Pulverization of coffee silverskin extract as a source of antioxidant

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Abstract. Coffee silverskin (CS) is waste from coffee roasting process that has a value as source of antioxidant. In this research, two types of variant coffee Robusta and Arabica CS were extracted for their phenolic content, flavonoid content, and antioxidant activity. The extraction was done at 40ºC for 60 minutes using hydroalcoholic solvent. The phenolic, flavonoid content, and antioxidant activity of Robusta CS extract were 816.75 ± 63.24 mg GAE/L and 32.82 ± 2.47 mg QE/L, and 54.80% inhibition respectively, while for Arabica CS extract were 473.51 ± 56.70 mg GAE/L, 18.58 ± 2.47 mg QE/L, and 26.30% inhibition respectively. Thus, the Robusta coffee silverskin extract has higher value of total phenolic content, flavonoid content, and antioxidant activity than Arabica coffee silverskin extract. To produce high antioxidant powder of CS extract, the effect of drying method (freeze drying and spray drying) affecting the phenolic content, flavonoid content, and antioxidant activity was evaluated. The effect of evaporation prior to both drying processes was also evaluated. Evaporation caused up to 23% of total phenolic content degradation. Spray drying resulted in dried CS extract with degradation of total phenolic content up to 17%. On the other hand, freeze drying resulted no major degradation of total phenolic content. However, the coffee silverskin extract can be directly spray dried without evaporation resulting in higher amount of phenolic content in the powder than the one which was evaporated first.

1. Introduction
Recently, coffee has become one of the most popular beverages in the world. Indonesia itself is the third biggest coffee producer in the world, after Brazil and Vietnam [1], but only two species are commercially traded worldwide. There are Coffeaarabica (Arabica) and Coffeaacanephora (Robusta) [1]. Robusta is considered to have a higher yield because it is easier to tend on the farm and less sensitive to insects. Also from the price perspective, Robusta's greenbean is about half the price of Arabica's green bean on the commodity market. However, Arabica has more preferable taste and aroma than Robusta. Robusta is often used in instant coffee while Arabica is used in coffee shops [15].

Commonly, coffee beans must go through several steps of processing until it is served. First, coffee cherries are harvested from the coffee plant, they are each composed of two coffee beans covered by a thin parchment like hull and further surrounded by pulp [16]. When the pulps are removed through pulping process, the parchment is removed through either wet or dry process which produces the dried beans, commonly known as the green bean. Then, the green bean enters another process called roasting that affects the overall color, aroma, and flavor of the final product [12].

The roasting process of green beans into brown is a crucial step of coffee processing. It is a process where a high temperature (around 210°C-240°C) is applied to the coffee beans. The water contained is evaporated and chemical reactions like Maillard reactions [17], oxidation, thermal degradation and hydrolysis of the coffee’s chemical components takes place. There are four main degrees of coffee roasting that will affect the organoleptic properties of the final product, which are light roast, medium roast, medium dark roast and dark roast [8].

Furthermore, the process of obtaining coffee bean from the whole fruit leaves the silverskin as waste. Silverskins, or commonly known as chaff in the industries is usually produced during the roasting
process. It is actually the outer layer of the green coffee beans that is usually still intact during the pulp and hull removing process. When the coffee beans come into contact with high temperature, the coffee beans crack as the result of swelling due to loss of moisture content, and also make the silverskin detach from the beans. Due to its lightness, silverskin usually escapes from the roasting container through the roaster exhaust or cyclone [11]. The silverskin, or the chaff is usually thrown away by the roasters due to some problems related to roaster cleanliness and air pollution. On the other hand, the silverskin is mostly used only as combustible or fertilizer [17]. However, coffee silverskin actually has a potential of antioxidant activity because it is highly rich in phenols [18]. Phenolic compound from coffee silverskin can be obtained by extraction and the extract has many application possibility for food and pharmaceutical based on previous research by Costa et al. [6] in which the total phenolic content and total flavonoid content of the coffee silverskin extract was 302.5 ± 7.1 mg GAE/L and 83.0 ± 1.4 mg ECE/L. Therefore, the extract of coffee silverskin has potential as antioxidant food or cosmetic products. Hence, the extract of coffee silverskin could be more applicable for commercial uses while in powder form instead of liquid form in terms of distribution and storage. The desired powder should be high in phenolic content, flavonoid content, and antioxidant activity. However, drying process affects the phenolic content based on previous research by Orphanides et al. [14]. The characteristics of the final powder form of coffee silverskin extract is then identified.

2. Methodology
The raw material was homogenized using blender. Then, the homogenized coffee silver skin was extracted. The extraction was done on a hotplate inside a beaker and stirred with a magnetic stirrer. The extraction condition was set at 40°C for 60 minutes using hydroalcoholic solvent with 1:1 ratio of alcohol and water. There were two ratio of solid to solvent which are 1:50 and 1:10. The extract with 1:50 solid to solvent ratio was analyzed for comparison of Robusta and Arabica variant, while the extract with 1:10 solid to solvent ratio was used for the drying step. The extract was filtered using filter paper and stored in a freezer prior to analysis. The two drying processes were done separately. Spray drying was done directly to the extract at inlet temperature 170°C, outlet temperature 125°C with feed flow 20ml/min. In the case of freeze drying, the alcoholic content of the extract was first removed using vacuum rotary evaporator at 50°C for 3 hours. Then, the extract was freeze dried at -50°C for 24 hours. As a comparison, spray drying was also done to the extract whose alcoholic content had been removed using vacuum rotary evaporator at the same condition. The resulting powder was immediately stored in desiccator until analysis.

3. Results and Discussion
The extract of coffee silver skin from both Arabica and Robusta were compared in terms of total phenolic content, total flavonoid content, and antioxidant activity. As shown in Figure 1, total phenolic content of Robusta coffee silver skin extract was 816.76 ± 63.24 mg GAE/ L while Arabica coffee silver skin was 473.51 ± 56.70 mg GAE/ L. Thus, Robusta coffee silver skin has the value of phenolic content almost twice than Arabica coffee silver skin. This finding is similar to the study conducted by Farah (2012) which reported higher amount of chlorogenic acid is originally present in the green bean of Robusta rather than in Arabica. Chlorogenic acid belongs to the phenolic group, therefore contributing to the absorbance reading of phenolic.
As shown in Figure 2, total flavonoid content of Robusta coffee silver skin extract was 32.82 ± 2.47 mg QE/L while Arabica coffee silver skin extract was 18.58 ± 2.47 mg QE/L. This result is also in agreement with the total phenolic content because flavonoid is one of the phenolic group. Robusta coffee silver skin extract has twice total flavonoid content than Arabica coffee silver skin extract.

The antioxidant activity of the Arabica and Robusta coffee silver skin extract can be seen in Figure 3. The inhibition to DPPH activity of Robusta coffee silver skin extract was 54.80 % and Arabica coffee silver skin extract was 26.30 %. As the total phenolic content gets higher, it also increases the antioxidant activity. The antioxidant activity of Robusta coffee silver skin extract is higher than of Arabica coffee silver skin extract. This indicates that Robusta coffee silver skin contain high amount of antioxidant activity.

Total phenolic content and total flavonoid content were analysed in this research as an approach to identify the amount of chlorogenic acid in coffee silver skin. Both chlorogenic acid and flavonoid belong to the phenolic group. Most of phenolic group has antoxidative property, so do chlorogenic acid and flavonoid. Based on the results from this research, the total flavonoid content is only around 4% from the total phenolic content found in Robusta and Arabica coffee silver skin extract. Therefore, it can be concluded that flavonoid does not have much contribution to the high antioxidant activity which means the antioxidative property comes from other compounds from the phenolic group. This other compounds
are assumed to be dominated mostly by chlorogenic acid, corresponding to 74% of chlorogenic acid detected in coffee silverskin based on Bresciani et al. [4].

The products from both drying method were compared. The total phenolic content results show in Table 1. First, the total phenolic content of the Robusta coffee silver skin after extraction with solid to solvent ratio 1:10 was 210.27 mg GAE/ g solid extract. The extract was evaporated using rotary vacuum evaporator. The total phenolic content was degraded by 22.61% to 162.72 mg GAE/g solid extract. After evaporation, the Robusta coffee silver extract was dried with freeze drying and spray drying. Total phenolic content of freeze dried extract was 162.91 mg/ g powder while spray dried extract was 134.76 mg/ g powder. Another spray dried product using extract without evaporation was also analysed and the result was 188.83 mg / g powder in total phenolic content. From the results, the total phenolic content from freeze drying process does not give major degradation while spray drying process degrade 17%. The result shows, phenolic compound affected by high temperature and in accordance to study by Orphanides et al. [14] on effect of drying method on the phenolic content and antioxidant capacity of Spearmint.

Table 1. Total phenolic content of Robusta coffee silverskin extract from different drying method

| Drying Method | After Extraction (mg/ g solid extract) | After Evaporation (mg/ g solid extract) | After Drying (mg/ g powder) |
|---------------|----------------------------------------|------------------------------------------|-----------------------------|
| Freeze drying | 210.27                                  | 162.72                                   | 162.91                      |
| Spray drying  | 210.27                                  | 162.72                                   | 134.76                      |

The total flavonoid content of Robusta coffee silver skin extract results show in Table 2. Total flavonoid content after extraction was 8.09 mg QE/ g solid extract. Thus, total flavonoid content of the extract was degraded 23.85% after evaporation to 6.16 mg QE/ g solid extract. After that, the extract was went to drying processes which are freeze drying and spray drying. Then, total flavonoid content of freeze dried product was 6.31 mg QE/ g powder while spray dried extract was 4.03 mg QE/ g powder. Another spray dried product using extract without evaporation was also analysed and the result was 7.22 mg/ g powder.

Table 2. Total flavonoid content of Robusta coffee silverskin extract from different drying method

| Drying Method | After Extraction (mg/ g solid extract) | After Evaporation (mg/ g solid extract) | After Drying (mg/ g powder) |
|---------------|----------------------------------------|------------------------------------------|-----------------------------|
| Freeze drying | 8.09                                    | 6.16                                     | 6.31                        |
| Spray drying  | 8.09                                    | 6.16                                     | 4.03                        |

The antioxidant activity of the product was determined using IC$_{50}$. The result of IC$_{50}$ each product can be seen in Figure 4. IC$_{50}$ is the amount of sample to inhibit 50% of Free Radical or in this case is DPPH. The IC50 of Robusta CSE freeze dried was 2139.80 ppm, Robusta CSE (with evaporation) spray dried was 2596.73 ppm, Robusta CSE (without evaporation) spray dried was 1721.32 ppm, Arabica CSE
(without evaporation) spray dried was 2236.77 ppm, Arabica CSE (with evaporation) spray dried was 2923.88 ppm, and Arabica CSE freeze dried was 2391.50 ppm. The smallest value means, the better the antioxidant. Robusta CSE (without Evaporation) Spray dried gives smallest value between the other Robusta CSE. This value correlated with the amount of phenolic content in the sample. The higher phenolic content means the better the antioxidant activity. Other study also revealed that the antioxidant activity was directly proportional to the content of phenolic compounds [3].

Figure 4. IC<sub>50</sub> and the phenolic content of the spray dried and freeze dried of the Arabica and Robusta coffee silverskin extract

The ascorbic acid was compared with the phenolic content in the spray dried and freeze dried of Robusta and Arabica coffee silverskin extract in terms of their antioxidant activity. As the result shown in Figure 5, ascorbic acid has greater antioxidant activity than the spray dried and freeze dried of the Robusta and Arabica coffee silverskin extract with the IC<sub>50</sub> value of ascorbic acid at 141.33 ppm and IC50 value of the phenolic content in the spray dried and freeze dried of Arabica and Robusta coffee silverskin extract at around 350 ppm. These results show that the coffee silver skin extract can substitute ascorbic acid in terms of antioxidant activity with twice more amount.

Figure 5. The IC<sub>50</sub> of the phenolic content in the spray dried and freeze dried of the Arabica and Robusta coffee silverskin extract and Ascorbic acid

The extract of coffee silverskin extract which was pulverized using spray dried gives moisture content, solubility value, and mass mean diameter were 5.30%, 8.47 mg/ml, and 240.53µm respectively while pulverized using freeze dried were 3.86%, 9.28 mg/ml, and 1343.33µm respectively. The physical properties of coffee silverskin extract which was pulverized using spray dried was light brown fine powder with rancid and medicinal aroma while using freeze dried was dark brown crystalline powder with mild rancid and medicinal aroma.

4. Summary
In summary, the total phenolic content, the total flavonoid content, and antioxidant activity of Robusta coffee silverskin extract were 816.76 ± 63.24 mg GAE/ L, 32.82 ± 2.47 mg QE/ L, and 54.80 % inhibition of DPPH respectively while Arabica coffee silverskin extract were 473.51 ± 56.70 mg GAE/ L, 18.58 ± 2.47 mg QE/ L, and 26.30 % inhibition of DPPH. Thus, the Robusta coffee silverskin extract
has higher value of total phenolic content, the flavonoid content, and antioxidant activity than Arabica coffee silverskin extract.

Prior to drying, the extract was evaporated first with total phenolic content 162.72 mg GAE/g solid extract, and total flavonoid content 6.16 mg QE/ g solid extract. Decrease of total phenolic content was 22.61% through evaporation. The total phenolic content, total flavonoid content, and IC50 value of spray dried of Robusta coffee silverskin extract were 134.76 mg GAE/ g powder, 4.03 mg QE/ g powder, and 2596.73 ppm respectively, while for freeze dried Robusta CS extract were 162.91 mg GAE/ g powder, 6.31 mg QE/ g powder, and 2139.80 ppm respectively. Moreover, freeze drying does not give major degradation to the total phenolic content and the total flavonoid content in the coffee silverskin extract while spray drying gives 17% of degradation to the total phenolic content and flavonoid content. However, the coffee silverskin extract can be directly spray dried. The resulting powder has higher amount of phenolic content than the one which was evaporated first.

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