Evaluation of fatty acids, phenolics and bioactivities of spent coffee grounds prepared from Vietnamese coffee

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ABSTRACT
Spent coffee ground (SCG) is a residue released during coffee brewing. Disposal of SCG is able to lead to a loss of bioactive constituents and have a negative impact upon the environment. This study aimed to explore fatty acids, bioactive phenolics, antioxidant and anti-aging potentials of SCG samples obtained from coffee shops in Ho Chi Minh city, Vietnam. The oil content of the SCG samples ranged from 6.3 to 10.5%, and linoleic (43%), palmitic (33.4%) and oleic (11%) acids were identified as major constituents of the oil. Chlorogenic acid was the most abundant phenolic acid examined (832.9–7657.7 μg/g of dry weight), followed by ferulic acid (40.5–1041.7 μg/g). Through anti-collagenase and anti-elastase assays, SCG showed a promising anti-aging activity, with IC50 values comparable with those of epigallocatechin gallate. The correlation analysis revealed gallic acid positively correlated with the free radical scavenging potential evaluated by DPPH (2,2-diphenyl-1-picrylhydrazyl) assay and the inhibitory effect on elastase. The results demonstrated that utilization of SCG prepared from Vietnamese coffee could open new avenues for food and cosmeceutical industry.

INTRODUCTION

Coffee is a dark-colored drink obtained by brewing roasted coffee beans. It is among the most consumed beverages worldwide and is known as a huge industry. The preparation of coffee brewing releases a large amount of residue also known as spent coffee ground (SCG) (910 kg/tonne of coffee). Different approaches to SCG valorization in order to reduce this waste disposal have been taken into consideration. For example, the utilization of SCG for productions of bioethanol, butanol, fertilizers and SCG-based sorbent materials for metal removal has been proposed. Spent coffee ground is also used for development of skin-whitening products due to its inhibition of tyrosinase activity and melanin synthesis. Sufficient amounts of dietary fiber, protein, lipid, and low glycemic sugars in SCG and acceptable rheological properties of SCG-supplemented dough give rise to its application in biscuit products. In addition, SCG reportedly contains a wide variety of bioactive constituents that can be exploited as a nutraceutical or used in food products.

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Coffee, introduced to Vietnam by the French in the late 19th century, has become a huge part of daily Vietnamese life. It is estimated that there are more than 20,000 modern and traditional coffee shops across the country. In 2017–2018, about 150 thousand tonnes of coffee were consumed in Vietnam, equivalent to 1.38 kg per capita per year. About 50% of the coffee consumed is reckoned into coffee shops, restaurants, or homes. As a result, Vietnam’s annual production of SCG as a waste is very high, and this waste often ends up in landfills or is reused as a nitrogen source for composting. Recently, several applications of SCG-derived biochar for remediating contaminated water from agricultural activity have been proposed. Beyond these, to our knowledge, there is a lack of efforts to convert SCG into other valuable products, such as food or cosmeceuticals in Vietnam. It could be because limited information about phenolics and fatty acids in SCG and how these compounds are related to bioactivities of SCG, such as antioxidant and anti-aging activities, restrains applications of SCG constituents in food and cosmeceutical industries. Therefore, we conducted a study on fatty acids, phenolics, antioxidant and anti-aging activities of SCG samples obtained during the brewing of Vietnamese roasted coffee. The goal is to gain a better understanding of phytochemical composition and their contribution to health benefits of coffee products, exploring the potential use of SCG in food and cosmeceutical productions.

**Materials and methods**

**Sample collection**

The SCG samples were collected from 10 well-known coffee shops located in Ho Chi Minh city, Vietnam. The samples collected were dried at 45°C until dryness (moisture ≤5%) in a convection oven. All the samples were kept in a freezer (−20°C) until analysis.

**Chemicals**

The analytical standards, with purity above 98%, used to determine phenolics were caffeic acid, chlorogenic acid, ferulic acid, cinnamic acid, p-coumaric acid, and gallic acid (Sigma–Aldrich, St. Louis, MO, USA). The solvents, including methanol, hexane, diethyl ether (99.5%, ACS grade), were purchased from Fisher Scientific (Pittsburg, PA, USA). Folin-Ciocalteu reagent was obtained from Merck KGaA (Darmstadt, Germany). Collagenase (EC 3.4.24.3), elastase (EC 3.4.21.36) and substrates were purchased from Sigma–Aldrich.

**Fatty acid composition**

Oil in SCG was extracted using the method described by Vu et al. 2019 with a minor modification. About 5 g of an SCG sample were weighed into a screw-capped tube, then 25 mL of 5 M HCl were added. The tube was vortexed and then placed in a water bath (80°C for 60 min). During the heating, the tube was shaken every 10 min. After the acid hydrolysis, the tube was cooled down with water. 25 mL of hexane-diethyl ether (1:1, v/v) were pipetted into the mixture. The tube was vortexed for 10 min and centrifuged at 5000 rpm for 5 min. The upper phase was collected and transferred into a clean tube. The addition of hexane-diethyl ether was repeated for two times, making a total of 50 mL of hexane-diethyl ether used. The combined upper phases were evaporated until dryness under a clean stream of nitrogen. The oil was methylated with 1 mL of BF₃ in methanol for 45 min at 60°C. The fatty acids were analyzed using Shimadzu gas chromatograph 2010 equipped with flame ionization detector set at 280°C. The chromatographic separation was performed at 100–230°C at the rate of 7°C/min with nitrogen as a carrier gas.
Phenolic acids

Phenolic acids in an SCG sample (30 g) were extracted with 100 mL of methanol in a precleaned flask. After 24 hr of extraction performed on a shaker at room temperature, the mixture was filtered through a Whatman filter paper (110 mm in diameter, GE Healthcare, IL, USA). An aliquot of the filtrate was transferred to an LC vial for analysis of phenolic acids.

For a qualitative analysis, the SCG extract was injected into a Shimadzu Nexera X2 high-performance liquid chromatograph (HPLC) coupled to a Sciex QTRAP 6500+ mass spectrometer. The retention time, molecular and product ions of the monitored phenolic acids were detailed in Table S1 (Supplemental data). Phenolic acids in the SCG sample were quantitatively analyzed using a Shimadzu LC-2030C HPLC interfaced to a diode array detection system and a VertiSep™ GES C18 reverse-phase column (250 × 4.6 mm, 5.0 µm particle size). The mobile phases consisted of (A) methanol and (B) 1% formic acid in water. The gradient elution was as follows: 0 to 3 min, 25% A; 3 to 5 min, 25% to 40% A; 5 to 16 min, 40% to 60% A; 16 to 21 min, 60% A; 21 to 24 min, 60% to 80% A, 24 to 27 min, 80% A, 27 to 35 min, 80 to 25% A. The flow rate was 0.8 mL/min and the column temperature was set at 40°C. The detection of phenolic acids was set at 270 nm. Chromatographic data obtained were processed using LabSolutions 5.87 SP1 software platform (Shimadzu, Kyoto, Japan). The quantification of phenolic acids was performed using their standard stock solutions in methanol prepared in the range from 0.1 to 5 µg/mL. The linear relationship successfully fitted every calibration curve. The correlation coefficients (R²) of the calibration were all 0.999. A representative HPLC-DAD chromatogram of a standard mixture containing phenolic acids was shown in Figure S1 (Supplemental data). The extraction efficiency was estimated based on the recovery rate of an internal standard (acetylsalicylic acid). A volume (10 µL) of the internal standard solution (10 µg/mL) was spiked and the recovery rate calculated was higher than 90%.

Total phenolic content

The filtrate collected above was evaporated using a rotary evaporator. The residue obtained was used for determination of total phenolic content (TPC). Total phenolic content of an SCG sample was determined using the Folin – Ciocalteu reagent, with gallic acid as an analytical standard. The solutions of gallic acid in methanol at concentrations ranging from 20 to 200 µg/mL were prepared. 100 µL of the sample (0.5 mg/mL) or standards were mixed with 100 µL of 2% Na₂CO₃ and 100 µL of 50% Folin – Ciocalteu solutions. The absorbance of the mixture was spectrophotometrically measured at 760 nm against a blank (methanol). The TPC was calculated using the calibration curve (y = 0.0072x + 0.1541; R² = 0.9994) fitted by a linear relationship between the absorbance and the concentrations of the gallic acid standard solutions, expressed as mg of gallic acid equivalent (mg GAE)/g of extract.[17]

Antioxidant activity

ABTS radical scavenging assay: ABTS radical scavenging activity was determined following the method previously described by Leung et al. (2009).[18] In brief, K₂S₂O₈ (2.45 mM) was added to ABTS (7 mM) at a ratio of 1:1 (v/v), and the mixture was then incubated for 12–16 hr at an ambient temperature in the dark. After the incubation, an ABTS radical working solution with an absorbance value of 0.75 ± 0.02 at 734 nm was prepared by diluting the mixture with the phosphate-buffered saline (PBS, pH = 7.4). The test sample (100 µL) was mixed with 3 mL of the working solution, and the absorbance at 734 nm was measured.

DPPH radical scavenging activity: DPPH radical scavenging activity was determined using the method by Xiao et al. (2014).[19] A solution of DPPH (40 µg/mL) in 80% methanol was prepared. The test sample (0.5 mL) was mixed with 0.75 mL of the DPPH solution. The mixture was vigorously
shaken for 30 min at an ambient temperature in the dark and the absorbance at 517 nm was then measured. Ascorbic acid was used as a reference standard. IC50 values were determined using the graph constructed for the concentrations (μg/mL) against the percentage inhibition.

**Anti-collagenase activity**

The assay was performed as described by Thring et al. (2009) with a minor modification.[20] Tricine buffer (50 mM tricine, 10 mM calcium chloride and 400 mM sodium chloride, pH 7.5) was prepared and used for the assay. N-[3-(2-furyl)acryloyl]-Leu-Gly-Pro-Ala (FALGPA) was prepared in Tricine buffer at a concentration of 1 mg/mL. A mixture containing 25 μL of collagenase (1 mg/mL), 25 μL of Tricin buffer and an SCG extract (1.5 mg/mL in DMSO) was incubated in at 37°C for 15 min. Afterward, 100 μL of FALGPA was added to the mixture, incubated for 60 min. Epigallocatechin gallate (EGCG) with concentrations ranging between 1 and 10 μg/mL was used as a standard and blank samples containing no inhibitors or samples were regarded as a negative control. Absorbance was spectrophotometrically measured at 335 nm. The percentage inhibition of collagenase was calculated as follows:

\[
\text{Percentage inhibition of collagenase} = \left[ 1 - \frac{A}{B} \right] \times 100
\]

where, A stands for the corrected absorbance values of the samples/standard while B shows the corrected absorbance values of the control.

**Anti-elastase activity**

The inhibitory effect of SCG extracts was investigated according to Thring et al. (2009) with a minor modification.[20] 25 μL of Tris-HCl buffer solution (pH 8.0), 25 μL of an SCG extract (1.5 mg/mL) and 25 μL of porcine pancreatic elastase (1 μg/mL) were mixed then incubated at ambient temperature for 30 min. After an addition of N-succinyl-Ala-Ala-Ala-p-nitroanilide (1 mM), the mixture was incubated at ambient temperature for 40 min then absorbance at 410 nm was measured. EGCG (1–10 μg/mL) was used as a standard and blank samples without inhibitors or samples were regarded as a negative control. The calculation of percentage inhibition of elastase resembled that of collagenase as described above.

**Statistical analyses**

Statistical analyses were performed using XLSTAT 2016 (Addinsoft, Paris, France). Box plot was used to graphically present oil content, phenolic contents and bioactivities of the SCG samples. Correlations between antioxidant, anti-aging activities, and concentrations of phenolic acids in SCG samples were examined. This helps gain a better understanding of antioxidative roles and skin-aging inhibitory effect of individual phenolic acids in the samples.

**Results and discussion**

**Oil content and fatty acid composition**

The results showed that the oil content of the 10 SCG samples investigated in this study ranged from 6.3 to 10.5 g/100 g DW (dry weight), with the median of 7.8 (Figure 1). Prior research revealed the SCG samples prepared from Caribbean and South American coffees had an oil content of 7–13%.[21] Recently, a study on SCG obtained from various Vietnamese coffees has indicated oil content ranged from 6 to 16 g/100 g DW.[22] Slight differences in oil content among the studies could be due to oil extraction methods. The present study employed acid hydrolysis combined with organic solvents to extract oil while the prior research took advantage of organic solvents with or without a Soxhlet apparatus.
As shown in Table 1, the oil extracted from SCG contained 33.4% palmitic acid, 11% oleic acid and 43% linoleic acid, followed by stearic and arachidic acids (<10%). The results also yielded evidence of eicosenoic, behenic, and lignoceric acids that were present at below 1% of the oil. The results are in agreement with those reported by Sung et al. (2015) on Vietnamese coffee. It is noted that studies conducted by Jenkins et al. (2014) and Dang and Nguyen (2019) indicated fatty acid composition of SCG obtained from Vietnamese coffee was different with respect to weight percentages of palmitic, oleic, and linoleic acids. In comparison with soybean and corn oils, the SCG oil consists of relatively similar linoleic acid and PUFA contents (Table 1). Conversely, the SCG oil and palm oil share similarities in fatty acid composition with respect to SFA content.

### Table 1. Fatty acid composition of the SCG oil.

| Fatty acid        | SCG oil | Soybean oil | Corn oil | Palm oil |
|-------------------|---------|-------------|----------|----------|
| Palmitic acid 16:0| 33.4    | 9.0         | 12.9     | 44       |
| Stearic acid 18:0 | 7.2     | 4.0         | 2.1      | 4        |
| Oleic acid 18:1   | 11.0    | 28.5        | 32.0     | 40       |
| Linoleic acid 18:2| 43.0    | 49.5        | 49.0     | 10       |
| α-Linolenic acid 18:3| 1.0     | 8.0         | 0.7      | -        |
| Arachidic acid 20:0| 3.0     | -           | 0.7      | -        |
| Eicosenoic acid 20:1| 0.4     | -           | -        | -        |
| Behenic acid 22:0 | 0.6     | -           | 0.4      | -        |
| Lignoceric acid 24:0| 0.3     | -           | 0.5      | -        |
| Total             | 99.9    | -           | -        | -        |
| SFA               | 44.5    | 13.5        | 16.6     | 48       |
| MUFA              | 11.4    | 28.5        | 33.7     | 40       |
| PUFA              | 44.0    | 57.5        | 49.7     | 10       |

1Kostik et al. (2013)
2Dorni et al. (2018)
3Gunstone (2012)
Total phenolic content

Figure 2A displays TPC of the 10 methanolic SCG extracts, and the data are presented as boxplot diagrams. The TPC of the samples ranged from 109.4 to 181.3 mg GAE/g of extract, with the median of 132.5. Prior studies have reported a large variation in TPC of SCG extracts and this could be due to different extraction methods. For example, the conventional solid–liquid extractions with aqueous methanol or ethanol at different concentrations, extraction times (30–120 min) and solvent/sample ratios resulted in TPC varying from 2.6 to 21.6 mg GAE/g.\[^{26,27}\] Reportedly, TPC of SCG extracts obtained by the solid–liquid extraction combined with ultrasonic treatment (120 min) ranged between 56.9 and 93.6 mg GAE/g.\[^{28}\] Notably, a combination of ethanolic extractions and a microwave-assisted technique (80 W, 40 s) resulted in SCG extracts with TPC of 398.9 mg GAE/g.\[^{29}\] Besides the uses of conventional solvents, applications of new techniques for SCG phenolic investigations have aroused much attention and been shown to be suitable for extracting natural compounds in coffee byproducts. For instance, the use of subcritical water extraction of SCG showed that TPC could contain up to 88.3 mg of GAE/g.\[^{30}\] A study conducted by Sung et al. (2015) revealed that the supercritical extract of SCG prepared from Vietnamese coffee had a TPC value of about 100 mg GAE/g.\[^{8}\] In general, extraction times employed in the prior studies often fell within 0.5–5 hr, while the extraction performed in the present study was prolonged for 24 hr. Evidence suggests that TPC depends on multiple variables, such as solvent, solvent/sample ratio, extraction time, extraction method and temperature.\[^{31}\] Perhaps, these factors may have affected the results among the studies and contributed to the much higher TPC values in the present study compared to the others.

Phenolic acid profiles

While the measurement of TPC is performed to glance at the total amount of phenolics in samples, determination of phenolic composition allows for a detailed look at individual phenolics. The results demonstrated that these compounds were all present in the investigated SCG samples (Figure S2, Supplemental data) and their levels were depicted as box plots in Figure 2B. Chlorogenic acid (CGA) predominated over the other phenolic acids in all the samples, with the concentration values ranging from 832.9 to 7657.7 μg/g DW and the median of 3066. Previously, many authors reported the compound was the most abundant phenolic acid detected in SCG.\[^{11,32–34}\] Among these, Ramón-Gonçalves et al. (2019) showed CGA was present in SCG prepared from a Spanish-branded coffee product at a concentration as high as 4800 μg/g DW.\[^{34}\] Through the use of microwave-assisted extraction, López-Barrera et al. (2016) indicated an average CGA level in lyophilized SCG was 5600 μg/
It should be noted that levels of CGA in SCG varied considerably among studies. While Mussatton et al. (2011) and Cruz et al. (2012) revealed CGA concentrations ranged between 370 and 2642, Okur et al. (2021) recorded the levels falling within only about 31–110 µg/g DW. As explained above, the variations could be due to multiple factors, including solvent, solvent/sample ratio, extraction time, extraction method and temperature. Indeed, a recent investigation by Angeloni et al. (2020) has shown CGA levels differ moderately among the phenolic extraction methods using different solvents and techniques. Interestingly, these authors have also noted negligible variations in CGA levels among the SCG prepared from coffee samples originating in five different countries (RSD = 2.2%, n = 5). Several investigations were also focused on the measurements of all CGA isomers, including 3-caffeoylquinic acid, 4-caffeoylquinic acid, 5-caffeoylquinic acid, 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid and 4,5-dicaffeoylquinic acid. Chlorogenic acid is a bioactive phenolic compound that exerts a wide range of potential health benefits, including free radical scavenging capacity, anti-inflammatory, antidiabetic, and anticancer effects. Its abundant presence in SCG may enable the development of dietary approaches to stop certain chronic diseases.

Following CGA, ferulic acid was identified as being the second most abundant phenolic, with the levels varying remarkably among the samples (40.5–1041.7 µg/g DW) and the median of 385.7. The present study reported p-coumaric acid at concentrations ranging from 9.7 to 267.5 µg/g DW. Notably, the compound was once recognized as one of the predominant phenolics, with concentrations ranging between 173 and 500 µg/g DW. Many authors have found these two acids to be at comparable levels in various SCG whereas Angeloni et al. (2020) revealed the compounds as minor phenolics at levels below 1 µg/g DW (Table 2). Caffeic and cinnamic acids have generally been reported to be phenolic constituents in SCG in aforementioned research. In this study, we showed that the SCG consisted of caffeic acid with the levels comparable with prior research (Table 2). Of the phenolics analyzed, cinnamic acid was detected at low concentrations with the median (range) of 3.9 (1.3, 45.9) µg/g DW. This result is in agreement with what was presented by Zengin et al. (2020).

Among the phenolic acids monitored in the present study, gallic acid, with the median concentration of 20.7 µg/g DW, is not a hydroxycinnamic acid. The presence of this acid in SCG as a minor constituent was previously indicated. Interestingly, according to these authors, water was shown to be able to extract gallic acid in SCG efficiently compared to methanol and ethanol. And though gallic acid is thought to be a constituent of SCG, it has not always been reported to be detected in SCG. This could be in part due to detection and quantification sensitivity of methods employed in those analyses.

Phenolic acids have attracted much attention due to their multiple bioactivities important to human health. It is known that the presence of chlorogenic, p-coumaric and ferulic acids has been linked to health benefits of coffee consumption, such as cardioprotective effect and neurodegeneration prevention. Since phenolic acids are mainly representative of phenolic composition of SCG and roasted coffee, the information about these constituents in SCG is of importance as it may help better understand bioactivities and nutraceutical applications of SCG.

| Phenolic acids | López-Barrera et al. (2016) | Ramón-González et al. (2019) | Angeloni et al. (2020) | Present study (2021) |
|----------------|-----------------------------|-----------------------------|------------------------|----------------------|
| Gallic acid    | 2500                        | n.a.                        | 0.2–0.5                | 15.2–202.3           |
| Cinnamic acid  | n.a.                        | n.a.                        | 0.12–0.15              | 1.3–45.9             |
| Chlorogenic acid| 5600                        | 20–4800                     | 396.6–414.2            | 832.9–7657.7         |
| Caffeic acid   | 70                          | n.a.                        | 5.8–8.1                | 69.1–230.7           |
| p-Coumaric acid| 10                          | 173–500                     | 0.14–0.22              | 9.7–267.5            |
| Ferulic acid   | 4                           | 89–160                      | 0.70–0.88              | 40.5–1041.7          |

n.a.: not reported or not detected
Antioxidant activity

As depicted in Figure 3, the DPPH values (IC\textsubscript{50}) fall within 8.5–44.9 μg/mL, with the median of 17.5. A study conducted by Balzano et al. (2020) revealed the figure for extracts of SCG ranged between 10.1 and 301.8 μg/mL.\textsuperscript{[40]} In this study, an ABTS test was also applied to the determination of antioxidant activity of SCG in addition to the DPPH assay. The results indicated that the ABTS values (IC\textsubscript{50}) of the extracts ranged from 76.9 to 590.8 μg/mL. Compared to prior research (1.5–185.7 μg/mL),\textsuperscript{[40]} the antioxidant activity measured through ABTS in the present study was weaker. In both assays, the IC\textsubscript{50} values for vitamin C as a positive control were 4.06 and 51.4 μg/mL, respectively. Prior research has shown that different assays have been employed to test antioxidant activity of SCG. In the present study, DPPH and ABTS assays were performed in part because these methods are widely accepted for measuring the capacity of trapping free radicals. Furthermore, they are among the commonly used methods for evaluating the scavenging ability of SCG extracts.

In vitro anti-collagenase and anti-elastase activities

The skin aging process is widely known to depend on multiple processes, among which the degradation of two proteins, namely collagen and elastin, plays an important role. Two enzymes involve the breakdown of peptide bonds in these biomolecules are collagenase and elastase. In the present study, we conducted enzyme assays to determine inhibitory effects of SCG extracts on collagenase and elastase. These assays have often been used as an approach to evaluating anti-aging potential of plant extracts. As seen in Figure 4, the extracts of SCG exhibited an anti-collagenase activity with IC\textsubscript{50} values ranging between 72.3 and 200.4 μg/mL (Figure 4). Additionally, the extracts showed an inhibitory effect on elastase demonstrated through IC\textsubscript{50} values falling within 58.2 and 111.0 μg/mL. In both assays, the IC\textsubscript{50} values for epigallocatechin gallate as a positive control were 62.4 and 48.3 μg/mL, respectively. In general, the enzyme inhibitory effects of the studied SCG were comparable with those of epigallocatechin gallate.
Correlation analysis

Correlations between phenolic acid levels, antioxidant, anti-collagenase, and anti-elastase activities were examined in order to assess the contribution of phenolic acids to radical scavenging capacity as well as anti-aging potential of SCG extracts. In the present study, a reciprocal of IC_{50} was used to investigate the correlations. The use of Pearson’s correlation revealed that the DPPH had positive correlations with gallic acid in the SCG extracts (r = 0.64, p < .05, Table S2, S3, Supplemental data). Previously, Choi and Koh (2017) evinced a positive correlation between DPPH radical scavenging potential and gallic acid in SCG.\textsuperscript{[33]} The results also indicated a positive correlation between gallic acid and anti-elastase activity (r = 0.68, p < .05, Table S2, S3, Supplemental data). Beyond these, no positive correlations between the other phenolic acids and the examined bioactivities were observed, hinting at unmonitored bioactive constituents potentially contributing to the radical scavenging activities and anti-aging potential of the SCG.

Conclusion

The results achieved in this study indicated that the SCG samples collected from coffee shops in Vietnam were a rich source of fatty acids and phenolic acids. The oil extracted from the SCG contained two major fatty acids, namely linoleic and palmitic acids. It also had similar linoleic acid and PUFA contents to those of soybean and corn oils. All the phenolic acids monitored were present in the SCG and among these, chlorogenic acid was the most abundant compound. The findings also showed that methanolic extracts of the SCG exhibited DPPH and ABTS radical scavenging activities and possessed inhibitory effects on collagenase and elastase. The correlation analysis unraveled the relationships between phenolic acid composition, antioxidant, and skin aging-related enzyme inhibitory activities. In general, this study explored fatty acids and phenolics of SCG and highlighted potential applications of SCG in cosmeceutical industry.
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