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Chemical characterization and antioxidant activity of a new potential functional ingredient of coffee silver skin extracts

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Abstract: The coffee industry still generates large amount of waste representing serious enviromental problem. Coffee silver skin, a byproduct of roasted coffee beans, might be an important source of several bioactive compounds such as dietary fiber, phenolic content, caffeine, chlorogenic acid, tannic acid, and antioxidant activity. The compositions of coffee silver skin extract were investigated in this study. Extraction was using water and ethanol solvent with maceration method. The percentage yield of extract from coffee silver skin in water and ethanol solvent are 16.97% and 2.65% respectively. The result showed that this material in water extract has 7.78 % of phenolic content, 0.14 % of chlorogenic acid, 3.12 % of caffeine, 4.15 % tannic acid, 23.82% of dietary fiber and antioxidant activity with IC_{50} = 52, 12 µg/ml. Extract of ethanol showed 0,62 % of phenolic content, 0,33 % of chlorogenic acid , 3.49 % of caffeine, 0.6 % of tannic acid, 8,48 % of dietary fiber and antioxidant activity with IC_{50} 13,29 µg/ml. The composition of extract from coffee silver skin can be used as ingredient for functional food.
Key words : Coffee silver skin, antioxidant, chemical ingredients.

1. Introduction

Coffee is one of the most consumed beverages in the world and widely used as non- alcoholic beverages in industrialized countries (Nurminem, et al., 1999). Inside the skin, there is epicarp with a sweet tasting mesocarb called pulp, within the mesocarpthere is a thin layer of endocarp called parchment. The endosperm of the coffee bean is also covered with a spermaderm called silver skin (Bondesson, et al., 2015). Coffee silver skin is a tegument of coffee beans that constitutes a byproduct of the roasting procedur (Borelli, et al., 2004). Coffee silver skin is main coffee industry residues. It isresidu with concentration of soluble dietary fiber and high antioxidant capacity (Musatto, et al., 2011). Coffee silver skin can be used in the preparation of functional beverages and bakery product by adding dietary fiber to the biscuit formulation and has an impact on its nutritional properties (Serna, et al., 2014), and sources of polyphenols (Regazzoni, et al., 2016).

It has been known that agroindustrial by- product are rich in dietary fibers, some of which contains appreciable amounts of colorants, antioxidant compounds or other substances with positive health effect (Oreopoulou, et al., 2007). Agro waste are great sources of dietary fiber which include cellulose, hemicellulose, lignin, pectin and other polysaccharides. The soluble and insoluble dietary fiber fractions are known to reduce the risks of gastrointesnal disease, cardiovascular diseases and obesity (Murthy, et al., 2012). One of beneficial role of dietary fiber is helping reducing risk of coronary herat disease. Formulation food product with high

dietary fiber content are now commercially available. Consumers today are highly aware of the close relationship between nutritional and health. They want to include health ingredients in their diets (Oreopoulou, et al., 2007). The ability of dietary fiber from different sources are having noticeable physiological effects, promoted a number of investigations, particularly those aiming to use the dietary fiber present in food industry waste products (Borelli, et al., 2004).

Polyphenols are secondary metabolites of plants used in their defense system against severe environments such as ultraviolet radiations and pathogens. These compounds are generally classified into flavonoids, phenolic acids and lignans (Wang,et al., 2009). Tannins (commonly refered to tannic acid) are water soluble polyphenols that are present in many plant foods (Chung, et al., 1998).

Chlorogenic acid are a family of ester formed between trans-cinnamic acid and quinic acid. Chlorogenic acid is formed between caffeic acid and quinic acid. There has been shown that both chlorogenic acid and caffeic acid are strong antoxidant in vitro (Ramalaksmi et al, 2008).

Antioxidant constituents of the plant material acts as radical scavengers, and helps in converting the radicals to less reactive species. Oxidation of biomolecules can cause generation of free radical in body. Natural antioxidants occur in all parts of plants. These antioxidants include carotenoids, vitamins, phenols, flavonoids. One method that is currently popular is based upon the use of the stable free radical diphenylpicrylhydrazyl (DPPH) (Maimulyanti and Prihadi, 2016). Antioxidant interfere with the oxidative processes by scavenging free radicals, chelating free catalytic metals and hence dietary intake of antioxidant compounds are importants. The therapeutic effects of several medicinal plants are usually attributed to their antioxidant phytochemicals (Padmanabhan and Jangle, 2012). Free radical can also effect food quality; reducing its nutritional content and promoting the development of food deterioration (Wettasingle, et al., 1999).

The aim of this study was to evaluate the potential use of the coffee silverskin as a food ingredient by studying its chemical characteristics and investigating its antioxidant properties.

2. Materials and Methods

2.1. Materials

Samples were collected from Pangalengan, West Java Province, Indonesia.

2.2. Sample extraction

Coffee silveskin was washed with aquadistillation and was dried in oven for 3 hours at 50 ^{o}C and grounded into 18 mesh. Sampel was the extracted with maseration method with water at 80^{o}C for four hours and with ethanol at 25^{0}C for two days.

2.3. Total phenolic content

Total phenolic content of coffee silver skin extract was determined using Folin-Ciocalteu's reagent. Sampel was diluted (1:10) briefly, 0.5 mL of each extract were mixed with 2.5 mL of Folin -Ciocalteu reagent (1:10) and 2 mL of sodium carbonate solution (7.5%). The mixture was incubated at 45^{o}C during 15 min, followed by 30 min incubation at room temperature before absorbance reading at 765 nm were performed. Total phenolic content was calculated from a calibration curve prepared with gallic acid (10-100 mg/L) and expressed as mg of gallic acid equivalent (Costa, et al., 2010).

2.4. Caffeine and chlorogenic acid.

Analysis of caffeine and chlorogenic acid (5-CQA dan 3-CQA) in extract of coffee silver skin with modification method (Narita dan Inouye, 2011).Extract coffee silver skin (10 mg/mL)was analysed with HPLC. Mobile fase used solvent A (50 mMacetic acid in aqua distillation and solvent B (50mM acetic acid in acetonitrile)with gradient elution : 0–30.0 min, 0–20% (v/v) of B; 30.0– 45.0 min, 20–35% (v/v) of B; 45.0–50.0 min, 35–80% (v/v) of B; 50.0–50.1 min, 80–5% (v/v) of B; and 50.1–60 min, 0% (v/v) of B. Volume injectionof sample was10 µL. Caffeine and chlorogenic acid was detectedat270 dan 325 nm.

2.5. Tannic acid

As much as 0,025 g of coffee silverskin extract diluted in water and 0,1 gram extract of coffee silver skin in ethanol was dilutted into volumetric flask. Sample (1 mL) was added with 0,5 mL reagenfolin–ciocalteu. After 3 minute, 0,2 mL of sodium carbonat (7.5% w/v) was added and diluted until 10 mL. Sample was incubated for 2 hours in dark condition. Detection was at 522 nm and calibration curve of tannic was at 1–5 mg/L.

2.6. Dietary fiber

Sample (0,5 gram) was added to 40 ml MES-TRIS (Buffer pH 8,2) and stirred until homogen. Solution was added 50 µL α amylase and stored in water bath at 95-100^{o}C for 35 minute. Solution was cooled at 60^{o}C and it was added 100 µL protease and incubation at 60^{o}C for 30 minute. After that, it was added 0,561 N HCl until pH 4,5 , 200 µL amyloglucosidase and incubation at 60^{o}C for 30 minute. Solution was precipited with 225 ml ethanol 95% at 60^{o}C for 1 hour at room temperature. supernatant was filtered with whatman 42. Supernatan was washed with 15 ml ethanol 78%, 15 ml ethanol 95% dan 15 ml aceton and was dried at 70^{o}C .

2.7. Antioxidant activity

The antioxidant activity was evaluated by free radical scavenging activity (DPPH) method.1,1-Diphenyl-2-picryl-hydrazyl (DPPH) is free radical yet stable. DPPH solution is initially violet in color which fades when antioxidants donated hydrogen. The color change is monitored by spectrophotometer and DPPH free radical scavenging activity was calculated. Stock solution of 0.1 mM DPPH in methanol was made. Test sample of extracts were made at 10, 20, 30, and 40 µg/mL in methanol. Test sample of n- hexane extract made at 100, 200, 300, 400, and 500 µg/mL. The absorbance was measure at 517 nm by spectrophotometer (UV-VIS Shimadzu). After 30 minutes and % scavenging was calculated by the equation.

$$\% \text{ Scavenging} = \frac{(A_0 - A_T)}{A_0} \text{ x } 100\%$$

Where, Ao = Absorbance of DPPH solution and A_T = Absorbance of test or reference sample. The % scavenging was then plotted against concentration and regression equation was obtained to calculate IC_{50}. IC_{50} is defined as the total antioxidant necessary to decrease the initial DPPH radical by 50 %.

3. Results and discussion

3.1. Yield of extraction

The yield of extraction of coffee silverskin with water and ethanol solvent was shown in figure 1.

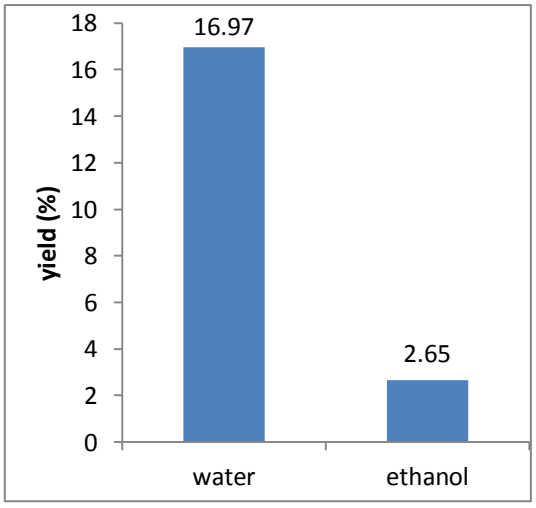

Fig.1. The yield of coffee silverskin extract

The yield of coffee silverskin extracts in water and ethanol were 16.97% and 2.65%. Differences in the yield of extract from different solvent might be attributed to availability of extractable component of different polarities (Maimulyanti et al, 2006).

3.2. Analysis of constituent

Chemical characterization of water extract and ethanol extract from coffee silverkin were shown in table 1.

Ingredients	**content**	
	Water extract	**Ethanol extract**
Phenolic content (%)	7.78	0.62
Chlorogenic acid (%)	0.14	0.33
Caffeine (%)	3.12	3.49
Tannic acid (%)	4.5	0.6
Dietery fiber (%)	23.82	8.48
Antioksidant IC_{50} (µg/ml)	52.12	13.29

Content of phenolic, caffeine, tannic acid and dietary fiber in water extract of coffee silverskin was shown in figure 2 and ethanol extract in figure 3.

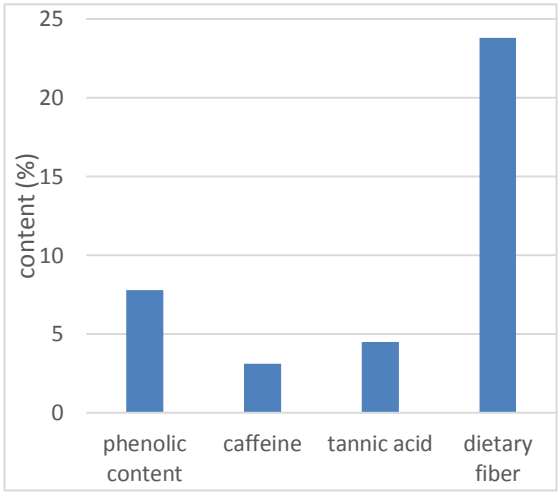

Fig. 2.Phenolic content, caffein, tannic acid and dietary fiber in water extract

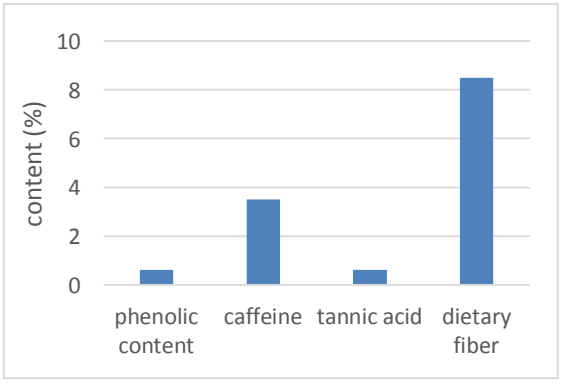

Fig. 3.Phenolic content, caffein, tannic acid and dietary fiber in ethanol extract

3.2.1. Phenolic content

Phenolic content of coffee silverskin in water extract was 7.78 % and ethanol extract was 0.62 %. Phenolic constitutes one of the most numerous and ubiquitous group of plants metabolites and are an integral part of both human and animal diets. However, recent interest in food phenolics has increased greadly, owing to their antioxidant capacity and their possible beneficial implications in human health, such as in the treatment and prevention of cancer, cardiovascular disease and other pathologies. Polyphenols are partially responsible for the sensory and nutritional qualities of plant foods. The astringency and bitterness of food and beverage depend on the content of polyphenolic compounds (Bravo, et al 1998).

Total phenolic content was measured by the folinciocalteu assay, provided an approximation of total amount of polyphenols in the sample. Phenolic compounds have shown potential protective activity against several chronic diseases, with mechanisms of action possibly involving antioxidant (Bresciani, et al., 2013). Polyphenols also acted as antioxidant, they scavenge free radicals which are responsible for serious disease and for oxidation of lipid, protein and DNA (Oreopoulou, et al., 2007). Polyphenols have powerful antioxidant activity in vitro being capable of scavenging a wide range of reactive oxygen, nitrogen and chlorine species, such as superoxide anion, hydroxyl radical, and peroxynitrousacis (Petti and Scully, 2009).

3.2.2. Caffeine

Fig. 3 showed caffeine in water extract was 3,12 % and ethanol extract was 3,49 %. Caffeine is used as an adjuvant in many prescription and over-the- counter drugs, e.g in combination with nonsteroidal anti-inflammatory drugs in analgesic formulations. Caffeine exerts variety of stimulatory effects upon the central nervous system and it is probably the most widely used psychoactive substance.

Caffeine (1,3,5-trimetrylxanthine), a mild addicting drug, though used for medicinal purposes, is the active ingredient that makes tea and coffee valuable to humans. Caffeine which is found in tea and coffee imparts bitterness and also acts as a flavor constituents. Caffeine is used as drug on the basis of its effects on respiratory, cardiovascular and the central nervous system (Wanyika, et al, 2010).

3.2.3. Total dietary fiber

In Fig 3.It was indicated dietary fiber in water extract was 23,88 % ethanol extract was 8,48 %. Dietary fiber is one of the main dietary factors contributing to costumers well-being. To increase dietary fiber public consumption, new dietary fiber enriched food has been developed in the past few years. The availability of dietary fiber from different sources, having noticeable physiological effects, promoted a number investigation, particularly those aiming to use dietary fiber.

Several studies have shown the role of insoluble fiber in the prevention of intestinal cancer, being able to reduce glucose and sterol absorption from the intestine, to increase calcium absorption from the colon. To increase the overall consumtion of dietary fiber and to provide their appropriate balance, a new generation of fuctional food should be developed (Borelli, et al., 2004). Dietary fiber from coffee is thought to be composed chiefly by cellulose, hemi cellulose, pectin substance and lignin. On the basic of the result of this study described that beverages made from coffee silverskin extract are both potential of interest in body weight control and prevention of obesity and diabetes (Saes, et al., 2014).

Natura lingedients recovered from agroindustry by-product have specific dietary and functional properties and can be utilized effectively to develop this new food category (Oreopoulou, et al., 2007).

Tannic acid

Callibration curve of tannic acid was shown in figure 4.

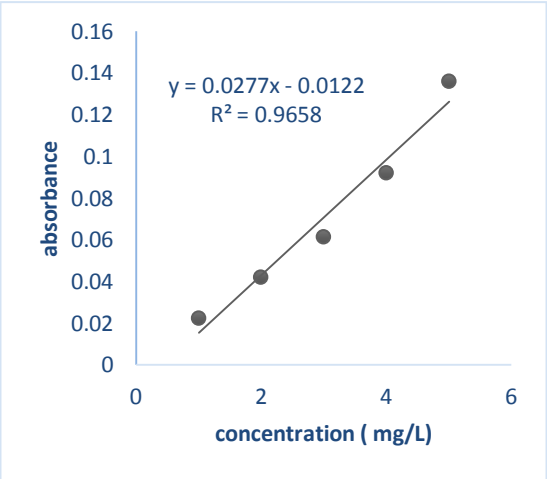

Fig. 4. Calibration curve of tannic acid

Tannic acid of coffee silverskin in water extract was 4,15 % and ethanol extract was 0,6 %. Tannins are water soluble polyphenols which differ from most other natural phenolic compounds in their ability to precipitate proteins such as gelatin from solution. (Scalbert, et al.,1991). Therefore, food rich in tannins are considered to be of low nutritional value. Incidences of certain cancers, such as esophageal cancer, have been reported to be related to consumption of tannins-rich food such as herbal teas, suggesting that tannins might carcinogenic. Tannic acid was found to be an effective inhibitor of tumor formation in reducing cumulative numbers of tumors per mouse and percentage of mice with tumors. The implication of total tannins on human health is public concern (Chung, et al,1998).

3.2.4. Chlorogenic acid.

Chlorogenic acid from extract coffee silverskin was shown in figure 5.

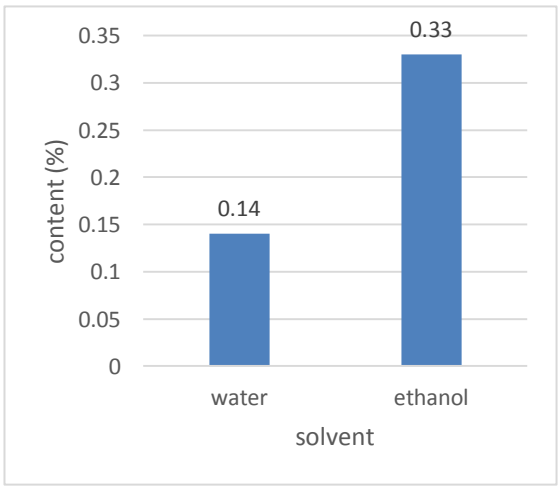

Fig.5. Chlorogenic acid from coffee silverskin

Chlorogenic acid of coffee silverskin in ethanol extract was 0,33 % and water extract was 0,14 %. Chlorogenic acid (CGA) one of the most abundant polyphenol compounds in the human diets, is a group of phenolic secondary metabolits produced by certain plant species and an important component of coffee. CGA is

an ester formed cinnamic acid and quinic acid and is also known as 5-O-caffeoylquinic acid (5-CGA). CGA exert its antidiabetic effects on stimulating glucose uptake in both insulin-sensitive and insulin-resistant adipocytes. CGA has been described as a potential antidiabetic agent. CGA, one of the abundant polyphenols compounds in the human diets, a group of phenolic secondary metabolits producer by certain plant species and is an important component of coffee (Meng, et al, 2013).

3.3. Antioxidant activity

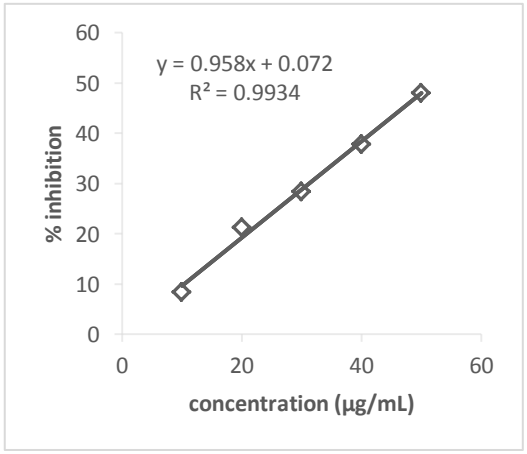

Fig 6. % inhibition of water extract at different concentration.

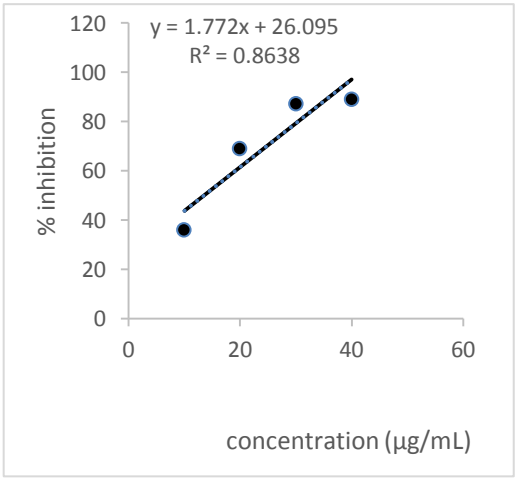

Fig. 7. % inhibition of ethanol extract at different concentration

Antioxidant activity of coffee silverskin may be explained by considering that its tegument keeps part of the polyphenolic compounds. It is normal constituent of coffee beans. In addition to health benefits, the supplementation of food product with antioxidants delays the formation of off-flavors and rancidity and extends the shelf life of the product. Polyphenols are extensively distributed in several plant by-product (Oreopoulou, et al., 2007). Phenolic and flavonoid compounds have recently attracted a lot of interest because they are potential antioxidant and exhibit various physiological activity like anti inflammatory, anti allergic, and anti hypertensive activities (Murthy, et al., 2012).

Antioxidant may defined as compounds that inhibit or delay the oxidation of other molecules by inhibiting the initiation or propagation of oxidizing chain reaction. Antioxidant can also protect the human body from free radical and ROS effects. Radical scavenging activities are very important due to the deleterious role of free radicals in food and biological system. Chemical assay are based on the ability to scavenge synthetic free

radicals, using a variety of radical generating system and methods for detection of the oxidation end-points. DPPH radical scavenging methds is common spectrophotometric procedures for determining the antioxidant capacities of component. In DPPH assay the antioxidant were able to reduce the stable radical DPPH to the yellow coloured diphenyl-picrilhydrazine (Gulcin, et al., 2010).

Table 2. IC_{50} of extract from coffee silverskin

No	Solvent	IC_{50} (µg/mL)
1	water	52.15
2	ethanol	13.29

The DPPH is a stable free radical, red in color and has an absorbance band at 515 nm. The DPPH free radical scavenging activity in water and ethanol extract from coffee silverskin was recorded in term of the percentage inhibition. The result showed that the absorbance decreased as a result of a color change from purple to yellow (Maimulyanti and Prihadi, 2016). The linier regression equation were used to determine the IC_{50}. The concentration of extract scavenging 50% is shown in table 2. Coffee silverskin in ethanol extract is a potent antioxidant (IC_{50}= 13.29 µg/ml) compared to water extract (IC_{50} = 52.15 µg/ml).

4. Conclusion

Coffee silverskin has potential ingredient such as phenolic, chlorogenic acid, caffeine, tannic acid, dietary fiber and antioxidant activity. Characteristically chemical and nutritionalcomposition of extract support its potential for other health promoting application.

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References

1. Bondenson E. A nutritional analysis on by-product coffee silverskin husk and its potential utilization in food production, Faculty of natural resources and agriculture science, Departement of Food Science, 2015, Swedish University of Agriculture Science.
2. Borrelli RC, Espositof, Napolitano A. Ritieni A, Fogliano V. Characterization of a new potential functional ingredient: coffee silverskin. J. Agric. Food. Chem., 2004, 52; 1338-1343.
3. BravoL. Polyphenols: chemistry, dietary sources, metabolism and nutritional significance. Nutrition Reviews,1998, 56 (11); 317-333.
4. Bresciani L, Calani, Bruni R, Bighenti F, Rio, D.P. Phenolic composition, caffeine content and antioxidant capacity of coffee silverskin. Food Research International,2013, http://dx.doi.org/10.1016/j.foodres.2013.10.047
5. Chung KT, Wong TY, Wei CI, Huang, YW, Lin Y. Tannins and human health: A review, Critical Reviews in Food Science and Nutrition, 1998, 38 (6); 421-464.
6. Costa ASG, Alves RC, Vinha AF, Barreira, SVP, Nunes MA, Cunha, LM, Oliveira BPP. Optimization of antioxidant extraction from coffee silverskin, a roasting by-product, having in view a sustainable process.Industrial Crops and Product, 2014, 53; 350-357.
7. Gulsin I, Huyut Z, ElmasterM, Enenin HYA. Radical scavenging and antioxidant activity of tannic acid, Arabian Journal of Chemistry,20103: 43-53.
8. Maimulyanti A, Prihadi AR, Safrudin I. Chemical composition, phytochemical screening and antioxidant activity of *Acmellauliginosa* (Sw) Cass leaves, Indonesian Journal of Chemistry,2016, 16, (2), 162-174).
9. MaimulyantiA,Prihadi AR. Chemical composition of essential oil and hexane extract and antioxidant activity of various extract of *Acmellauliginosa* (Sw.) Cass Flower from Indonsia, Agriculture and Natural Resources,2016, 50 , 264-269.

10. Mussatto SI, Machado EMS, Martins S, Teixeira JA. Production, composition and application of coffee and its industrial residues, Food Bioprocess Technol, 2011, 4: 661-672.
11. Meng S, Cao J, Feng Q, Peng J, Hu Y. Roles of chlorogenic acid and regulating glucose and lipid metabolism: A review., Evidence-based Complementary and Alternative Medicine, 2013; 1-12.
12. Murthy PS, Naidu MM. Sustainable management of coffee industry by-product and value addition a review, Resources Conservation and Reciding,2012, 66, 45-58.
13. Nurminem ML, Niittynen L, KorpelaR, VaapaotaloH. Coffee, caffeine and blood pressure: a critical review, European Journal of Clinica Nutrition, 1999, 53; 831-839.
14. Oreopoulou V, Rus W. Utilization of by-product and treatment of waste in the food industry,Springer Science Business Media, 2007, LLC, New York, USA ; 209-230.
15. Padmanabhan P, Jangle SN, Evaluation of DPPH radical scavenging activity and reducing power of four selected medicinal plants and their combination. International Journal of Pharmaceutical Science and Drug Research , 2012, 4(2); 143-146.
16. Petti S, Scully C. Poliphenols, oral health and disease: A review, Journal of Dentistry, 2009, 37, 413-423.
17. Pourfarzad A, Mehr HM, Sedaghat N. Coffee Silverskin as a source of dietary fiber in bread making: optimization of chemical threatment using response surface methodology, Food Science and Technology ,2013, 50; 599-606.
18. Ramalaksmi K, Kubra IR, Rao JM. Antioxidant potential of low-grade coffee beans, Food Research International,2008, 4; 96-103.
19. SaezNM, UllateM, CabrejasMAM, Martorell, P., Genous, S., Ramon, D. Castillo, MD, A Novel antioxidant beverage for body weight control based on coffee silverskin, Food Chemistry, 2014, 150; 227-234.
20. Scalbert A, (1991). Antimicrobial properties of tannins. Phytochemistry, 1991, 30 (12); 3875-3883.
21. Serna EG, Saez NH, Mesias M, MorakesFJ,Castillo MD. Use of coffee silverskin and stevia to improve the formulation of biscuits, Pol. J. Food. Sci.2014,64 (2); 243-251.
22. Thom E. The effect of chlorogenic acid enrich coffee on glucose absorption in healthy volunteers and its effect on body mass when used long term in overwheight and obese people, The Journal of InternationalMedical Research, 2007, 35; 900-908.
23. Wanyika HN, Gatebe EG, Gitu LM, Ngumba EK, Maritim CW. Determination of caffeine content of tea and instant coffee brands found in the Kenyan market, African Journal of Food Science,2010, 4(6); 353-358.

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