Biointerface Research in Applied Chemistry
Platinum Open Access Journal (ISSN: 2069-5837)

Article
Volume 12, Issue 5, 2022, 6308 - 6320
https://doi.org/10.33263/BRIAC125.63086320

Spent Coffee Ground Oil as a Potential Alternative for Vegetable Oil Production: Evidence from Oil Content, Lipid Profiling, and Physicochemical Characterization

Laila Bijla [1], Rabha Aissa [2], Hasna Ait Bouzid [1], El Hassan Sakar [3], Mohamed Ibourki [1], Abdellatif Laknifli [1], Said Gharby [1,*]

[1] Equipe Laboratory Biotechnology, Materials and Environment (LBME), Faculty Polydisciplinary of Taroudant, University Ibn Zohr, Agadir, Morocco; bijla.laila@gmail.com (L.B.), hasna.aitbouzid@edu.uca.ac.ma (H.A.B), a.laknifli@uiz.ac.ma (A.L.), ibourkimohamed.91@gmail.com (M. I),s.gharby@gmail.com (S.G.);
[2] Equipe Bioprocédés and Environnement, Ecole Supérieure de Technologie, Université Ibn Zohr, Agadir, Maroc; r.aissa@uiz.ac.ma (R.A.);
[3] Department of Biology, Faculty of Sciences of Tetuan, Abdelmalek Essaâdi University, Mhannech II. 93002, Tetuan, Morocco; hassan.sce@gmail.com (E.H.S.);
* Correspondence: s.gharby@yahoo.fr, s.gharby@uiz.ac.ma (S.G.);

Scopus Author ID 25927057100
Received: 31.08.2021; Revised: 15.10.2021; Accepted: 20.10.2021; Published: 18.11.2021

Abstract: In this work, routinely measured physicochemical indices and lipid profiling of oil extracted from spent coffee grounds (SCG) were evaluated to assess the suitability of SCG as a new candidate for oil production. The obtained results reveal that the oil yield was 18.55±1.5 g/100g. Physicochemical indices were comparable to those of widely consumed vegetable oils in the range set in several studies. The main fatty acids of SCG oil were linoleic acid 43.20±2.19 g/100g, palmitic acid 31.78±2.02 g/100g, and oleic acid 12.68±1.15 g/100g dry basis. For sterol composition, β-sitosterol was the most abundant sterol (44.70±0.01%), followed by stigmasterol (27.57±0.01%) and campesterol (12.16±0.01%). In conclusion, this composition is typical for many other vegetable oils. Therefore, this oil may be considered a good alternative for vegetable oil production for new multi-purpose products such as cosmetic and industrial pharmaceutical uses.

Keywords: spent coffee ground oil; fatty acids; sterols; vegetable oil; environment.

1. Introduction

With coffee on every street in the world, it is no surprise that it is one of the most consumed beverages in the world [1]. Furthermore, it is the third most consumed beverage around the globe. Recent estimates from the International Coffee Organization show that the global consumption of coffee exceeded 10.16 billion kilograms in 2019-2020. Europe ranked first in terms of consumption (32.71%), followed by Asia and Oceania (21.9%), North America (22.15%), South America (16.02%), Africa (7.07%), and both Central America and Mexico (3.23%). In Morocco, coffee consumption exceeds 35 million kilograms in the same period [2]. Unfortunately, coffee consumption leads to the generation of millions of tons of wastes, such as; aluminum capsules, plastic cups, and spent coffee grounds (SCG).

Previous studies showed that one ton of raw green coffee produces almost 650 kg of SCG through the process of soluble coffee preparation [3]. SCGs are reported to be involved in serious environmental issues. For instance, phytotoxic substances and organic acids in these

by-products affect soil, water quality and restrict crop growth [4]. When SCGs are sent to landfill, they can produce greenhouse gases like methane and carbon dioxide that contribute to global warming [5]. Furthermore, SCGs discarded in the environment may pose a risk to human and environmental health [6]. However, SCG chemical composition reveals a rich product in sugars, proteins, antioxidants, polyphenols components, and oil [7-9].

In this context, SCGs may present promising valorization opportunities to reduce their environmental impacts on one hand and obtain added-value products on the other hand. In fact, several works were devoted to SCGs valorization globally. For instance, several options can be considered to manage this waste material, for example; antioxidants [10], anti-inflammatory additives [11], metal scavengers [12], production of biofuels [13,14], cosmetics, soap [15], and other food and health applications [16].

This work had as goals to (i) assess the potentiality of using SCGs as a raw material to produce vegetable oil, (ii) evaluate the quality of obtained oil, and (iii) compare SCGs oil quality attributes to commonly consumed vegetable oils (soybean, sunflower, rapeseed, and coconut oils).

2. Materials and Methods

2.1. Plant material and chemicals reagents.

All samples were a concoction of Robusta beans (*Coffea canephora*) and Arabica beans (*Coffea arabica*). Indeed, samples are collected by taking an average of 4 kg for each brand of coffee. After collection, the samples were dried in ambient air (until 2.5% of moisture). Then, they were grounded in order to obtain a homogeneous structure. Afterward, the SCG oil (SCGO) was extracted using a Soxhlet extractor with n-hexane as a solvent. Later, various analyses were carried out, namely, oil yield, physicochemical indices, fatty acids, and sterols.

All the chemical reagents were analytical or HPLC grade and purchased from Professional Labo (Casablanca, Morocco).

2.2. Oil yield.

A Soxhlet system was used to extract the oil from the crushed SCGs (dry matter, DM). n-Hexane was used as extraction solvent with a solvent ratio of 20 g of weight for 200 mL of solvent, with a solid to solvent ratio of 1:10 [17]. The extraction was carried out for 8 hours. The hexane was evaporated in a rotavapor under reduced pressure. The yield of oil (%) was then calculated as follows:

$$Oil\ Yield\ (\%, DM) = \frac{extracted\ oil\ (g)}{SCGs\ sample\ (g)} \times 100$$

2.3. Physicochemical indices.

Routinely measured physicochemical indices in oil consist mainly of free fatty acids (FFA), acidity or acid value, peroxide value, iodine, saponified values, refractive index, and density.

Acidity (a measure of the amount of free fatty acids in oil) was determined using the official analytical method [18]. Acidity was expressed as the oleic acid (C18:1) in the mass percentage of oil by titration of a solution of oil in ethanol with NaOH (0.1N). Peroxide value, expressed as milliequivalents of active oxygen per kilogram of oil (meq O_2/kg oil), was

determined by iodine titration of a solution of oil in iso-octane/acetic acid (3:2) [19]. Iodine value (a measure of the relative degree of unsaturation in oil) was calculated from the relative percentage of fatty acids using the formula [20]:

$$IV = (0.998 \times C16:1) + (0.899 \times C18:1) + (1.811 \times C18:2) + (2.736 \times C18:3) + (0.818 \times C20:1)$$

The saponification value was determined according to the ISO 3657 standard method, and the iodine value (a measure of the relative degree of unsaturation in Argan oil) was determined using the ISO 3961, 2018 method [20]. The extinction coefficient was determined according to the ISO 3656, 2011 standard method [21]

The density and the refractive index were measured at 20 °C ± 0.2 °C [22]. The saponified value (a measure of the content of ester linkages) was determined following the official analytical method ISO 3657, 2020 [23]. In a 250 mL round-bottomed flask, 1g of fatty substance is placed with 3 mL of solvent (ethanol-ether (v: v)) and 25 mL of alcoholic potassium hydroxide with a concentration of 0.5 N. the flask is then placed in a water bath for 60 minutes. After cooling the flask to room temperature, 2 to 3 drops of phenolphthalein are added. The excess of potassium hydroxide was determined with hydrochloric acid at a concentration of 0.5 N up to the endpoint (discoloration of the solution). Under the same conditions, a blank test was carried out.

For the identification of p-anisidine value, the absorbance of the oil samples was determined at 350 nm with a spectrophotometer (CARY 100 Varian UV). The value of para-anisidine was determined following the official analytical method ISO 6885, 2006 [24].

2.4. Fatty acid determination.

The composition of fatty acids was determined following the official analytical method ISO 12966-2, 2011 [25]. Prior to analysis, fatty acids (FAs) were converted to fatty acid methyl esters by shaking a solution of 60 mg oil and 3 mL of hexane with 0.3 mL of 2N methanolic potassium hydroxide for 25 min. The fatty acid composition was measured as their corresponding methyl esters by gas chromatography on a CPWax 52CB column (60 m x 0.25 mm i.d., 0.25 µm film thickness), Helium (with a flow rate of 1 mL/mn) was used as a carrier gas. Oven, injector, and detector temperatures were sand at 185, 200, and 230 °C, respectively. The injection volume of the samples was 1 µL in a split mode (split ratio 1:50). Results were expressed as the relative percentage of the area of each individual fatty acid peak [26].

2.5. Sterols determination.

Sterols composition was determined following the official analytical method ISO 12228-1, 2014 [27]. After trimethylsilylation of the crude sterol fraction, we used an Agilent 6890 GC-System equipped with a VF-1 column (30 m x 320 µm i.d., 0.25 µm film thickness) and applied Helium (flow rate 1.6 mL/min) as a carrier gas. The program of column temperature was prepared as follows: from 200 to 280 °C (5 °C/min). Injector and detector temperature were 300 ºC. The injection volume was 1 µL in a split mode (split ratio 1:50). Peaks were determined either by standard compounds (β-sitosterol, campesterol, stigmasterol) by a mixture of sterols isolated from sunflower oil (Δ-7-stigmasterol, Δ-7-campesterol, and Δ-7-avenasterol) or by a mixture of sterols isolated from rapeseed oil (brassicasterol). The results

were expressed as the relative percentage of the area of each individual sterol peak and individual sterol [19].

2.6. Statistical analysis.

All determinations and measurements were performed in triplicate. Values were represented as means ± SD (standard deviations). Differences were considered significant at 5% as a probability level. In addition, principal component analysis (PCA) was carried out on fatty acids mean values of studied SCGO and various plant oils (soybean, sunflower, rapeseed, and coconut oils) from published literature. All statistical analyses were carried out using version XVII of STATGRAPHICS package (Statpoint Technologies, Inc., Virginia, USA).

3. Results and Discussion

3.1. Oil yield.

The economic value of vegetable oil is dependent on yield oil [28]. Oil extracted from SCGs has a significant potential for cosmetics, food soap production, and other industrial uses [15]. Moreover, it may be utilized as a substrate for producing poly 3-hydroxybutyrate), which is a whole biodegradable alternative to synthetic polymers [29]. Furthermore, other studies reported that SCGO could be a good source of essential fatty acids needed in the human body [30].

The oil yield of SCG extracted by the Soxhlet method is presented in Table 1. The SCGO yield was 18.5 ± 1.5 g/100g. However, such yield is much lower than that reported for sunflower oil (44 g/100g), coconut oil (38.1 g/100g), and rapeseed oil (28.27 g/100g), but similar to that of soybean seed oil (19g/100g) (Table 1). This result is similar to the SCGO yield reported in other studies [31, 32].

3.2. SCGO physicochemical indices.

Parameters used systematically to measure physicochemical properties of oils are the density, the refractive index, the iodine value, the saponification value, the free fatty acids (acidity), and the peroxide value. The density and the refraction index depend on the temperature and the fatty acid composition of the oil [33]. The refraction index rises as the oil's unsaturation level rises [34]. Table 1 summarizes the ranges of the main physicochemical parameters of SCGO and as well as other vegetable oils reported in the literature. Density and refractive index were similar to that of other vegetable oils (Table 1). The iodine value is a measure of the total number of double bonds present in fats and oils. SCGO showed a low iodine value (92.275 g (I_2)/100 g), likely due to its important content of saturated fatty acids (SFA) (Table 2). This value is lower than that of rapeseed oil (94-120 g (I_2)/100 g), sunflower oil (130 g (I_2)/100 g), and soybean seed oil (134.5 g (I_2)/100 g) but higher than that of coconut oil (6.3-10.6 g (I_2)/100 g) [35]. In addition, a high iodine value indicates that SCGO contains a greater number of double bonds than low iodine-value oil and usually has reduced oxidative stability [36]. These results suggest that SCGOs have a very good oxidative stability, and its significant content of SFA is likely responsible for this higher stability.

The saponification value is a measure of the average chain length of fatty acids. In fact, the shorter fatty acid has a higher saponification value. The saponification value of SCGO

analyzed is 187.5 ± 1.5 mg KOH/g, and it is lower than that of soybean, sunflower, and coconut oil (Table 1).

It is noteworthy that a high saponification value indicates that oil has a high triglyceride content and hence is very appreciated in cosmetology [22]. The oxidative state of oil can be examined from peroxide value which indicates the presence of primary oxidation products [37]. The peroxide value of SCG oil was determined as 5.5 Meq O_2/kg. Another parameter index used to evaluate the secondary oxidation products is the p-anisidine value [38]

This parameter has registered a value of 9.5, suggesting that over-oxidation was currently occurring at the time of extraction. On top of that, this value is close to that reported in the literature [39] and higher than that found in all studied oils; sunflower oil, rapeseed oil, coconut oil and, soybean oil. After extraction, free-fatty acids (FFA) quantity was found to be 7.5% (Table 1). Furthermore, high FFA contents have already been announced in other scientific researches [40]. This important value is generally an indication for strong enzymatic hydrolysis of SCGO during handling, harvesting, and oil processing [41].

A high level of free fatty acids, peroxide value, and p-anisidine value in SCGO indicate that this oil ought to be refined before its use [17]. Thus, the oil obtained using solvent extraction is frequently refined before consumption to remove impurities such as free fatty acids and oxidation products [42].

3.3. Fatty acids.

Fatty acids are the main important abundant components present in vegetable oils [19], [22]. They are closely related to stability, nutritional, and cosmetic quality [50, 51] . Table 2 shows the fatty acid profile of SGCO. Our results showed that SCGO contained three types of fatty acids. Indeed, the polyunsaturated fatty *acids* were the most abundant, accounting for 44.98 ± 2.5g/100g followed by saturated fatty acids (42.29 ± 2.3g/100g), and monounsaturated fatty acids (12.68 ± 1.15g/100g). The main unsaturated fatty acid in SCGO was linoleic acid (43.20 ± 2.19%). This value is similar to that reported by [39, 52]. Linoleic acid is considered the main essential fatty acid, also often referred as omega-6 fatty acid [53]. The linoleic acid content of SCGO is higher than that observed in rapeseed oil (16.22 ± 0.41%) and coconut oil (1.91 ± 0.04%) and similar to that of soybean oil but is much lower than that of sunflower oil (73.24 ± 0.35%). Linolenic acid is only a minor polyunsaturated in SGCO with a concentration less than 1 g/100 g. This value is lower than that reported by other authors [39, 52].

Unsaturated fatty acids are the major component of SCGO (54.59%). Both oleic and linoleic acids constitute 53.3% of total SCGO fatty acids.

The main saturated fatty acids of the SCGO in ascending order were arachidic acid (3.03 ± 0.99), stearic acid (7.25 ± 0.78 mg/100g), and palmitic acid (31.78 ± 2.02mg/100g). It is noteworthy that palmitic acid is an important element for cosmetic uses [54]. This result is similar to those reported in other works [39, 52]. However, the SFA composition observed in SCGO was higher than that of other vegetable oils (Table 2).

Additionally, palmitic acid is an important component of the saturated fatty acids fraction in SGGO.

Table 1. Mean values of physical and chemical parameters of SCGO and other vegetable oils found in the literature. Results are presented as means ± SD.

	SCGO		**Sunflower oil**	**Rapeseed oil**	**Coconut oil**	**Soybean oil**
	Our study	[15, 32, 39, 40]	[22, 43]	[35, 44–46]	[35, 47, 48]	[22, 49]
Oil yield [g/ 100g]	18.55±1.5	10–20	44	28.27	19	19
Density [20 °C]	0.909±0.01	0.917	0.919	0.91–0.92	0.908–0.921	0.91
Refraction index [20 °C]	1.469±0.01	--	1.463	1.464	1.4543	1.46
Saponification value [mg KOH/g]	187.5 ±1.5	167.28	191	168–181	248–265	190.5
Iodine value [g (I_2)/100 g]	92.22	79	130	94–120	6.3–10.6	134.5
Peroxide value [meq O_2/*kg*]	5.21±0.1	3.77	0.7	3.62	2.2	0.06
Para anisidine value	9.5±0.5	8	1.08	0.14	0.16 – 0.19	4.75
FFA [g/100g]	7.5±0.5	6.14	0.05	0.08	0.13–0.27	0.06

Table 2. Mean values of fatty acids of SCGO and other vegetable oils. Results are presented as means ± SD.

Fatty acids	**SCG oil**			**Sunflower oil**	**Rapeseed oil**	**Coconut oil**	**Soybean oil**
Source	Our study	[39]	[52]	[58]	[59]	[58]	[60]
C14: 0	0.09±0.02	0.05	0.1	0.87 ± 0.00	--	11.39	--
C16: 0	31.78±2.02	32.45	32.80	5.29 ± 0.02	2.69±0.01	7.76 ± 0.02	14.04 ± 0.62
C16: 1	0.08±0.00	0.03	--	--	--	--	--
C18: 0	7.25±0.78	8.35	7.10	4.75 ± 0.05	1.51±0.01	1.7 ± 0.02	4.07 ± 0.29
C18: 1	12.68±1.15	9.00	10.30	11.37 ± 0.08	46.29±1.21	6.49 ± 0.02	23.27 ± 2.43
C18: 2	43.20±2.19	45.04	44.20	73.24 ± 0.35	16.22±0.41	1.91 ± 0.04	52.18 ± 2.64
C18: 3	0.80±0.17	4.12	1.50	--	5.15±0.62	--	5.63 ± 3.48
C20: 0	3.03±0.09	--	2.60	--	0.54±0.08	--	--
C20: 1	0.39±0.01	--	--	--	--	--	--
SFA	42.29±2.3	41.0	42.5	11.61	7.54	91.2	18.26
USFA	57.84±3.3	59	56	88.39	92.46	8.8	81.14

This fatty acid is the principal constituent of refined palm oil [55] and, the biological and nutritional properties of palmitic acid have been extensively studied [55-57]. Indeed, similar to palm oil, the saturated fatty acid of SGGO is mostly palmitic acid, this last considered to be important and valuable by the industry, notably for cosmetics uses. With such an approach, the commercial success of palm oil has been global. Therefore, this SGGO is perfectly suitable for large-scale use and could follow the path of cosmetic palm oil.

3.4. Principal component analysis of fatty acids.

Principal component *analysis* was carried to visualize similarities among various plant oils, including SCGO and those from literature based on fatty acids as the major fraction. As summarized in Figure 1, the points plotted on the surface were delimited by the first two components, which accounted for more than 80% of the total variability. The second component (PC2, 35.74%) seemed to separate between plant oils. On its negative side, sunflower oil and SCGO interacted with higher values of C16: 0, C18: 0, C20: 0, and C18:2. In contrast, coconut oil was associated mainly with the best score of C14: 0, while both rapeseed and soybean oils were linked to the greatest content of C18:1 and C18:3. PCA was successfully used as a discriminative approach as well as the reduction and explanation of data variability [38, 61–64].

The two segments are representing C16: 0 and C20: 0 (Figure 1) are pointing almost in the same direction indicating thus a positive association between these fatty acids. However, C18: 2 and C14: 0 are pointing in opposite directions, so they are negatively correlated. Nevertheless, C18: 2 and C18: 3 are unrelated (they are orthogonal).

The dendrogram of the hierarchical classification shows that the five studied oils are divided into two main classes which are found on the factorial plane of axes 1 and 2 of the PCA (Figure 2 and 3). The first class has two subclasses, one containing rapeseed oil and the other containing sunflower oil and soybean oil. The second class also has two underclasses, one containing coconut oil and the other one containing SCGO. Therefore, the results of the hierarchical classification categorized our samples into four groups according to their fatty acids content. The first one represents rapeseed oil, the second encompasses both soybean and sunflower oil, the third is related to coconut oil, and the fourth is linked to SCGO.

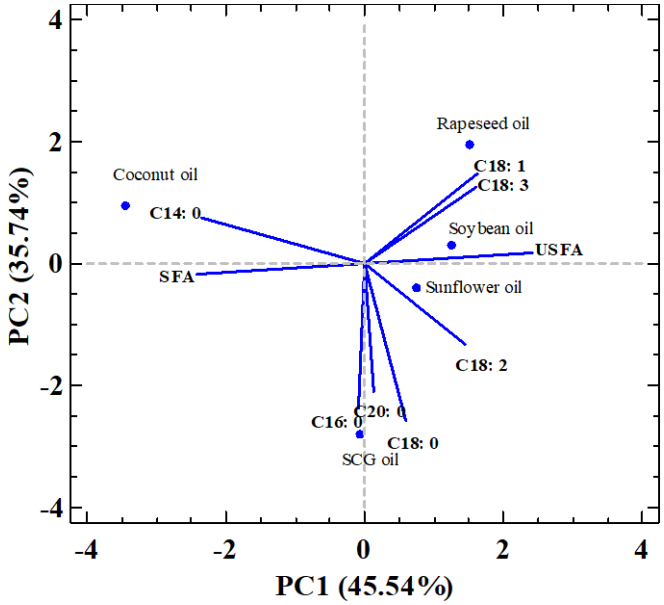

Figure 1. Principal component projections on PC1 and PC2 for the studied spent coffee grounds along with other vegetable oils (coconut, soybean, rapeseed, and sunflower oils). Points plotted are related to vegetable oils, and blue segments represent various fatty acids.

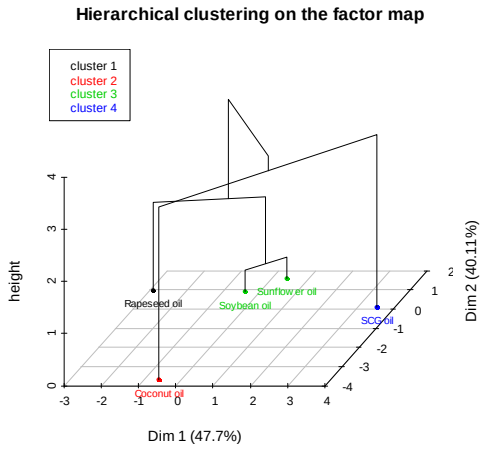

Figure 2. 3D Hierarchical classification.

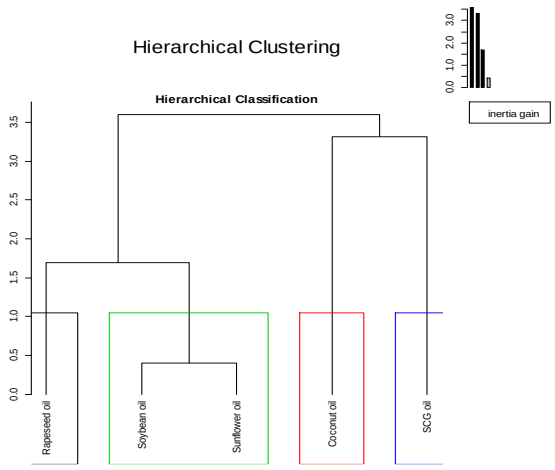

Figure 3. 2D Hierarchical classification.

3.5. Phytosterols.

Phytosterols are a minor component of oils [65]. Analysis of these compounds is a useful parameter for detecting alterations or verifying authenticity, as they can be considered an oil impression [56]. Furthermore, these important molecules are endowed with potent biological properties [66–68].

The total content of phytosterols in the unsaponifiable fraction of SCGO is about 1138 ± 0.01 mg/100g. Generally, SCGO phytosterols composition was found to be satisfactory and within the range of published values by [69]. This value is higher than that reported for all other oils (sunflower, soybean, rapeseed, and coconut oil) (Table 3)

A higher level of phytosterols in SGG oil than other vegetable oils could be explained by dehydration of some β-sitosterol during refining, especially in the bleaching step [70].

Δ-5-Avenasterol, Campesterol, *Stigmasterol* and β -Sitosterol were found to be the major sterols of SGG oil. The β-Sitosterol is significantly the sterol present in high amount. It represents 44.70 ± 0.01% of the total sterol fraction, which is similar to coconut oil (32.6-50.7 %). Nevertheless, β-sitosterol detected in SCGO is lower than that observed in sunflower oil (58-64%). This sterol is also found in coconut oil but *with* contents lower than that found in SCGO (Table 3).

Table 3. Sterols profile of SCGO and other vegetable oils (g/100g). Results are presented as means ± SD.

Vegetable oil	**SCG oil**		**Sunflower oil**	**Rapeseed oil**	**Soybean oil**	**Coconut oil**
Sterols/Reference	Our study	[69]	[22]	[35]	[22]	[35]
Cholesterol	0.41±0.01	--	< 0.4	< 0.05	< 1	< 0.05
Campesterol	15.87±0.01	18.36	8-11	24.7-38.6	19-23	6.0-11.2
Stigmasterol	21.57±0.01	22.48	7-10	0.2-1.0	17-19	11.4-15.6
β-Sitosterol	44.70±0.01	48.00	58-64	45.1-57.9	47-59	32.6-50.7
Δ-5-Avenasterol	12.16±0.01	9.07	2-7	2.5-6.6	2-4	20.0-40.7
Δ-7-Stigmasterol	0.25±0.01	0.62	9-14	< 0.05	1-3	< 0.05
Δ-7-Avenasterol	0.51±0.01	0.80	4-6	< 0.05	1-2	< 0.05
Total mg/100g	1382±0.01	1900	325-515	450-1130	250-418	40-120

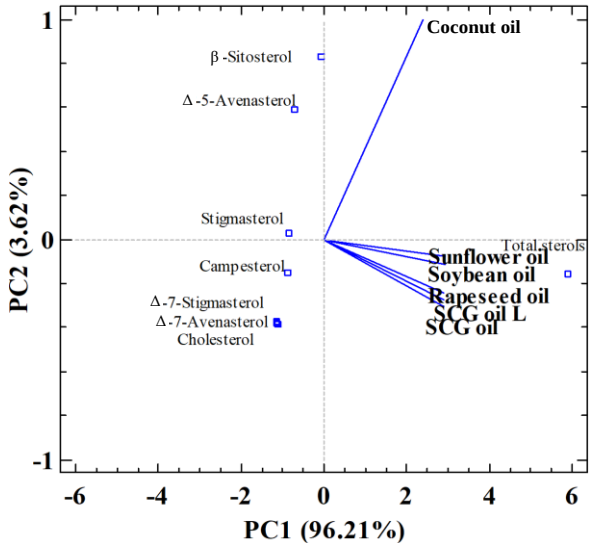

Figure 4. Principal component projections on PC1 and PC2 for sterols in spent coffee grounds oil along with other plant oils (coconut, soybean, rapeseed, and sunflower oils). Points plotted are related to vegetable oils, and blue segments represent various sterols. SCG oil L = spent coffee grounds oil reported in the literature.

β-sitosterol has beneficial and *physiological* effects on human health. It reduces cholesterol levels [41], inhibits breast cancer development [71], enhances the efficacy of

vitamin D [72], and has anti-carcinogenic, antipyretic, and anti-inflammatory effects. Generally, all phytosterols composition in SCGO analyzed were found to be satisfactory and within the range of published values [69].

The second major phytosterol detected in SCGO is stigmasterol with 21.57±0.01%. This amount is higher than that found in sunflower oil, rapeseed oil, and coconut oil. Finally, Δ-7- stigmasterol, Δ-7-avenasterol, and cholesterol are detected but with a minor component (less than 0.5%).

3.6. Principal component analysis of sterols.

Principal component analysis for sterols (Figure 4) shows that most data variability can be explained by the first two components (PC 1 + PC 2 = 99.84%). Both SCG oil investigated in our study and that from the literature [69] presented high similarity with vegetable oils and were rich in total sterols compared to coconut oil.

4. Conclusions

Recycling is reprocessing and recovery of waste materials for another use in new products. The present study demonstrated that SCG could offer potential and cheap alternative raw material for vegetable oil production, oil yield was encouraging since it reached (18.55 g/100g). Likewise, fatty acids composition showed an interesting fatty acid profile (linoleic and palmitic) and are a very good source of phytosterols (β-sitosterol, stigmasterol, and campesterol). Its high amounts of phytosterols, linoleic acid, and palmitic acid could open important applications for SCGO, and it can be a new source of palmitic acid. Such compositional attributes found in this oil are even more important than some plant oils, which could open important applications of SCGO, such as in the food industry, pharmaceutical applications, and cosmetics uses.

Funding

This research received no external funding.

Acknowledgments

We thank Ibn Zohr University for their interest in this work and technical support.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Madiga Bala, D.; Padigapati Venkata, N. S.; Yannam, P. Global and regional trading blocs of coffee and tea: Outlook, trading signals, and policies. *World Food Policy* **2020**, *6*, 119-156, https://doi.org/10.1002/wfp2.12018.
2. ICO, International Coffee Organization - Trade Statistics Tables **2020**. Available online: https://www.ico.org/trade_statistics.asp?section=Statistics (accessed on 05/20/2021).
3. Murthy, P. S.; Madhava Naidu, M. Sustainable management of coffee industry by-products and value addition - A review. *Resources, Conservation and Recycling* **2012**, *66*, 45-58, https://doi.org/10.1016/j.resconrec.2012.06.005.

4. Preethu D. C.; Srinivasamurthy, C. A.; Vasanthi, B. G. Maturity Indices as an Index to Evaluate the Quality of Compost of Coffee Waste Blended with Other Organic Wastes. *Proceeding of international conference on sustainable solid waste management*, Chennai, India, Citeseer **2007,** 270-275.
5. Atabani, A. E.; Al-Rubaye, O. K. Valorization of spent coffee grounds for biodiesel production: blending with higher alcohols, FT-IR, TGA, DSC, and NMR characterizations. *Biomass Conversion and Biorefinery* **2020,** 1-20, https://doi.org/10.1007/s13399-020-00866-z.
6. Fernandes, A. S.; Mello, F. V. C.; Thode Filho, S.; Carpes, R. M.; Honório, J. G.; Marques, M. R. C.; Felzenszwalb, I.; Ferraz, E. R. A. Impacts of discarded coffee waste on human and environmental health. *Ecotoxicology and Environmental Safety* **2017,** *141*, 30-36, https://doi.org/10.1016/j.ecoenv.2017.03.011.
7. McNutt J.; He, Q. Spent coffee grounds: A review on current utilization. *Journal of Industrial and Engineering Chemistry* **2019**, *71*, 78-88, https://doi.org/10.1016/j.jiec.2018.11.054.
8. Zhang, S.; Yang, J.; Wang, S.; Vasantha Rupasinghe, H.P.; He, Q. Experimental exploration of processes for deriving multiple products from spent coffee grounds. *Food and Bioproducts Processing* **2021**, 128, 21-29, https://doi.org/10.1016/j.fbp.2021.04.012.
9. Alsanad, M.A.; Sassine, Y. N.; El Sebaaly, Z.; Abou Fayssal, S. Spent coffee grounds influence on *Pleurotus ostreatus* production, composition, fatty acid profile, and lignocellulose biodegradation capacity. *CyTA-Journal of Food* **2021,** *19*, 11-20, https://doi.org/10.1080/19476337.2020.1845243.
10. Castaldo, L.; Lombardi, S.; Gaspari, A.; Rubino, M.; Izzo, L.; Narváez, A.; Ritieni, A.; Grosso, M. In Vitro Bioaccessibility and Antioxidant Activity of Polyphenolic Compounds from Spent Coffee Grounds-Enriched Cookies. *Foods* **2021**, *10*, 1837, https://doi.org/10.3390/foods10081837.
11. López-Barrera, D. M.; Vázquez-Sánchez, K.; Loarca-Piña, G. F.; Campos-Vega, R. Spent coffee grounds, an innovative source of colonic fermentable compounds, inhibit inflammatory mediators in vitro. *Food Chemistry* **2016,** *212*, 282-290, https://doi.org/10.1016/j.foodchem.2016.05.175.
12. Serrano-Gómez, J.; López-González, H.; H.; Olguín, M. T.; Bulbulian, S. Carbonaceous material obtained from exhausted coffee by an aqueous solution combustion process and used for cobalt (II) and cadmium (II) sorption. *Journal of Environmental Management* **2015,** *156*, 121-127, https://doi.org/10.1016/j.jenvman.2015.03.013.
13. Battista, F.; Barampouti, E. M.; Mai, S.; Bolzonella, D.; Malamis, D.; Moustakas, K.; Loizidou, M. Added-value molecules recovery and biofuels production from spent coffee grounds. *Renewable and Sustainable Energy Reviews* **2020**, *131*, 110007, https://doi.org/10.1016/j.rser.2020.110007.
14. Park, J.; Kim, B.; Lee, J.W. In-situ transesterification of wand spent coffee grounds for sustainable biodiesel production. *Bioresource Technology* **2016**, *221*, 55-60, https://doi.org/10.1016/j.biortech.2016.09.001.
15. Muangrat, R.; Pongsirikul, I. Recovery of spent coffee grounds oil using supercritical CO_2: Extraction optimisation and physicochemical properties of oil. *CyTA - Journal of Food* **2019**, *17*, 334-346, https://doi.org/10.1080/19476337.2019.1580771.
16. Salazar-López, N. J.; López-Rodríguez, C. V.; Hernández-Montoya, D. A.; Campos-Vega, R. Health Benefits of Spent Coffee Grounds. *Food Wastes and By-products: Nutraceutical and Health Potential* **2020**, John Wiley & Sons Ltd, 327-351, https://doi.org/10.1002/9781119534167.ch11.
17. Gharby, S.; Ravi, H. K.; Guillaume, D.; Vian, M. A.; Chemat, F.; and Z.; Charrouf, 2-methyloxolane as alternative solvent for lipid extraction and its effect on the cactus (Opuntia ficus-indica L.) seed oil fractions. *OCL* **2020**, *27*, 27, https://doi.org/10.1051/ocl/2020021.
18. ISO 660:**2009**, Animal and vegetable fats and oils - Determination of acid value and acidity.
19. Gharby, S.; Hajib, A.; Ibourki, M.; Sakar, E.H.; Nounah, I.; EL Moudden, H.; Elibrahimi, M.; Harhar, H. Induced changes in olive oil subjected to various chemical refining steps: A comparative study of quality indices, fatty acids, bioactive minor components, and oxidation stability kinetic parameters, *Chemical Data Collections* **2021**, *33*, 100702, https://doi.org/10.1016/j.cdc.2021.100702.
20. ISO 3961:**2018**, Animal and vegetable fats and oils - Determination of iodine value.
21. ISO 3656:**2011**, Animal and vegetable fats and oils - Determination of ultraviolet absorbance expressed as specific UV extinction.
22. Zine, S.; Gharby, S.; El Hadek, M. Physicochemical Characterization of Opuntia ficus-indica Seed Oil from Morocco, *Biosciences Biotechnology Research Asia* **2013**, *10*, http://dx.doi.org/10.13005/bbra/1099.
23. ISO 3657:**2020**, Animal and vegetable fats and oils - Determination of saponification value.
24. ISO 6885:**2006**, Animal and vegetable fats and oils - Determination of anisidine value.

25. ISO 12966-2:**2011**, Animal and vegetable fats and oils - Gas chromatography of fatty acid methyl esters - Part 2: Preparation of methyl esters of fatty acids.
26. Harhar, H.; Gharby, S.; El Idrissi, Y.; Pioch, D.; Matthäus, B.; Charrouf, Z.; Tabyaoui, M. Effect of maturity stage on the chemical composition of argan fruit pulp. *OCL* **2019**, *26*, 15, https://doi.org/10.1051/ocl/2019012.
27. ISO 12228-1:**2014**, Determination of individual and total sterols content - Gas chromatographic method – Part 1: Animal and vegetable fats and oils.
28. Taoufik, F.; Zine, S.; El Hadek, M.; Idrissi Hassani, L. M.; Gharby, S.; Harhar, H.; Matthäus, B. Oil content and main constituents of cactus seed oils Opuntia Ficus Indica of different origin in Morocco. *MNM* **2015,** *8*, 85-92, http://dx.doi.org/10.3233/MNM-150036.
29. Obruca, S.; Petrik, S.; Benesova, P.; Svoboda, Z.; Eremka, L.; Marova, I. Utilization of oil extracted from spent coffee grounds for sustainable production of polyhydroxyalkanoates. *Appl Microbiol Biotechnol.* **2014,** *98*, 5883-5890, https://doi.org/10.1007/s00253-014-5653-3.
30. Koushki, M.; Nahidi, M.; Cheraghali, F. Physico-chemical properties, fatty acid profile and nutrition in palm oil, *Archives of Advances in Biosciences* **2015,** *6*, 117-134, https://doi.org/10.22037/jps.v6i3.9772.
31. Cruz, R.; Cardoso, M.M.; Fernandes, L.; Oliveira, M.; Mendes, E.; Baptista, P.; Morais, S.; Casal, S. Espresso Coffee Residues: A Valuable Source of Unextracted Compounds. *J. Agric. Food Chem.* **2012,** *60*, 7777-7784, https://doi.org/10.1021/jf3018854.
32. Najdanovic-Visak, V.; Lee, F. Y. L.; Tavares, M.T.; Armstrong, A. Kinetics of extraction and in situ transesterification of oils from spent coffee grounds, *Journal of Environmental Chemical Engineering* **2017,** *5*, 2611-2616, https://doi.org/10.1016/j.jece.2017.04.041.
33. Kanda, L. R. S.; Yamamoto, C. I.; Lopes, A. R.; Voll, F. A. P.; Corazza, M. L.; Wypych, F. Density, refractive index and viscosity as content monitoring tool of acylglycerols and fatty acid methyl esters in the transesterification of soybean oil. *Anal. Methods* **2016,** *8*, 5619-5627, https://doi.org/10.1039/C6AY00663A.
34. Raiser, A. L.; Torres, M. D. P. R.; Ribeiro, E. B.; Valladão, D. M. D. S. Characterization of munguba oil obtained by ultrasound. *Ciência Rural* **2020,** *50*, e20191028, https://doi.org/10.1590/0103-8478cr20191028.
35. Standard for named vegetable oils CXS 210-**1999**.
36. Sanders, T. H. Ground nut oil, in *Encyclopedia of Food Sciences and Nutrition (Second Edition)*, Editor-in-chief Caballero, B., Academic Press **2003**, 2967-2974.
37. Gharby, S.; Harhar, H.; Guillaume, D.; Roudani, A.; Boulbaroud, S.; Ibrahimi, M.; Ahmad, M.; Sultana, S.; Ben Hadda, T.; Chafchaouni-Moussaoui, I.; Charrouf, Z. Chemical investigation of *Nigella sativa* L. seed oil produced in Morocco. *Journal of the Saudi Society of Agricultural Sciences* **2015,** *14*, 172-177, https://doi.org/10.1016/j.jssas.2013.12.001.
38. Gharby, S.; Guillaume, D.; Nounah, I.; Harhar, H.; Hajib, A.; Matthäus, B.; Charrouf, Z. Shelf life of Moroccan prickly pear (Opuntia ficus-indica) and argan (Argania spinosa) oils: a comparative study. *Grasas y Aceites* **2021,** *72*, e397, https://doi.org/10.3989/gya.1147192.
39. Acevedo, F.; Rubilar, M.; Scheuermann, E.; Cancino, B.; Uquiche, E.; Garcés, M.; Inostroza, K.; Shene, C. Spent coffee grounds as a renewable source of bioactive compounds. *Journal of Biobased Materials and Bioenergy* **2013,** *7*, 420-428, https://doi.org/10.1166/jbmb.2013.1369.
40. Phimsen, S.; Kiatkittipong, W.; Yamada, H.; Tagawa, T.; Kiatkittipong, K.; Laosiripojana, N.; Assabumrungrat, S. Oil extracted from spent coffee grounds for bio-hydrotreated diesel production. *Energy Conversion and Management* **2016,** *126*, 1028-1036, https://doi.org/10.1016/j.enconman.2016.08.085.
41. Gharby, S.; Harhar, H.; Bouzoubaa, Z.; Asdadi, A.; El Yadini, A.; Charrouf, Z. Chemical characterization and oxidative stability of seeds and oil of sesame grown in Morocco. *Journal of the Saudi Society of Agricultural Sciences* **2017,** *16*, 105-111, https://doi.org/10.1016/j.jssas.2015.03.004.
42. Aluyor, E.O.; Aluyor, P.; Ozigagu, C.E. Effect of refining on the quality and composition of groundnut oil. *African Journal of Food Science* **2009,** *3*, 201-205.
43. Tehseen, M.; Hina, S.; Nisa, A.; Zahra, N. Study of antioxidant activity of spinach extract in stabilization of sunflower oil under accelerated storage conditions. *Pakistan Journal of Agricultural Research* **2021,** *34*, 414-423, http://dx.doi.org/10.17582/journal.pjar/2021/34.2.414.423.
44. Aniołowska, M.; Zahran, H.; Kita, A. The effect of pan frying on thermooxidative stability of refined rapeseed oil and professional blend. *J Food Sci Technol.* **2016,** *53*, 712-720, https://doi.org/10.1007/s13197-015-2020-z.

45. Bubalo, M.C.; Jokić, S.; Lepojević, Ž.; Vidović, S.; Marić, B.; Radojčić Redovniković, I. Optimization of the Supercritical CO_2 Extraction of Oil from Rapeseed Using Response Surface Methodology. *Food Technology and Biotechnology* **2012,** *50,* 208-215.
46. Zheng, C.; Yang, M.; Zhou, Q.; Liu, C. S.; Huang, F.H. Changes in the content of canolol and total phenolics, oxidative stability of rapeseed oil during accelerated storage: Changes in the canolol content of rapeseed oil. *Eur. J. Lipid Sci. Technol.* **2014,** *116,* 1675-1684, https://doi.org/10.1002/ejlt.201300229.
47. Patil U.; Benjakul, S. Coconut Milk and Coconut Oil: Their Manufacture Associated with Protein Functionality, *Journal of Food Science* **2018,** *83,* 2019-2027, https://doi.org/10.1111/1750-3841.14223.
48. Marina, A. M.; Che Man, Y. B.; Nazimah, S. A. H.; Amin, I. Chemical Properties of Virgin Coconut Oil, J *Am Oil Chem Soc*. **2009,** *86,* 301-307, https://doi.org/10.1007/s11746-009-1351-1.
49. Li, Y.; Ma, W. J.; Qi, B. K.; Rokayya, S.; Li, D.; Wang, J.; Feng, H.X.; Sui, X.N.; Jiang, L. Z. Blending of Soybean Oil with Selected Vegetable Oils: Impact on Oxidative Stability and Radical Scavenging Activity. *Asian Pacific Journal of Cancer Prevention* **2014,** *15*, 2583-2589, https://doi.org/10.7314/APJCP.2014.15.6.2583.
50. Gharby, S.; Harhar, H.; Mamouni, R.; Matthäus, B.; Ait Addi, E. H.; Charrouf, Z. Chemical Characterization and Kinetic parameter determination under Rancimat test conditions of four monovarietal virgin olive oils grown in Morocco. *OCL* **2016,** *23,* A401, https://doi.org/10.1051/ocl/2016014.
51. Hajib, A.; Harhar, H.; Gharby, S.; Nounah, I.; Matthäus, B.; Guillaume, D.; Charrouf, Z. Is geographic origin a good marker for cumin seed oil (Cuminum cyminum L.) ? Rivista Italiana delle Sostanze Grasse, **2018**, *95*, 155-159.
52. Cruz, R.; Morais, S.; Mendes, E.; Pereira, J. A.; Baptista, P.; Casal, S. Improvement of vegetables elemental quality by espresso coffee residues. *Food Chemistry* **2014,** *148,* 294-299, https://doi.org/10.1016/j.foodchem.2013.10.059.
53. Marmouzi, I.; Ali, K.; Harhar, H.; Gharby, S.; Sayah, K.; El Madani, N.; Cherrah, Y.; Faouzi, M. E. A. Functional composition, antibacterial and antioxidative properties of oil and phenolics from Moroccan *Pennisetum glaucum* seeds. *Journal of the Saudi Society of Agricultural Sciences* **2018,** *17*, 229-234, https://doi.org/10.1016/j.jssas.2016.04.007.
54. Khan, N. R.; Gawas, S. D.; Rathod, V. K. Enzyme-catalysed production of n-butyl palmitate using ultrasound-assisted esterification of palmitic acid in a solvent-free system, *Bioprocess Biosyst Eng.* **2018,** *41*, 1621-1634, https://doi.org/10.1007/s00449-018-1988-y.
55. Suryani, S.; Sariani, S.; Earnestly, F.; Marganof, M.; Rahmawati, R.; Sevindrajuta, S.; Indra Mahlia, T. M.; Fudholi, A. A comparative study of virgin coconut oil, coconut oil and palm oil in terms of their active ingredients. *Processes* **2020,** *8,* 402, https://doi.org/10.3390/pr8040402.
56. Korbecki J.; Bajdak-Rusinek, K. The effect of palmitic acid on inflammatory response in macrophages: an overview of molecular mechanisms. *Inflamm. Res.* **2019,** *68*, 915-932, https://doi.org/10.1007/s00011-019-01273-5.
57. Carta, G.; Murru, E.; Banni, S.; Manca, C. Palmitic Acid: Physiological Role, Metabolism and Nutritional Implications. *Front Physiol.* **2017,** *8,* 902, https://doi.org/10.3389/fphys.2017.00902.
58. Devi A.; Khatkar, B. S. Effects of fatty acids composition and microstructure properties of fats and oils on textural properties of dough and cookie quality. *J Food Sci Technol.* **2018,** *55,* 321-330, https://doi.org/10.1007/s13197-017-2942-8.
59. Li, J.; Liu, J.; Sun, X.; Liu, Y. The mathematical prediction model for the oxidative stability of vegetable oils by the main fatty acids composition and thermogravimetric analysis. *LWT* **2018,** *96,* 51-57, https://doi.org/10.1016/j.lwt.2018.05.003.
60. Chowdhury, K.; Banu, L.; Khan, S.; Latif, A. Studies on the Fatty Acid Composition of Edible Oil. *Bangladesh J. Sci. Ind. Res*. **2007,** *42*, 311-316, https://doi.org/10.3329/bjsir.v42i3.669.
61 Shin, E. C.; Craft, B. D.; Pegg, R. B.; Phillips, R. D.; Eitenmiller, R. R. Chemometric approach to fatty acid profiles in Runner-type peanut cultivars by principal component analysis (PCA). *Food Chemistry* **2010,** *119*, 1262-1270, https://doi.org/10.1016/j.foodchem.2009.07.058.
62. Sakar, E. H.; El Yamani, M.; Rharrabti, Y. Geometrical Traits in Almond Fruit as Affected by Genotypic and Environmental Variations in Northern Morocco. *Erwerbs-Obstbau* **2019,** *61,* 103-112, https://doi.org/10.1007/s10341-018-0401-y.

63. Sakar, E.H.; El Yamani, M.; Boussakouran, A.; Ainane, A.; Ainane, T.; Gharby, S.; Rharrabti, Y. Variability of oil content and its physicochemical traits from the main almond [*Prunus dulcis* Mill. DA Webb] cultivars grown under contrasting environments in north-eastern Morocco. *Biocatalysis and Agricultural Biotechnology* **2021**, *32*, 101952, https://doi.org/10.1016/j.bcab.2021.101952.
64. Zeroual, A.; Sakar, E. H.; Eloutassi, N.; Mahjoubi, F.; Chaouch, M.; Chaqroune, A. Phytochemical Profiling of Essential Oils Isolated Using Hydrodistillation and Microwave Methods and Characterization of Some Nutrients in *Origanum compactum* Benth from Central-Northern Morocco. *Biointerface Research in Applied Chemistry* **2021,** *11*, 9358-9371, https://doi.org/10.33263/BRIAC112.93589371.
65. Charrouf, Z.; Guillaume, D. The argan oil project: going from utopia to reality in 20 years. *OCL* **2018,** *25*, D209, https://doi.org/10.1051/ocl/2018006.
66. Awad, A. B.; Fink, C. S. Phytosterols as anticancer dietary components: evidence and mechanism of action. *The Journal of nutrition* **2000,** *130*, 2127-2130, https://doi.org/10.1093/jn/130.9.2127.
67. Nickavar, B.; Mojab, F.; Javidnia, K.; Amoli, M. A. R. Chemical composition of the fixed and volatile oils of *Nigella sativa* L. from Iran. *Zeitschrift für Naturforschung C* **2003,** *58*, 629-631, https://doi.org/10.1515/znc-2003-9-1004.
68. Trautwein, E. A.; Duchateau, G. S. M. J. E.; Lin, Y.; Mel'nikov, S. M.; Molhuizen, H. O. F.; Ntanios, F. Y. Proposed mechanisms of cholesterol-lowering action of plant sterols. *European Journal of Lipid Science and Technology* **2003**, *105*, 171-185, https://doi.org/10.1002/ejlt.200390033.
69. Campos-Vega, R.; Loarca-Piña, G.; Vergara-Castañeda, H.A.; Oomah, B.D. Spent coffee grounds: A review on current research and future prospects. *Trends in Food Science & Technology* **2015,** *45*, 24-36, https://doi.org/10.1016/j.tifs.2015.04.012.
70. Gharby, S.; Guillaume, D.; Elibrahimi, M.; Charrouf, Z. Physico-Chemical Properties and Sensory Analysis of Deodorized Argan Oil. *ACS Food Sci. Technol.* **2021,** *1*, 275-281, https://doi.org/10.1021/acsfoodscitech.0c00107.
71. Xu, H.; Li, Y.; Han, B.; Li, Z.; Wang, B.; Jiang, P.; Zhang, J.; Ma, W.; Zhou, D.; Li, X.; Ye, X. Anti-Breast-Cancer Activity Exerted by β-Sitosterol-d-glucoside from sweet potato via upregulation of microRNA-10a and via the pi3k–akt signaling pathway. *Journal of agricultural and food chemistry* **2018,** *66*, 9704-9718, https://doi.org/10.1021/acs.jafc.8b03305.
72. Alappat, L.; Valerio, M.; Awad, A. B. Effect of vitamin D and β-sitosterol on immune function of macrophages. *International Immunopharmacology* **2010,** *10*, 1390-1396, https://doi.org/10.1016/j.intimp.2010.08.003.
73. Klippel, K. F.; Hiltl, D. M.; Schipp, B. A multicentric, placebo-controlled, double-blind clinical trial of β-sitosterol (phytosterol) for the treatment of benign prostatic hyperplasia, *British Journal of Urology* **1997,** *80*, 427-432, https://doi.org/10.1046/j.1464-410X.1997.t01-1-00362.x.
74. Kritchevsky D.; Chen, S. C. Phytosterols-health benefits and potential concerns: a review. *Nutrition Research* **2005,** *25*, 413-428, https://doi.org/10.1016/j.nutres.2005.02.003.