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Physicochemical characteristics and bioactive compound profiles of Arabica Kalosi Enrekang with different postharvest processing

Yulianti YULIANTI[1,2,3], Nuri ANDARWULAN[1,2*], Dede Robiatul ADAWIYAH[1,2], Dian HERAWATI[1,2], Dias INDRASTI[1,2]

Abstract

This work aimed to understand and evaluate the impacts of postharvest procedures on physicochemical characteristics and bioactive compounds (CQAs and alkaloids) of green bean and roasted bean. Arabica green bean of kalosi Enrekang was obtained from different procedures: natural, honey and full-washed, and followed with medium roasting, powdered, and extracted using boiling water. A single-factor ANOVA and t-test was arranged to evaluate data, and OPLS-DA was applied to produce mapping. As the results, full washed processed green beans demonstrated a high lightness, while honey processed green beans showed a high chromaticity a*. Natural processed green beans contained a high CQAs, whereas honey processed green beans contained the highest quantity of alkaloids. In terms of caffeine, natural and honey processed green beans exhibited equal levels. In addition, honey roasted beans contained a high content of 3-CQA and 4-CQA, while full-washed processed roasted beans contained a high level of theobromine. The roasting process was reported to reduce the content of total CQAs and alkaloids.

Keywords: green bean; roasted bean; Kalosi; caffeoylquinic acid; alkaloid.

Pratical Application: Different postharvest processing (natural, honey and full-washed) affect the physicochemical characteristics and bioactive components of Arabica Kalosi Enrekang coffee.

1 Introduction

Indonesia is a prominent producer and exporter of coffee in the world. As reported by International Coffee Organization, Indonesia ranked 4th of coffee exporter after Brazil, Vietnam, and Columbia. There are three popular coffee beans of Indonesia, i.e. Arabica, Robusta, and Liberica (Ferry et al., 2015). Among the beans, Arabica is deemed to be the most superior bean regarding organoleptic profiles, which make it more precious in global market. Arabica coffee brew is characterized with odoriferous and sweet-smelling, mild, and low acidity taste, as well as able to exert miscellaneous aroma (Portaluri et al., 2020). In this regard, South Sulawesi becomes the main producer of Arabica coffee in Indonesia. Directorate General of Estate Crops reported 14 regencies in the province as producer of Arabica coffee (Direktorat Jenderal Perkebunan, 2017). In this province, Regency of Enrekang shows the highest contributor, which has been registered as Geographical Indication since 2013 regarding the coffee bean "Arabica kalosi Enrekang" from Ministry of Law and Human Rights of the Republic of Indonesia.

Coffee bean quality strongly determines its economic value in global market, which depends on geographical condition (40%) and postharvest processing (60%, comprising of 40% primary method and 20% secondary method) (Duguma & Chewaka, 2019). In Indonesia, the most popular postharvest process applied by coffee processors includes full-washed and dry (natural) method, while few farmers used honey technique. Dry processing is performed by drying the coffee cherry without exocarp removal; on the contrary, full-washed processing removes the outer skin of cherry and pulpy matter from the cherry prior to drying (Duguma & Chewaka, 2019). There are 3 types of honey processing, i.e. red, yellow, and black, depending on mucilage removal and drying periods. Yellow honey processing removes most mucilage from the bean, with drying for 8-10 days. In red honey, 50-60% of mucilage is removed, followed with drying for 12-15 days. Furthermore, black honey leaves mucilage in coffee beans during 30 days of drying (Sanz-Uribe et al., 2017). After drying, the beans are dehulled to collect green beans. The physical and chemical quality of green beans may vary greatly, depending on the preparation procedures.

In terms of chemical composition, chlorogenic acid (CGA) and alkaloid are regarded as main components. CGA content in coffee reaches 6-12% in various forms, such as caffeoylquinic acid (3-CQA, 4-CQA, and 5-CQA), feruloylquinic acids (3-FQA, 4-FQA, and 5-FQA), and dicaffeoylquinic acids (3,4-diCQA, 3,5-diCQA and 4,5-diCQA); however, caffeoyquinic acid (CQA) becomes the most abundance of CGA in coffee (Pereira et al., 2019; Duarte et al., 2010). In addition, caffeine and trigonelline are the major alkaloid founds in coffee, enabling to affect quality, aroma and characteristics of coffee. Meanwhile, theobromine is also alkaloid able to determine flavour of coffee, despite at low concentration (Yisak et al., 2018). In this regard, postharvest technique of coffee cherry substantially alters chemical profile of coffee beans, especially on water-soluble compounds such

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[1]*Department of Food Science and Technology, Faculty of Agricultural Engineering and Technology, IPB University, IPB Dramaga Campus, Bogor, Indonesia*
[2]*South-East Asia Food & Agricultural Science and Technology Center, IPB University, IPB Dramaga Campus, Bogor, Indonesia*
[3]*Department of Agricultural Technology, Faculty of Agriculture, Gorontalo University, Gorontalo, Indonesia*
*Corresponding author: andarwulan@apps.ipb.ac.id

as sugar, trigonelline, caffeine, and CGA (Duarte et al., 2010). A study conducted De Bruyn et al. (2016) distinguishing dry/natural and full-washed post-harvest processes revealed that green beans with natural processing demonstrated a higher level of caffeine, trigonelline, 3-CQA, 4-CQA, 3,4-diCQA, and 4,5-diCQA than that with full-washed. Besides, Kassaye et al. (2019) compared natural, full-washed, and semi-washed processing, finding that total CGA and caffeine was higher in green beans with full-washed processing than in natural and semi-washed processing. Numerous researches discussing the effects of full-washed and natural processing on content of CGA and caffeine have been made, but few studies discussed the role of honey processing on the chemicals.

Besides postharvest processing, condition of roasting also determines the roasted bean properties. Roasting is often conducted in 180-240 °C for 8-15 min which induces endothermic and exothermic process, leading to reduction of moisture content and changes in coffee bean characteristics (Sunarharum et al., 2014). When roasted, two mechanisms occurred in the beans, i.e. heat transmission and temperature profile, which markedly alter physical and chemical quality of roasted beans (Bastian et al., 2021; Somporn et al., 2011). Therefore, this present work aimed to understand and evaluate the effects of postharvest processes (natural, full-washed, and honey) on physical and chemical properties of Arabica green bean and roasted bean. The work provides scientific evidences on quality of green bean and roasted bean as affected by postharvest treatments, meaningful for coffee industries in developing their products.

2 Materials and method

2.1 Materials

Chemicals including 3-O-caffeoylquinic (3-CQA), 4-O-caffeoylquinic (4-CQA), and 5-O-caffeoylquinic(5-CQA), trigonelline, theobromine were purchased from Sigma-Aldrich (St Louis, USA), while caffeine, formic acid, methanol LC, and water LC were purchased from Merck (Darmstadt, Germany). All chemicals used were analytical grade.

2.2 Post-harvest process

Coffee cherry "Arabica kalosi Enrekang" was harvested in May 2021, then processed under different methods, i.e. natural, full-washed, and honey. Stages of natural process for producing green bean include sortation, sun-drying ± 15 days, and skin removal. In honey process, coffee cherry is depulped, fermented for 24 h, sun-dried for ± 6 days, and finally, the mucilage and parchment are removed to collect green bean. Full-washed processing removes skin and involves fermentation (soaking) for 24 h, washing, and sun-drying for ± 4 days, and the hull and testa of dried beans are removed to produce green bean.

2.3 Roasting process

Green bean from previous stages was roasted at medium level (12 min, initial temperature 155 °C, final temperature 196 °C) using a roaster from PT Kemenady Industri Mandiri (IKRI, Jember, Indonesia).

2.4 Sample extraction

Befero extraction, the green bean was added with liquid nitrogen before grinding. The grinding of green bean and roasted bean was conducted by coffee grinder (Gemilai crm905, China). Extraction of green and roasted bean followed procedures of Herawati et al. (2019). Bean powder (5 g) was dissolved in 100 mL of boiling distilled water under constant stirring for 1 min. To reduce temperature, ice cube was added and left for 2 min. Coffee filtrate was obtained through passing the mixture through filtering paper (Whatman no. 1), and then stored in freezer at -22 °C for further analyses.

2.5 Moisture content analysis

Procedure for moisture analysis conformed to Association of Official Analytical Chemists (2012). Moisture content was expressed as g/100 g dry basis (db).

2.6 Determination of Bulk Density, pH, and Total Dissolved Solid (TDS)

Bulk density of coffee bean and roasted bean was measured (g/mL). The bean volume was determined via a measuring cylinder. The pH meter (PHT-027, China) apparatus was used to measure pH, while refractometer (HM digital SCM-1000, Korea) was applied to determine TDS expressed as g/100 mL (Herawati et al., 2019).

2.7 Color analysis

Color of samples (green bean, roasted bean, coffee brew) was tested using a chromameter (Konica Minolta CR400, Konica Minolta inc, Japan). Samples were transferred into a special chamber to detect color displayed as L* (lightness), a* (red - green), and b* (yellow – blue) (Herawati et al., 2018).

2.8 Quantification of CQA (Caffeoylquinic Acid)

Quantification of CQA conformed to method of Herawati et al. (2019) with modification, using LC-40B XR (Shimadzu Corp, Japan). Sample was filtered using a membrane PTFE 0.22 µm, and 5 µL of the resultant was eluted into Column ACQUITY UPLC® BEH C18 (2.1 × 50 mm, 1.7 µm, Ireland) at temperature of 30 °C and pressure of 430-570 kgf/cm^2. Mobile phase consisting of methanol LC (A) and formic acid 0,05% (B) was set at 0.3 mL/min. Gradient elution was set 5% A (0 min), 90% A (8.30-9.30 min), 5% A (10.30-12.30 min), and 5% A (12.30-14.00 min). Detection was performed using PDA SPD-M40 at 320 nm. Standard curve plotting 5 points of 3-CQA, 4-CQA, and 5-CQA at concentration of 5-83 mg/L (triplicates: 3-CQA = LoD 4.78 mg/L, LoQ 1.43 mg/L, r^2 0.99; 4-CQA = LoD 2.39 mg/L, LoQ 0.72 mg/L, r^2 0.99; and 5-CQA = LoD 0.65 mg/L, LoQ 0.20 mg/L, r^2 0.99). Concentration of CQAs was expressed as g/100 g dry basis coffee (db).

2.9 Quantification of alkaloid

The alkaloid was quantified using a modified method of Caprioli et al. (2014) employing LC-40B XR (Shimadzu Corp,

Japan). Brewed coffee was filtered using a filter membrane of PTFE 0.22 µm, and 1 µL of the sample was eluted into column ACQUITY UPLC® BEH C18 (2.1 × 50 mm, 1.7 µm, Ireland) at 30°C and 430-570 kgf/cm^2. Mobile phase of methanol LC (A) and formic acid 0.3% (B) was operated at 0.3 mL/min. The gradient was programmed at 25% A (0 min), 60% A (1.00-1.50 min), 25% A (2.00-2.50 min), and 25% A (2.50-4.00 min). Detection using PDA SPD-M40 was performed at 265 nm. A 5 points-standard curve was made plotting trigonelline, theobromine, and caffeine at 15-250 mg/L (triplicates: trigonelline = LoD 6.81 mg/L, LoQ 2.04 mg/L, r^2 1; Theobromine = LoD 4.63 mg/L, LoQ 1.39 mg/L, r^2 0.99; and caffeine = LoD 4.99 mg/L, LoQ 1.50 mg/L, r^2 0.99). Concentration of alkaloid was expressed as g/100 g dry basis coffee (db).

2.10 Statistical analysis

Means were analyzed using single factor ANOVA. Significant difference between means was verified using Duncan test at $P < 0.05$ and T-Test between green beans and roasted beans with the same post-harvest processing (significant $P < 0.05$) in software Microsoft Excel 2019. Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) using software SIMCA Umetrics 14.1 was applied to create a profiling.

3 Results and discussion

3.1 Characteristics of green bean and roasted bean

Moisture content of green bean and roasted bean ranged 8.14-10.01 g/100 g db and 2.19-3.10 g/100 g db, respectively (Table 1). The difference in moisture content of green beans depends on the drying time of each process. The longest drying process was found in natural processing, while the shortest was found in full-washed processing. Gloess et al. (2014) stated that moisture content of coffee bean was desirable at 8-12 g/100 g wet basis, while other works suggested moisture content of < 12% wet basis on green bean before roasting and storage (Pereira et al., 2019; Kulapichitr et al., 2019, 2022). These records are in line with standard issued by Indonesian National Standards for upper limit of moisture level in green bean reaching 12%. High level of moisture in beans is not desirable, which make it highly susceptible to microbial growth and aflatoxin production. To exterminate the disadvantage, moisture content shall be controlled between 8.0-12.5% (Adnan et al., 2017; Reh et al., 2006). For roasted beans, the desirable moisture level could vary, depending on degree of roasting as follows: medium 2-3% and dark 1-2% (Wang & Lim, 2015). Roasting process includes three phases: drying, taste and color development, and cooling, and in the first phase, water evaporation in the beans caused reduction of moisture content from 12% to 2% (Fadai et al., 2017).

Bulk density of Arabica green bean differed significantly between three different processes, ranging 0.72-0.73 g/mL ($P < 0.05$), being higher than roasted bean 0.39-0.41 g/mL (Table 1). It is profoundly affected by moisture content. The moisture content of coffee beans from each processing varied, thus the bulk density was also different. Roasted coffee bean with low bulk density resulted from initial drying process of green bean (Wang & Lim, 2015). The bulk density of green bean reaches 0.48-0.76 g/mL, and it brings down 0.28-0.40 g/mL (Yusianto et al., 2007). Acidity of coffee depends on geographical origin, maturity of coffee cherry, drying condition, and postharvest processing (Bicho et al., 2013; Worku et al., 2018). The results show differences in pH level between treatments, i.e. 5.37 (natural), 5.32 (honey), and

Table 1. Physicochemical Characteristics of Kalosi Enrekang Arabica Coffee.

Parameters	Post-harvest processing		
	Natural	Honey	Full-washed
Green Bean			
Moisture content (% DB)	8.14 ± 0.37^{a*}	8.73 ± 0.26^{b*}	10.01 ± 0.10^{c*}
Bulk density (g/mL)	0.72 ± 0.00^{a*}	0.73 ± 0.01^{b*}	0.72 ± 0.00^{a*}
pH	5.37 ± 0.05^{a*}	5.32 ± 0.11^{a*}	5.45 ± 0.06^{a*}
TDS (g/100 mL)	1.88 ± 0.03^{a*}	1.73 ± 0.06^{a}	1.73 ± 0.06^{a}
Color			
L*	61.01 ± 0.64^{a*}	61.82 ± 1.62^{ab*}	64.30 ± 0.27^{c*}
a*	2.50 ± 0.18^{b*}	4.24 ± 0,44^{c*}	1.64 ± 0.19^{a*}
b*	21.19 ± 0.30^{a**}	20.59 ± 0.37^{a}	20.22 ± 0.82^{a*}
Roasted Bean			
Moisture content (% DB)	2.19 ± 0.03^{a*}	3.10 ± 0.61^{a*}	2.58 ± 0.85^{a*}
Bulk density (g/mL)	0.41 ± 0.01^{a*}	0.41 ± 0.02^{a*}	0.39 ± 0.01^{a*}
pH	4.69 ± 0.01^{a*}	4.65 ± 0.03^{a*}	4.67 ± 0.07^{a*}
TDS (g/100 mL)	1.78 ± 0.03^{a*}	1.80 ± 0.00^{a}	1.82 ± 0.10^{a*}
Color			
L*	36.44 ± 0.76^{a*}	37.82 ± 3.48^{a*}	36.43 ± 1.28^{a*}
a*	9.63 ± 0.41^{a*}	10.45 ± 0.58^{a*}	9.45 ± 0.37^{a*}
b*	15.65 ± 0.65^{a*}	18.71 ± 3.01^{a}	15.15 ± 1.07^{a*}

Notes: Means followed by the same superscript letter on the same row are not significantly different at Duncan's test ($P < 0.05$). The ANOVA test on green beans and roasted beans was carried out separately. Numbers followed by a sign * are significant between green beans and roasted beans with the same post-harvest processing by T-Test ($P < 0.05$). Values are the mean and standard deviation of 3 replications.

5.45 (full-washed). The pH tends to decline after roasting process, namely 4.69, 4.65, and 4.67, respectively. Bicho et al. (2013) reported that pH of Arabica green bean reached 5.62, and it was affected by the roasting process; longer roasting would produce lower pH, which altered the final taste (Rodriguez et al., 2020). The pH changes result from formation of organic acid during roasting process. Content of Formic acid, lactic acid, and acetic acid increased significantly as the glucose level of coffee beans decreased during roasting (Diviš et al., 2019).

Postharvest processing affects color profile of green bean (Figure 1). Full-washed resulted in the highest lightness (L*) compared with honey and natural, while honey processing yielded beans with distinct chromaticity of red (a*) over natural and full-washed process. High lightness in full-washed samples related to the absence of mucilage and short drying time. High chromaticity was found in honey processing samples. Honey treatment retained presence of mucilage which caused formation of brown color, and had a relatively long drying time. According to Kulapichitr et al. (2022), UV light and oxygen contributed to the rise of oxidation of chlorogenic acid isomers, leading to synthesis of ortho-quinones that polymerize into brown pigments. Such reaction occurs in long drying process. Intriguingly, roasting process reduced L* values of samples from all processes, with lower lightness. Variation of green bean colors is affected by postharvest processing. Coffee bean processing without mucilage removal produced more color variation, but the appearance of beans is similar due to caramelization induced by roasting process. (Rodriguez et al., 2020). Kim et al. (2018) showed that L* value of roasted coffee relied heavily on degree of roasting, i.e. light 50.79, medium 40.80, medium to dark 36.79, and dark 34.45. Noticeably, roasting process prompts meaningful physical and chemical changes of the beans through diverse mechanisms such as Maillard and Strecker reaction, hydrolysis, pyrolysis, and compound degradation that account for color and aroma of coffee (Toci et al., 2017).

Total dissolved solid (TDS) represents amount of dissolved component in coffee extract, which determines the coffee strength (Jung et al., 2021). Table 1 exhibits that TDS of green bean is not significantly different between procedures, and this also occurs in roasted bean. This is in accordance with Amorim et al. (2009), reporting that soluble solid of beans prepared with full-washed and dry did not differ significantly. Cordoba et al. (2020) found that TDS of coffee was affected by some factors, i.e. coffee bean structure, particle size, water temperature, and extraction time. According to Jung et al. (2021) the linear relation between TDS and roasting degree. The increase in TDS was associated with the pore structure of the coffee beans. TDS of coffee beans in honey and full-washed processing increased after roasting, in contrast to natural processing where TDS decreased. This possibly related to water pressure and low surface area of coffee powder; therefore, TDS was not sufficiently eluted (Jung et al., 2021).

3.2 Concentration of Caffeoylquinic Acid (CQAs)

As exhibited in Table 2, postharvest processing did not affect level of 3-CQA and 5-CQA ($P > 0.05$), but significantly altered content of 4-CQA and total CQAs ($P < 0.05$). The highest amount of CQAs is found in natural process, reaching up to 5.53 ± 0.12 g/100 g coffee db, while the lowest one occurred in honey process, reaching up to 5.11 ± 0.17 g/100 g coffee db. The results are in line with previous work of Bicho et al. (2013) reporting quantity of 3-CQA, 4-CQA, and 5-CQA in green bean, namely

Figure 1. Green beans and roasted beans of Kalosi Enrekang Arabica coffee with different post-harvest processing (A: Green bean; B: Roasted bean).

Table 2. CQAs content of green beans and roasted beans for Kalosi Enrekang Arabica coffee (g/100 g dry basis coffee).

Coffee sample	Post-harvest processing	3-CQA	4-CQA	5-CQA	Total CQAs
Green Bean	Natural	$0.75 \pm 0.04^{a*}$	0.68 ± 0.03^{c}	$4.11 \pm 0.05^{a*}$	$5.53 \pm 0.12^{bc*}$
	Honey	$0.67 \pm 0.03^{a*}$	$0.59 \pm 0.01^{a*}$	$3.85 \pm 0.13^{a*}$	$5.11 \pm 0.17^{a*}$
	Full-washed	0.74 ± 0.03^{a}	$0.64 \pm 0.04^{ab*}$	$3.93 \pm 0.14^{a*}$	$5.30 \pm 0.20^{ab*}$
Roasted Bean	Natural	$0.66 \pm 0.01^{a*}$	0.66 ± 0.02^{a}	$1.71 \pm 0.11^{a*}$	$3.03 \pm 0.14^{a*}$
	Honey	$0.78 \pm 0.02^{c*}$	$0.81 \pm 0.05^{c*}$	$1.73 \pm 0.18^{a*}$	$3.32 \pm 0.24^{a*}$
	Full-washed	0.71 ± 0.03^{b}	$0.72 \pm 0.03^{ab*}$	$1.75 \pm 0.10^{a*}$	$3.18 \pm 0.16^{a*}$

Notes: Means followed by the same superscript letter on the same row are not significantly different at Duncan's test ($P < 0.05$). The ANOVA test on green beans and roasted beans was carried out separately. Numbers followed by a sign * are significant between green beans and roasted beans with the same post-harvest processing by T-Test ($P < 0.05$). Values are the mean and standard deviation of 3 replications.

0.56 g/100 g, 0.71 g/100 g, and 4.43 g/100 g, respectively, with total CQAs of 5.70 g/100 g. In addition, Santiago et al. (2020) reported content of 5-CQA in Arabica green bean reaching 3.47-5.25 g/100 g. Discrepancy in chlorogenic acid content among postharvest procedures relates to loss of water-soluble compounds during lixiviation and fermentation in full-washed processing, as well as results from degradation of components due to sun-drying (Duarte et al., 2010). The growing acidity in fermentation leads to isomerization of 5-CQA into 4-CQA and 3-CQA following mechanism of intramolecular ortho-acyl migration. UV light also caused 5-CQA isomerization into cis/trans 5-CQA (Xie et al., 2011). Drying condition affects metabolism of coffee bean, which reduce metabolite stresses such as phenolics (Kulapichitr et al., 2022). In addition, CQAs become substrate for polyphenol oxidase responsible for formation of dark color in the green bean (Cheng et al., 2019; Kulapichitr et al., 2022). In this regard, temperature demonstrated strong impact to amount of CGA isomers through metabolism pathway without altering quantity of CGA (Joët et al., 2010).

The highest content of CQAs isomers in green bean is found in natural process, while the lowest one is honey process (Table 2). CGA isomers (3-CQA, 4-CQA, 3,4-diCQA, and 4,5-diCQA) are lower in full-washed process than in dry process (De Bruyn et al., 2016). Nevertheless, content of chlorogenic acid and trigonelline in full-washed process relies on soaking time. Quantity of chlorogenic acid in Arabica coffee bean was higher in full-washed process than in semi dry (pulped natural) (Duarte et al., 2010). Meanwhile, Rodriguez et al. (2020) found that concentration of chlorogenic acid in Arabica green bean var. Castillo did not differ significantly between full-washed and semi dry process. Duarte et al. (2010) and Worku et al. (2018) reported that some isomers of CGA and caffeine did not change due to postharvest processing. The chlorogenic acid in Arabica coffee bean varied depending on coffee variety and geographical condition (Monteiro & Farah, 2012).

Roasting can markedly alter content of CQAs (Tfouni et al., 2014). Table 2 demonstrates reduction of CQAs following roasting process. Concentration of 3-CQA and 4-CQA in roasted bean relied heavily on postharvest processing ($P<0.05$). During roasting, CQA diminished significantly due to decomposition and degradation (Farah et al., 2005; Wei et al., 2012; Wei & Tanokura, 2015). Isomerization and degradation occur as a result of carbon-carbon bond breakage in CGA induced by high temperature during roasting. Quantity of 5-CQA diminished after 5 min of roasting; conversely, concentration of 3-CQA and 4-CQA almost doubled in comparison with green bean. Additionally, roasting induced transformation such as dehydration of quinic acid and formation of lactone rings (Farah et al., 2005). The main constituent of CGA degradation was melanoidin and low molecular weight compounds (Diviš et al., 2019). Roasting process also prompted formation of quinic acid lactone, chlorogenic acid lactone, feruloylquinic acid, caffeoylquinic acid lactone, and p-coumaroylquinic acid lactone, and cinnamic acid as chlorogenic acid products (Wei & Tanokura, 2015).

Concentration of 5-CQA decreased significantly, while 3-CQA and 4-CQA content was relatively unchanged, even they tended to increase during roasting (Table 2). 5-CQA in green bean was found to be more abundant than in roasted bean; indeed, its content could be twice, depending on roasting duration (Jeszka-Skowron et al., 2016). Changes in characteristic result from degradation and formation/release of chemical compounds generated through some reactions such as Maillard, Strecker, breakdown of constituents, i.e. amino acids, trigonelline, and quinic acid, pigment, lipid, as well as interaction of intermediate products (Sunarharum et al., 2014; Toci et al., 2017). The decrease of CGA relates to breakage of carbon-carbon bonds, resulting inisomerization, epimerization, lactonization, and degradation in initial phase of roasting (Hu et al., 2020; Sittipod et al., 2019). However, CGA isomers could still exist in dark roasted bean, while quinic acid and syllo-quinic content increased as a result of CGA breakdown (Hu et al., 2020). Light roasting in green beans (Ethiopian, Nicaragua, and Sumatra) could raise content of 4-CQA (Moon et al., 2009). In short, roasting process markedly induced most changes of CGA due to hydrolysis, degradation, isomerization, decarboxylation, and polymerization. During roasting, CGA could transform into some aromatic compounds, taste-active chlorogenic lactone and melanoidin (Kulapichitr et al., 2022). Roasting supressed content of 5-CQA, trigonelline, furfural, and hydroxymethylfurfural, but increased melanoidin (Vignoli et al., 2014).

3.3 Concentration of alkaloid content

In addition to chlorogenic acid, main constituent of coffee is alkaloid, primarily in form of caffeine and trigonelline (Mehari et al., 2016; Rodrigues & Bragagnolo, 2013). Caffeine, theobromine, and theophylline are secondary metabolite of methylxanthine, derived from purine nucleotide (Mehari et al., 2016), while trigonelline is derived from pyridine. Caffeine is

dominant constituent of coffee (Rodrigues & Bragagnolo, 2013; Yisak et al., 2018), reaching up to 2.78-2.80 g/100 g db in Arabica green bean. This work reveals that caffeine content is not affected by postharvest processing ($P > 0.05$) (Table 3). De Luca et al. (2018) reported that caffeine in Arabica green bean reached 7.31-44.69 mg/g; and Jeszka-Skowron et al. (2016) reported its concentration reaching up to 34.1-38.5 g/kg, depending on where these beans come from. Furthermore, postharvest treatment was responsible for content of caffeine in coffee bean (Joët et al., 2010; Worku et al., 2018).

Trigonelline is also main alkaloid of coffee bean (Rodrigues & Bragagnolo, 2013; Yisak et al., 2018). Table 3 exhibits content of trigonelline in Arabica green bean, i.e. 1.10-1.25 g/100 g db, relying on postharvest process ($P < 0.05$). Duarte et al. (2010) argued that the difference in trigonelline concentration between green bean and processed bean came from lixiviation and degraded compounds due to heat exposure. High temperature could degrade trigonelline into nicotinate acid and nicotinamide (Taguchi et al., 1985; Wei & Tanokura, 2015). In this work, the greatest trigonelline content was found in honey process. Yellow Bourbon coffee planted in altitude greater than 1200 m combined with shade had a higher content of trigonelline in full-washed process than in dry process (Ribeiro et al., 2016). Moreover, trigonelline was found more abundant in Brazilian arabica coffee bean processed with full washed than semi dry process, since full-washed process cause loss of water-soluble components, giving rise to trigonelline concentration (Joët et al., 2010; Mehari et al., 2016). Besides processing, concentration of trigonelline in green bean differs due to location of cultivation and genetic feature (Mehari et al., 2016).

Furthermore, theobromine in coffee is lower than caffeine and trigonelline (Rodrigues & Bragagnolo, 2013). In this case, its content reaches 0.12-0.13 g/100 g db (Table 3). This finding is in accordance with Gebrekidan et al. (2020) examining 18 coffee samples that contain theobromine of 0.0186-0.320% (w/w). Our work reveals that postharvest processing has no effect on theobromine in green bean. The increases in theobromine concentration in roasted beans deemed as the result of caffeine degradation due to the oxidation induced by roasting. According to Chung & Cha (1997) theobromine was arranged from the demethylation of caffeine due to oxidation. Additionally, Jeszka-Skowron et al. (2020) revealed that decaffeinated coffee contains smaller theobromine and theophylline. Theobromine in green beans was detected but it could not be quantified. Meanwhile, in roasted beans it could be quantified (Mehari et al., 2016). Total alkaloid in green bean was not significantly different (Table 3). Concentration of coffee alkaloid relies on species, maturity, harvesting technique (fermentation, washing, drying, and storage), roast degree (light, medium, and dark), cultivating method, and environmental condition (Jeszka-Skowron et al., 2020; Mehari et al., 2016; Ribeiro et al., 2016)

The content of alkaloids in coffee beans decreased due to the roasting process, but the decline was lower than CQAs (Figure 2). Although concentration of trigonelline and caffeine showed a decline, the caffeine seemed to be more stable (Herawati et al., 2018; Vignoli et al., 2014). The content of caffeine differs in green bean and roasted bean as a consequence of water loss during roasting as well as formation of carbon dioxide and volatile compounds (Jeszka-Skowron et al., 2020; Wei & Tanokura, 2015). Medium and dark roasting showed a higher retaining of caffeine which could relate to decrease in water content as higher period of roasting (Bolka & Emire, 2020; Vignoli et al., 2014). Theobromine, having a similar chemical structure to caffeine, showed a heat-stable feature during roasting process (Mehari et al., 2016; Santos & Rangel, 2012).

Similar to caffeine, trigonelline also decline in roasted bean (Table 3), which is a precursor for generating taste and aroma of coffee. During roasting, trigonelline accounts for composing furan, pyrazine, alkyl-pyridine, and pyro. High temperature leads to decline of trigonelline during roasting process, inducing pyrolysis that facilitates formation of nicotinate acid and N-methylpyridinium (Wei et al., 2012; Wei & Tanokura, 2015; Bastian et al., 2021; Jeszka-Skowron et al., 2020). A study

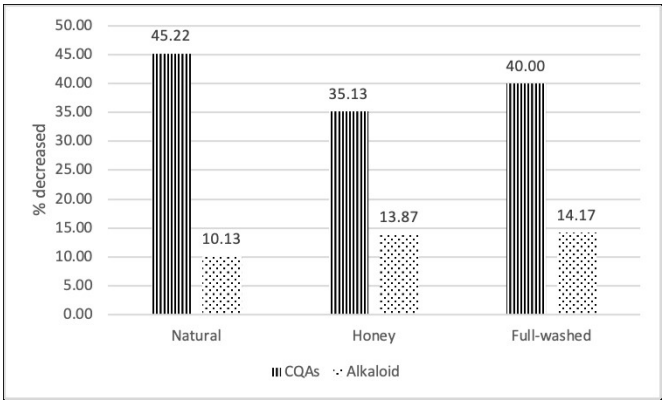

Figure 2. Percentage decrease in CQAs and alkaloids during roasting.

Table 3. Alkaloids content of green beans and roasted beans for Kalosi Enrekang Arabica coffee (g/100 g dry basis coffee).

Coffee sample	Post-harvest processing	Trigonelline	Theobromine	caffeine	Total Alkaloid
Green Bean	Natural	$1.10 \pm 0.02^{a*}$	$0.13 \pm 0.01^{a*}$	$2.80 \pm 0.06^{a*}$	$4.03 \pm 0.09^{a*}$
	Honey	$1.25 \pm 0.02^{bc*}$	$0.12 \pm 0.00^{a*}$	$2.80 \pm 0.08^{a*}$	$4.17 \pm 0.10^{a*}$
	Full-washed	$1.21 \pm 0.05^{ab*}$	$0.12 \pm 0.01^{a*}$	$2.78 \pm 0.08^{a*}$	$4.12 \pm 0.15^{a*}$
Roasted Bean	Natural	$0.84 \pm 0.01^{a*}$	$0.46 \pm 0.01^{a*}$	$2.32 \pm 0.08^{a*}$	$3.63 \pm 0.10^{a*}$
	Honey	$0.83 \pm 0.01^{a*}$	$0.53 \pm 0.03^{b*}$	$2.23 \pm 0.09^{a*}$	$3.59 \pm 0.13^{a*}$
	Full-washed	$0.83 \pm 0.03^{a*}$	$0.55 \pm 0.01^{bc*}$	$2.15 \pm 0.18^{a*}$	$3.53 \pm 0.21^{a*}$

Notes: Means followed by the same superscript letter on the same row are not significantly different at Duncan's test ($P < 0.05$). The ANOVA test on green beans and roasted beans was carried out separately. Numbers followed by a sign * are significant between green beans and roasted beans with the same post-harvest processing by T-Test ($P < 0.05$). Values are the mean and standard deviation of 3 replications.

reported that decline of trigonelline did not differ significantly between light and medium roasting, but dark roasting promoted a more intensive degradation of trigonelline (Hu et al., 2020). Dark roasting reduced 40-60% of caffeine and also suppressed content of chlorogenic acid and trigonelline (Somporn et al., 2011). However, Perrone et al. (2008) reported that trigonelline was unstable in high temperature process, make it more easily degraded during roasting process.

3.4 OPLS-DA

This work employs OPLS-DA to distinguish physical and chemical characteristics of green bean and roasted bean. This OPSL-DA has excellent performance R^2X: 0.999, R^2Y: 0,9 and an acceptable Q^2: 0.485 (see Figure 3). Tunnisa et al. (2022) and Worley & Powers (2016) Q^2 and R^2 are reliable when the value is > 0.4. Natural-processed green bean shows different characteristics from honey and full-washed processing. In natural process, coffee cherry was sun-dried directly after harvested in which metabolic activities still occurred during drying process (Bastian et al., 2021). Characteristic of green bean and roasted bean differed clearly as presented in OPLS-DA biplot (Figure 3), but showed relation. Moisture content serves a key parameter of green bean, which alters final properties of roasted bean. The low content of moisture limits water mobility, which leads to restriction of bean swelling; in contrast, excessive moisture content would delay water evaporation, giving increment of bean surface hardness (Herawati et al., 2018). Maillard reaction and pyrolysis present during roasting facilitate production of miscellaneous compounds including chemicals that form aroma and taste. Roasting also generates CO_2, which raises bean porosity (Fadai et al., 2017), while higher roast degree would induce bean weight loss, increase level of TDS, remove thermolabile compounds, as well as enhance remaining compound (Jung et al., 2021). Difference in physical, chemical, and biological properties of roasted beans occurs due to dissimilar characteristic of green beans; thus, this complexity challenges researchers in determination of optimum roasting condition (Bolka & Emire, 2020).

CQAs decreased after the roasting process due to degradation and isomerization as indicated by the increase of 4-CQA content in roasted beans. Herawati et al. (2022) stated that the roasting process enhanced content of 3-CQA and 4-CQA. This increase was due to CQA undergoing isomerization before forming lactones (Farah et al., 2005). Similarly, caffeine and trigonelline were high in green beans but they decreased after roasting, while theobromine increased. Oxidation prompted degradation of caffeine into theobromine (Chung & Cha, 1997). Trigonelline was degraded to form pyrrole and alkyl-pyridine (Buffo & Cardelli-Freire, 2004). The loading plot results showed the increase in theobromine in line with an increase in a* chromaticity. Overall, natural processed green beans contained higher of 5-CQAs and CQAs compared to honey and full-washed process. Honey processed green beans contained a high level of trigonelline and alkaloids compared to other processes. Natural and honey green beans contained caffeine in the same concentration. Honey roasted beans contained a high 3-CQA and 4-CQA, while full-washed roasted beans contained a high content of theobromine.

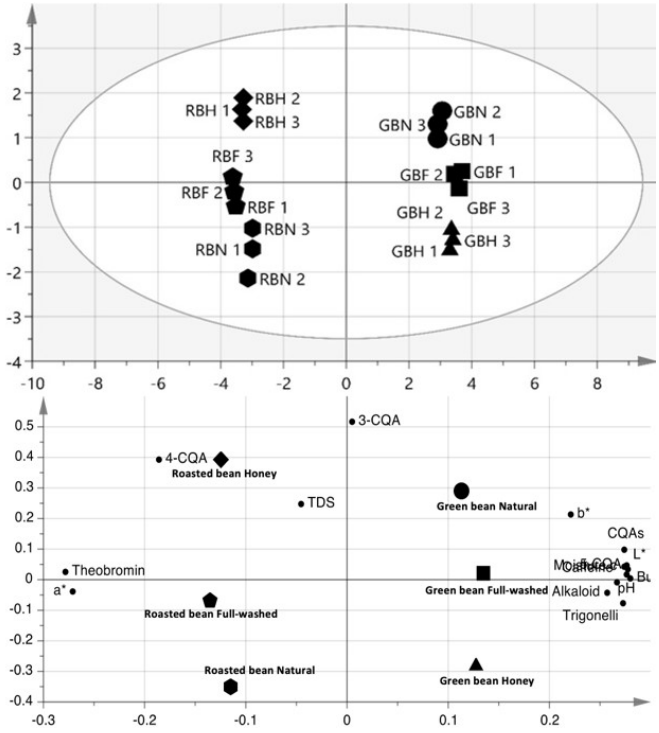

Figure 3. OPLS-DA physicochemical characteristics and bioactive compound of green beans and roasted beans for Arabica Kalosi Enrekang coffee (GBN: Green bean Natural, GBF: Green bean Full-washed, GBH: Green bean Honey, RBN: Roasted bean Natural, RBF: Roasted bean Honey, RBF: Roasted bean Full-washed).

4 Conclusion

Post-harvest processing affects the physicochemical characteristics of coffee beans. Physical characteristic of green bean, especially bulk density, color, was affected by postharvest processing ($P < 0.05$). Moisture content of green bean obtained in all procedures ranged 8-10% db, then decreased up to 2-3% db following the roasting process. Moisture content affected bulk density of bean. Level of pH also differed, ranging 5.32-5.45 for green bean and 4.65-4.69 for roasted bean. TDS for green bean and roasted bean was found at 1.73-1.88 g/100 mL. The difference of green bean post-harvest processing showed significant effects on 4-CQA, total CQAs, and trigonelline, while the treatments also significantly affected 3-CQA, 4-CQA, and theobromine in roasted samples ($P < 0.05$). Roasting caused the decline of CQAs and alkaloid reaching up to 45.22% and 14.17%, respectively.

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