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Chemical composition of green and roasted coffee bean of Gayo arabica civet coffee (kopi luwak)

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Abstract. Kopi luwak, is an Indonesian exotic coffee, is known as one of the most popular coffee in the world. This coffee is prepared from the finest and ripest coffee berries that are eaten by Asian civet (\textit{Paradoxurus hermaphroditus}), cat like-animal. The aim of this study was to determine the chemical attributes of kopi luwak both in green and roasted coffee bean. This study conducted by collecting the six samples of kopi luwak from different farms in Gayo Highland, which then processed onto green and roasted coffee beans. The examined parameters are protein, lipid, caffeine and chlorogenic acids. The results of this study showed that the differences existed in chemical attributes of green and roasted of Gayo kopi luwak. The average contents of lipid, protein, caffeine and chlorogenic acids of Gayo arabica kopi luwak in green bean were 12.30\%, 13.36\%, 1.20\% and 3.73\%, while in roasted bean were 14.79\%, 13.66\%, 1.10\% and 0.88\% respectively. To conclude with, lipids and caffeine survived during thermal treatments in roasting process, meanwhile chlorogenic acids and protein (N-compounds) are degraded and formed smaller fragments with lower molecular weights.

1. Introduction

Coffee is one of the most widely consumed beverages in the world. It is consumed by a million people because of its complex aroma and taste. Recently, coffee is considered as a functional food, primarily because of its chemical compounds and other beneficial properties. There are many compounds in coffee that are often thought to have implications to health, include caffeine, micronutrients and chlorogenic acids [1,2]. In global trade \textit{Coffea arabica} and \textit{Coffea robusta} are the two common coffee varieties have grown in commercial production and both of them are differed distinctly in flavor, caffeine contents and other chemical compounds. For the consumers, flavor is arguably the most important aspect of a good coffee. The flavor of coffee varies due to influences of many factors such as genetic, environmental (geographical location), differing agricultural practices and variations in post-harvest methods [2,3].

Gayo Highland is one of the largest arabica coffee producing regions in Indonesia even in Southeast Asia. It is located on the ridges of Bukit Barisan that lies across Sumatera Island and in the center of Aceh Province, Indonesia. Administratively Gayo Highland covers three district areas: Aceh Tengah, Bener Meriah and Gayo Lues. The perfect climates and altitude in Gayo Highland support
and suitable for Arabica coffee production. As a result, reputation of Gayo Arabica coffee as specialty coffee is well known in domestic and international markets. It has a distinctive taste and aroma, complex flavor, light acidity, and strong heavy body [7]. Usually in this area, the green bean of Arabica coffee is processed through semi-washed, natural and herbivorous coffee processing.

As mentioned above, good post-harvest methods are important to produce good-quality coffee. Each applied method contributed towards the coffee sensory quality. Dry and wet processing methods are the common ways to produce green bean. The dry process is simple and inexpensive while the wet process requires more cares and investment but the result of wet process is superior. However, in Gayo Highland, the common post harvest process done by farmers is semi-washed process, which comprises component a both dry and wash processing[4]. As well as the above-mentioned of coffee bean processing, there is an unique method called as “herbivorous method of coffee processing” that produce kopi luwak from Indonesia. This coffee is prepared from excreted beans, which previously had been eaten as coffee berries by civet (Paradoxurus hermaphroditus) or luwak (Indonesian). The berries are digested but the beans present inside them pass undigested and excreted. The excreted beans are manually collected, washed, dried and finally roasted to produce one of the most expensive coffee in the world [2,5]. According to some resources, Indonesia was the country that discovered kopi luwak for the first time. Natural process of getting kopi luwak only take place in Indonesia, usually in Sumatera, Java, Bali and Sulawesi Island. One of the reasons that kopi luwak has high price because of its high demand and limited supply [6].

Eventhough the kopi luwak processing method mig originally come from Indonesia, scientific information about kopi luwak characteristics are still lacking, especially kopi luwak from Gayo Highland. Therefore this research aims to collect and identify chemical composition of kopi luwak as green bean and roasted bean. This information is required in order to study the quality of kopi luwak holistically as premium brewed drink. Coffee quality as brewed drink is measured by its sensory properties, not mentioned its beneficial functional properties. It sensory properties are manifestation of its chemical composition such as lipids, proteins, peptides and free sugar through the whole process from post harvest practices to roasting and brewing techniques. Therefore the information related its chemical compounds during these processing sequences should be well known.

2. Materials and Methods

2.1 Sampling Procedures
The six samples of kopi luwak were obtained from two district areas at Gayo Highland, Aceh Tengah and Bener Meriah, Aceh Indonesia (A: Arul Badak, Aceh Tengah, B: Jejem 1, Aceh Tengah, C: Wih Pongas, Bener Meriah, D: Blang Panas, Bener Meriah , E: Jejem 2, Aceh Tengah, F: Kenawat Redelong, Bener Meriah). The collected samples were cleaned, washed, dried up to moisture content about 12% and manually hulled to produce green coffee bean. Since the experimental coffee set also include roasted bean, the samples are roasted at medium degree based on SCAA protocol standard [9].

2.2 Sample Analysis
2.2.1 Analysis of Total Lipid. Total lipid analysis of kopi luwak was conducted by soxhlet method based on Indonesian Nasional Standard SNI No 01-2891-1992 (10). Briefly, 2 g of sample was wrapped and dried using oven oven at 80°C and placed into the lipid flask within the soxhlet extractor. The sample was then extracted by hexane solvent. The extract obtained was distilled and subsequently dried using oven at 105°C. The step was repeated until a contant weight was achieved. Total lipid content of the sample was calculated as:

\[
\text{Lipid content (%)=(Weight of n-hexane extract)/(Weight of sample)×100} \quad (1)
\]

2.2.2 Analysis of Protein Analysis. Crude protein analysis of kopi luwak was conducted by measuring nitrogen content with Kjeldahl method based on SNI No 01-2891-1992 (10). Briefly, 0.51 g of sample was placed in the kjeldahl flask. Subsequently, mixture of selenium 2 g (2.5 g of SeO₂, 100 g of
K₂SO₄, 30 g of CuSO₄·5H₂O and 25 ml of H₂SO₄ were added into the kjeldahl flask, mixed thoroughly and heated until it clear and greenish. Distilled water was added until the mixture reached 100 ml. The mixture then pipetted 5 ml and placed into distillation system. Subsequently added 5 ml of 30% NaOH solution and few drops of indicator solution (10 ml of 0.1 ml bromcresol green and 2 ml of methyl red). Distillation was done within 10 min and the produced NH₃ (in the form of NH₄OH) was collected in the conical flask supplemented with 10 ml of 0.2% boric acid solution and few drops of mixed indicator solution. The distillate then subjected to titration against 0.01 N HCl. Protein of sample was calculated as:

\[
\text{Crude protein content (\%) = 6.25 \times \left( \frac{V_1 - V_2}{W} \right) \times 0.014 \times f \times N} \times 100
\]

Where V₁, V₂, N, f and W are the sample titration reading, blank titration reading, HCl normality, sample dilution and sample weight, respectively. The 0.014 is the mili equivalent of nitrogen.

2.2.3 Caffeine and Chlorogenic Acids Analysis by High Performance Liquid Chromatography (HPLC). Each sample (green bean or roasted bean) is grounded and weighed for 1 g in 100 ml beakers and added 50 ml distilled water. The samples were boiled for 5 minutes in stirring hotplate. The coffee samples were cooled for some minutes and continued by centrifugation with 8000 rpm for 10 minutes. The supernatant was pipetted 1 ml to microcentrifuge tube and centrifugated at 13000 rpm for 10 minutes. The resulted supernatant is ready to be injected to chromatography column. The following were HPLC condition: column is Sunfire C 18:5 m (150 x 4.6 mm), combination of 0.1% acetic acids and methanol with ratio 80:20 as active phase at 1 ml per minutes with injection volume of 10 ml (11).

2.4 Data Analysis
All of parameters were measured triplicates. The obtained data for each samples were tabulated and calculated. Results were presented as means with corresponding standar deviation in table form and analyzed descriptively.

3. Results and Discussion
3.1 Total Lipid Content of Gayo Kopi Luwak
The total lipid content of Gayo kopi luwak are shown in Table 1. The total lipid content of the green bean samples are ranged from 12.03±0.82% to 12.63±0.19 % with average 12.30±0.33%. Lipid contents of this kopi luwak is in the range of regular Arabica coffee from previous report, as mentioned within 12-18% [12]. The lipid fractions in coffee, also known as coffee oil, is divided into the oil coated the bean surface and tryglycerides, as linoleic acid (40-45%) and palmitic acids (25-35%) [23]. The other lipid fractions are free fatty acids, diterpene alcohols, sterols and tocopherols, which are generally found in edible vegetable oils [1,2]. From Table 1, the total lipid of roasted bean of Gayo kopi luwak ranged from 14.53±0.01% to 15.10±0.12% with average 14.79± 0.08%. This report is in agreement with content reported by Wei and Tanokura [12], which was in the range of 14.5 -20%. Lipid fraction is reported relatively heat stable. During roasting, lipid form aldehydes as result of thermal degradation. The aldehydes will react further with other coffee constituents [23]. As roasting done and water content evaporated, the bean has porous wall and lipid fractions appeared in bean surface [12]. This lipid fraction migration together with aldehydes formation are also reported to retain the generation of aroma components [24].
Table 1. Lipid content of kopi luwak (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lipid content (%) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green Bean</td>
</tr>
<tr>
<td>A</td>
<td>12.63 ± 0.19</td>
</tr>
<tr>
<td>B</td>
<td>12.18 ± 0.26</td>
</tr>
<tr>
<td>C</td>
<td>12.16 ± 0.14</td>
</tr>
<tr>
<td>D</td>
<td>12.16 ± 0.18</td>
</tr>
<tr>
<td>E</td>
<td>12.03 ± 0.82</td>
</tr>
<tr>
<td>F</td>
<td>12.66 ± 0.43</td>
</tr>
<tr>
<td>Average</td>
<td>12.30 ± 0.33</td>
</tr>
</tbody>
</table>

3.2 Protein Content of Gayo Arabica Kopi Luwak

The crude protein content of Gayo kopi luwak are shown in Table 2. The protein content of green bean of Gayo kopi luwak ranged from 12.49 ± 0.59% to 13.90 ± 0.20% with average 13.36 ± 0.47%. While, the total protein of roasted bean of Gayo kopi luwak ranged from 12.68 ± 0.21% to 13.79 ± 0.01% with average 13.66 ± 0.12%. The results are within the literature reported range 11-13% (green bean) and 13-15% (roasted bean) [12]. Crude protein content is calculated the protein, peptide and amino acids. All of these N-compounds have a vital contribution to coffee flavor during roasting through Maillard reactions and Stecker degradations. Maillard reactions refers as non-enzymatic browning, is forming the carbondioxide as lower molecular weight compounds and also the flavor components. Maillard reaction is a joint degradation of N-amino (free amino acids, peptide or proteins) catalyzed sugar degradation. As a result of maillard reactions, N-amino decreased to form melainoidin and flavor [24]. Nitrogen compounds serve as precursors for volatile compounds formation such as furans, pyridines, pyrazines, pyrrols, aldehydes and melanoidsins [1, 2, 13]. Composition of coffee bean changes as consequence of thermal process which destruction of various compounds and formation of others. Roasting leads to protein denaturation with degradation, at the same time the green coffee bean protein subunits are integrated with reducing sugars into polymeric structure of melanoidsins formed during roasting [1, 12]. As an active components involved of flavor formation, N-compounds formed flavor quality such as roasty, nutty from pyrazines and thiazoles, and malty or honey from aldehydes [24].

Table 2. Protein content of kopi luwak (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Protein content (%) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green Bean</td>
</tr>
<tr>
<td>A</td>
<td>13.49 ± 1.10</td>
</tr>
<tr>
<td>B</td>
<td>12.49 ± 0.59</td>
</tr>
<tr>
<td>C</td>
<td>13.45 ± 0.54</td>
</tr>
<tr>
<td>D</td>
<td>13.13 ± 0.27</td>
</tr>
<tr>
<td>E</td>
<td>13.90 ± 0.20</td>
</tr>
<tr>
<td>F</td>
<td>13.73 ± 0.15</td>
</tr>
<tr>
<td>Average</td>
<td>13.36 ± 0.47</td>
</tr>
</tbody>
</table>

3.3. Caffeine Content of Gayo Arabica Kopi Luwak

The caffeine content of Gayo kopi luwak are presented in Table 3. The caffeine content of green bean of Gayo kopi luwak ranged from 1.13 ± 0.05% - 1.24 ± 0.01% with average 1.20± 0.02%. While, the caffeine content of roasted bean of Gayo kopi luwak ranged from 1.00 ± 0.01% to 1.17 ± 0.01% with average 1.10 ± 0.02%. In present study, the caffeine content of green and roasted bean are relatively similar. This result is in agreement with caffeine content reported by Tawfik and El Bader [14], 1.2% and 1.1% in green and roasted bean respectively. Caffeine is actually heat stable. Roasting is not significantly affected caffeine level but small losses may occur due to sublimation (1). Caffeine is
main alkaloid compounds in coffee bean. Caffeine reported having a contribution towards the bitterness of coffee liquor and may give a physiological stimulating effect [15].

**Tabel 3. Caffeine content of kopi luwak (%)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Green Bean</th>
<th>Roasted Bean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.24± 0.01</td>
<td>1.16± 0.00</td>
</tr>
<tr>
<td>B</td>
<td>1.13± 0.05</td>
<td>1.03± 0.04</td>
</tr>
<tr>
<td>C</td>
<td>1.21± 0.01</td>
<td>1.15± 0.06</td>
</tr>
<tr>
<td>D</td>
<td>1.23± 0.02</td>
<td>1.17± 0.01</td>
</tr>
<tr>
<td>E</td>
<td>1.18± 0.02</td>
<td>1.00± 0.01</td>
</tr>
<tr>
<td>F</td>
<td>1.19± 0.02</td>
<td>1.08± 0.01</td>
</tr>
<tr>
<td>Average</td>
<td>1.20± 0.02</td>
<td>1.10± 0.02</td>
</tr>
</tbody>
</table>

**3.4 Chlorogenic Acids Content of Gayo Arabica Kopi Luwak**

The chlorogenic acids content of Gayo kopi luwak are presented in Table 3. The chlorogenic acids content of green bean of Gayo kopi luwak ranged from 3.61±0.60% to 4.84±0.21% with average 3.73±0.61%. The chlorogenic acids of roasted bean of Gayo kopi luwak ranged from 0.55±0.73% to 1.18±0.04% with average 0.88± 0.44%. The results are lower than the literature reported 5.5-8.0% and 1.2-2.3% for green and roasted bean respectively [13, 24]. Chlorogenic acids has been reported heavily degraded during roasting process due to thermal instability. The degradation rate of chlorogenic acids depend on roasting condition. Roasting causes isomerization of the compound prior to the formation of lactones. Losses of about 60% were observed in mild roasting and almost 100% in heavy roasting [16, 17, 18]. Farah et al., [25] added that after 7 minutes of roasting, almost 90% of chlorogenic acids have reacted.

**Tabel 4. Chlorogenic acids content of kopi luwak (%)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chlorogenic acids content (%) + SD</th>
<th>Roasted Bean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.84± 0.21</td>
<td>0.55± 0.73</td>
</tr>
<tr>
<td>B</td>
<td>4.06± 0.16</td>
<td>0.79± 0.10</td>
</tr>
<tr>
<td>C</td>
<td>3.61± 0.60</td>
<td>0.91± 0.04</td>
</tr>
<tr>
<td>D</td>
<td>3.92± 0.27</td>
<td>0.98± 0.02</td>
</tr>
<tr>
<td>E</td>
<td>3.71± 0.15</td>
<td>1.18± 0.04</td>
</tr>
<tr>
<td>F</td>
<td>3.76± 0.50</td>
<td>0.94± 0.04</td>
</tr>
<tr>
<td>Average</td>
<td>3.73± 0.61</td>
<td>0.88± 0.44</td>
</tr>
</tbody>
</table>

Chlorogenic acids (CGA) are secondary metabolits which presents in coffee beans. A number of chlorogenic acids present in coffee, and its hydrolisis products such as quinic acids and ferulic acids might have large contribution towards bitterness of coffee liquor [17, 19]. The formation of lactones and caffeic acids as results of CGA breakdown during roasting is reported as key intermediate of in formation of harsh bitterness and darker color in coffee. In addition, the phenols compounds in CGA contributes towards the formation of smoky and ashy flavor.

Furthermore due to its chlorogenic acids contents, coffee has been reported as functional food. This brewed beverage is claimed as one of the richest sources of chlorogenic acids in human diets compared to other beverages [20] and reported being used as bioactive compounds which act as antioxidant [21, 22]. By doing so, the lower roasting degree is implemented in order to gain its functional properties, which is also questioning its sensory performance.
4. Conclusions
Taking everything into considerations, the lipids, protein and caffeine compounds of kopi luwak for both green and roasted beans are in the range of regular Arabica coffee. The samples of Gayo kopi luwak in form of green bean has 12.30% lipid, 13.36% protein, 1.20% caffeine and 3.73% chlorogenic acids. Meanwhile the roasted bean has 14.79% lipid, 13.66% protein, 1.10% caffeine and 0.80% chlorogenic acids. However the chlorogenic acids of kopi luwak is lower than the regular Arabica coffee. Furthermore, lipids and caffeine survived during thermal treatments in roasting process, meanwhile chlorogenic acids and protein (N-compounds) are degraded and formed smaller fragments with lower molecular weights.

Acknowledgments
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