-0.158535
Unknown 9	-0.15771	Unknown 2	-0.158503
Sucrose	-0.154883	Unknown 26	-0.157218
Tyrosine	-0.151285	Xylitol	-0.150272
Unknown 3	-0.149951	Unknown 24	-0.145052
Unknown 20	-0.149719	Unknown 10	-0.142565
Unknown 24	-0.145538	Quinic acid	-0.140934
Phenylalanine	-0.142359	Lysine	-0.13955
Serotonin	-0.142265	Unknown 1	-0.135088
Unknown 1	-0.140863	Serotonin	-0.122838
Maltose	-0.139227	Leucine	-0.12001
Malic acid	-0.136969	Maltose	-0.119349
Unknown 6	-0.13452	Glycerol	-0.118149
Proline	-0.127996	Unknown 27	-0.098947
Citric acid	-0.126744	Unknown 8	-0.0892675
Leucine	-0.123823	Alanine	-0.0852867
Unknown 13	-0.119069	Unknown 13	-0.0826655
Unknown 17	-0.117801	Unknown 25	-0.0800212
Unknown 23	-0.116456	Valine	-0.0735252
Mannitol	-0.115628	Unknown 19	-0.0693872
Unknown 29	-0.111216	Glucose	-0.0590888
Unknown 15	-0.103468	Isoleucine	-0.0589142
Unknown 21	-0.101244	Melezitose	-0.0495608
Unknown 2	-0.0986693	Sorbose	-0.041822
Lysine	-0.0952696	Caffeine	-0.0414002
Melezitose	-0.080149	Fructose	-0.0389173
Unknown 8	-0.075608	Unknown 9	-0.0368645
Galactinol	-0.0731536	Unknown 4	-0.0336594
Raffinose	-0.0701564	Gluconic acid	-0.0300988
Unknown 12	-0.0598063	Unknown 3	-0.0192544
4-Aminobutyric acid	-0.0523923	Galactose+Glucose	-0.0189933
Tryptophan	-0.048468	Phosphate	-0.0162782
Glycolic acid	-0.0471189	Unknown 29	-0.0149274
Unknown 5	-0.0446862	Unknown 16	-0.010079
Threitol	-0.0385308	Unknown 14	-0.00319174
Unknown 7	-0.038129	Sorbitol	0.00511072

N-Methylnicotinate	-0.0348933	Citric acid	0.0128189
Unknown 28	-0.0325176	Galactose	0.0144476
Aspartic acid	-0.0309778	Unknown 12	0.0167334
Chlorogenic acid	-0.0257154	Unknown 20	0.0210998
Unknown 11	-0.0255209	2-Aminoethanol	0.0219276
Pyroglutamic acid	-0.0248785	Unknown 22	0.0347787
Lactic acid	-0.02029	Unknown 6	0.0378724
Glutamic acid	-0.0109485	Unknown 18	0.0423178
Glucarate	-0.00800366	Unknown 21	0.0461024
Putrescine	-0.0063161	Glycolic acid	0.0467216
Serine	0.0109511	Phenylalanine	0.0497467
Phosphate	0.0214054	Putrescine	0.0580133
Quinic acid	0.0240014	Lactic acid	0.0586803
Unknown 22	0.0299799	Proline	0.0604241
Caffeine	0.0315169	Succinic acid	0.0770036
Succinic acid	0.0320562	Glucarate	0.0840909
Asparagine	0.0444262	Sucrose	0.085185
Unknown 14	0.0608345	Unknown 5	0.0937916
Glyceric acid	0.073846	Threitol	0.0949723
Inositol	0.0779691	Unknown 15	0.096267
Galactose	0.0826678	Malic acid	0.100078
Glycine	0.0832642	Unknown 28	0.101036
Gluconic acid	0.0929123	N-Methylnicotinate	0.112334
Unknown 16	0.105723	Raffinose	0.115851
Xylitol	0.108438	Inositol	0.117014
2-Aminoethanol	0.115875	Unknown 11	0.121991
Alanine	0.116801	Pyroglutamic acid	0.123746
Sorbitol	0.119583	Unknown 23	0.141676
Meso-erythritol	0.12513	Unknown 17	0.148282
Fumaric acid	0.134731	Asparagine	0.162908
Unknown 10	0.136864	Serine	0.166775
Galactose+Glucose	0.144199	Galactinol	0.167378
Fructose	0.148559	Chlorogenic acid	0.17863
Sorbose	0.150061	Unknown 7	0.182492
Glycerol	0.164488	Aspartic acid	0.195228
Glucose	0.175569	Glutamic acid	0.214525

Table S15. List of metabolites based on principal component loading coefficient in **Fig. 3.3.4-1**

PC1		PC2	
Metabolite	Coefficient	Metabolite	Coefficient
Inositol	-0.184725	Gluconic acid	-0.177504
Unknown 24	-0.183424	Sorbitol	-0.167979
Unknown 26	-0.181132	Glyceric acid	-0.165236
Unknown 15	-0.178045	Mannitol	-0.15202
Unknown 18	-0.174319	Unknown 4	-0.14934
2-Aminoethanol	-0.171294	Unknown 9	-0.148259
Unknown 19	-0.170902	Glucarate	-0.131241
Phenylalanine	-0.170479	Unknown 14	-0.130024
Unknown 25	-0.163935	Unknown 1	-0.127981
Unknown 22	-0.163046	Unknown 2	-0.112411
Phosphate	-0.160091	Fumaric acid	-0.108081
Tyrosine	-0.154681	Maltose	-0.100837
Unknown 5	-0.149204	Unknown 6	-0.100579
Unknown 29	-0.144283	Unknown 13	-0.0860048
Unknown 4	-0.144127	Unknown 16	-0.0856158
Maltose	-0.138485	Unknown 27	-0.0777031
Unknown 27	-0.137696	Xylitol	-0.0685478
Unknown 1	-0.13632	Phenylalanine	-0.0496171
Unknown 6	-0.1342	Inositol	-0.049561
Unknown 10	-0.133638	Unknown 26	-0.0492378
Isoleucine	-0.130592	Putrescine	-0.0486031
Unknown 9	-0.130483	Glycolic acid	-0.0465941
Unknown 13	-0.13009	Raffinose	-0.0389647
Sorbitol	-0.129498	Unknown 10	-0.0387339
Raffinose	-0.128468	Unknown 29	-0.0302569
Lysine	-0.125366	2-Aminoethanol	-0.0295485
Fumaric acid	-0.123533	Unknown 25	-0.027306
Mannitol	-0.12246	Unknown 12	-0.0213942
Valine	-0.121972	Fructose	-0.0140798
Gluconic acid	-0.121465	Unknown 24	-0.0110695
Malic acid	-0.119355	Unknown 19	-0.00903257
Unknown 2	-0.1111	4-Aminobutyric acid	-0.00687254
Unknown 3	-0.108024	Sorbose	-0.00555643
4-Aminobutyric acid	-0.102333	Glucose	-0.00422528
Chlorogenic acid	-0.101745	Phosphate	0.000741248
Unknown 23	-0.0913739	Glycerol	0.00561983
Unknown 17	-0.0896107	Unknown 7	0.00720578
Galactinol	-0.0864046	Quinic acid	0.00865989
Proline	-0.0838761	Galactose+Glucose	0.00930206
Unknown 21	-0.0830587	Unknown 20	0.0101063
Leucine	-0.0805162	Galactose	0.0101633
Threitol	-0.0774493	Unknown 5	0.0158073
Serine	-0.0755248	Glycine	0.0161288

Serotonin	-0.0667158	Unknown 21	0.0178957
Asparagine	-0.0585475	Unknown 17	0.0266628
Quinic acid	-0.0537206	N-Methylnicotinate	0.0297065
Unknown 20	-0.0487928	Malic acid	0.0405064
Unknown 14	-0.0383217	Unknown 22	0.0495524
Citric acid	-0.038027	Unknown 8	0.0501332
Unknown 16	-0.0376189	Unknown 11	0.0526781
Sucrose	-0.0374348	Melezitose	0.0564595
Unknown 28	-0.0369217	Unknown 18	0.0622567
Glutamic acid	-0.02767	Lactic acid	0.0721338
N-Methylnicotinate	-0.0182897	Unknown 15	0.0741901
Pyroglutamic acid	-0.0123869	Citric acid	0.077202
Glucarate	-0.00210226	Unknown 28	0.0820311
Caffeine	-0.000818966	Threitol	0.104607
Meso-erythritol	0.00445047	Tryptophan	0.121121
Melezitose	0.00693617	Tyrosine	0.121464
Unknown 11	0.0136704	Sucrose	0.121712
Aspartic acid	0.0158733	Chlorogenic acid	0.129522
Putrescine	0.017162	Succinic acid	0.13038
Unknown 12	0.0229653	Asparagine	0.145775
Unknown 8	0.0265826	Meso-erythritol	0.146448
Lactic acid	0.0313606	Unknown 3	0.153649
Glyceric acid	0.0317348	Unknown 23	0.16468
Galactose	0.0366073	Leucine	0.16515
Alanine	0.0486894	Isoleucine	0.165532
Unknown 7	0.0656533	Lysine	0.171819
Glycerol	0.0702648	Aspartic acid	0.179331
Tryptophan	0.0749528	Valine	0.179492
Glycolic acid	0.0917677	Pyroglutamic acid	0.183405
Glycine	0.112833	Galactinol	0.186058
Xylitol	0.122589	Alanine	0.187182
Succinic acid	0.148316	Serotonin	0.189853
Galactose+Glucose	0.157377	Proline	0.206185
Glucose	0.169042	Caffeine	0.210998
Fructose	0.172276	Serine	0.220004
Sorbose	0.173319	Glutamic acid	0.241195

Table S16. List of detected metabolites

No	Class	Metabolite name	RT[a] (min)	RI[b]	Quant. *m/z*	MSI Level[c]
1	Amino Acid	Alanine	6.85	1108.95	116.10	1
2	Amino Acid	Asparagine	12.61	1683.95	116.11	1
3	Amino Acid	Aspartic acid	11.39	1532.12	232.07	1
4	Amino Acid	Glutamic acid	12.19	1630.48	246.10	1
5	Amino Acid	Glycine	9.38	1316.71	174.10	1
6	Amino Acid	Isoleucine	7.81	1180.81	86.10	1
7	Amino Acid	Leucine	7.54	1160.40	86.10	1
8	Amino Acid	Lysine	14.44	1939.73	174.09	1
9	Amino Acid	Phenylalanine	12.28	1641.92	218.05	1
10	Amino Acid	Proline	9.26	1305.52	142.13	1
11	Amino Acid	Pyroglutamic acid	11.40	1533.60	156.08	1
12	Amino Acid	Serine	9.93	1372.28	204.06	1
13	Amino Acid	Tryptophan	16.37	2248.71	202.06	1
14	Amino Acid	Tyrosine	14.56	1958.02	218.04	1
15	Amino Acid	Valine	8.35	1225.05	144.14	1
16	Organic Acid	Chlorogenic acid	20.94	3173.08	345.15	1
17	Organic Acid	Glucarate	15.22	2059.72	333.09	1
18	Organic Acid	Gluconic acid	15.11	2042.33	147.07	1
19	Organic Acid	Citric acid	13.76	1840.83	273.08	1
20	Organic Acid	Lactic acid	6.22	1067.58	147.09	1
21	Organic Acid	Malic acid	11.11	1498.90	147.10	1
22	Organic Acid	Quinic acid	14.12	1891.69	345.15	1
23	Organic Acid	Succinic acid	9.39	1317.76	147.09	1
24	Sugar	Arabionose	12.64	1686.90	103.06	1
25	Sugar	Fructose	14.28	1915.38	103.06	1
26	Sugar	Galactose	14.36	1927.30	205.04	1
27	Sugar	Galactose+Glucose	14.53	1953.33	205.04	1
28	Sugar	Glucose	14.40	1933.44	205.04	1
29	Sugar	Melezitose	23.23	3586.53	361.13	1
30	Sugar	Panose	24.74	3774.40	204.05	1
31	Sugar	Raffinose	22.68	3503.29	361.14	1
32	Sugar	Sorbose	14.21	1905.33	103.06	1
33	Sugar	Sucrose	18.83	2708.25	361.24	1
34	Sugar Alcohol	Galactinol	20.52	3077.81	204.05	1
35	Sugar Alcohol	Inositol	15.68	2132.54	217.05	1
36	Sugar Alcohol	Mannitol	14.63	1968.61	205.05	1
37	Sugar Alcohol	Sorbitol	14.69	1976.43	205.07	1
38	Other	2-Aminoethanol	8.94	1276.59	174.09	1
39	Other	2-Dehydro gluconate	14.35	1925.73	103.06	1
40	Other	4-Aminobutyric acid	11.47	1541.81	174.10	1
41	Other	Caffeine	13.93	1864.76	194.05	1
42	Other	Glycerol	9.04	1285.16	147.10	1
43	Other	Nicotinic acid	9.16	1296.00	180.01	1
44	Other	N-Methylnicotinate	11.24	1514.12	210.04	1
45	Other	Phosphate	9.02	1283.72	299.05	1
46	Other	Putrescine	13.16	1757.02	174.09	1
47	Other	Serotonin	17.72	2490.44	174.09	1
48	Unknown	Unknown_1	5.93	1049.56	117.10	4
49	Unknown	Unknown_2	10.25	1404.33	147.08	4
50	Unknown	Unknown_3	10.48	1429.72	160.09	4
51	Unknown	Unknown_4	11.43	1536.65	174.06	4
52	Unknown	Unknown_5	11.59	1556.50	120.10	4
53	Unknown	Unknown_6	11.90	1593.48	210.04	4
54	Unknown	Unknown_7	13.08	1746.00	117.13	4
55	Unknown	Unknown_8	13.32	1779.24	217.02	4
56	Unknown	Unknown_9	13.82	1849.49	204.06	4

57	Unknown	Unknown_10	14.61	1964.26	204.06	4
58	Unknown	Unknown_11	14.73	1983.10	147.08	4
59	Unknown	Unknown_12	15.09	2039.18	217.05	4
60	Unknown	Unknown_13	15.40	2087.14	333.11	4
61	Unknown	Unknown_14	16.25	2227.71	204.05	4
62	Unknown	Unknown_15	17.29	2410.03	217.04	4
63	Unknown	Unknown_16	19.73	2899.99	191.03	4
64	Unknown	Unknown_17	20.14	2991.15	355.11	4
65	Unknown	Unknown_18	20.20	3002.96	355.11	4
66	Unknown	Unknown_19	20.29	3025.54	345.13	4
67	Unknown	Unknown_20	20.71	3120.91	204.06	4
68	Unknown	Unknown_21	20.72	3123.61	191.02	4
69	Unknown	Unknown_22	20.82	3146.17	345.15	4
70	Unknown	Unknown_23	21.05	3198.24	204.04	4
71	Unknown	Unknown_24	21.07	3202.27	249.06	4
72	Unknown	Unknown_25	21.16	3220.26	307.10	4
73	Unknown	Unknown_26	21.19	3227.88	249.07	4
74	Unknown	Unknown_27	21.26	3242.55	307.10	4
75	Unknown	Unknown_28	22.56	3483.77	255.06	4
76	Unknown	Unknown_29	22.96	3545.82	361.14	4
77	Unknown	Unknown_30	23.42	3613.07	204.08	4
78	Unknown	Unknown_31	23.43	3614.72	361.13	4
79	Unknown	Unknown_32	24.83	3784.47	204.04	4

There are 79 metabolites detected in all samples

a Retention time in minute(s)

b Retention indices (RI) are calculated using a standard alkane mixture (C9–C40).

c Mass spectra of metabolite peaks that are compared only with the in-house library are considered Metabolic Standards Initiative (MSI) level 1 identification. Several unknown compounds are considered MSI level 3 based on similarity to known compounds of a chemical class in library and MSI level 4 if there are no similarities with any chemical class compound in library.

Table S17. List of metabolites sorted based on VIP value

Metabolite	VIP Score	Coefficient
Unknown_2	1.94322	-0.0519212
Unknown_13	1.93544	-0.052012
N-Methylnicotinate	1.90852	-0.05365
Arabionose	1.90187	-0.0540962
Unknown_6	1.884	-0.0524361
Phosphate	1.88027	-0.0482134
Putrescine	1.77635	0.0457321
Serotonin	1.66465	-0.0378469
Galactinol	1.66028	-0.0499557
Unknown_11	1.61061	-0.0382275
Inositol	1.60287	0.0356457
Glucarate	1.52705	-0.0432385
Citric acid	1.50944	-0.0356244
Proline	1.47552	-0.0270537
Succinic acid	1.41877	-0.0383416
Gluconic acid	1.39505	0.0285693
Unknown_9	1.39341	-0.052736
Pyroglutamic acid	1.38412	-0.0273308
Tyrosine	1.36877	-0.0342047
Unknown_8	1.26856	0.0385994
Nicotinic acid	1.26306	-0.0251916
Unknown_23	1.2265	0.0342118
Valine	1.14927	-0.0236135
2-Dehydro gluconate	1.13444	-0.028652
Mannitol	1.11751	0.0326222
Alanine	1.04266	-0.0166258
Unknown_12	0.983766	-0.0328652
Unknown_10	0.93586	0.0286599
Raffinose	0.933368	-0.00973574
Unknown_3	0.932243	-0.0175312
Unknown_19	0.909776	-0.00763988
Unknown_30	0.890618	-0.0314516
4-Aminobutyric acid	0.876171	-0.0275822
Galactose	0.814316	0.0244249
Lactic acid	0.803134	0.0356973
Caffeine	0.782688	-0.00588669
Unknown_28	0.777516	0.0398356
Unknown_31	0.7446	-0.0326355
Leucine	0.713852	-0.0149373
Isoleucine	0.701684	-0.0214655
Unknown_20	0.675228	0.0414729
Lysine	0.662077	-0.00703807
Glycine	0.640915	-0.00701749
Unknown_25	0.5761	0.0166348
Tryptophan	0.566893	-0.00311743
Glycerol	0.557457	-0.00384981
Unknown_18	0.555741	0.00919977

Chlorogenic acid	0.542826	0.00330773
Sorbitol	0.535405	0.0274912
Unknown_7	0.52952	-0.00249059
Unknown_22	0.526493	0.0136347
Unknown_5	0.5128	-0.0172168
Galactose+Glucose	0.50556	0.0266969
Glucose	0.486295	0.0266776
Unknown_32	0.47699	-0.00270392
Unknown_27	0.471729	0.0177515
Unknown_14	0.467471	-0.0219886
Quinic acid	0.451635	0.0116626
Unknown_24	0.439443	0.0156975
Aspartic acid	0.42229	-0.000238925
Fructose	0.39177	0.0245164
Sorbose	0.366128	0.0237945
Unknown_16	0.355415	0.00987123
Unknown_21	0.34803	0.00407855
Unknown_26	0.346155	0.0133857
Unknown_1	0.344223	-0.00146409
2-Aminoethanol	0.338886	-0.00283442
Glutamic acid	0.307515	0.00785171
Melezitose	0.30086	-0.0108212
Phenylalanine	0.252298	0.00827259
Panose	0.244228	0.00520064
Unknown_17	0.215348	-0.009582
Unknown_29	0.21138	-0.00218763
Unknown_4	0.157201	-0.00736752
Serine	0.146786	0.0181318
Asparagine	0.144213	0.0148263
Unknown_15	0.142711	0.0159875
Malic acid	0.082737	0.0105386
Sucrose	0.0739957	0.00416982

Table S18 Data matrix of 10 different specialty Arabica green coffee bean samples for quality-related metabolite investigation

Metabolite name	2-Aminoethanol	2-Dehydro gluconate	4-Aminobutyric acid	Adenosine	Alanine	Asparagine	Aspartic acid	beta-Glutamic acid	Caffeine	Chlorogenic acid
1_1	0.01774548	0.007405428	0.2679591	0.001801865	0.1320177	0.0500524	0.05347589	6.40289E-05	0.3994656	1.089637
1_2	0.01690132	0.007127517	0.2552368	0.001662474	0.1364383	0.05113846	0.06459538	7.50797E-05	0.3918832	1.078525
1_3	0.01789113	0.007421904	0.2590145	0.001799226	0.1193992	0.04794322	0.06102937	0.000103484	0.3944541	1.119558
2_1	0.0409716	0.000420616	0.1677714	0.00621974	0.2068074	0.03951268	0.04228346	0.002315482	0.2852974	1.079508
2_2	0.04281246	0.000488119	0.1660786	0.005264169	0.2107897	0.05796247	0.05429776	0.00286346	0.2936097	0.9935347
2_3	0.04195349	0.00052186	0.1673117	0.005474132	0.2235426	0.04890045	0.06586275	0.003237142	0.2948924	1.108166
3_1	0.03962261	0.00018196	0.2279527	0.00396537	0.2755838	0.05155567	0.1158252	0.002253372	0.353926	1.079343
3_2	0.03815691	0.000131612	0.220022	0.003759458	0.2595641	0.06085772	0.1035786	0.002098145	0.3532136	1.048734
3_3	0.04072062	0.000168287	0.2447262	0.003821363	0.2417402	0.06406968	0.09723209	0.002060874	0.3726175	1.060661
4_1	0.01143725	0.007632396	0.1202971	0.001959988	0.1354576	0.06979255	0.08279135	5.02436E-05	0.312006	1.018306
4_2	0.01211651	0.008264238	0.1224096	0.001900549	0.1302455	0.09450593	0.1161115	5.99364E-05	0.3190588	1.05538
4_3	0.01090455	0.008186075	0.1194484	0.002145358	0.1242894	0.05677581	0.06658376	9.09489E-05	0.3047244	1.12562
5_1	0.02181457	0.000104653	0.1737803	0.00328158	0.1487342	0.0507885	0.1044751	7.93765E-05	0.3622337	1.016609
5_2	0.02035061	0.000123873	0.1672304	0.003885023	0.09999039	0.03016495	0.08045413	0.000120994	0.3235382	1.154452
5_3	0.0186448	0.000171245	0.1680905	0.00385008	0.1534122	0.0388958	0.08500521	0.000158255	0.330326	1.119716
6_1	0.02124784	0.000266576	0.05754013	0.002381685	0.08252814	0.02635192	0.05930454	0.005334122	0.2719614	1.079483
6_2	0.02113584	0.000147112	0.05686129	0.002205309	0.0768081	0.02423312	0.06182829	0.004795101	0.2673295	1.040633
6_3	0.02400101	0.00017747	0.05985187	0.00194386	0.07922002	0.03797132	0.0663128	0.005359068	0.2959005	1.004511
7_1	0.03999681	0.000352788	0.3509921	0.004074302	0.2020873	0.02737613	0.03987486	0.002079728	0.292954	1.124487
7_2	0.03915871	0.000312888	0.3346568	0.003704045	0.2322493	0.03278443	0.04515178	0.002341637	0.2806923	1.048566
7_3	0.0358113	0.000317873	0.3175156	0.004354664	0.2273385	0.02341513	0.03603481	0.002193968	0.2713305	1.141949
8_1	0.03346384	0.000128232	0.2326165	0.00281551	0.2961067	0.09600637	0.4700699	0.001502731	0.2759652	1.063908
8_2	0.03491602	0.000161395	0.2475476	0.00243587	0.3096713	0.1232797	0.4735307	0.001484777	0.2977474	1.011344
8_3	0.03658311	0.00018362	0.2600138	0.00271015	0.3194378	0.1263048	0.505221	0.001606583	0.30119	0.9857355
9_1	0.03095689	0.001255367	0.1916507	0.001430585	0.3998216	0.04332029	0.0480523	0.002177805	0.305866	1.080564
9_2	0.03326752	0.001181571	0.1970025	0.00136077	0.3638336	0.0616703	0.07050976	0.002721539	0.3067502	1.085312
9_3	0.03156722	0.00133076	0.2000262	0.001606779	0.4262974	0.04986956	0.08546223	0.002928279	0.2991374	1.124914
10_1	0.03343483	0.001200919	0.230639	0.004392927	0.2703176	0.02362461	0.06092735	0.00791937	0.306723	1.045767
10_2	0.03148997	0.001206138	0.2434773	0.00490275	0.3048776	0.01862682	0.06006511	0.008101088	0.3116992	1.064082
10_3	0.03010477	0.001083912	0.2321798	0.00470236	0.269886	0.01647606	0.04251854	0.00604664	0.2962036	1.132499

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Ferulic acid	Fructose	Fumaric acid	Galactinol	Galactitol	Galactose	Galactose+Glucose	Galacturonic acid	Gentiobiose	Glucarate	Gluconic acid
1_1	0.002421569	0.1619958	0.003686109	0.2011201	0.01170026	0.004929476	0.01844094	0.002758494	0.001925845	0.01262803	0.0526906
1_2	0.002516797	0.1532449	0.00345692	0.2087372	0.0112041	0.004923099	0.01697184	0.00266018	0.001657956	0.01244271	0.05298858
1_3	0.00321787	0.1587993	0.004482152	0.2013817	0.0117563	0.004894989	0.0177801	0.003102796	0.001943805	0.01252166	0.05606936
2_1	0.004282823	0.051503	0.01128472	0.2553149	0.01028087	0.03763438	0.01253264	0.01629165	0.005326077	0.01975585	0.04281608
2_2	0.003594703	0.05001197	0.009261198	0.2408009	0.008371464	0.03534599	0.01157828	0.0163794	0.004702006	0.01921611	0.04381765
2_3	0.004740543	0.0502157	0.01047882	0.2539194	0.009342921	0.03827351	0.01195253	0.0161886	0.004921085	0.01948415	0.04325485
3_1	0.003755671	0.03063498	0.007547672	0.2451236	0.01444718	0.02006155	0.01074802	0.006286163	0.001708531	0.007893948	0.01436642
3_2	0.003079462	0.02991626	0.006424022	0.2386971	0.01448232	0.01949648	0.01048791	0.00604081	0.001845045	0.008282604	0.01443665
3_3	0.003149705	0.03176994	0.006336458	0.2547944	0.009400707	0.01956534	0.01104492	0.006341314	0.001682357	0.008534366	0.01588791
4_1	0.001732538	0.1597465	0.003471657	0.1331929	0.01306043	0.00455682	0.02318894	0.002374422	0.003016569	0.01674321	0.05130484
4_2	0.00162956	0.1603743	0.002968862	0.1358281	0.01298547	0.004618697	0.025269	0.002388691	0.00318281	0.01664039	0.05028315
4_3	0.002622233	0.16095	0.004358659	0.1403329	0.01168846	0.004616819	0.02421238	0.002392731	0.003225162	0.0165919	0.05268893
5_1	0.002593117	0.03221704	0.00283788	0.22708	0.01492899	0.0056111	0.006773725	0.005871837	0.004180531	0.01079024	0.01702427
5_2	0.004494169	0.03041318	0.006104029	0.2493294	0.01057865	0.005897236	0.006700483	0.005310473	0.004732508	0.0105555	0.016354
5_3	0.004165929	0.03261472	0.005254462	0.2344951	0.01106937	0.005889932	0.007010863	0.005526478	0.004245076	0.01064606	0.01774385
6_1	0.00315876	0.008334974	0.006644153	0.1731571	0.0112891	0.009740221	0.0027082	0.003582144	0.002021937	0.01394605	0.008880396
6_2	0.003531416	0.008224858	0.005723875	0.1564169	0.01105564	0.008933421	0.002624225	0.003626517	0.002106053	0.01326907	0.008648196
6_3	0.001730147	0.008584447	0.003734889	0.1518365	0.01481647	0.009240136	0.002677739	0.003773928	0.002214524	0.01365048	0.00829825
7_1	0.003661105	0.09070421	0.03017185	0.01723268	0.003003098	0.02979048	0.01909394	0.03008771	0.005792864	0.01205311	0.07975081
7_2	0.00340634	0.08241344	0.02835437	0.01623974	0.01197903	0.02720513	0.0165987	0.02857234	0.005522225	0.01104286	0.07367169
7_3	0.004625046	0.0812122	0.03067748	0.01777591	0.007532123	0.02755981	0.01707049	0.02884193	0.006114715	0.01166637	0.07586303
8_1	0.004590586	0.04428863	0.007981588	0.02274376	0.009639901	0.01187401	0.01603556	0.01056311	0.0057362	0.02152462	0.01792161
8_2	0.002802273	0.04647348	0.006276384	0.02218099	0.01118868	0.01203659	0.01609185	0.01125659	0.005350983	0.02216982	0.01828898
8_3	0.002550566	0.04787884	0.00564344	0.02211938	0.009551492	0.01242326	0.01660701	0.01175784	0.00554839	0.0232604	0.01873966
9_1	0.005057918	0.06182105	0.01234127	0.01934871	0.01282058	0.0497383	0.0150405	0.004726231	0.003522877	0.01600327	0.0157831
9_2	0.003890325	0.05976063	0.01092713	0.01744614	0.01265319	0.04910368	0.01422181	0.0043774	0.002963186	0.01544888	0.01504514
9_3	0.005440343	0.06322472	0.01257837	0.02027532	0.01442633	0.05168978	0.01681648	0.004538761	0.003283931	0.01605443	0.01530707
10_1	0.008959308	0.1736618	0.02070838	0.004966323	0.01011827	0.02020819	0.02590512	0.04215544	0.004290342	0.01261313	0.1227433
10_2	0.009507718	0.1821193	0.02161296	0.005297434	0.01023942	0.02039578	0.02682679	0.04405577	0.00472349	0.01318543	0.126215
10_3	0.008874261	0.1786073	0.02067095	0.005077537	0.00621779	0.01923383	0.02478143	0.04138171	0.004850635	0.01224451	0.1139804

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Glucono-1,5-lactone	Glucose	Glutamic acid	Glutamine	Glyceric acid	Glycerol	Glycine	Glycolic acid	Inositol	Citric acid	Isoleucine	Lactic acid
1_1	0.01487637	0.1042586	0.1793049	0.005320158	0.006348737	0.07413305	0.03019954	0.01078802	0.1897164	0.9141718	0.01995849	0.02096939
1_2	0.01443276	0.100772	0.1896397	0.005420402	0.005890942	0.07396924	0.02968294	0.01006213	0.1910152	0.9231348	0.0224553	0.02142187
1_3	0.01513289	0.1035411	0.1881586	0.004596441	0.006332609	0.07727155	0.03018111	0.01080278	0.1939157	0.9488336	0.01853997	0.01941177
2_1	0.01070013	0.06458388	0.09713184	0.0024442	0.004240169	0.09029029	0.02359439	0.003184685	0.291393	0.8715734	0.02018964	0.02306951
2_2	0.01017529	0.06567711	0.1189895	0.003114404	0.004194843	0.08904489	0.02362403	0.003039574	0.2881747	0.9046372	0.02225707	0.02321385
2_3	0.01061029	0.06716507	0.1188527	0.002334009	0.004274941	0.08982676	0.02397659	0.003387459	0.2960297	0.9090164	0.0290178	0.02375086
3_1	0.00394106	0.06054639	0.1435618	0.0071668	0.002947502	0.05450776	0.02862644	0.00154175	0.2751659	0.8296849	0.03413745	0.01620999
3_2	0.00379178	0.05806971	0.1418498	0.009305766	0.002724746	0.04997624	0.02816909	0.001454558	0.2646653	0.8297338	0.02622055	0.01181037
3_3	0.003910577	0.06034247	0.1472314	0.01050771	0.002819358	0.05713884	0.03024028	0.001610178	0.2889688	0.8701258	0.02617524	0.0138248
4_1	0.0122958	0.1344952	0.1948105	0.005660411	0.00521984	0.08770585	0.01658899	0.008629933	0.1680054	0.9389238	0.01631505	0.01896461
4_2	0.01298195	0.1330232	0.2407503	0.006792358	0.005421814	0.08881714	0.01694857	0.008856265	0.1747842	0.9827577	0.0178297	0.01771716
4_3	0.01374602	0.1345699	0.1729141	0.004434484	0.005478903	0.09068983	0.01654967	0.008671586	0.1733418	0.9643829	0.01459532	0.01828132
5_1	0.004132684	0.03844619	0.1736597	0.003186267	0.001991465	0.06351718	0.0166347	0.00152306	0.2346756	0.8434443	0.01492891	0.01122639
5_2	0.003924111	0.03949514	0.1305498	0.002264905	0.001880596	0.0654487	0.01662446	0.001557796	0.234239	0.8055427	0.01037215	0.01520391
5_3	0.004277085	0.0398169	0.1570735	0.002694068	0.001962183	0.06511062	0.01963948	0.001582783	0.2314472	0.7971934	0.01659779	0.01353941
6_1	0.002932654	0.0155957	0.1504779	0.002681298	0.002322769	0.05422515	0.01572706	0.003044468	0.2480174	0.9331456	0.02054439	0.01524846
6_2	0.002661365	0.01519248	0.1411609	0.002447903	0.001996309	0.05802675	0.01575797	0.002918182	0.2385602	0.8659185	0.01769784	0.01317592
6_3	0.002671201	0.01502874	0.16375	0.003603676	0.002237162	0.05672864	0.0163761	0.003100478	0.2479642	0.9533519	0.0202015	0.01416335
7_1	0.02086994	0.1018789	0.06034409	0.001484205	0.0127646	0.1914166	0.03518549	0.002084387	0.3597995	0.8201429	0.009829072	0.07131315
7_2	0.01904428	0.09306277	0.06304546	0.001639754	0.01185583	0.1747831	0.03416274	0.001737579	0.3421768	0.826757	0.01044133	0.06335163
7_3	0.0194072	0.09703535	0.05867233	0.001378185	0.01204866	0.1749079	0.03195018	0.001899087	0.3401832	0.7924214	0.009324363	0.06592101
8_1	0.004277735	0.08789329	0.08645289	0.004233622	0.0148944	0.1001539	0.02680232	0.001581596	0.3783172	1.031302	0.05566506	0.02003358
8_2	0.004506544	0.09174427	0.09067357	0.005874141	0.0151741	0.1038862	0.02874293	0.001761578	0.3874654	1.049274	0.05135974	0.02143389
8_3	0.004630854	0.09317235	0.09796539	0.006122797	0.01563172	0.1026676	0.02976516	0.001757616	0.3829067	1.102848	0.05339137	0.01995757
9_1	0.004443645	0.09199113	0.03986743	0.001481435	0.007663598	0.1078127	0.05466055	0.003088481	0.2394337	0.7836533	0.01851846	0.03784412
9_2	0.004262209	0.08958736	0.04928565	0.001971494	0.007211674	0.0982589	0.05185485	0.003241593	0.2279922	0.8388026	0.0162671	0.0338823
9_3	0.00414804	0.09747761	0.0521651	0.001639995	0.007620555	0.1028612	0.05289418	0.003048971	0.2319392	0.7976752	0.02052238	0.0328957
10_1	0.03330257	0.1398641	0.07997745	0.000834241	0.008709425	0.3815747	0.03921853	0.004519096	0.3510316	0.8781841	0.01846393	0.03620206
10_2	0.03486123	0.147657	0.07912056	0.000393439	0.009256015	0.3830466	0.04020023	0.004689232	0.3657995	0.886005	0.02009049	0.04152722
10_3	0.03532007	0.1317821	0.06902911	0.000350529	0.008640076	0.3759212	0.03790339	0.004642318	0.347502	0.8386492	0.01767344	0.03799681

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Leucine	Lysine	Malic acid	Mannitol	Mannose	Melezitose	Meso erythritol	Methyl succinic acid	Nicotinic acid	N-Methylnicotinate	Paeoniflorin
1_1	0.02007071	0.01575674	0.6079541	0.06701001	0.004620271	0.0194774	0.002773276	0.000443693	0.04819572	0.04112663	0.003066837
1_2	0.02236873	0.01475023	0.5950141	0.06511902	0.004651304	0.01863745	0.002890396	0.005812953	0.04262467	0.03820879	0.002915588
1_3	0.01850025	0.01512161	0.6021998	0.06799702	0.004500893	0.01957748	0.002838782	0.006273285	0.05022883	0.04185412	0.00508636
2_1	0.01920587	0.01361968	0.5358701	0.08542118	0.008476223	0.01220669	0.004806187	0.004240169	0.06133057	0.05409513	0.005011719
2_2	0.02058049	0.0147628	0.5426176	0.08233039	0.008184164	0.01201683	0.004653404	0.004194843	0.05280419	0.0565918	0.004759738
2_3	0.02886779	0.01409946	0.5434058	0.08748513	0.008647517	0.01245732	0.004872556	0.004274941	0.06680822	0.05031972	0.004810222
3_1	0.03555291	0.01976028	0.550437	0.09311774	0.006046413	0.01013503	0.002172197	0.002989496	0.06086439	0.03952287	0.004219144
3_2	0.02561671	0.01943484	0.5428157	0.09300591	0.005491788	0.01016687	0.002375393	0.002724746	0.04679168	0.03909668	0.00389047
3_3	0.02609441	0.02105627	0.5885677	0.09703843	0.005790594	0.01101186	0.002506558	0.002870232	0.04560789	0.03507685	0.003978213
4_1	0.01443634	0.0108423	0.692654	0.0938508	0.005031276	0.02005083	0.00289269	0.005262712	0.04671756	0.04422787	0.005289789
4_2	0.01515585	0.01149559	0.6983562	0.09406861	0.005807578	0.02004379	0.003052394	0.005421814	0.04639119	0.04614943	0.005204854
4_3	0.01222878	0.01073945	0.7173104	0.09766626	0.005386482	0.02068408	0.003132741	0.005478903	0.05828362	0.04636072	0.004746814
5_1	0.01503082	0.01121999	0.8097286	0.07791607	0.003515363	0.01141469	0.003923035	0.001991465	0.02853248	0.03608678	0.006235093
5_2	0.01056621	0.01108927	0.7805827	0.07258689	0.003581525	0.0112043	0.003700208	0.001857321	0.06144958	0.04433839	0.006889476
5_3	0.01812247	0.01106579	0.7767881	0.07572592	0.003906981	0.01155592	0.003964581	0.001962183	0.05069122	0.04126153	0.006968936
6_1	0.01527925	0.009823482	0.6716293	0.04502792	0.00355477	0.01564443	0.002165805	0.002322769	0.06772037	0.06133328	0.00356889
6_2	0.01252764	0.009773998	0.6344103	0.04421563	0.003331759	0.01431167	0.001892744	6.13158E-05	0.06227138	0.04972089	0.002946895
6_3	0.01511068	0.01046716	0.6850205	0.04628299	0.003569285	0.0133085	0.002304393	0.002237162	0.04134398	0.0688583	0.003161776
7_1	0.0108551	0.01200609	0.7269508	0.02437006	0.008864633	0.009538182	0.01511857	0.003530733	0.04289275	0.04503665	0.007627978
7_2	0.01236992	0.0110585	0.6955588	0.02297249	0.00789929	0.009586219	0.01443009	0.001958458	0.04290222	0.04760182	0.00674205
7_3	0.01132709	0.01107842	0.6846756	0.02306139	0.008855745	0.01033378	0.01425662	0.000283829	0.06019913	0.04759445	0.007388295
8_1	0.0349022	0.03160142	0.315896	0.005103592	0.02595667	0.006195082	0.004267953	0.000169966	0.06679557	0.04523386	0.003818891
8_2	0.03272794	0.03308083	0.3225448	0.005145146	0.02585626	0.006731973	0.004260716	0.002389126	0.04853344	0.06117166	0.004370124
8_3	0.03447381	0.03428673	0.3260841	0.005116615	0.02763356	0.006594845	0.004530455	0.001162037	0.04449886	0.05954366	0.00389513
9_1	0.02040487	0.01293528	0.6698285	0.2681816	0.00749102	0.01420249	0.007501345	0.00679368	0.06448209	0.05374328	0.004456999
9_2	0.01753307	0.01311653	0.668175	0.2586435	0.007142365	0.01354817	0.007057697	0.007211674	0.04896323	0.06774815	0.00572476
9_3	0.02279062	0.01316748	0.6595221	0.2585328	0.007631785	0.01446467	0.007616102	0.007610152	0.07043111	0.05712039	0.005883352
10_1	0.01809782	0.01582313	0.5557314	0.05522339	0.01561309	0.007203324	0.008425675	0.008688636	0.04619851	0.05525995	0.006882419
10_2	0.01975169	0.01509621	0.5720377	0.05705	0.01758781	0.007922216	0.008327205	0.009256015	0.06038409	0.05421407	0.007251565
10_3	0.01781368	0.01489649	0.5517498	0.05170632	0.0160845	0.007098149	0.007807751	0.008591688	0.05994279	0.05221363	0.006434455

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Panose	Phenylalanine	Phosphate	Proline	Psicose+Tagatose	Putrescine	Pyroglutamic acid	Quinic acid	Raffinose	Serine	Serotonin	Shikimic acid
1_1	0.04423762	0.02200138	0.2383821	0.05935862	0.2680004	0.09359539	0.05101719	1.012219	0.06176372	0.02137662	0.008398248	0.003160547
1_2	0.04577009	0.02487244	0.2359938	0.06708989	0.2559041	0.09281807	0.04863396	0.9827706	0.05584586	0.01708555	0.007524586	0.003088337
1_3	0.04637697	0.02493803	0.2443627	0.05327199	0.2673023	0.0958983	0.05615512	1.014252	0.06244027	0.02163703	0.009040445	0.003276212
2_1	0.02995911	0.01631127	0.2920204	0.05902996	0.0867868	0.07734262	0.0458309	0.8873433	0.0638842	0.01723125	0.0138254	0.004393195
2_2	0.03033946	0.0193767	0.2989983	0.06807326	0.08615614	0.08077171	0.03635392	0.9066578	0.05386629	0.01414306	0.01281841	0.004075937
2_3	0.02963576	0.02238036	0.3052615	0.09364109	0.08826637	0.08253779	0.04782427	0.9567207	0.05756616	0.01134115	0.01539894	0.004356041
3_1	0.03312902	0.02961345	0.2616366	0.102104	0.05601453	0.0791887	0.05974361	0.9631006	0.04685552	0.02239387	0.01112015	0.00300036
3_2	0.03720023	0.02810062	0.2420269	0.06628284	0.05330892	0.07677004	0.04916568	0.8984102	0.04379715	0.03104734	0.009745711	0.002853359
3_3	0.03669392	0.02992952	0.2717778	0.06551412	0.05815831	0.07892351	0.049346	0.9783229	0.04698207	0.03568004	0.01033613	0.003111872
4_1	0.03230063	0.01718424	0.2558056	0.09868117	0.2592009	0.07153077	0.06281645	0.954972	0.07588921	0.02996449	0.01063904	0.003408251
4_2	0.03374587	0.02208677	0.2743046	0.1022968	0.2635197	0.0762303	0.05655103	1.019443	0.07365431	0.02650198	0.01142782	0.003510452
4_3	0.03089937	0.01496362	0.254288	0.08379495	0.2674115	0.07267164	0.0744466	1.016085	0.081623	0.03567166	0.01119459	0.003559106
5_1	0.02795237	0.01801491	0.236453	0.07341236	0.05737259	0.1037307	0.03314089	0.7729052	0.0390348	0.01660138	0.006717795	0.004138937
5_2	0.02766965	0.01420855	0.2168076	0.03808745	0.05276899	0.09646457	0.05656274	0.8376468	0.04190521	0.02290491	0.009154259	0.004699543
5_3	0.02790876	0.01514546	0.2435791	0.09972953	0.05910701	0.09251814	0.04833668	0.8012431	0.04219613	0.01234253	0.008037206	0.004509508
6_1	0.03203423	0.02454807	0.2647875	0.05875538	0.01653929	0.06549368	0.0512759	0.9303499	0.06635708	0.01964386	0.008452136	0.003780876
6_2	0.02558268	0.02406778	0.234992	0.04953935	0.01519145	0.06394864	0.05034443	0.9330725	0.05761298	0.02119692	0.007993132	0.003558261
6_3	0.02862382	0.02726894	0.2617835	0.05424629	0.01678361	0.06779806	0.03125269	0.9133899	0.05398133	0.02060629	0.00734155	0.003627069
7_1	0.0363052	0.01371937	0.3236798	0.09525736	0.1529181	0.1171305	0.04064276	0.9097547	0.04648526	0.01526328	0.008319497	0.003062138
7_2	0.03648601	0.01368802	0.3108543	0.1206819	0.141506	0.110642	0.03675199	0.8844454	0.04456736	0.01259507	0.008625082	0.002926319
7_3	0.03258758	0.01252149	0.3069032	0.09762785	0.1420747	0.1069919	0.04797523	0.8779396	0.04633246	0.01343523	0.009807935	0.003092136
8_1	0.02775533	0.0274793	0.7769017	0.2173226	0.07453573	0.1132345	0.05258606	0.758608	0.01142023	0.01222426	0.004864005	0.00406964
8_2	0.03476952	0.02724306	0.8439113	0.2080692	0.07882588	0.1182862	0.043409	0.772654	0.01179853	0.01568232	0.004485454	0.004104904
8_3	0.04145319	0.02834842	0.8414267	0.2137565	0.08201194	0.1212307	0.04413998	0.7854009	0.01179197	0.01515632	0.004456162	0.003921577
9_1	0.04444294	0.01271049	0.2699386	0.07149872	0.1138023	0.0723943	0.05325931	0.9825083	0.08775643	0.01522507	0.01506938	0.005327228
9_2	0.04421281	0.01678326	0.2667371	0.06297622	0.1073496	0.07417832	0.04183287	0.9378087	0.07475232	0.01549928	0.01514143	0.005270741
9_3	0.0457861	0.01906254	0.2614101	0.0867822	0.1138206	0.0741649	0.05658794	0.9919163	0.09081703	0.01396646	0.01874574	0.005939974
10_1	0.03790569	0.01171089	0.4453502	0.05893955	0.2897801	0.05160253	0.05787379	1.064531	0.0198665	0.02160767	0.007324581	0.004495473
10_2	0.04094978	0.01205955	0.4658359	0.07321345	0.3016092	0.0532059	0.06549285	1.077715	0.02407042	0.02021026	0.008495578	0.004555895
10_3	0.04144549	0.009061869	0.4560151	0.06013437	0.2973564	0.04920033	0.06261769	1.038638	0.02222331	0.02180514	0.007569117	0.004704132

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Sorbitol	Sorbose	Succinic acid	Sucrose	Threitol	Threonine	Trehalose	Tryptophan	Tyrosine	Unknown_1	Unknown_2 (apigenin)	Unknown_3
1_1	0.006973694	0.2680004	0.06395968	2.725132	0.003044683	0.003054603	0.00467536	0.145466	0.03575793	0.02046374	0.03073475	0.004565064
1_2	0.006711957	0.2559041	0.06163798	2.677825	0.003023709	0.003641423	0.005320895	0.1302019	0.0339907	0.02006925	0.0305749	0.005797944
1_3	0.007127009	0.2675606	0.06359054	2.783312	0.003016638	0.003145895	0.004469934	0.1414225	0.03497057	0.0194934	0.03054236	0.00467812
2_1	0.07574626	0.08697172	0.0431752	2.737506	0.005540594	0.003637838	0.005635867	0.05258748	0.02800268	0.0137031	0.01556358	0.008075047
2_2	0.07759719	0.08615614	0.04216693	2.64326	0.005524878	0.004495549	0.005293877	0.05758701	0.02924619	0.01355437	0.01574552	0.00637005
2_3	0.07713437	0.08826637	0.04463332	2.819752	0.005826718	0.005275555	0.005481092	0.05461104	0.02892913	0.01359671	0.01603228	0.008004873
3_1	0.03191432	0.05601453	0.04751791	2.606162	0.0024806	0.00591211	0.004693404	0.1094916	0.0450617	0.002407901	0.003593822	0.006995935
3_2	0.03102874	0.0534214	0.04585228	2.450898	0.002693999	0.004200415	0.005032571	0.1093179	0.04373783	0.002595871	0.00355739	0.006476105
3_3	0.03243157	0.05810379	0.04850312	2.61415	0.002932463	0.004048865	0.004679205	0.1163678	0.0475655	0.002855428	0.003978527	0.007847943
4_1	0.005852547	0.2592009	0.03715184	2.545804	0.005397234	0.003644877	0.00566891	0.1431417	0.02578563	0.009825436	0.01360679	0.008512184
4_2	0.006220915	0.2637706	0.03883904	2.671003	0.005587103	0.004421973	0.006364152	0.1517695	0.02742138	0.009689119	0.0135186	0.006092971
4_3	0.00612864	0.2679195	0.03899	2.709369	0.005702434	0.002599068	0.005113237	0.1392552	0.02583736	0.009511699	0.01368727	0.01050418
5_1	0.02959747	0.0573732	0.02813678	2.532492	0.003575143	0.003699164	0.003430001	0.06293707	0.02155891	0.001741936	0.00260383	0.008305934
5_2	0.02813364	0.05287162	0.03105772	2.700436	0.003574591	0.002285463	0.003971349	0.06819604	0.0204281	0.001699916	0.002427623	0.007737568
5_3	0.02993337	0.05924243	0.03020426	2.567835	0.003551072	0.003898269	0.003991689	0.06298754	0.02014747	0.00166333	0.00228581	0.008018226
6_1	0.01252798	0.01653929	0.02445887	2.625948	0.004576908	0.002141066	0.004227858	0.0805025	0.02833197	0.002354626	0.003299718	0.01483034
6_2	0.01177294	0.01538985	0.02560045	2.517558	0.004360781	0.001764049	0.003236239	0.075726	0.02696038	0.002168436	0.002894807	0.01252036
6_3	0.01237111	0.016794	0.02403219	2.451409	0.004497754	0.002287689	0.003214987	0.07775434	0.02988739	0.002435871	0.003097757	0.01249726
7_1	0.1200106	0.1529453	0.05928044	2.754979	0.00662842	0.002127844	0.005403353	0.02441351	0.02440588	0.008514664	0.008598212	0.007648218
7_2	0.1111568	0.1414947	0.05608284	2.599997	0.006040318	0.002441879	0.004449439	0.02449505	0.0223406	0.007703112	0.007632935	0.005111852
7_3	0.1104586	0.1420563	0.05722664	2.704717	0.006234893	0.002177661	0.004520672	0.02722547	0.02305007	0.007559984	0.007414069	0.005924555
8_1	0.02134517	0.07442464	0.03987177	2.276787	0.002594182	0.01023147	0.003210871	0.03682277	0.02768379	0.003855907	0.005655647	0.0129978
8_2	0.02205846	0.07870904	0.03897293	2.284406	0.002688149	0.009837531	0.00319565	0.04072414	0.03109923	0.004078231	0.00579499	0.0139393
8_3	0.0228316	0.08196526	0.03973163	2.23495	0.00283937	0.01044989	0.003482229	0.04082412	0.03131362	0.004547973	0.006084897	0.01770443
9_1	0.02915087	0.1141901	0.15442	2.587199	0.006312509	0.003213121	0.003328911	0.1173443	0.03679925	0.00579489	0.01065007	0.009845712
9_2	0.02654495	0.1076614	0.149786	2.597317	0.005938262	0.003469362	0.003264631	0.1212813	0.03821499	0.005291012	0.009850689	0.00789775
9_3	0.02857298	0.1141721	0.1513657	2.722274	0.006255396	0.00410383	0.003850547	0.1233494	0.03736972	0.005549135	0.0102208	0.00843411
10_1	0.2689511	0.2900442	0.05775957	2.529956	0.00742278	0.003582839	0.003478894	0.03968598	0.03328594	0.01032983	0.009415909	0.008138902
10_2	0.2786416	0.3016092	0.06070069	2.585857	0.007946559	0.004056688	0.003669626	0.03812381	0.03327942	0.01095487	0.01000568	0.009910761
10_3	0.2716643	0.2975479	0.06053877	2.627288	0.007889606	0.003486867	0.003632937	0.0373667	0.03122719	0.01019192	0.009525318	0.01002341

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Unknown_4	Unknown_5	Unknown_6	Unknown_7	Unknown_8	Unknown_9	Unknown_10	Unknown_11	Unknown_12	Unknown_13	Unknown_14	Unknown_15 (genistic acid)
1_1	0.03045703	0.0150667	0.02181533	0.02025809	0.0037054	0.04443331	0.07555816	0.01780394	0.006452092	0.02309606	0.01028402	0.002328133
1_2	0.02755276	0.0146083	0.02062467	0.01478075	0.003502902	0.03559616	0.07186793	0.01383032	0.005980571	0.02035437	0.009006233	0.002004524
1_3	0.02914607	0.01468316	0.02117689	0.01769571	0.003988422	0.03820958	0.07579873	0.01535718	0.006503119	0.02337889	0.008656092	0.002269265
2_1	0.03226565	0.02757131	0.02979937	0.01486458	0.005077701	0.02450522	0.0475559	0.01254196	0.01170194	0.02874785	0.009419297	0.004236734
2_2	0.03117756	0.02765159	0.03110176	0.01110831	0.005154356	0.01807955	0.04823358	0.009070792	0.01131409	0.03093489	0.008104058	0.001858675
2_3	0.03306825	0.02780142	0.03016116	0.01366585	0.004896052	0.01549942	0.05154417	0.008698046	0.01106589	0.02690936	0.005842369	0.00407448
3_1	0.03527533	0.01761648	0.02454888	0.02440491	0.003546935	0.02420819	0.06729595	0.01620706	0.005199179	0.02282502	0.00864633	0.002579691
3_2	0.02761868	0.01676833	0.02369843	0.0285502	0.003396268	0.0279756	0.06432781	0.01757172	0.005234264	0.02068155	0.009988649	0.003309652
3_3	0.03018757	0.01803126	0.02504697	0.0323104	0.003116689	0.03021259	0.06994417	0.01965417	0.005487466	0.01763003	0.01191886	0.001822171
4_1	0.02682164	0.01693569	0.03049201	0.02245319	0.004180294	0.04139088	0.03456287	0.01098548	0.004857003	0.02381225	0.01359453	0.002281005
4_2	0.0293685	0.01707234	0.03044049	0.0172206	0.004227295	0.02765495	0.0352339	0.007455405	0.005251351	0.02571354	0.01031154	0.002751013
4_3	0.02742015	0.01721783	0.03201571	0.02847189	0.004066946	0.04827574	0.03368447	0.01344901	0.004986067	0.02503633	0.0126395	0.005519382
5_1	0.03233477	0.01655602	0.02753639	0.01810065	0.003207198	0.0267451	0.04797518	0.007851559	0.006029179	0.01938173	0.008083284	0.007233056
5_2	0.03244482	0.0162841	0.0271592	0.02605444	0.003866452	0.03395558	0.04787251	0.01052935	0.005992807	0.02329392	0.007543629	0.005397569
5_3	0.03046107	0.01599258	0.02510101	0.0221177	0.003889518	0.0297769	0.04787927	0.009710065	0.006042703	0.02285141	0.006454811	0.002372385
6_1	0.03189229	0.03497424	0.04051586	0.02625159	0.005933742	0.03829771	3.98016E-05	0.02117575	0.006580557	0.03278959	0.00532893	0.004784647
6_2	0.03117691	0.03325593	0.0363518	0.02326305	0.004478761	0.0370575	6.5434E-05	0.01977148	0.005916479	0.02604979	0.005524904	0.002680202
6_3	0.02888749	0.03624616	0.04357059	0.02169182	0.006325253	0.03629374	7.62261E-05	0.01820156	0.006272193	0.03683923	0.006096499	0.003081431
7_1	0.026447	0.02554971	0.02561533	0.01990797	0.004140506	0.01997487	0.09833712	0.01453413	0.02316981	0.02400274	0.009061483	0.002700267
7_2	0.030616	0.02397646	0.0254986	0.01898986	0.004436332	0.0180879	0.09527297	0.01241022	0.02231609	0.02677636	0.007777859	0.006468065
7_3	0.03130558	0.02400894	0.02703929	0.02172699	0.004495207	0.01881848	0.08891628	0.01433193	0.02227807	0.02642615	0.006349198	0.004863702
8_1	0.03318896	0.02227721	0.02463127	0.1117174	0.004302437	0.01279818	0.06852569	0.01198379	0.004625109	0.02365761	0.01207605	0.002740596
8_2	0.03294675	0.02432689	0.02493758	0.1324909	0.005623107	0.01523914	0.07139611	0.01407848	0.005010914	0.03300961	0.01642524	0.002383995
8_3	0.02643442	0.02508993	0.02537685	0.1195791	0.005908849	0.01483161	0.07038679	0.01345495	0.005147206	0.03474193	0.01770737	0.005511131
9_1	0.03038225	0.02254444	0.02750815	0.03103883	0.005031096	0.01606134	0.05406961	0.01636865	0.01204456	0.02880777	0.0140209	0.005650687
9_2	0.03184438	0.02175442	0.02874184	0.02328667	0.006101322	0.01172411	0.05485978	0.01185037	0.01178562	0.03678924	0.01311497	0.005542209
9_3	0.0328438	0.0218139	0.02822438	0.02154824	0.005411776	0.0108334	0.05705928	0.01159136	0.01241161	0.0308478	0.009494092	0.007556525
10_1	0.02961439	0.02037526	0.02026266	0.02624341	0.005251547	0.02075366	5.32574E-05	0.009689189	0.02065856	0.02999021	0.004417457	0.006211277
10_2	0.02868142	0.02161953	0.02028954	0.02529697	0.004979664	0.02172767	0.07014413	0.01074827	0.02124616	0.03073537	0.004208378	0.006730388
10_3	0.03148299	0.02074777	0.01951389	0.02869844	0.005042574	0.02438019	5.35066E-05	0.01181232	0.02023243	0.02964112	0.004706455	0.003471354

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Unknown_16 (2,5-dimethylpyrazines)	Unknown_17	Unknown_18 (galactopyranoside)	Unknown_19	Unknown_20	Unknown_21	Unknown_22	Unknown_23	Unknown_24	Unknown_25	Unknown_26
1_1	0.01504317	0.002113854	0.05206902	0.006426959	0.00196925	0.001468546	0.1797305	0.007941498	0.006569132	0.004521424	0.004181676
1_2	0.014297	0.002118005	0.04982597	0.006454595	0.001796017	0.001290291	0.1772448	0.007739411	0.00647527	0.004675769	0.003793573
1_3	0.01438905	0.00206544	0.05027955	0.006606956	0.001828024	0.001414991	0.1763178	0.007804135	0.006504062	0.00521491	0.004020206
2_1	0.01476746	0.005853102	0.05604511	0.003752363	0.003144597	0.006966943	0.2076547	0.01000743	0.007281754	0.004935697	0.003998625
2_2	0.01338278	0.005646178	0.05458755	0.003835919	0.003434977	0.006563636	0.2000357	0.00964055	0.008239501	0.003504233	0.004565141
2_3	0.01467846	0.005442292	0.05717539	0.003867212	0.003227567	0.007012142	0.2144595	0.00989366	0.007381301	0.004317702	0.004218144
3_1	0.01176169	0.002261	0.03322661	0.004108535	0.000239634	0.002662599	0.1571576	0.005435847	0.006199633	0.005946977	0.002917144
3_2	0.01138981	0.002162714	0.03422298	0.00388777	0.00020908	0.002479333	0.1545052	0.005511774	0.006510864	0.00593657	0.003351572
3_3	0.01136042	0.002353936	0.03648666	0.004453818	0.001754927	0.00276543	0.1703779	0.005177524	0.006965232	0.00372408	0.003772878
4_1	0.01300259	0.002364832	0.04329085	0.002949402	0.001913054	0.001107652	0.1601817	0.0111203	0.004065103	0.007324052	0.004524027
4_2	0.01340008	0.002734986	0.04376642	0.002922944	0.002203707	0.001057963	0.1612836	0.01140082	0.004342302	0.004540803	0.004881073
4_3	0.0131329	0.002639826	0.04002856	0.003068738	0.001527543	0.001197102	0.1613958	0.01174809	0.004033194	0.004767034	0.004331992
5_1	0.01219389	0.002789537	0.04710993	0.000971275	0.001765345	0.002208435	0.1711965	0.007628947	0.006355492	0.005004643	0.003456765
5_2	0.01285057	0.002697791	0.04638223	0.000983643	0.000309175	0.00220157	0.1663294	0.007288463	0.005485841	0.004079205	0.00300137
5_3	0.01164253	0.002824982	0.04573892	0.000873806	0.001604057	0.002265197	0.1614155	0.00697897	0.005875114	0.004088494	0.003406157
6_1	0.01155705	0.002183621	0.04242819	0.00261668	0.001044831	0.001520405	0.1977552	0.01084574	0.003271479	0.004864841	0.003983228
6_2	0.01021076	0.002104184	0.04481273	0.002415682	0.000943569	0.001444239	0.1861017	0.009216816	0.003237993	0.003729777	0.003485162
6_3	0.0100321	0.002154927	0.04833538	0.002464895	0.001047362	0.00168423	0.2036841	0.009433516	0.003762212	0.004913653	0.004246326
7_1	0.01364729	0.00704792	0.02198558	0.004173471	0.005015017	0.01260392	0.1926062	0.008196838	0.006131753	0.001147313	0.004289044
7_2	0.01398172	0.006162391	0.01994106	0.003826344	0.004876279	0.01162547	0.1907702	0.007024873	0.006600827	0.004332993	0.003952005
7_3	0.01484901	0.006487113	0.01957866	0.003863556	0.004222313	0.01196032	0.1881015	0.007545029	0.005741351	0.002436952	0.003697084
8_1	0.009676725	0.004572711	0.006947367	0.002821418	0.002039672	0.004491084	0.1536019	0.01218107	0.006386797	0.004998145	0.004612029
8_2	0.009954598	0.004813489	0.007693667	0.002866861	0.002847545	0.004415433	0.164792	0.01243008	0.007265657	0.005138053	0.005638047
8_3	0.009011632	0.004727411	0.008153733	0.002763873	0.003258826	0.004785127	0.1672378	0.01261114	0.006944868	0.005095518	0.00531425
9_1	0.0113915	0.002826585	0.02782486	0.01913565	0.00143963	0.001916026	0.1740936	0.01095082	0.004724678	0.005145255	0.004962041
9_2	0.01153376	0.002719746	0.02455556	0.01902688	0.002072262	0.001893102	0.1636369	0.01127601	0.005215154	0.006328156	0.005480033
9_3	0.01183389	0.002800061	0.02704166	0.01900363	0.001230361	0.00173275	0.1774186	0.01094188	0.005117001	0.005592991	0.004312667
10_1	0.01170254	0.008609336	0.009783003	0.004527071	0.008900192	0.01781486	0.206547	0.008680698	0.007883084	0.004924443	0.003332578
10_2	0.0122156	0.00884916	0.00997675	0.004694209	0.008497367	0.01853042	0.2177995	0.009226501	0.006791827	0.003922379	0.003282213
10_3	0.01193559	0.007933427	0.009654339	0.004404826	0.008563891	0.01652637	0.2094164	0.008097135	0.007146734	0.002769981	0.002820337

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Unknown_27	Unknown_28	Unknown_29	Unknown_30	Unknown_31	Unknown_32	Unknown_33	Unknown_34 (alpha-1,2-mannobiose)	Unknown_35	Unknown_36	Unknown_37
1_1	0.008622721	0.009299043	0.001442707	0.002814525	0.00673883	0.002368793	0.002975322	0.006396258	0.007054544	0.007084107	0.003133571
1_2	0.008639985	0.008811202	0.001474028	0.002799427	0.005458191	0.002204648	0.003439692	0.006182838	0.00626523	0.007154088	0.002857776
1_3	0.008792853	0.009486912	0.00152979	0.00307887	0.006220521	0.002301638	0.00229441	0.006360504	0.006788584	0.00766207	0.003145738
2_1	0.01059602	0.01169322	0.006394735	0.003263953	0.009764607	0.007333845	0.008437381	0.01009138	0.008489019	0.009376567	0.002755198
2_2	0.01033509	0.01166426	0.005976929	0.003177374	0.008557418	0.006353213	0.008372063	0.008955703	0.007929104	0.008651367	0.00263201
2_3	0.01034473	0.01275026	0.006487782	0.003242987	0.009309543	0.007054249	0.007094472	0.009426636	0.008404257	0.009161034	0.003003034
3_1	0.003094057	0.009910151	0.001716776	0.003068822	0.006241858	0.002422233	0.004345279	0.007409247	0.006760732	0.00782591	0.002652544
3_2	0.003163303	0.009534343	0.001559735	0.002995732	0.006839257	0.002473333	0.004466864	0.00718831	0.006529012	0.007396902	0.002655566
3_3	0.00294711	0.009681981	0.001726768	0.003029159	0.006098068	0.00220014	0.002938808	0.006751711	0.006126854	0.007303372	0.002774986
4_1	0.01885965	0.009739391	0.002122189	0.006125578	0.005908018	0.002598074	0.004205566	0.0106044	0.006162245	0.007523559	0.002415301
4_2	0.01803222	0.01020167	0.002167289	0.006190368	0.00577425	0.002203359	0.002973341	0.0102024	0.006424977	0.007304791	0.002673119
4_3	0.01866577	0.01025887	0.002133418	0.006237779	0.006214494	0.002489133	0.004145039	0.01032646	0.00677786	0.007622868	0.002602172
5_1	0.007519223	0.00731716	0.001933667	0.00425457	0.007438359	0.003494547	0.004460027	0.007998913	0.007057794	0.007688269	0.002569708
5_2	0.007435976	0.008018482	0.002196501	0.00461788	0.00945423	0.004077422	0.00594488	0.008841678	0.008409035	0.009775245	0.003386775
5_3	0.007498384	0.008011265	0.002031957	0.004635949	0.009022167	0.004009035	0.0051344	0.008463977	0.007742359	0.009295039	0.002841122
6_1	0.007577484	0.00812165	0.001844599	0.005418091	0.008254584	0.003220429	0.005748617	0.009575627	0.008683159	0.01023267	0.003660016
6_2	0.007474197	0.007780509	0.001807214	0.005158535	0.008099176	0.002557837	0.004421258	0.009376817	0.007899785	0.008743145	0.003643867
6_3	0.006843416	0.007739725	0.001632644	0.005340247	0.006462739	0.003181201	0.006764621	0.008780814	0.007738931	0.008555499	0.003388527
7_1	0.008163246	0.01144255	0.00522921	0.003972706	0.01279709	0.007348833	0.006527606	0.009848687	0.009677676	0.009733193	0.002764827
7_2	0.00749632	0.01149187	0.005139613	0.003965792	0.01229219	0.007221693	0.006610421	0.00869624	0.008740054	0.009527978	0.002487996
7_3	0.00798397	0.01183137	0.005196955	0.004037525	0.01368869	0.007859309	0.008328313	0.01057495	0.01067662	0.01135545	0.003095459
8_1	0.004389243	0.01135552	0.003703355	0.01189622	0.007297657	0.008126813	0.001058156	0.01186987	0.01111421	0.0130006	0.009946884
8_2	0.004815225	0.01161556	0.003861264	0.01241163	0.007362766	0.008827434	0.001342094	0.0116222	0.01115706	0.01235025	0.009818367
8_3	0.004715544	0.01173203	0.003508148	0.01228583	0.007369598	0.007894577	0.004052981	0.01179238	0.01065709	0.01199789	0.009240272
9_1	0.003434958	0.009021752	0.002868507	0.00395479	0.01455952	0.007207309	0.004673789	0.01001243	0.008510033	0.009434139	0.004281819
9_2	0.003111472	0.008624991	0.002743915	0.003467998	0.01338648	0.006641529	0.005464909	0.009304441	0.007848673	0.008914936	0.004224046
9_3	0.003576735	0.009365678	0.002944277	0.003866072	0.01644007	0.006947865	0.005754977	0.01049115	0.009125161	0.01011185	0.005157114
10_1	0.005983922	0.01152205	0.004331202	0.003097058	0.003203384	0.004872546	0.006399096	0.01001017	0.007359959	0.007816787	0.002065965
10_2	0.006224649	0.01172292	0.004875375	0.003194605	0.003722276	0.005231796	0.006565866	0.01092963	0.008264717	0.008552311	0.002383268
10_3	0.00610117	0.01126725	0.004397424	0.002987629	0.003659789	0.004851029	0.00565351	0.009980576	0.007758103	0.00841227	0.001997265

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Unknown_38	Unknown_39	Unknown_40	Unknown_41	Unknown_42	Unknown_43	Unknown_44	Unknown_45 (D-lactitol)	Unknown_46	Unknown_47	Unknown_48
1_1	0.04397566	0.002519239	0.005297377	0.009935372	0.01400726	0.3845346	0.008168991	0.01223743	0.08567252	0.5324136	0.06007533
1_2	0.0399736	0.002602061	0.00528908	0.009764611	0.01227356	0.3455826	0.007521446	0.01156656	0.07739852	0.5267158	0.05741058
1_3	0.04553311	0.002768378	0.005695793	0.01062932	0.01420589	0.3692139	0.007592767	0.01300687	0.07830057	0.5257761	0.05654046
2_1	0.02849679	0.002309858	0.003534374	0.004344388	0.01063917	0.3177455	0.007095963	0.01129008	0.06756194	0.5206565	0.04890117
2_2	0.02593876	0.002325542	0.003018659	0.003982549	0.009279457	0.3072092	0.007547657	0.01007969	0.06524803	0.5022102	0.05137496
2_3	0.02899777	0.002557505	0.003615569	0.00475554	0.01062594	0.3304867	0.006525582	0.011722	0.07193433	0.5527	0.05677177
3_1	0.05077501	0.002001987	0.005639844	0.001401514	0.003387012	0.3290407	0.007837468	0.01196565	0.05924165	0.4981889	0.0437738
3_2	0.04748078	0.002230882	0.005636262	0.001223955	0.002653203	0.3123603	0.007294087	0.0109856	0.05669476	0.4638116	0.04046781
3_3	0.04625715	0.00219877	0.005338527	0.001335875	0.003045764	0.3026041	0.008457253	0.0113744	0.05916415	0.4767989	0.04109247
4_1	0.04819986	0.002412593	0.007067908	0.0152851	0.02753054	0.3223144	0.007595202	0.01232784	0.07067577	0.5360094	0.05202375
4_2	0.0493702	0.002137359	0.007203108	0.01408186	0.02689674	0.3177489	0.00815375	0.01192055	0.07244863	0.5618266	0.05610456
4_3	0.05177032	0.002380074	0.007342738	0.01602026	0.02940029	0.3156122	0.00755791	0.0124715	0.0707427	0.5704964	0.05321353
5_1	0.03781789	0.002598111	0.00366569	0.002766243	0.007557119	0.3351858	0.01035878	0.008216721	0.0651004	0.4992284	0.05073578
5_2	0.0480995	0.00310059	0.004868991	0.003434702	0.009124376	0.3446566	0.007589569	0.01080552	0.06434792	0.5593442	0.05346106
5_3	0.04293318	0.00249976	0.004269228	0.00319423	0.008807089	0.3349711	0.007985012	0.00968914	0.06636477	0.5497386	0.04898063
6_1	0.05724386	0.003974378	0.008946077	0.007663813	0.01310302	0.2903153	0.007184935	0.009571379	0.06743106	0.580981	0.05623376
6_2	0.05344995	0.00302762	0.007625885	0.007127008	0.01178945	0.2742897	0.007536695	0.008799579	0.06091267	0.5547423	0.049158
6_3	0.05223663	0.003512371	0.00762771	0.006326084	0.01090456	0.2706625	0.009649723	0.00785155	0.06254511	0.5467886	0.04963009
7_1	0.04291225	0.002565902	0.003941659	0.006373979	0.01631467	0.2784264	0.008472616	0.004058328	0.05206664	0.5406008	0.03664061
7_2	0.04149457	0.002202756	0.003695433	0.006123677	0.01567896	0.2594787	0.008769968	0.0033501	0.04824036	0.5147994	0.03626812
7_3	0.04585302	0.002387219	0.004554716	0.007056704	0.01756932	0.2861641	0.007321946	0.004622959	0.05120825	0.5553395	0.03983669
8_1	0.03325394	0.008687537	0.01575458	0.002313321	0.01550487	0.1735125	0.006677554	0.004124607	0.1311802	0.8370578	0.1146646
8_2	0.03163371	0.009435138	0.01657826	0.002142129	0.01522051	0.1733056	0.007476135	0.003479771	0.1384934	0.8760185	0.1212883
8_3	0.03162254	0.009300738	0.01634081	0.002329272	0.01511902	0.1693839	0.007732092	0.003240517	0.1403581	0.8486059	0.1182434
9_1	0.03953062	0.004245992	0.006453181	0.00932685	0.009814658	0.2876206	0.007665034	0.004362092	0.07314109	0.599794	0.06580751
9_2	0.03842136	0.004014793	0.005766119	0.008291932	0.0092899	0.2766637	0.008387827	0.00346718	0.07464638	0.5932297	0.06003724
9_3	0.04412691	0.004562285	0.006784658	0.009541967	0.01100106	0.3080379	0.006775871	0.004656419	0.08030161	0.6451296	0.06468838
10_1	0.03877388	0.00181801	0.005095479	0.002777703	0.007420323	0.3256792	0.008315494	0.001871343	0.07252326	0.5135476	0.05203849
10_2	0.04438893	0.002176632	0.005402657	0.002944224	0.008224898	0.3276873	0.007317942	0.00274626	0.07415342	0.5442914	0.05628836
10_3	0.0414414	0.00179253	0.005213252	0.002658794	0.007426236	0.3225028	0.007527934	0.002554104	0.06852503	0.5359318	0.05494833

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Unknown_49	Unknown_50	Unknown_51	Unknown_52	Unknown_53	Unknown_54	Unknown_55	Unknown_56	Valine
1_1	0.006688172	0.5057243	0.004344904	0.00332903	0.00951144	0.005622344	0.01649388	0.007865746	0.03725926
1_2	0.006366383	0.4548003	0.004268363	0.003032592	0.008520914	0.005641506	0.0160419	0.007739871	0.04084466
1_3	0.006187559	0.5050184	0.004236721	0.002918575	0.009759805	0.005305154	0.0164682	0.008486683	0.03515797
2_1	0.005864313	0.4921796	0.0050603	0.004117378	0.0099202	0.003450688	0.01033236	0.008193498	0.03412877
2_2	0.006603521	0.4669452	0.005677869	0.004294854	0.009238187	0.003311245	0.009605268	0.007590909	0.0355083
2_3	0.00713308	0.5551201	0.004228027	0.003681441	0.009130424	0.003346698	0.009586374	0.007719351	0.04446289
3_1	0.006461459	0.4683403	0.003508562	0.003126804	0.00942884	0.002932284	0.008638663	0.006044757	0.06154268
3_2	0.006563771	0.4373143	0.004610099	0.003657318	0.009388633	0.00292149	0.008764394	0.006037773	0.04977144
3_3	0.007295304	0.441355	0.004320974	0.003402663	0.009595703	0.002815403	0.008781685	0.006135822	0.05292098
4_1	0.00689905	0.5302014	0.003145638	0.002472088	0.007791588	0.004915332	0.01549378	0.005473013	0.03387243
4_2	0.007110191	0.5149986	0.003482956	0.002815159	0.008448643	0.005153761	0.01518647	0.005588609	0.03436458
4_3	0.00660432	0.5434919	0.00320952	0.002488257	0.008145317	0.005232844	0.01506746	0.005554448	0.03141306
5_1	0.007755789	0.4703439	0.008449552	0.004868156	0.009357539	0.002823583	0.008532016	0.006457362	0.02819484
5_2	0.006725866	0.5419497	0.005887829	0.003584241	0.008607678	0.00309463	0.009296094	0.006186462	0.02175587
5_3	0.005987514	0.4891785	0.007109106	0.004138043	0.00971621	0.003188785	0.009016255	0.006450028	0.03132803
6_1	0.007001305	0.5980236	0.005298017	0.004804666	0.009397424	0.003757082	0.01191452	0.004511818	0.04121923
6_2	0.007059934	0.530578	0.004092715	0.003715173	0.008720723	0.00340909	0.01006143	0.003800245	0.03354065
6_3	0.008020065	0.5427348	0.005814081	0.00551938	0.00843226	0.003852686	0.01108891	0.004170062	0.03873392
7_1	0.007551986	0.4979616	0.009326533	0.004276007	0.01405246	0.003546902	0.01111866	0.0330158	0.02398172
7_2	0.00678507	0.4775548	0.009305171	0.004456691	0.01179154	0.003372082	0.01021981	0.02864467	0.02351612
7_3	0.006972154	0.4948251	0.007834501	0.003957071	0.01489835	0.003625905	0.01103028	0.03052995	0.02279171
8_1	0.008734028	0.9204301	0.002374388	0.002501661	0.00786494	0.00143568	0.004512795	0.009294598	0.1222604
8_2	0.008804911	0.9418702	0.002932619	0.003157546	0.008245498	0.001437354	0.004633231	0.01064507	0.1092337
8_3	0.009969252	0.9344653	0.002618755	0.002989574	0.008203952	0.001705174	0.005310784	0.01086599	0.113779
9_1	0.007370029	0.6092487	0.00492928	0.002162084	0.0094223	0.003878864	0.0116128	0.01854699	0.03899748
9_2	0.008206251	0.5821009	0.005818316	0.002270093	0.00877702	0.003812596	0.01106594	0.01688352	0.03525243
9_3	0.007320461	0.6407731	0.004863009	0.002614433	0.009573765	0.004421971	0.0120004	0.01710361	0.04053907
10_1	0.006939116	0.4915065	0.00406106	0.002154715	0.01344786	0.003019875	0.008300715	0.02915442	0.03758683
10_2	0.006631309	0.5287055	0.003983234	0.002137825	0.01437913	0.002996797	0.008952983	0.02903286	0.04316545
10_3	0.007024642	0.5098739	0.00341958	0.001972736	0.01398247	0.002858686	0.008197141	0.03039096	0.03582025

Table S18 Data matrix of 10 different green coffee bean samples (cont.)

Metabolite name	Xylitol	Xylonic acid	Final Score	Fragrance /Aroma	Flavor	Aftertaste	Acidity	Body	Balance	Overall
1_1	0.002085584	0.004728685	86.75	8.5	8	7.75	8	8.5	8	8
1_2	0.002168237	0.004394172	86.75	8.5	8	7.75	8	8.5	8	8
1_3	0.002174032	0.004691596	86.75	8.5	8	7.75	8	8.5	8	8
2_1	0.003528712	0.006704526	84.5	7.75	7.75	7.75	7.75	8	7.75	7.75
2_2	0.003519162	0.006573552	84.5	7.75	7.75	7.75	7.75	8	7.75	7.75
2_3	0.003463752	0.006738349	84.5	7.75	7.75	7.75	7.75	8	7.75	7.75
3_1	0.00182361	0.004404764	84.25	8	8	7.75	7.5	8	7.5	7.5
3_2	0.002005717	0.003859348	84.25	8	8	7.75	7.5	8	7.5	7.5
3_3	0.001899441	0.004395151	84.25	8	8	7.75	7.5	8	7.5	7.5
4_1	0.001407986	0.004902433	83	7.75	7.75	7.5	7.5	7.5	7.5	7.5
4_2	0.001443765	0.004874894	83	7.75	7.75	7.5	7.5	7.5	7.5	7.5
4_3	0.001515284	0.004949807	83	7.75	7.75	7.5	7.5	7.5	7.5	7.5
5_1	0.00345951	0.005277848	82.75	8.5	8.25	8	8.5	8	3	8.5
5_2	0.003222476	0.005769836	82.75	8.5	8.25	8	8.5	8	3	8.5
5_3	0.003450767	0.00597429	82.75	8.5	8.25	8	8.5	8	3	8.5
6_1	0.001238097	0.00475869	82.75	7.75	7.5	7.5	7.5	7.5	7.5	7.5
6_2	0.00125419	0.004938819	82.75	7.75	7.5	7.5	7.5	7.5	7.5	7.5
6_3	0.001130088	0.004648014	82.75	7.75	7.5	7.5	7.5	7.5	7.5	7.5
7_1	0.0304937	0.01219292	82.75	7.75	7.25	7.25	7.5	8	7.5	7.5
7_2	0.02853804	0.01152477	82.75	7.75	7.25	7.25	7.5	8	7.5	7.5
7_3	0.02938852	0.0119793	82.75	7.75	7.25	7.25	7.5	8	7.5	7.5
8_1	0.05199672	0.006140114	81.5	7.5	7	7	7	8	7.5	7.5
8_2	0.05466937	0.006463396	81.5	7.5	7	7	7	8	7.5	7.5
8_3	0.05542057	0.006260229	81.5	7.5	7	7	7	8	7.5	7.5
9_1	0.008633974	0.005339494	80.5	8	7.25	7	7	7.25	7	7
9_2	0.008420299	0.005482489	80.5	8	7.25	7	7	7.25	7	7
9_3	0.008663396	0.005714116	80.5	8	7.25	7	7	7.25	7	7
10_1	0.01284155	0.007649682	80.25	7.5	7	7	7	7.75	7	7
10_2	0.01398592	0.007303088	80.25	7.5	7	7	7	7.75	7	7
10_3	0.01220529	0.007134765	80.25	7.5	7	7	7	7.75	7	7

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method

Metabolite name	Alanine	Asparagine	Aspartic acid	Glutamic acid	Glycine	Isoleucine	Leucine	Lysine	Phenylalanine	Proline	Pyroglutamic acid	Serine
400-DB	0.117839	0.09177326	0.07803469	0.1039995	0.1951186	0.05557378	0.07790178	0.09236801	0.04812463	0.04463737	0.1304415	0.0246394
400-DB	0.1140101	0.08408859	0.05804001	0.09440661	0.1829397	0.04964713	0.06343701	0.08837667	0.04421223	0.0366859	0.2159289	0.02003448
400-DB	0.09127099	0.07821588	0.05180931	0.09120097	0.1802295	0.0368936	0.05220227	0.087105	0.03597497	0.03228118	0.1062125	0.01543269
400-HB	0.177626	0.09402367	0.07553315	0.2393861	0.08516011	0.04844961	0.0440882	0.04502074	0.03456732	0.05385746	0.1620968	0.02499771
400-HB	0.2356112	0.1010096	0.0974089	0.2645972	0.07881043	0.05402632	0.0515075	0.04036835	0.04606496	0.06374485	0.1589919	0.03405096
400-HB	0.2043643	0.0993866	0.1035074	0.2679303	0.08120389	0.05082666	0.05064654	0.04242044	0.04939542	0.06480931	0.1384896	0.03307594
400-WB/BM	0.1766438	0.1021462	0.08579716	0.1867344	0.08996478	0.05717643	0.06206666	0.05164764	0.05900981	0.04902407	0.1045608	0.02396986
400-WB/BM	0.1623746	0.08628967	0.07312985	0.1700808	0.09080753	0.05221951	0.05259906	0.05321665	0.0486263	0.05263008	0.09755838	0.02113795
400-WB/BM	0.1499077	0.08207942	0.06015829	0.1605287	0.08962576	0.05056902	0.04816342	0.05361828	0.04100373	0.03843907	0.1135461	0.02094677
800-DK	0.2651487	0.1515962	0.1075383	0.1919933	0.1813302	0.05770277	0.06116481	0.06862431	0.04836085	0.1138133	0.2517677	0.0450865
800-DK	0.315776	0.1570795	0.1213967	0.2266383	0.1943992	0.06865768	0.07635136	0.07589103	0.05735754	0.1463498	0.2478254	0.06007325
800-DK	0.2926661	0.1607431	0.1256856	0.2149853	0.1951787	0.06697092	0.07552988	0.07951036	0.05717525	0.1375052	0.2746991	0.05620342
800-HK	0.2816791	0.1033117	0.1348052	0.3642028	0.100128	0.05862344	0.06437249	0.04382541	0.06310905	0.1064898	0.1709429	0.04195282
800-HK	0.271506	0.1213405	0.1356514	0.329666	0.09515801	0.05635996	0.06021326	0.04432822	0.06182914	0.1010556	0.1552744	0.03591667
800-HK	0.2237205	0.1087982	0.1271762	0.369261	0.1020749	0.05237057	0.05316161	0.05762454	0.06172375	0.09147783	0.2061396	0.03466741
800-WK/KB	0.2173627	0.117156	0.1422164	0.4095419	0.05589971	0.04446382	0.03838197	0.03015281	0.04866906	0.06834606	0.1704342	0.02888703
800-WK/KB	0.1604839	0.09689482	0.1071144	0.341317	0.05416783	0.03378253	0.02708174	0.02516954	0.03583728	0.04594636	0.1630136	0.02085961
800-WK/KB	0.1604726	0.1108848	0.1048334	0.3464724	0.05447531	0.03203497	0.02730637	0.02564138	0.0406034	0.04521239	0.1396218	0.01966517
1000-B	0.2118402	0.1074812	0.1370228	0.3876305	0.07226645	0.02793694	0.02340483	0.02024338	0.03138174	0.04435116	0.1358297	0.02993117
1000-B	0.2173723	0.11079	0.1476215	0.3827967	0.06884244	0.02533378	0.02025979	0.02055723	0.03795071	0.04035506	0.1295442	0.03189411
1000-B	0.1885519	0.08352555	0.10462	0.2904246	0.0613434	0.02314854	0.0162972	0.02056369	0.02636689	0.03432283	0.1400899	0.02421173
1000-AG	0.1833517	0.1033181	0.1009089	0.329226	0.05921277	0.02546426	0.01625565	0.02675855	0.02790091	0.0349564	0.1160436	0.02630669
1000-AG	0.1664515	0.1042576	0.1061029	0.370835	0.06797782	0.02101143	0.01707469	0.02440329	0.02906623	0.03114022	0.1391588	0.0232298
1000-AG	0.1510958	0.09442674	0.09347376	0.3290301	0.06423239	0.02170345	0.01447929	0.02310433	0.02637351	0.03091724	0.1425734	0.02244809
1200-B	0.2439859	0.1554485	0.1651672	0.5191506	0.0527637	0.04609192	0.03399626	0.0413379	0.05207924	0.07370115	0.1646393	0.05157121
1200-B	0.2064975	0.142438	0.140337	0.4880545	0.05947595	0.0377439	0.0339722	0.03601054	0.04992552	0.07403698	0.1316217	0.04715423
1200-B	0.2318557	0.1473596	0.1426386	0.5082757	0.06236231	0.04708203	0.02691997	0.03822456	0.05449988	0.06790707	0.1550674	0.05170658
1200-AS	0.3263082	0.1048891	0.07822433	0.2164589	0.1130724	0.01937226	0.01956884	0.03157655	0.02615675	0.02967509	0.1193184	0.02455027
1200-AS	0.3188896	0.1058933	0.07773197	0.2430166	0.1232892	0.01903339	0.02233676	0.03568692	0.02840921	0.03288546	0.152035	0.02979882
1200-AS	0.3930931	0.1174572	0.09388704	0.2576213	0.1171906	0.02222713	0.02213655	0.03094228	0.03502773	0.03716707	0.1163165	0.03154069
1200-F	0.1631406	0.1945391	0.1860832	0.5336106	0.0586445	0.02559783	0.02162703	0.03226239	0.04415436	0.0419575	0.2130809	0.08918266
1200-F	0.1700827	0.2384761	0.1876345	0.647008	0.05787168	0.0272766	0.02188073	0.03158189	0.0499216	0.04853813	0.2008158	0.07936578
1200-F	0.1380429	0.203667	0.1713439	0.5477788	0.06101025	0.02772552	0.01775096	0.02887526	0.04830884	0.03268831	0.2602471	0.07426386
1400-B	0.196891	0.1462096	0.1311637	0.2986345	0.0587534	0.03532133	0.01811957	0.0276289	0.05863849	0.05111915	0.1255773	0.02384533
1400-B	0.213123	0.141099	0.1415179	0.3046895	0.05071454	0.03642396	0.01807494	0.02860156	0.06701272	0.04988421	0.1269815	0.0305709
1400-B	0.2022747	0.1526071	0.1490818	0.3016829	0.06354954	0.03283158	0.01706916	0.02563711	0.06251854	0.05245517	0.1288916	0.03070175
1400-M1	0.1563018	0.1428743	0.0959785	0.2172275	0.07142853	0.02672137	0.03108638	0.02456459	0.03852222	0.0411679	0.06889631	0.02988811
1400-M1	0.1281076	0.1149142	0.07541987	0.2027756	0.059122	0.02379213	0.02274395	0.02486066	0.03142275	0.03304959	0.09012636	0.0215946
1400-M1	0.130685	0.130571	0.06543158	0.2126574	0.05776036	0.02320296	0.02314359	0.02673833	0.02978283	0.02918969	0.07764781	0.02638444
1400-M2	0.1564775	0.1234276	0.09650651	0.2677442	0.09135056	0.02455382	0.02692305	0.03346767	0.03761817	0.0389385	0.109251	0.03597247
1400-M2	0.1683381	0.1243254	0.09106715	0.26858	0.07861289	0.02793322	0.02435921	0.02926137	0.03397545	0.04153778	0.08195706	0.03765704
1400-M2	0.1637403	0.1156743	0.09239521	0.2774797	0.08114075	0.02583093	0.02508156	0.02656576	0.03746492	0.03562997	0.1046806	0.03376253
1600-B	0.1116163	0.07909925	0.08567806	0.2733942	0.05457591	0.02779058	0.02098221	0.02457533	0.05054446	0.03261032	0.1083091	0.02623043
1600-B	0.1131363	0.07233182	0.07863212	0.3202208	0.0585097	0.03005615	0.02520793	0.02440481	0.05960065	0.03958662	0.1422032	0.03373169
1600-B	0.1272839	0.09236804	0.1020085	0.33635	0.06379066	0.03626693	0.03004026	0.0313427	0.07163524	0.04377254	0.1400681	0.03318966
1600-M1	0.2650865	0.2416253	0.1012578	0.3786367	0.06942807	0.03041679	0.03116552	0.0338813	0.04747087	0.04359779	0.116313	0.03464015
1600-M1	0.2128497	0.198853	0.09688116	0.3252656	0.07145374	0.02841748	0.02603988	0.03471306	0.04230313	0.03840762	0.1360789	0.0308914
1600-M1	0.297363	0.240954	0.1239055	0.3778301	0.06865369	0.03113933	0.03198614	0.03329039	0.06137833	0.05431363	0.1026718	0.04070777
1600-M2	0.2219782	0.1290405	0.1006134	0.402825	0.05508898	0.03337924	0.02875196	0.03546605	0.04309886	0.04027757	0.1196596	0.03327904
1600-M2	0.211512	0.1348326	0.0845765	0.3556845	0.05349063	0.02973119	0.02971022	0.03186478	0.03822779	0.03691055	0.1013088	0.03205411
1600-M2	0.2427484	0.1312592	0.09377726	0.3796251	0.06309424	0.0355952	0.03223728	0.03226124	0.0392158	0.0451616	0.1190603	0.03691103

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method (cont.)

Metabolite name	Tryptophan	Tyrosine	Valine	Chlorogenic acid	Fumaric acid	Glucarate	Gluconic acid	Glyceric acid	Glycolic acid	Citric acid	Lactic acid	Malic acid
400-DB	0.2559143	0.1290933	0.09139512	14.7335	0.03852701	0.0535218	0.3592571	0.03229737	0.06769023	4.98988	0.3830858	2.096932
400-DB	0.2374748	0.1358849	0.09497366	14.37821	0.03697607	0.05872075	0.3993488	0.03710108	0.08115409	5.094843	0.3020603	2.238024
400-DB	0.1590932	0.1261621	0.07409169	13.15179	0.03352574	0.06178396	0.3416509	0.02849242	0.0670865	4.761033	0.2353549	2.016639
400-HB	0.1144173	0.1178509	0.07809699	16.22447	0.00778142	0.03732715	0.03425613	0.01457009	0.01951636	5.710635	0.2259273	2.164011
400-HB	0.1138838	0.1147367	0.09627333	14.946	0.008939163	0.03598609	0.02910023	0.0137839	0.02188502	5.563939	0.5208998	2.074644
400-HB	0.09765998	0.1096763	0.08580326	16.14405	0.009601647	0.03752955	0.02803681	0.01097858	0.01772301	5.436934	0.2608314	2.128219
400-WB/BM	0.3524836	0.1288444	0.09397934	14.01771	0.007943672	0.0363983	0.03233233	0.01148066	0.01669457	4.651245	0.3607955	1.982525
400-WB/BM	0.1932678	0.1302822	0.09308103	14.7473	0.008693227	0.03834808	0.03454404	0.0181981	0.014194	4.499258	0.2559355	2.075114
400-WB/BM	0.2879302	0.1354932	0.07932685	15.75181	0.007364153	0.03395712	0.03375951	0.01587314	0.01555902	4.693004	0.3177518	2.017575
800-DK	0.1638815	0.1644113	0.1086781	14.55642	0.06597352	0.06771893	0.1595054	0.03912687	0.06620766	5.442229	0.3105137	2.214498
800-DK	0.1502777	0.1603446	0.1399825	15.01358	0.06866832	0.07921831	0.1428578	0.04488256	0.06065837	5.321452	0.2805334	2.264908
800-DK	0.2090732	0.1703315	0.1273876	14.99398	0.06707556	0.06954067	0.1578201	0.05022597	0.06403279	5.51726	0.4336415	2.284688
800-HK	0.1064084	0.1508795	0.09586429	15.83766	0.01003923	0.03162311	0.03014891	0.012134	0.0144504	5.017606	0.1595702	2.172801
800-HK	0.1038295	0.1409216	0.09874097	12.69691	0.007194472	0.03936558	0.02689028	0.009541323	0.01212325	4.646197	0.2147044	2.029389
800-HK	0.1394909	0.1462579	0.08278666	15.89699	0.007465483	0.04267538	0.02028165	0.01399432	0.01294629	5.349401	0.2389288	2.147051
800-WK/KB	0.09797713	0.08167338	0.0704316	14.09671	0.007373824	0.03207839	0.02258372	0.005934412	0.009830818	5.221074	0.2632671	2.452825
800-WK/KB	0.05748866	0.07473302	0.06179111	15.05778	0.01045922	0.03146916	0.02068844	0.005652572	0.01147539	4.988211	0.2414948	2.317568
800-WK/KB	0.06343143	0.07196537	0.05404747	14.26758	0.007884957	0.03233669	0.02196698	0.007405367	0.01019581	4.998182	0.2678468	2.327243
1000-B	0.09591883	0.05282454	0.04774462	17.7315	0.006507741	0.03488871	0.02140117	0.009993615	0.01664289	4.277158	0.5157553	2.643184
1000-B	0.09349892	0.05448855	0.0456994	16.27167	0.005584199	0.03615535	0.02337614	0.01007064	0.01277243	4.502831	0.1809681	2.745205
1000-B	0.08354276	0.05026133	0.04190072	13.58822	0.007704259	0.02884956	0.01893932	0.009412521	0.01868576	3.925846	0.3394924	2.411265
1000-AG	0.06750258	0.06100148	0.04621005	16.36339	0.0139276	0.02715546	0.07011893	0.007878635	0.01374976	4.02041	0.1723604	2.259701
1000-AG	0.08926281	0.06099667	0.04220532	17.57044	0.01795234	0.02612475	0.06317895	0.008779601	0.01675996	4.219182	0.1988263	2.30024
1000-AG	0.07932246	0.05785913	0.03447424	14.82305	0.01458526	0.02515168	0.06118353	0.008421452	0.01132277	3.689527	0.2580914	2.122309
1200-B	0.1025227	0.08844314	0.08360725	17.19239	0.008933297	0.02886182	0.02007959	0.00680493	0.01304228	4.314259	0.3057017	2.750331
1200-B	0.05276656	0.08132415	0.06891643	19.3117	0.009933445	0.02810038	0.02413066	0.008420272	0.01552332	4.094368	0.4058169	2.762685
1200-B	0.08800066	0.0952367	0.08039406	20.85591	0.01027629	0.03077233	0.02389468	0.007107704	0.01346761	4.44668	0.2993717	2.856239
1200-AS	0.1656954	0.07316456	0.03736243	12.65755	0.04680156	0.02144491	0.05220976	0.02320807	0.01189576	3.424752	0.275703	1.472561
1200-AS	0.1782752	0.07967935	0.04390124	14.60688	0.05382545	0.02679225	0.06104359	0.0235257	0.01016343	3.676256	0.2366972	1.6954
1200-AS	0.1655977	0.07212415	0.04175099	11.92712	0.04868643	0.02416266	0.06109736	0.02485879	0.01096821	3.449965	0.2237786	1.570417
1200-F	0.1053878	0.05533012	0.04826248	17.91288	0.007738274	0.0340677	0.0308288	0.0104344	0.01548306	3.754858	0.3800216	2.335073
1200-F	0.0991952	0.0578187	0.04714786	20.07401	0.009261556	0.04060788	0.03700303	0.01458	0.01590777	4.103763	0.3478379	2.670534
1200-F	0.1026048	0.05988206	0.04439923	20.98374	0.01136107	0.04390832	0.04039026	0.0144025	0.01460066	3.999612	0.3595227	2.636193
1400-B	0.0539178	0.07295576	0.05049479	17.93211	0.01603829	0.03228162	0.03359801	0.01122314	0.01229647	4.358912	0.1625514	2.653181
1400-B	0.0606143	0.07409997	0.06049317	18.46839	0.01880367	0.03257485	0.03307361	0.009484451	0.01146831	4.236408	0.2250122	2.652054
1400-B	0.0802894	0.08003921	0.05762281	15.86271	0.01379984	0.03375767	0.03580099	0.00969672	0.01326842	4.178913	0.1538699	2.636859
1400-M1	0.06625385	0.05582408	0.0507146	16.99877	0.01236344	0.04450013	0.02298152	0.008199017	0.01234765	3.73691	0.2461439	1.807616
1400-M1	0.06647799	0.05005148	0.03926998	19.97714	0.01432658	0.05009656	0.02692294	0.01031197	0.01379327	3.897684	0.4061024	1.823809
1400-M1	0.06148531	0.04922264	0.03951743	18.57503	0.01349158	0.03625542	0.02247872	0.008719077	0.0140618	3.945266	0.273151	1.805888
1400-M2	0.1267777	0.06599934	0.04452442	19.60072	0.01208628	0.05008987	0.01963	0.007923052	0.008685033	5.199481	0.1447216	2.002221
1400-M2	0.1167058	0.05918211	0.04606102	16.97931	0.01038707	0.04683932	0.0189133	0.00723541	0.01251676	4.746504	0.3497997	1.799079
1400-M2	0.09725299	0.05749267	0.04385562	19.61489	0.01441092	0.0536142	0.02153389	0.008388634	0.01138411	4.826285	0.2284913	2.001132
1600-B	0.05197327	0.06048983	0.04915503	15.09881	0.01254445	0.03319367	0.03437679	0.007833339	0.01657043	3.91194	0.2508614	2.677011
1600-B	0.07596581	0.07704918	0.05474457	17.92981	0.01098171	0.03818649	0.03669145	0.01115413	0.01554013	4.404533	0.2712986	3.036747
1600-B	0.09124225	0.07270322	0.06745486	16.30323	0.01116037	0.03488347	0.03770199	0.01009022	0.01420415	4.350583	0.4719269	2.803401
1600-M1	0.08897107	0.06289422	0.05041241	18.9347	0.008364076	0.03949128	0.08196132	0.009700621	0.01747141	4.477656	0.3083225	1.566711
1600-M1	0.1250172	0.06261547	0.04179502	18.7865	0.01070187	0.04258167	0.07633844	0.01037384	0.01454092	4.38927	0.384298	1.617054
1600-M1	0.1146718	0.05552488	0.05846786	17.76401	0.007305611	0.03320663	0.06062004	0.00894181	0.0147017	4.591912	0.3310921	1.584997
1600-M2	0.0376678	0.05654234	0.05174056	18.06366	0.01095284	0.03651975	0.07792506	0.007356441	0.01100349	3.737894	0.2342839	1.575241
1600-M2	0.03943059	0.04703175	0.04895144	15.07207	0.008491802	0.04008636	0.07073486	0.006193749	0.01586319	3.308439	0.3594984	1.41451
1600-M2	0.03907529	0.05835867	0.05588645	16.89659	0.01079112	0.03813663	0.08511874	0.009449257	0.01470992	3.81084	0.2928947	1.612557

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method (cont.)

Metabolite name	Quinic acid	Succinic acid	Fructose	Galactose	Galactose+Glucose	Glucose	Maltose	Melezitose	Raffinose	Sorbose	Sucrose	Galactinol
400-DB	4.65943	0.302208	0.7483746	0.05615462	0.05373228	0.3009171	0.03736283	0.02448175	0.06423272	1.342515	66.16897	0.109345
400-DB	4.898037	0.3086264	0.7772606	0.05259776	0.05792717	0.3212746	0.03684032	0.02429795	0.0686762	1.416459	68.14067	0.1133421
400-DB	4.579365	0.2717252	0.6788468	0.05112895	0.04793044	0.273093	0.03118914	0.02417608	0.05985117	1.239832	64.19293	0.09864445
400-HB	4.773921	0.1101195	0.08441287	0.01562722	0.006939841	0.0449329	0.03151793	0.03390975	0.08913135	0.1605854	66.77605	1.325124
400-HB	4.654214	0.09928728	0.08260596	0.01405485	0.008325303	0.04006474	0.02530885	0.0358156	0.08308531	0.1422329	68.59079	1.225033
400-HB	4.779124	0.1018545	0.07366583	0.01639485	0.007794099	0.03584421	0.03793053	0.03541968	0.0795094	0.1464441	68.03534	1.267548
400-WB/BM	5.124784	0.09456623	0.05169335	0.01206954	0.004994998	0.03448769	0.03425742	0.03898864	0.1254582	0.09335098	71.57663	0.3746229
400-WB/BM	5.055946	0.09242924	0.04982635	0.01088189	0.009513104	0.03176216	0.04570355	0.03265389	0.1213221	0.08935265	75.05778	0.350856
400-WB/BM	5.325395	0.09723435	0.05142999	0.0125186	0.005365198	0.03249303	0.04312633	0.03697469	0.13844	0.08315771	71.90062	0.3693725
800-DK	5.9846	0.3276836	0.7842812	0.0939546	0.05164032	0.2867679	0.02790433	0.02567925	0.1049085	1.393816	61.39715	0.1146114
800-DK	5.869924	0.3172939	0.7443907	0.0874094	0.05128351	0.2747414	0.02742156	0.03178738	0.1093443	1.335678	60.14792	0.1170671
800-DK	6.077082	0.3393723	0.7805061	0.08250266	0.05236141	0.2827758	0.02989529	0.02500032	0.1176444	1.403312	60.70111	0.1275573
800-HK	5.623213	0.1506896	0.06868721	0.01606315	0.007978748	0.03057265	0.04079142	0.03581432	0.09955453	0.1211008	70.73524	1.438797
800-HK	5.559454	0.1393779	0.06796241	0.01528783	0.00832676	0.03175609	0.02499119	0.02463746	0.08447573	0.1216892	71.0463	1.27601
800-HK	5.325642	0.1526007	0.06677154	0.01377428	0.007922669	0.03697427	0.03867887	0.03324587	0.1033935	0.1211917	70.75516	1.548266
800-WK/KB	5.145824	0.08193837	0.02766878	0.01463493	0.004928217	0.02513949	0.03674189	0.03002501	0.102477	0.04934821	70.03799	1.108914
800-WK/KB	4.729759	0.07768878	0.03068019	0.01184949	0.007369631	0.02599492	0.04534942	0.03106082	0.09296771	0.04965374	70.95467	1.046439
800-WK/KB	4.742495	0.07908117	0.02840638	0.01225754	0.00662971	0.02509873	0.04087289	0.03193967	0.09904721	0.05030973	67.7112	1.070027
1000-B	4.432765	0.1131056	0.159471	0.0986543	0.0197111	0.09619939	0.02462091	0.03324471	0.1096714	0.3016115	71.0883	0.6001178
1000-B	4.492457	0.1115875	0.172285	0.00670482	0.01987769	0.09785866	0.02073333	0.0265368	0.08489969	0.31822	73.92763	0.5987366
1000-B	3.746367	0.1058677	0.1723767	0.00612103	0.01884709	0.1054608	0.02040209	0.02603347	0.08956295	0.3120626	66.56256	0.5277705
1000-AG	4.872335	0.08980507	0.08899488	0.03810152	0.01575436	0.06431836	0.02161782	0.03105976	0.1146269	0.1563732	67.15025	0.4662067
1000-AG	5.023819	0.0846151	0.09104377	0.0329976	0.014433	0.06713655	0.02862543	0.03435187	0.1220433	0.1695782	69.39108	0.5497388
1000-AG	4.799576	0.08644176	0.07862104	0.03044702	0.01078033	0.05948926	0.01974785	0.02994976	0.1011255	0.1354516	66.7692	0.453907
1200-B	4.27173	0.09542284	0.05616838	0.01359966	0.009762481	0.04590888	0.02253241	0.02796896	0.1183169	0.1117058	71.55934	1.16253
1200-B	4.19553	0.09092983	0.05836087	0.01417417	0.008140098	0.04966781	0.034151	0.02685083	0.1397025	0.1119307	73.26714	1.151218
1200-B	4.457754	0.09785705	0.06280828	0.01489059	0.01263001	0.0534544	0.03251849	0.02882772	0.1342833	0.1109835	73.15358	1.207811
1200-AS	4.727195	0.08446115	0.3287643	0.04069024	0.04399918	0.2311235	0.02666113	0.02162868	0.07477176	0.5909737	55.1861	0.08578111
1200-AS	5.413226	0.09362707	0.3721588	0.04807624	0.04830112	0.2649542	0.033485	0.02840724	0.09013315	0.6781216	58.07753	0.09002861
1200-AS	5.112623	0.08681425	0.3545235	0.04404467	0.04757996	0.2543696	0.0231096	0.0214003	0.07653575	0.6400424	58.06919	0.0799433
1200-F	4.250038	0.1092548	0.0809611	0.02310384	0.009572293	0.04802009	0.01684267	0.02504055	0.211225	0.1375224	66.70183	0.7598839
1200-F	4.522305	0.1157197	0.08088538	0.02421106	0.01000736	0.04757632	0.01811503	0.02669598	0.2451593	0.138957	65.10062	0.8699154
1200-F	4.536459	0.1197185	0.08478726	0.02311985	0.01324549	0.05918908	0.01916294	0.02778597	0.2445006	0.1402657	67.36604	0.8904145
1400-B	4.040058	0.08182894	0.03862944	0.01531717	0.007419412	0.0321814	0.04273469	0.02957656	0.1720069	0.07336845	73.70483	0.5262477
1400-B	4.021016	0.08362126	0.0496534	0.008031724	0.008522107	0.03739802	0.03643009	0.03174536	0.1869915	0.0921735	69.29327	0.5282648
1400-B	3.964747	0.07727852	0.03682211	0.009474536	0.007827519	0.03917687	0.02300413	0.02695703	0.1590037	0.06702895	68.76289	0.474049
1400-M1	4.454571	0.099378	0.1157263	0.2646385	0.0791249	0.1239271	0.01914605	0.02857346	0.1141117	0.2019394	69.40705	0.2705845
1400-M1	4.278568	0.09460252	0.1059247	0.2623837	0.07246857	0.1114224	0.0275772	0.03333631	0.1188757	0.1826526	66.62309	0.3056026
1400-M1	4.414678	0.09581079	0.1016447	0.25789	0.07973117	0.1279221	0.02362357	0.03081864	0.1294453	0.1871942	69.07069	0.3211159
1400-M2	5.22266	0.1029955	0.08113464	0.2902569	0.07810248	0.1018976	0.03060097	0.03815908	0.155365	0.148259	70.48166	0.2896792
1400-M2	5.288722	0.1006704	0.07002085	0.2885371	0.07935994	0.09928055	0.01531882	0.03678055	0.134424	0.129919	70.43269	0.2462448
1400-M2	5.09953	0.1041799	0.07641262	0.2594111	0.07361859	0.1033639	0.02531406	0.04005266	0.1437123	0.1344199	72.77776	0.2661805
1600-B	4.560719	0.07113649	0.08711782	0.01445566	0.01014922	0.06021868	0.03715425	0.02363272	0.1144813	0.1479902	66.9606	0.6974835
1600-B	4.712169	0.08369824	0.08389763	0.01551655	0.01387211	0.05914518	0.03856896	0.02830837	0.1260877	0.1545103	71.93213	0.8371832
1600-B	4.521836	0.08157096	0.08439137	0.06389789	0.01249035	0.06350759	0.03410773	0.02664264	0.1266124	0.1528718	69.80341	0.7917796
1600-M1	4.649773	0.1107775	0.4639654	0.06150267	0.04761071	0.2527139	0.02239205	0.03174266	0.08307402	0.7999279	69.68214	1.238864
1600-M1	4.561718	0.1111347	0.4102801	0.05669395	0.04344056	0.2253242	0.02633554	0.03026155	0.08511544	0.7115248	67.22663	1.23676
1600-M1	4.722272	0.1079819	0.3577315	0.05348334	0.03817126	0.1971733	0.01550425	0.0260282	0.07339869	0.6308473	71.93234	1.190668
1600-M2	5.173352	0.07277705	0.3198301	0.05182183	0.04333237	0.2023639	0.0303712	0.02126332	0.08496422	0.599015	69.42966	1.109998
1600-M2	4.625041	0.06400817	0.3180363	0.04879356	0.03266255	0.1858985	0.01969088	0.02359736	0.06594492	0.5682179	70.58224	0.8516793
1600-M2	5.208483	0.07875938	0.3190575	0.04696347	0.03446189	0.2080336	0.02922637	0.02000579	0.08790454	0.5532504	73.01077	0.9169704

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method (cont.)

Metabolite name	Inositol	Mannitol	Meso-erythritol	Sorbitol	Threitol	Xylitol	2-Aminoethanol	4-Aminobutyric acid	Caffeine	Glycerol	N-Methylnicotinate	Phosphate
400-DB	0.6821902	1.187832	0.01428521	0.09735645	0.02932977	0.009290936	0.04226007	1.370565	1.003295	2.213524	0.1093119	0.7755775
400-DB	0.7189463	1.192839	0.01759943	0.09024807	0.04007971	0.01025269	0.05023087	1.453606	1.067533	2.547415	0.1186652	0.8335791
400-DB	0.6627191	1.124934	0.01426195	0.09057435	0.02682586	0.007512403	0.04299156	1.281078	0.922036	2.020917	0.1065864	0.7447624
400-HB	0.6556771	0.3140466	0.009865169	0.02944148	0.01613388	0.007837456	0.05163348	0.458595	0.8265084	0.2663343	0.1196245	0.5035563
400-HB	0.6334877	0.2947602	0.01200652	0.02130244	0.01497398	0.00451843	0.04554769	0.3989517	0.8126164	0.4370567	0.1479845	0.4858151
400-HB	0.6053507	0.3076221	0.009735488	0.01672432	0.01285956	0.008614049	0.047648	0.4206023	0.7839355	0.2757238	0.1089248	0.4618636
400-WB/BM	0.490333	0.5911964	0.008980889	0.02399115	0.01397702	0.004376302	0.06339577	1.475314	1.051416	0.3521528	0.1273611	0.5728109
400-WB/BM	0.4928169	0.56635	0.009032574	0.02277042	0.01535987	0.006169335	0.0761903	1.404645	0.9923014	0.3274224	0.09725607	0.5496752
400-WB/BM	0.5152409	0.609671	0.007988114	0.0239809	0.01724442	0.006002293	0.06573481	1.422101	1.054749	0.3449456	0.1181617	0.5791801
800-DK	1.539107	0.420174	0.01853394	0.06875922	0.03788152	0.008269249	0.05716044	1.060271	0.9817362	0.7572669	0.1768794	1.088348
800-DK	1.561302	0.4477652	0.01721488	0.05860886	0.03736025	0.01011208	0.06450348	1.042842	1.0407	0.7402949	0.1495184	1.126089
800-DK	1.581261	0.448956	0.01942163	0.07408447	0.03691567	0.01020734	0.06626541	1.157471	1.077308	0.8993548	0.166965	1.133563
800-HK	0.7475858	0.1667617	0.01716964	0.01745233	0.01784541	0.005906281	0.0758862	0.5026664	0.8820183	0.2380463	0.1035882	0.4539938
800-HK	0.7590187	0.1802516	0.01376319	0.01818152	0.01443652	0.005753506	0.0644967	0.4710969	0.8436221	0.2058694	0.1841086	0.4564365
800-HK	0.7823938	0.1807124	0.01703924	0.02034929	0.0159195	0.005450927	0.0735071	0.5473395	0.6367672	0.2775988	0.1543387	0.4604441
800-WK/KB	0.8434812	0.08799461	0.006708626	0.01782287	0.01298517	0.004507523	0.04887372	0.1459841	0.8049987	1.031729	0.1545335	0.5955398
800-WK/KB	0.7396957	0.07989478	0.006348795	0.02183408	0.01402063	0.004991206	0.05402747	0.1542384	0.7305987	0.2809047	0.1180426	0.5153974
800-WK/KB	0.7430074	0.08012462	0.008719715	0.01828946	0.008540718	0.004065769	0.04748422	0.1542051	0.7492372	0.2875838	0.135034	0.5574023
1000-B	0.7634591	0.2894926	0.008495864	0.01502691	0.01273963	0.0127943	0.04258977	0.2682596	0.9464551	0.5078874	0.1016085	0.4689548
1000-B	0.7291446	0.2632565	0.01044681	0.01928733	0.01122484	0.009762472	0.03893616	0.3120666	0.9106556	0.3462062	0.1176195	0.453776
1000-B	0.6758317	0.3021432	0.00788119	0.0183319	0.01139263	0.01231358	0.03846698	0.2403109	0.7564033	0.4280946	0.08065621	0.3932054
1000-AG	0.9558239	0.2580799	0.006045528	0.1225891	0.01443972	0.003073236	0.08279212	0.2147988	0.9222812	0.5359961	0.07663984	0.5948957
1000-AG	0.9626516	0.2427303	0.00763939	0.1386038	0.01295605	0.004349613	0.09070197	0.2297548	0.9842626	0.5470734	0.09550478	0.6323575
1000-AG	0.8783149	0.2383586	0.008963619	0.1149803	0.01415716	0.002858932	0.08079194	0.196614	0.8719159	0.5396305	0.09233197	0.5690169
1200-B	0.9588501	0.3186869	0.01016577	0.01980448	0.01426235	0.006948825	0.05218179	0.5027357	0.9283869	0.3404913	0.1095523	0.5485011
1200-B	0.9450051	0.3048611	0.008892843	0.02211685	0.0149609	0.007009652	0.0593397	0.4883211	0.8987898	0.4170785	0.08168175	0.5919716
1200-B	0.9865291	0.3090138	0.009269894	0.02205539	0.01238055	0.009021551	0.0581355	0.5260372	0.9904715	0.3462567	0.1128117	0.579634
1200-AS	0.735186	0.2703905	0.05704733	0.0752157	0.009863243	0.02998047	0.08166143	0.6717195	0.9055886	1.963197	0.07670272	0.6720851
1200-AS	0.8410187	0.310898	0.06179931	0.0777982	0.009823874	0.02935844	0.1023028	0.7830544	0.9823773	2.18432	0.07727948	0.6804159
1200-AS	0.8079295	0.3084534	0.06087188	0.07979265	0.009096197	0.03013637	0.08726594	0.7196275	1.049032	2.056069	0.09411671	0.6432965
1200-F	0.8240576	0.04007525	0.006561566	0.05141141	0.01603679	0.007856655	0.07436905	0.3048688	1.019658	0.6725997	0.1317022	0.6776789
1200-F	0.872928	0.04258637	0.005973769	0.05245435	0.01708367	0.00580097	0.08760305	0.3207534	1.040764	0.6819385	0.1387204	0.7472906
1200-F	0.9074671	0.03642888	0.006993303	0.05994391	0.01873361	0.001790937	0.08820959	0.3461919	1.076791	0.7081434	0.1307566	0.7631857
1400-B	1.033896	0.4524853	0.007147552	0.0329126	0.01118945	0.009243233	0.05105032	0.2307785	0.8371496	0.3108941	0.1095909	0.4935859
1400-B	1.059162	0.4431961	0.009212885	0.02917204	0.01099691	0.007517339	0.05412713	0.2365413	0.8316001	0.3579823	0.100021	0.4989359
1400-B	1.024215	0.3675952	0.007977747	0.0295024	0.0117719	0.007377933	0.0495503	0.2109583	0.8421053	0.3248411	0.143132	0.5495344
1400-M1	1.436315	0.1542208	0.009192022	0.03732044	0.01714162	0.005699253	0.1390418	0.7335892	0.8651832	0.5833618	0.1504648	0.4861359
1400-M1	1.281184	0.1331358	0.006921653	0.03714145	0.01632288	0.00499242	0.1494361	0.7303739	0.8542788	0.6851224	0.09592973	0.4992546
1400-M1	1.367807	0.1478058	0.00749957	0.03235088	0.01670539	0.002874909	0.1430747	0.7019019	0.8721887	0.6203483	0.1064719	0.50665
1400-M2	1.265641	0.2287655	0.004797657	0.03843438	0.01409748	0.007035734	0.1566831	0.8113868	1.050202	0.6679524	0.1286644	0.6479776
1400-M2	1.214103	0.2231316	0.007364297	0.03907176	0.01302208	0.004552832	0.1408122	0.7497472	1.061751	0.6510508	0.1442344	0.6043307
1400-M2	1.250426	0.2401849	0.006589299	0.04006634	0.01682713	0.006861123	0.1523403	0.7816702	1.059499	0.6818497	0.1117827	0.5905153
1600-B	1.017676	0.3684499	0.008420792	0.0351399	0.01285692	0.008367711	0.06107017	0.6834747	0.7487574	0.376915	0.08293424	0.6230237
1600-B	1.055769	0.5124352	0.009155593	0.03970597	0.0135107	0.01123164	0.06410459	0.7182193	0.8152291	0.3292823	0.1073246	0.6034233
1600-B	1.023021	0.4525427	0.008216519	0.04020584	0.01375848	0.009507879	0.06509498	0.747647	0.8153839	0.4944437	0.08885509	0.606257
1600-M1	1.065492	0.1266756	0.006798206	0.1128562	0.0141648	0.005612995	0.1486383	0.5290489	0.9433982	0.6249446	0.1217408	0.5088007
1600-M1	1.041326	0.1240938	0.007468327	0.1127374	0.01299974	0.007382171	0.1414573	0.5245644	0.918483	0.6375437	0.1173853	0.4971462
1600-M1	1.040226	0.1170038	0.007064145	0.1169945	0.01312601	0.00452819	0.1476179	0.5232977	0.9806135	0.536078	0.1519721	0.4823067
1600-M2	1.068155	0.2521384	0.005959296	0.1069834	0.01410838	0.003866919	0.1466303	0.4489767	0.8983825	0.8286157	0.09792539	0.531342
1600-M2	0.9696361	0.230151	0.003931345	0.1072191	0.01530418	0.004078138	0.1462099	0.4065157	0.8610959	0.8075618	0.1335184	0.5174131
1600-M2	1.048121	0.2537925	0.005659733	0.1041214	0.01609261	0.005016016	0.1627519	0.4750489	0.9500889	0.8547702	0.1188239	0.5685854

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method (cont.)

Metabolite name	Putrescine	Serotonin	Unknown 1	Unknown 2	Unknown 3	Unknown 4	Unknown 5	Unknown 6	Unknown 7	Unknown 8	Unknown 9	Unknown 10
400-DB	0.1514193	0.03790113	0.1040788	0.1523066	0.02698	0.06540553	0.00508937	0.09153026	0.03848391	1.370653	0.03403572	0.009334312
400-DB	0.1709423	0.03425509	0.1122971	0.161484	0.03700945	0.06701549	0.003348837	0.08324806	0.03869673	1.453678	0.03730216	0.01364762
400-DB	0.1482751	0.02103809	0.1055566	0.1510997	0.03015246	0.06833459	0.00257406	0.08409565	0.03900495	1.281231	0.04010486	0.0105261
400-HB	0.139801	0.02603189	0.0300107	0.03785024	0.03603702	0.07803209	0.01061188	0.04967953	0.05245838	0.06695863	0.038537	0.02085236
400-HB	0.1394511	0.02388325	0.03083802	0.04473318	0.03471104	0.07293753	0.01440384	0.0505106	0.04240311	0.05145519	0.02600353	0.024134
400-HB	0.141911	0.0191947	0.03234938	0.03511709	0.04374582	0.07497736	0.01817247	0.0457479	0.04096564	0.0498047	0.02866168	0.02196075
400-WB/BM	0.1965449	0.04427666	0.04158836	0.06973065	0.03371226	0.0586759	0.005350202	0.061488	0.0330859	1.475335	0.03279373	0.01726017
400-WB/BM	0.2080876	0.02043899	0.04571811	0.06630493	0.04126576	0.05746704	0.006593836	0.06189564	0.04068489	0.04408722	0.0433718	0.01538203
400-WB/BM	0.2156885	0.02992009	0.04540172	0.0717708	0.03541407	0.06778231	0.004306894	0.06432012	0.04172935	0.04459899	0.04570984	0.01741233
800-DK	0.1455455	0.01997475	0.09472298	0.1681467	0.03447225	0.09382419	0.04147246	0.05857847	0.0567791	0.05077301	0.04034823	0.02117033
800-DK	0.1759666	0.02109594	0.07410894	0.1510612	0.03576332	0.09475575	0.05235139	0.05921872	0.04970297	1.042912	0.03440187	0.01765049
800-DK	0.1667936	0.03151156	0.08127455	0.1792545	0.03225606	0.1026031	0.04150791	0.05253227	0.05540704	1.157471	0.04011868	0.02066551
800-HK	0.1985139	0.01894967	0.03804681	0.04777658	0.05137399	0.08072	0.0270285	0.04132389	0.05285572	0.06513914	0.03906966	0.02225407
800-HK	0.1794781	0.02137605	0.04305125	0.0486959	0.0414421	0.07410687	0.02866175	0.04145189	0.04471302	0.05188455	0.03318838	0.01765036
800-HK	0.2056208	0.03177489	0.0477718	0.05000993	0.05177484	0.08330605	0.02385195	0.04208427	0.05327924	0.06305592	0.0391328	0.01694769
800-WK/KB	0.1245777	0.03083167	0.01622293	0.01938611	0.03450805	0.07207368	0.02725719	0.04033316	0.05187835	0.0607895	0.02900088	0.01966021
800-WK/KB	0.1217899	0.01813884	0.01616594	0.02133517	0.04434633	0.06878011	0.02056519	0.04924074	0.05894833	0.08154368	0.03425529	0.02033083
800-WK/KB	0.1242469	0.0187945	0.01433991	0.02011111	0.03950679	0.07104889	0.01760457	0.04888991	0.05698553	0.07850402	0.02969414	0.01985067
1000-B	0.2086784	0.01145529	0.001305989	0.01602902	0.03066659	0.03616361	0.005019147	0.06953847	0.06113225	0.06282204	0.02102791	0.01860992
1000-B	0.24457	0.01103859	0.01089269	0.01150789	0.02503436	0.0374007	0.006472851	0.06813326	0.05450633	0.06004228	0.01739997	0.01392917
1000-B	0.1645805	0.01068653	0.009478938	0.01038053	0.02448842	0.03447019	0.003167534	0.06980728	0.05741598	0.07112	0.02361964	0.0142141
1000-AG	0.159789	0.01045006	0.02969174	0.05998993	0.02367713	0.04002896	0.006685807	0.02875312	0.05619371	0.07816932	0.02430763	0.02587358
1000-AG	0.1641547	0.01484165	0.03838336	0.06495935	0.02367201	0.03878694	0.007009072	0.02678299	0.05779178	0.06711738	0.02188061	0.0253004
1000-AG	0.1466508	0.01304829	0.03077807	0.05486633	0.02310294	0.03555774	0.004846881	0.02696532	0.04856279	0.06105552	0.01992105	0.02672799
1200-B	0.1734113	0.02689196	0.01183158	0.01686981	0.04363166	0.04441122	0.01112975	0.07330392	0.04598827	0.05148161	0.02227411	0.01898963
1200-B	0.1774907	0.01403674	0.01600239	0.01993989	0.05125014	0.0440141	0.008370916	0.07828302	0.05514006	0.07659518	0.03235499	0.01940555
1200-B	0.1911572	0.02143509	0.01537259	0.01883525	0.04542595	0.04717682	0.007484653	0.07566917	0.05704706	0.07887711	0.03214432	0.02019143
1200-AS	0.1719641	0.009426082	0.009991636	0.02338216	0.02560159	0.02898162	0.002358455	0.03318472	0.03543074	0.04778253	0.02159289	0.08596269
1200-AS	0.197445	0.01237919	0.01113069	0.02540684	0.03076312	0.03281182	0.003118768	0.03382727	0.04688187	0.06208401	0.02363246	0.102306
1200-AS	0.1914041	0.01076464	0.01051504	0.02387023	0.01826821	0.03046179	0.00382797	0.03568915	0.03047139	0.03592078	0.01657121	0.08357976
1200-F	0.2474356	0.009129844	0.01033171	0.01393789	0.02263327	0.03197413	0.008047248	0.04849658	0.06107308	0.07761447	0.02223877	0.02729216
1200-F	0.2915632	0.008947204	0.01016576	0.01585805	0.02447134	0.03337752	0.01141827	0.06022973	0.07572208	0.08750306	0.02404152	0.03096269
1200-F	0.2759762	0.01069748	0.01055419	0.01643945	0.02897741	0.03516886	0.005753724	0.0596131	0.08850851	0.1041646	0.0312962	0.0268162
1400-B	0.2336359	0.009828711	0.01826587	0.01837703	0.02982423	0.0664127	0.007606891	0.07741841	0.06313916	0.05749029	0.04344055	0.02456472
1400-B	0.2163279	0.01005549	0.0189008	0.01826528	0.03112297	0.06166038	0.01010406	0.07209433	0.06105807	0.04928219	0.03504603	0.02386435
1400-B	0.2139554	0.01008479	0.01823803	0.01856101	0.02348915	0.06446024	0.01000761	0.07310098	0.05723501	0.04525878	0.03448684	0.02375198
1400-M1	0.2138821	0.01102218	0.01120815	0.01687114	0.0211037	0.03130978	0.003951259	0.06582285	0.03479582	0.03711225	0.01918816	0.02130253
1400-M1	0.2225482	0.01033451	0.01193524	0.01426637	0.02691222	0.02696308	0.004143535	0.06059435	0.03590551	0.04426267	0.02491702	0.02042931
1400-M1	0.2029461	0.009838355	0.001379697	0.01630154	0.03391281	0.02943365	0.003212632	0.06235827	0.04226654	0.04910212	0.02026339	0.0176636
1400-M2	0.173818	0.01657156	0.009465274	0.01539013	0.02787262	0.03923095	0.002947488	0.04593079	0.05387681	0.05827162	0.0270174	0.02411363
1400-M2	0.1700459	0.01469623	0.009072474	0.01433861	0.01899046	0.03370246	0.00451494	0.04104242	0.04670131	0.05266333	0.02627815	0.02317848
1400-M2	0.1750538	0.01264264	0.009476213	0.01351766	0.0301217	0.03597388	0.004516431	0.04546947	0.04939495	0.05782148	0.02662873	0.02501774
1600-B	0.170112	0.009802003	0.02444536	0.03631645	0.03164528	0.06332941	0.009060232	0.08523972	0.04619861	0.06931914	0.04783867	0.01741809
1600-B	0.1957506	0.01667995	0.03098648	0.04526576	0.04060709	0.0642714	0.007590909	0.08567404	0.0473609	0.06657799	0.04314227	0.02133609
1600-B	0.1962875	0.0142606	0.03354997	0.04690573	0.03320829	0.05892665	0.01190936	0.08453857	0.04115309	0.04983662	0.03095996	0.01898605
1600-M1	0.1929731	0.01175497	0.01401319	0.02386652	0.02294046	0.04427892	0.01332659	0.04576653	0.05663402	0.08017571	0.03407833	0.01780445
1600-M1	0.1890235	0.01335346	0.000949327	0.02488024	0.02510875	0.04328885	0.009554279	0.04211744	0.0481393	0.0775532	0.03501033	0.01835188
1600-M1	0.1949758	0.01042422	0.01470422	0.02350709	0.02293312	0.03879593	0.01642922	0.03758216	0.04087416	0.05169728	0.02824845	0.01989882
1600-M2	0.1580026	0.008335277	0.005545719	0.01223866	0.031991	0.04927552	0.02040778	0.03184322	0.04637463	0.07426076	0.02600471	0.0209029
1600-M2	0.1462605	0.008938471	0.006270141	0.01271254	0.02828274	0.04379752	0.01811211	0.03152356	0.0397095	0.06496741	0.02651254	0.01786496
1600-M2	0.1663814	0.01288024	0.001632069	0.01339498	0.02825902	0.04900348	0.02294895	0.03452549	0.04827131	0.08766254	0.0354955	0.01832343

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method (cont.)

Metabolite name	Unknown 11	Unknown 12	Unknown 13	Unknown 14	Unknown 15	Unknown 16	Unknown 17	Unknown 18	Unknown 19	Unknown 20	Unknown 21	Unknown 22
400-DB	0.04737919	0.03160448	0.04114594	0.02342962	0.6666911	0.01430023	0.02579691	0.02056852	0.06233227	0.07584006	0.01176222	0.8371983
400-DB	0.05808724	0.02947633	0.04585116	0.02652344	0.7146899	0.01798887	0.02758372	0.02465628	0.05556819	0.08347347	0.01324659	0.881837
400-DB	0.04687395	0.03057718	0.03711776	0.01564356	0.6455795	0.0099505	0.02222648	0.01951781	0.04703623	0.07057891	0.01168735	0.7572101
400-HB	0.05828298	0.03277835	0.03871527	0.02183703	0.6158122	0.003281874	0.02863091	0.02013589	0.04035543	0.08321423	0.0195651	0.5561755
400-HB	0.06965927	0.0335431	0.02280194	0.03021531	0.6110248	0.003830398	0.02937727	0.01943678	0.03649395	0.0765407	0.02139128	0.4912859
400-HB	0.05117138	0.03311252	0.04167835	0.02361506	0.5837674	0.003592928	0.02763833	0.01590022	0.03538338	0.07331834	0.02075757	0.4968934
400-WB/BM	0.05417836	0.03298312	0.03360948	0.03005744	0.6205681	0.004531615	0.01916765	0.03404873	0.156485	0.07638753	0.03045893	0.7967403
400-WB/BM	0.04052059	0.03128447	0.0631647	0.03720753	0.5892572	0.003415943	0.02073497	0.03758581	0.1564477	0.06520016	0.03239147	0.7396071
400-WB/BM	0.05591708	0.03796531	0.04392649	0.03117343	0.6208163	0.003961931	0.01613643	0.03879916	0.1539305	0.07884939	0.03534754	0.8527638
800-DK	0.07520511	0.02694889	0.0389326	0.0314653	0.7229761	0.01146567	0.05229357	0.02265972	0.03078027	0.1008688	0.01954365	0.5130466
800-DK	0.06215782	0.02738734	0.05422809	0.02417047	0.7109193	0.01271708	0.05052415	0.02408709	0.02346201	0.09549671	0.01381659	0.5258547
800-DK	0.07664905	0.02589245	0.04045467	0.02852613	0.7694227	0.01385126	0.060171	0.02363174	0.03052597	0.1093638	0.01382288	0.5524398
800-HK	0.05001799	0.03504683	0.04487363	0.0341826	0.608825	0.003498159	0.02698584	0.01565446	0.02470903	0.09950128	0.02113783	0.4332836
800-HK	0.07831643	0.03467496	0.02473205	0.03526181	0.6046091	0.002858703	0.02676322	0.01611536	0.0249828	0.07307421	0.02298744	0.371124
800-HK	0.06792578	0.03607266	0.0370161	0.05054807	0.6174238	0.004291797	0.0316904	0.01790607	0.02239645	0.09470612	0.02390329	0.4848209
800-WK/KB	0.07183971	0.03007738	0.02860694	0.04740926	0.6099666	0.002818198	0.02548475	0.02002028	0.0448404	0.06661034	0.03175987	0.4494259
800-WK/KB	0.05396428	0.03007578	0.05974602	0.03679027	0.5400634	0.002830332	0.02209831	0.02017708	0.03952879	0.06484024	0.02858218	0.3893104
800-WK/KB	0.06212274	0.02973204	0.04348858	0.02626264	0.5421168	0.002966049	0.01920085	0.01633603	0.04114831	0.07508553	0.02914358	0.4402568
1000-B	0.05254786	0.03218349	0.02615418	0.03844729	0.4767332	0.003189209	0.02102264	0.02584031	0.04097102	0.0757193	0.05006104	0.5224673
1000-B	0.05327452	0.03670648	0.0232342	0.03176937	0.455522	0.004117317	0.01917868	0.02253039	0.04171076	0.05931137	0.04475882	0.4753565
1000-B	0.03877136	0.03765977	0.02420071	0.0315054	0.4360344	0.005342322	0.0193397	0.01824101	0.03676113	0.05780077	0.04429223	0.3875329
1000-AG	0.04010269	0.03649831	0.02901737	0.1151544	0.5729872	0.002575123	0.01807184	0.02396384	0.115875	0.05315984	0.03774187	0.6809619
1000-AG	0.03972776	0.03542073	0.02847286	0.04695173	0.5901917	0.00474416	0.01950515	0.0297648	0.1144685	0.06157425	0.0387844	0.8136187
1000-AG	0.04384476	0.03234015	0.02353661	0.03806749	0.5219178	0.003425921	0.01577725	0.02544759	0.1027007	0.05390192	0.03594484	0.6369923
1200-B	0.05712409	0.03249061	0.02334864	0.01873492	0.7307074	0.004377197	0.01935074	0.05295171	0.1096731	0.06933387	0.1087835	0.6428572
1200-B	0.03433571	0.03460702	0.04499707	0.03583765	0.7328574	0.004377856	0.02597041	0.05813921	0.114053	0.06491745	0.1088326	0.6597945
1200-B	0.04657841	0.03802943	0.0339193	0.03485724	0.7399759	0.004026978	0.02283645	0.057855	0.1159539	0.0732226	0.113856	0.8271523
1200-AS	0.03885575	0.02911122	0.02123722	0.04617218	0.4703756	0.008268131	0.01358807	0.006468704	0.01763159	0.04791116	0.00887455	0.5886112
1200-AS	0.03326184	0.03361795	0.04127574	0.04623167	0.5129991	0.01129281	0.01613333	0.008359387	0.02135541	0.04982171	0.01511194	0.6734432
1200-AS	0.03896229	0.02657892	0.0222744	0.04299801	0.4925197	0.004987117	0.01616628	0.008598223	0.01959499	0.03982211	0.008356007	0.5170609
1200-F	0.0627763	0.02905633	0.0205036	0.03004067	0.6221173	0.005067597	0.02026003	0.02229204	0.03104987	0.0612912	0.01984274	0.7190104
1200-F	0.06576417	0.0310586	0.02666773	0.02643217	0.6544802	0.004144171	0.02620748	0.02426485	0.03532585	0.06994963	0.01825087	0.8617812
1200-F	0.05232817	0.0304297	0.02805018	0.05633741	0.6472313	0.005065505	0.02419262	0.02372691	0.03543755	0.07541611	0.02005603	0.9640862
1400-B	0.0463112	0.03539275	0.03978743	0.0402652	0.6481296	0.004349181	0.01884991	0.04662799	0.1115443	0.05075052	0.1790856	0.582006
1400-B	0.04649452	0.03306105	0.03928782	0.03502426	0.6214467	0.003867798	0.02075823	0.04743984	0.124105	0.05270818	0.1768651	0.6118068
1400-B	0.06372888	0.03234849	0.0250362	0.04317728	0.6048958	0.003144905	0.02010009	0.05165597	0.1395952	0.04969065	0.1897102	0.5675626
1400-M1	0.06781558	0.0243526	0.0246143	0.03993161	0.5992648	0.004622912	0.01726998	0.01405149	0.01522871	0.04181908	0.01145289	0.861307
1400-M1	0.04928396	0.03129272	0.04246402	0.04960559	0.5501707	0.006137369	0.01595837	0.01355466	0.01709232	0.05097348	0.01469274	1.038541
1400-M1	0.0469588	0.03098353	0.03568285	0.04485399	0.5861396	0.007203291	0.01789786	0.01109343	0.0134763	0.05579192	0.009922712	0.9372655
1400-M2	0.0487582	0.03728892	0.03402159	0.04486059	0.6482457	0.00588806	0.01942885	0.01097679	0.01345253	0.06989252	0.01182924	1.128356
1400-M2	0.06106287	0.03421386	0.02272765	0.04453013	0.6207907	0.00480065	0.020562	0.009305356	0.01104534	0.05980277	0.00947988	0.8844686
1400-M2	0.04920917	0.03234073	0.03920898	0.03898331	0.606081	0.006824366	0.01945048	0.01013155	0.01180096	0.06424866	0.009696179	1.023214
1600-B	0.0378662	0.03392559	0.04334809	0.02899832	0.6526355	0.0046988	0.02256289	0.04882998	0.1210973	0.06902499	0.04341458	0.6909411
1600-B	0.04793993	0.03707448	0.03841957	0.04886296	0.6783987	0.006581109	0.02200386	0.04661282	0.1016376	0.09688574	0.04686779	0.7374689
1600-B	0.0422127	0.03545015	0.0406669	0.0386098	0.6721128	0.005482541	0.02409125	0.04141374	0.09373989	0.08551203	0.04694409	0.6727147
1600-M1	0.0556453	0.04008484	0.02669504	0.04187894	0.6841023	0.01486345	0.01862405	0.03050354	0.05883423	0.05575804	0.0286142	0.9754389
1600-M1	0.05519049	0.03573597	0.02866578	0.04925131	0.6683594	0.01445156	0.01848272	0.03114586	0.06640154	0.06470302	0.03146292	1.015935
1600-M1	0.07277738	0.03239008	0.02370065	0.04307425	0.6732358	0.006344228	0.01824834	0.03315761	0.06152652	0.05411978	0.02535506	0.9171292
1600-M2	0.04391154	0.03945348	0.03874043	0.04057648	0.6477347	0.01000573	0.01913254	0.02371918	0.05382654	0.05314967	0.02440606	0.8758231
1600-M2	0.0606535	0.03273834	0.02248413	0.04450842	0.6033865	0.01017542	0.01759893	0.02806884	0.05806636	0.04245661	0.02116869	0.763723
1600-M2	0.04938953	0.03661846	0.03168231	0.04820032	0.6430929	0.009156684	0.02366574	0.03351702	0.0641246	0.05419581	0.02839303	0.8967381

Table S19 Data matrix for the green coffee beans obtained from different altitude, geographical origin, and postharvest process method (cont.)

Metabolite name	Unknown 23	Unknown 24	Unknown 25	Unknown 26	Unknown 27	Unknown 28	Unknown 29	Altitude (m)
400-DB	0.02074619	0.3131597	3.688426	0.2234157	2.486231	0.03231266	0.06552313	400
400-DB	0.01362754	0.306951	3.692092	0.2091421	2.426009	0.03195494	0.07055665	400
400-DB	0.01455586	0.2957195	3.473805	0.2005243	2.20789	0.02964444	0.05779627	400
400-HB	0.05087661	0.1584323	3.168515	0.1128129	1.962906	0.03481309	0.05265542	400
400-HB	0.04593876	0.1366292	2.80633	0.1025179	1.827699	0.0318114	0.04114495	400
400-HB	0.04537076	0.1655352	3.111557	0.1086555	1.86662	0.02426349	0.04503602	400
400-WB/BM	0.03842957	0.2537332	3.212726	0.1800607	2.112231	0.02641057	0.04591753	400
400-WB/BM	0.03460165	0.249901	3.128267	0.1839994	2.006777	0.02912177	0.0450869	400
400-WB/BM	0.03271177	0.2664731	3.32602	0.2071312	2.248727	0.03512737	0.05561239	400
800-DK	0.01455745	0.1805408	3.2315	0.1422192	2.247726	0.03486978	0.06770933	800
800-DK	0.01441033	0.1938095	3.673144	0.1430631	2.42122	0.04487451	0.06072622	800
800-DK	0.01369473	0.1698539	3.628533	0.1319778	2.455284	0.04010607	0.064904	800
800-HK	0.04576154	0.1352008	2.991124	0.09737139	1.915008	0.02567668	0.0419414	800
800-HK	0.03802649	0.09964741	2.525957	0.08682705	1.606697	0.0200848	0.03621164	800
800-HK	0.04304808	0.1374062	3.215107	0.09682933	2.033781	0.02902036	0.04781147	800
800-WK/KB	0.04532315	0.1153651	2.593605	0.08582453	1.667394	0.03312927	0.04710897	800
800-WK/KB	0.04278706	0.117873	2.561462	0.09022421	1.56101	0.03095874	0.04522555	800
800-WK/KB	0.03880975	0.1182718	2.50034	0.08922608	1.704732	0.03258073	0.04997605	800
1000-B	0.03893294	0.1046919	2.260515	0.06700448	1.36076	0.03222594	0.03417827	1000
1000-B	0.0269316	0.1045906	2.125893	0.07551481	1.377919	0.02192083	0.03104948	1000
1000-B	0.02873555	0.08680172	1.912858	0.06051441	1.151417	0.01930851	0.02806037	1000
1000-AG	0.03069774	0.126709	1.850129	0.07932727	1.06789	0.02182869	0.03991956	1000
1000-AG	0.03468861	0.1295918	2.037524	0.07988279	1.170747	0.03284955	0.05228757	1000
1000-AG	0.02935181	0.1061963	1.715265	0.07051279	1.015076	0.03040352	0.0385034	1000
1200-B	0.04810451	0.1415431	2.372311	0.09771027	1.422502	0.02794112	0.04107051	1200
1200-B	0.04627411	0.1388135	2.379401	0.09309793	1.323382	0.02355229	0.03532518	1200
1200-B	0.03944659	0.1648866	2.622118	0.1047538	1.608776	0.02660151	0.04579652	1200
1200-AS	0.02148142	0.1111061	1.588813	0.06792901	0.9272811	0.02218311	0.02635574	1200
1200-AS	0.01565291	0.1276355	1.83519	0.08163512	1.108401	0.02556179	0.03554679	1200
1200-AS	0.01328454	0.1018807	1.501145	0.07013866	0.9058968	0.0130054	0.02027684	1200
1200-F	0.03299813	0.09762058	1.696878	0.06138828	0.8704017	0.03364301	0.0235235	1200
1200-F	0.04251762	0.1204755	1.943236	0.06721665	1.038103	0.03916789	0.03311587	1200
1200-F	0.04894305	0.1259615	1.994334	0.07936659	1.070037	0.04736453	0.03506587	1200
1400-B	0.0351782	0.1479277	2.701203	0.108064	1.796501	0.01967931	0.0368108	1400
1400-B	0.03920744	0.1501969	2.759227	0.1061758	1.789527	0.02572708	0.04026859	1400
1400-B	0.02794519	0.1348648	2.356334	0.1009481	1.621981	0.01992542	0.03837657	1400
1400-M1	0.01862645	0.1351934	1.680791	0.06896151	0.8958523	0.01797117	0.02030924	1400
1400-M1	0.02708184	0.1459504	1.951482	0.08292101	0.9804916	0.03135815	0.03016839	1400
1400-M1	0.0238884	0.1386005	1.86965	0.07590982	1.014138	0.0182103	0.02654051	1400
1400-M2	0.02413825	0.1763792	2.144655	0.09431603	1.148856	0.02935093	0.03491444	1400
1400-M2	0.02597197	0.1390078	1.919569	0.08203478	1.078666	0.01847463	0.02704096	1400
1400-M2	0.02977009	0.1554722	2.246107	0.09115577	1.150874	0.03313626	0.03369102	1400
1600-B	0.0302129	0.1601329	2.350732	0.1053283	1.447722	0.02287235	0.04033668	1600
1600-B	0.03572406	0.1551346	2.684291	0.1090505	1.699623	0.02984807	0.05698854	1600
1600-B	0.0395765	0.1510575	2.579352	0.1206029	1.609772	0.02756288	0.05026041	1600
1600-M1	0.04814133	0.1334071	1.948251	0.07491026	1.05897	0.03270785	0.04912841	1600
1600-M1	0.04836379	0.1418923	1.927943	0.07318544	1.019895	0.04415978	0.04958256	1600
1600-M1	0.04007133	0.140256	1.80079	0.07340318	0.9725477	0.02944794	0.04252185	1600
1600-M2	0.04392574	0.1259735	1.924835	0.07180323	0.995454	0.04351216	0.05762221	1600
1600-M2	0.03873917	0.1122901	1.433119	0.05715085	0.8450422	0.03301695	0.04957905	1600
1600-M2	0.03546533	0.1314027	1.768953	0.06673171	0.9175461	0.03505147	0.05903463	1600