Pertanika J. Sci. & Technol. 26 (2): 799 - 810 (2018)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Comparison Extraction of Peanut Skin between CO_2 Supercritical Fluid Extraction and Soxhlet Extraction in Term of Oil Yield and Catechin

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ABSTRACT

The objective of this study was to compare the extraction of peanut skin using supercritical carbon dioxide extraction and soxhlet extraction in terms of oil yield and catechin. For supercritical fluid extraction, the temperatures used were 40 and 70°C, while pressure used was 10 and 30 MPa, the flow rate was CO_2 3 mL/min, and the concentration of co-solvents was 0 and 5%. Meanwhile, for soxhlet extraction, the extraction time was 6 hr with ethanol, hexane and water as the solvents. The results showed that soxhlet extraction gave the highest yield of extract (36.282%) using ethanol as solvent as compared with supercritical CO_2 extraction (15.47%) at pressure 30 MPa, temperature 70°C and 5% concentration of co-solvent. This study reveals that the extracts from SC-CO_2 extraction yielded the highest amount of catechin (208.73 µg/g sample) compared with that yielded in the soxhlet extraction (42.24 73 µg/g sample) with distilled water as a solvent analysed with High Performance Liquid Chromatography (HPLC).

Keywords: Catechin, peanut skin, soxhlet extraction, supercritical fluid extraction

Article history:
Received: 23 August 2017
Accepted: 5 December 2017

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ISSN: 0128-7680

INTRODUCTION

Peanuts are usually served as a side dish in Asian countries, especially Malaysia and Indonesia. Approximately 0.74 million metric tons of peanuts are globally produced and the quantity is still increasing (Sobolev & Cole, 1999). Peanut skin is usually peeled off the

seed because peanut skin gives an astringent taste to dishes. Peanut skin is commonly used for forage in villages. In the peanut butter industry, peanut skin is removed from peanuts because it reduces the quality of peanut butter in terms of taste. Peanut skin is a renewable raw material; it contains antioxidant compounds that protect human health and enhance a sustainable environment (Hoang, Dostálová, Pudil, & Pokorný, 2008).

Although peanut skin is a product waste, it is a rich source of antioxidants such as phenolics, flavonoids and tannins. Peanut skin contains procyanidins, epicatechin, oleic acid and catechin (Hoang, Apostolova, Dostalova, Pudil, & Pokorny, 2008; Nepote, Grosso, & Guzman, 2002; Sobolev & Cole, 1999; Yu et al., 2006). In this study, catechin was detected in the extract of peanut skin. Most antioxidant activities have been associated with reduced risk of cardiovascular diseases, antidiabetic indications and anti-inflammatory effects; antioxidants also help in the prevention of cancers (Nepote et al., 2002).

Carbon dioxide supercritical fluid extraction (SFE) is a green technology that was developed to extract oil, antioxidants and bioactive compounds from plants and herbs. This method has been used by many researchers to effectively extract bioactive compounds from plants and herbs such as lycopene from tomato skin (Kassama, Shi, & Mittal, 2008) and djencolic acid from *Pithecellobium Jiringan* (Jack) prain seeds (Yunus et al., 2013). Carbon dioxide supercritical fluid extraction is beneficial as it allows the extract to retain high purity of solute content, keeps it free of organic solvents and allows easy separation of the extract from the solvent. Its important advantage is that it provides high amounts of bioactive compounds that are available in the extract because supercritical carbon dioxide uses low critical temperature and pressure, ensuring that bioactive compounds are not easily degraded. Based on the temperature and pressure, the solubility of supercritical carbon dioxide as the solvent can be manipulated in order to obtain the maximum yield of the selected compound (Yunus et al., 2012). The presence of ethanol is needed to enhance the polarity of supercritical carbon dioxide as a solvent because ethanol can extract two kinds of compound, polar and nonpolar, found in the solute but carbon dioxide can only extract nonpolar compounds (Trabelsi et al., 2016).

Soxhlet extraction is a conventional method to extract compounds from herbs and plants. The benefit of soxhlet extraction is that this process exhausts the extraction process, providing a high amount of yield compared with other methods. However, soxhlet extraction yields only low quality extracts because compounds in the extracts are degraded due to the high temperature needed for this extraction process (De Castro & Garcıa-Ayuso, 1998). In this research, the aim of the study was to compare the extraction of peanut skin using supercritical fluid extraction and soxhlet extraction in order to obtain the maximum amount of oil and catechin.

MATERIALS AND METHOD

Materials

Raw peanut skin was obtained from G-Tachfood Industries Sdn Bhd, Johor Bahru, Malaysia. The peanut skin was dried in an oven at 60^{o}C for 4 hr and then blended into powder, classified as 425 µm size of particle with shaving process, stored in a plastic sample and placed in the

freezer until it was ready to be used. Catechin was purchased from Sigma-Aldrich (St. Louis, MO). Denatured ethanol 95%, absolute ethanol 99.86%, N-hexane and distilled water were purchased from Fisher Scientific (Atlanta, GA).

Soxhlet Extraction

Soxhlet extraction was carried out to compare the extraction performance with SC-CO_2 extraction. Denatured ethanol 95%, N-hexane and distilled water were used to extract the peanut skin. A volume of 100 mL of solvent was placed in a thimble that was put into the soxhlet apparatus containing 5.0+0.005 g of peanut skin powder. The extraction process was done for 6 hr at a temperature based on the boiling point of each solvent; for N-hexane this was 68^{o}C, for denatured ethanol it was 78^{o}C and for water it was 100^{o}C. Vacuum-drying temperature was set at 40°C and pressure was set at 80 mBar in order to avoid degradation of bioactive compounds (Danlami, Zaini, Arsad, & Yunus, 2015).

Supercritical Carbon Dioxide Extraction

The extraction process was performed at temperature 40 and 70^{o}C, with a pressure of 10 and 30 MPa, co-solvent concentration of 5% (Vethanol/Vtotal) and CO_2 flow rate of 3 ml/min. The extraction time of this method was 180 min. The chiller temperature was set at 6°C, while the heater on the back pressure regulator (Jasco BP 2080 Plus Automated BPR) was set at 50°C. Next, 5 ±0.005 g of peanut skin was placed in an extraction vessel. Then, liquid CO_2 was continuously pumped from the CO_2 tank into the system with a supercritical pump at a flow rate of 3 mL/min; ethanol 98.86% as modifier was also pumped. The extracted oil was collected in a vial and recorded every 30 min of the extraction process. After each extraction process, the extract obtained was sealed and stored at 4°C to prevent any possible degradation (Yunus et al., 2013).

Analysis of Catechin by High Performance Liquid Chromatograph (HPLC)

The analysis of catechin was developed by Chang and Wu (2011). High performance liquid chromatogram (HPLC) with ultraviolet-visible detection (Perkin Elmer Series 200, Connecticut, United States of America) was used to identify catechin. The column temperature controller was set at 30°C and the detection of wavelength was set at 210 nm. The injection volume and solvent flow rate was set at 10 µL and 1.0 mL/min, respectively. The RP C18) Merck, Darmsract, Germany – LiChrosper ® 1100 NH_2 column with C_{18} guard column was used, while HPLC grade methanol (A) and 0.5% ortho-phosphoric acid in water were used in the mobile phase. The programme was set up as follows: A:B (20:80 v/v for minute 0 to 5, linear gradient to 24/76 v/v at minute 5 to 7, hold at 24:76 v/v at minute 7 to 10 and back 20:80 v/v minute 10 to 15).

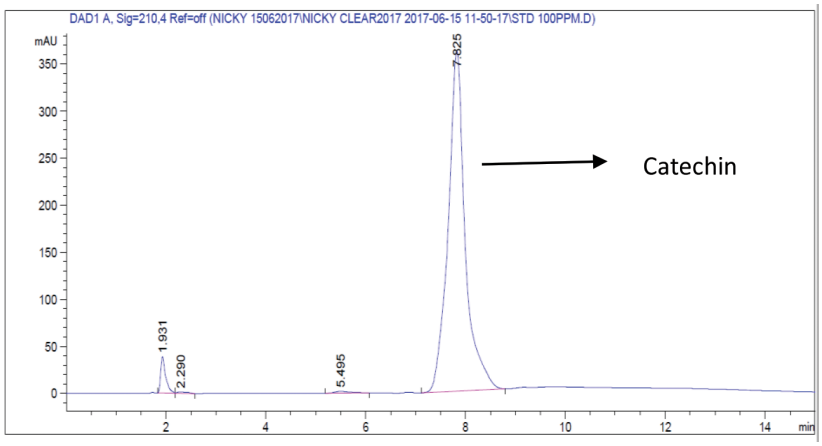


Figure 1. Peak area of catechin standard at concentration of 100 ppm

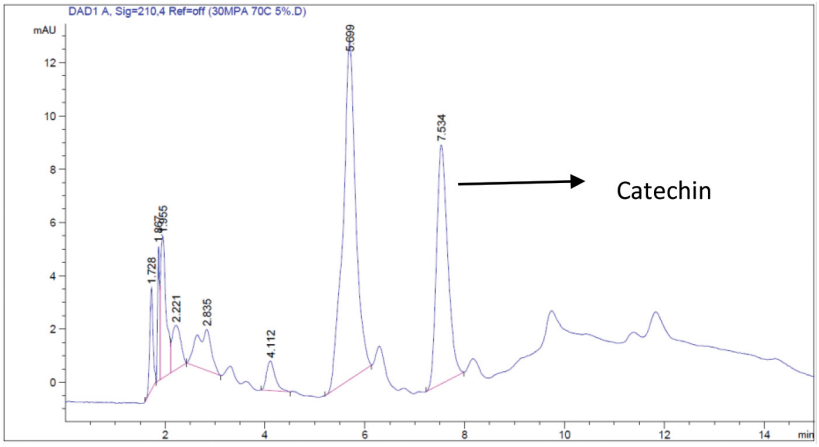


Figure 2. Peak area of catechin at 30 MPa, 70°C and 5% ethanol

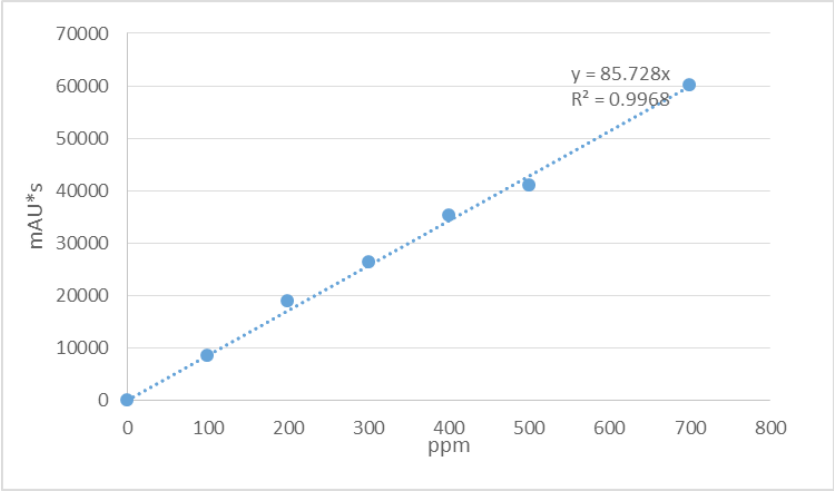


Figure 3. Calibration curve of the catechin standard

Calculation of Yield Extract

The extract yield was calculated using Equation (1):

$$\text{Extract Yield (\%)} = \frac{W_x}{W_{xy}} \times 100\ \% \quad (1)$$

where, W_x is mass of dry extract in gramme and W_{xy} is mass of sample in gramme. Based on the calculation of the extract, the extract yielded from using soxhlet extraction and supercritical carbon dioxide was compared.

Quantification of Catechin by High Performance Liquid Chromatograph (HPLC)

The slope on the calibration curve was used to denote quantification of catechin. The catechin peak area of the sample was substituted in the equation of calibration of the catechin standard curve. The equation of calibration standard is written as follows:

$$\text{Peak Area (mAU*s)} = 85.73*x \quad [2]$$

where, x is the concentration of catechin (mg/g_{sample}).

RESULTS AND DISCUSSION

Soxhlet Extraction

In this study, 5 ±0.005 g of peanut skin was used in soxhlet extraction, with 100 mL of N-hexane, denatured ethanol and distilled water used as solvent. The extraction time was 6 hr.

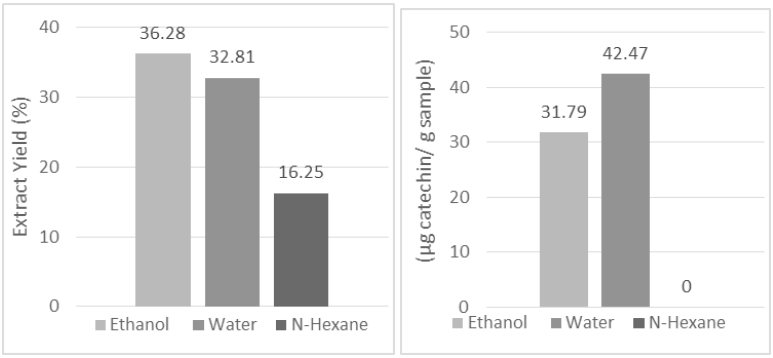


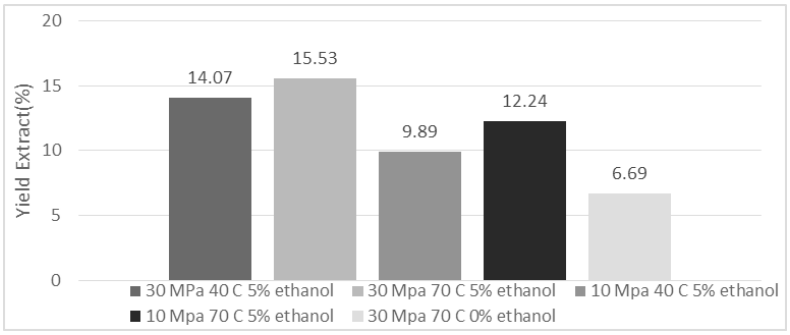
Figure 4. Extract yield (%) of soxhlet extraction using N-hexane, denatured ethanol and distilled water

The results obtained using the soxhlet extraction method are reported in Figure 4. Generally, every solvent used gives a high percentage yield in the range between 16.25% and 37%. Figure 1 shows that ethanol gave the highest amount of extract yield (36.28 ± 3.4%) compared with N-hexane and distilled water due to the polarity of the solvent. Ethanol is a bipolar solvent that can extract and make a bond between polar and nonpolar compounds in a solute (Mandana et

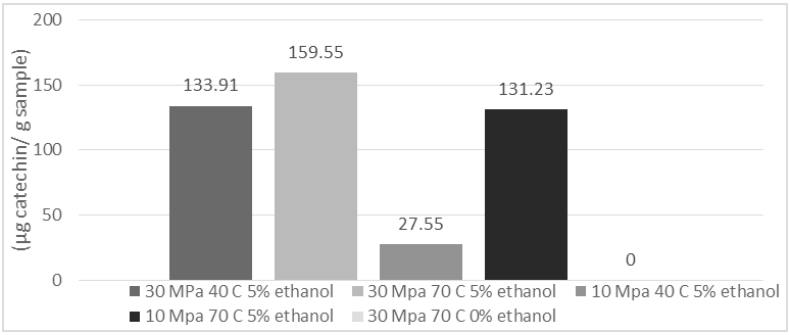
al., 2012). As a result, the extract yield from using water (32.81 ± 2.3%) was lower than from using denatured ethanol. Based on the polarity, polarity of water as solvent was higher than that of denatured ethanol and hexane, but the extract yield of water was not much more than ethanol and catechin in the peanut skin extract obtained from using distilled water (42.47 µg catechin/g sample). The amount was higher than the amount of extract obtained from using ethanol (31.79 µg catechin/g sample). N-hexane had the smallest extract yield (16.25 ± 1.3%); in addition, catechin was not extracted from the peanut skin because N-hexane is a nonpolar solvent. Polar solvents give higher results in the extraction of plants and herbs than nonpolar solvents because most of the components in plants and herbs are polar compounds; this creates difficulties for N-hexane when it is used to extract bioactive compounds in the solute (Saim, Dean, Abdullah, & Zakaria, 1997). Furthermore, peanut skin contains high oil content, thus, ethanol as a bipolar compound could extract the oil in the solute, but water as a pure polar solvent could not extract the oil in the solute. Therefore, ethanol could give a higher percentage of extract compared with water. However, water gave the higher concentration of catechin in the extract because water and catechin are polar compounds that bond easily lift catechin from the solute. This finding is similar to that reported in the extraction of *Artocarpus heterophyllus* L using various solvents. Ethanol as solvent gave the highest percentage of antioxidant activity (43%), total flavonoids (381.4 mgQE /g dry extract) and total phenolic compound (79 mg GAE/g dry extract) compared with N-hexane as solvent (Daud, Fatanah, Abdullah, & Ahmad, 2017). Siilarly, extraction of blackberry with ethanol as solvent led to high antioxidant activity and phenolic compound extraction (Wajs-Bonikowska et al., 2017).

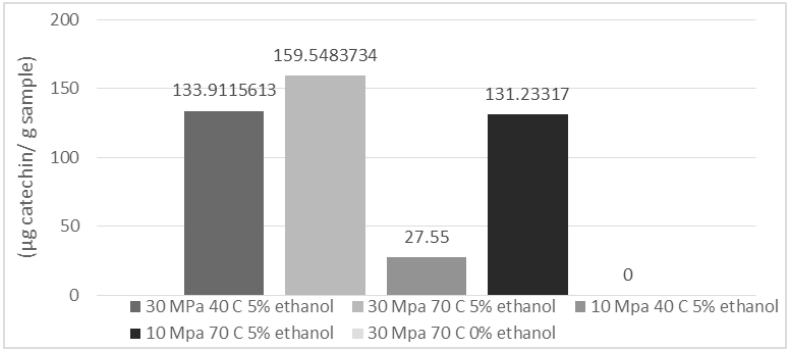
Supercritical Carbon Dioxide Extraction

Figure 5(a) illustrates the percentage of yield of SC-CO_2 extraction with ethanol as co-solvent in different pressure conditions of 10 and 30 MPa, temperature of 40 and 70°C, flow rate of CO_2 3 mL/min and co-solvent concentration of 5% ($V_{ethanol}/V_{total}$). The highest extracted yield obtained (15.528%) was at the highest pressure of 30 MPa, temperature 70 °C and 5% concentration of co-solvent ethanol. Meanwhile, the lowest yield extract obtained (6.692%) was at the lowest pressure, 30 MPa, temperature 70 °C and did not use ethanol as co-solvent. In this work, an increase in pressure increased the extract due to density and solubility. Increasing pressure will increase the density of carbon dioxide and the solubility of solvent. Increasing density enhances the amount of carbon dioxide in the solvent, and this helps to create a bond between the solvent and the extract in the solute as increasing the solubility of the solvent can lift the extract. This condition is similar to that needed for extraction of *Pithecellobium Jiringan* (Jack) prain seeds with supercritical carbon dioxide as an increase in the pressure and temperature increased the solubility and yield extract (Yunus et al., 2013).



(a)





(b)

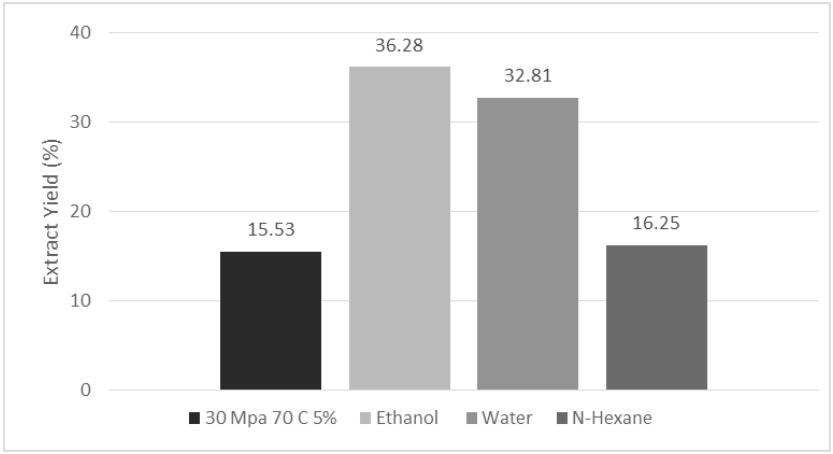
Figure 5(a), (b). Yield extract and concentration of catechin of supercritical carbon dioxide extraction with co-solvent and without co-solvent ethanol

Increasing the temperature from 40°C to 70°C at the low pressure of 10 MPa and high pressure of 30 MPa increased the yield and concentration of catechin in the extract due to the solute vapour pressure, which contributed to the increase of the mass transfer between the extract and solvent. Without ethanol as co-solvent, the amount of yield was lower as ethanol is needed to enhance the solvating power of the solvent and the polarity of the solvent (Mohd-Setapar, Yian, Yunus, Muhamad, & Zaini, 2013). Increasing the polarity gave the solvent power to extract polar and nonpolar compounds in the solute, while ethanol enhanced the porosity

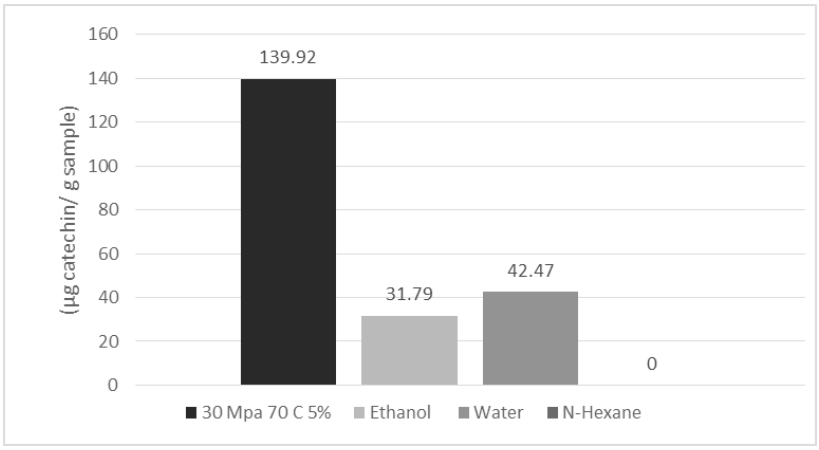
of the solute, helping the solvent to penetrate the solute to lift the extract. Supercritical carbon dioxide was not adequate for penetrating the inner solute of peanut skin, but ethanol as modifier encouraged the supercritical carbon dioxide to absorb the extract from the solute (Baumann, Ferrante, Deeg, & Bräuchle, 2001). The additional ethanol in the supercritical carbon dioxide caused the swelling of the matrix, increasing the internal volume and the surface area between the solute and the solvents (Machmudah, Shotipruk, Goto, Sasaki, & Hirose, 2006). Without a co-solvent, the supercritical carbon dioxide was unsuccessful at extracting the catechin due to differences in polarity. Catechin is a highly polar compound, but carbon dioxide is a nonpolar solvent; hence, there was no interaction between the catechin and the supercritical carbon dioxide.

Comparison Between Supercritical Carbon Dioxide Extraction and Soxhlet Extraction

The overall total percentage of oil yield obtained from optimum conditions of supercritical carbon dioxide was compared with that obtained from using soxhlet extraction with different solvents, namely, water, ethanol and N-hexane. The conditions of the supercritical carbon dioxide and co-solvent ethanol were selected at higher conditions (30 MPa, flow rate of CO_2 3 mL/min, co-solvent concentration of 0 and 5% and temperature of 40 and 70°C) in order to compare the performance of using the supercritical carbon dioxide method and other methods. The highest overall extraction of oil yield was 36.28% using soxhlet extraction with ethanol as the co-solvent, followed by water (32.82%), N-hexane (16.25%) and CO_2 supercritical fluid extraction (15.52%) at pressure 30 MPa, temperature 70°C and 5% rate of co-solvent ethanol, respectively. Finally, the lowest oil yield, 16.25%, was obtained from using N-hexane as the solvent in the soxhlet extraction as presented in Figure 6(a). The soxhlet extraction with ethanol as a co-solvent generated higher oil yield than other extraction media. This is because most of the compounds in peanut skin are polar compounds such as procyanidin, catechin and epicatechin (Yu, Ahmedna, Goktepe, & Dai, 2006). Ethanol and water are polar molecules that easily interact and extract compounds from peanut skin.



(a)



(b)

Figure 6(a),(b). Comparison of extract yield (%) and concentration of catechin in the extract using supercritical carbon dioxide and soxhlet extraction with various solvents

Although extraction of peanut skin using soxhlet extraction gave the maximum yield extract, the concentration of catechin in the extract was lower than the concentration of catechin in the extract obtained using supercritical fluid extraction as the temperature of extraction using soxhlet was relatively high compared with that used in supercritical fluid extraction. High temperatures lead to the degradation of bioactive compounds in extracts and also compromises the antioxidant activity of extracts (Hasmida et al., 2015). Bioactive compounds, especially flavonoids, are sensitive to high temperatures. This finding is similar to that obtained in previous research, which showed that catechin had degraded at below 100°C due to the decarboxylation of benzoid acid process in the structural molecules of catechin (Khuwijitjaru et al., 2014). Supercritical carbon dioxide extraction was preferable because it needed less solvent and a shorter extraction time. Moreover, the quality of the extract obtained using supercritical carbon dioxide was better than that obtained from soxhlet extraction.

CONCLUSION

In conclusion, the maximum peanut skin extract came from soxhlet extraction (36.28%) compared with using supercritical carbon dioxide extraction (15.53%). Although soxhlet extraction yielded a more extract (31.79 µg catechin/g sample), the bioactive compounds derived from this extraction were lower in quality than those extracted using supercritical carbon dioxide (139.92 µg catechin/g sample). Carbon dioxide supercritical fluid extraction was preferred in this work due to its benefits of shorter time of extraction, lower amount of solvent used and higher amount of catechin extracted. Both methods used ethanol as the extraction solvent, thus, toxicity of solvent should be ruled out.

ACKNOWLEDGEMENT

The authors are grateful to the Centre of Lipid Engineering and Applied Research (CLEAR) for the use of their equipment and thank Universiti Teknologi Malaysia for financial support under grant no. R.J130000.7709.4J260 and R.J130000.7909.4F766.

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