Received: 13 October 2023 | Accepted: 16 February 2024

DOI: 10.1002/fpf2.12007

REVIEW

WILEY

Valorization of spent coffee ground and coffee silverskin as a source of nutrients and bioactive compounds

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Funding information
European Union—NextGenerationEU under the Italian Ministry of University and Research National Innovation Ecosystem grant, Grant/Award Number: ECS00000041 - VITALITY - CUP J13C22000430001

Abstract

In a world where a greener approach is increasingly necessary, it is mandatory to reduce waste production and reuse residues from the company's supply chain. *Spent Coffee grounds* (SCG) and *Coffee Silverskin* (CS) are two important by-products of coffee production, being sources of important dietary fibers and bioactive compounds, which is why some authors have proposed their reuse in the nutraceutical, food and cosmetic industries. However, their nutrients chemical content has been insufficiently studied. Therefore, the aim of the present review was to investigate the main components, such as carbohydrates, dietary fibers, lipids, and bioactive compounds of SCG and CS. In addition, the most common extraction methods to obtain these aforementioned nutrients were evaluated.

KEYWORDS
bioactive compounds, carbohydrates, coffee silverskin, dietary fibers, lipids, spent coffee ground, valorization, waste

1 | INTRODUCTION

Coffee is one of the most consumed beverages in the world, and moreover, coffee beans are considered an important agricultural product of international trade (Mussatto et al., 2011; Mustafa et al., 2022). According to the latest statistics from the International Coffee Organization (ICO), global coffee consumption will reach 171.3 million bags in 2022–2023, with Europe accounting for about one-third of global consumption (Tea and Coffee, 2023; ICO, 2023). Nowadays, coffee beverages are consumed and prepared by a lot of various hot and cold brewing methods, depending on the geographic, cultural, and social context, as well as on personal preference (Santanatoglia, 2023a, 2023b, 2023c, 2023d, 2024). Therefore, in order to satisfy the enormous product demand, coffee companies must process a huge amount of raw materials, releasing a significant amount of solid and liquid residues, since about 90% of the weight of coffee berries is disposed of as agricultural waste and byproducts during the manufacturing process (Pavlić et al., 2023). For this reason, several authors have proposed the possibility of recycling various coffee residues to reuse them in different industries while reducing the amount that ends up in landfills (Iriondo-De Hond et al., 2016; Nzekoue, Khamitova, et al., 2020a, 2020b; Severini et al., 2020; Malara et al., 2018; Dos Santos Polidoro et al., 2018). Both the processing of the coffee cherries in the producing countries, as well as the processing of the green beans into coffee are sources of unavoidable waste. Processing of coffee cherries results in the

generation of husks, peel, and pulp, which together represent 45% of the cherry (Angeloni et al., 2021; Campos-Vega et al., 2015). Among this waste, *Spent Coffee Grounds* (SCG) and *Coffee Silverskin* (CS) are two important byproducts generated during coffee processing (Figure 1); the first one is the residue that comes largely from the soluble coffee company and the brewing process, is the solid residue

FIGURE 1 Coffee production chain.

that remains after ground roasted beans are brewed to make coffee, representing approximately 45% of the cherry. It was estimated that for each ton of green coffee beans, 650 kg of SCG are generated, and for each kg of soluble coffee, 2 kg of wet SCG are generated (Murthy & Naidu, 2012), with coffee shop chains and soluble coffee producers being responsible for half of this amount. The CS also known as coffee chaff, is the thin skin covering green coffee beans, which is released during the roasting process; this component represents approximately 4% of the weight of the bean (Ballesteros et al., 2014; Zengin et al., 2020). Some authors have proposed the use of both by-products for different purposes involving different fields; for example, some researchers have proposed to use them as adsorbents for the removal of potentially toxic metals (Malara et al., 2018), as raw material to produce fuel ethanol (Mussatto et al., 2012). While some studies have addressed the possibility of obtaining bioactive compounds from these two byproducts and using them in the food, nutraceutical, pharmaceutical and cosmetic industries (Angeloni, Scortichini, et al., 2020; Bertolino et al., 2019; Bessada et al., 2018; Iriondo-De Hond et al., 2016; Nzekoue, Khamitova, et al., 2020a, 2020b; Zengin et al., 2020). Despite these possible applications, SCG and CS are still underutilized as valuable materials for industrial processes. Nowadays, it is necessary to focus on the recycling of SCG and CS and to profitably utilize these unused materials and reduce their impact on the environment. Although some properties of SCG and CS have been recently described in the literature, to our knowledge, there is no study showing a detailed descriptions of the possible valorization and the most common extraction methods for SCG and CS, in specific terms of main nutrients, such as carbohydrates, dietary fibers, lipids, and bioactive compounds. This information is of great importance to identify the possible applications of these residues. Some summary values of these nutrients expressed as g/100 g dry material have been reported in Table 1. It is hoped that the results of this review can contribute to increase knowledge on SCG and CS and to facilitate the development of new applications that exploit these valuable by-products.

2 | CARBOHYDRATES AND FIBERS

The coffee bean is a rich source of polysaccharides, estimated around 50% of the green bean's dry weight. The saccharide fraction of coffee is mainly composed of galactomannans, arabinogalactans, and cellulose (Campos-Vega et al., 2015). After roasting, the resulting hydrophilic polysaccharides are crucial for preserving organoleptic characteristics of the coffee cup. In fact, preparing the coffee using hot water at high pressures, about the 13.9% (w/w) of carbohydrates from the roasted and ground coffee is extracted representing the water-soluble fraction, while cellulosic compounds are not extracted (Ishwarya & Nisha, 2022). Galactomannans are primary polysaccharide compounds in coffee extract. Galactomannans can go through several chemical events during roasting, including depolymerization, debranching, Maillard reactions, caramelization, isomerization, oxidation, decarboxylation, and the production of

TABLE 1 Summary table reporting the content of carbohydrates, fibers, lipids and other components inside SCG and CS expressed as percentage.

Chemical components	SCG	CS	References
Carbohydrates	45%–46%	40%–50%	Simões et al., 2013; Pourfarzad et al., 2013
Cellulose	10%–20%	25%–35%	Mussatto et al., 2011
Glucose	10%–20%	20%–58%	Mussatto et al., 2011
Hemicellulose	39%–40%	16%–17%	Mussatto et al., 2011; Simões et al., 2013; Ballesteros et al., 2014; Bijla et al., 2022; Alghooneh et al., 2017
Arabinose	1%–7%	8%–9%	Mussatto et al., 2011; Simões et al., 2013; Ballesteros et al., 2014; Bijla et al., 2022
Galactomannans[a]	50%	-	Simões et al., 2013
Mannose	21%–46%	4.37%	Mussatto et al., 2011; Simões et al., 2013; Ballesteros et al., 2014; Bijla et al., 2022
Galactose	15%–32%	9.29%	Mussatto et al., 2011; Simões et al., 2013; Ballesteros et al., 2014; Bijla et al., 2022
Xylose	-	18.81%	Mussatto et al., 2011
Lignin	23%–24%	28%–30%	Borrelli et al., 2004; Ateş & Elmacı, 2019; Gottstein et al., 2021
Insoluble	17%–20%	20%–21%	Ballesteros et al., 2014
Soluble	6%–7%	7%–10%	Ballesteros et al., 2014
Total dietary fiber	43%–58%	28%	Vázquez-Sánchez et al., 2018; Ateş & Elmacı, 2019; Murthy & Naidu, 2012
Insoluble	35%	20%–45%	Murthy & Naidu, 2012; Ballesteros et al., 2014
Soluble	8%	8%–10%	Murthy & Naidu, 2012; Ballesteros et al., 2014
Lipids	18%–20%	2%–3%	Couto et al., 2009; Efthymiopoulos et al., 2018; Quijote et al., 2021; Angeloni, Scortichini, et al., 2020
Saturated fatty acids (SFA)			
Palmitic (C16:0)	32%	34%–35%	Campos-Vega et al., 2015; Mota et al., 2020; Quijote et al., 2021; Toschi et al., 2014; Angeloni, Scortichini, et al., 2020
Stearic (C18:0)	7%–10%	6%–9%	Campos-Vega et al., 2015; Mota et al., 2020; Quijote et al., 2021; Toschi et al., 2014; Angeloni, Scortichini, et al., 2020
Arachidic (C20:0)	2%–5%	-	Campos-Vega et al., 2015; Mota et al., 2020; Quijote et al., 2021
Behenic acid (C22:0)	-	8%–10%	Toschi et al., 2014; Angeloni, Scortichini, et al., 2020
Monounsaturated fatty acids (MUFA)			
Oleic (C18:1)	10%–12%	5%–8%	Campos-Vega et al., 2015; Mota et al., 2020; Quijote et al., 2021; Toschi et al., 2014; Angeloni, Scortichini, et al., 2020
Polyunsaturated fatty acids (PUFA)			
Linoleic (C18:2)	36%–42%	27%–36%	Campos-Vega et al., 2015; Mota et al., 2020; Quijote et al., 2021; Toschi et al., 2014; Angeloni, Scortichini, et al., 2020
Sterols	10%–20%	0.2%–0.4%	Cholakov et al., 2013; Toschi et al., 2014
Sitosterol	48%–52%	71%	Campos-Vega et al., 2015; Toschi et al., 2014
Stigmasterol	21%–22%	11%	Campos-Vega et al., 2015; Toschi et al., 2014
Campesterol	16%–18%	14%	Campos-Vega et al., 2015; Toschi et al., 2014
5-avenasterol	-	4%	Toschi et al., 2014
Diterpenes	0.1%–0.5%	0.1%–0.5%	Ballesteros et al., 2014
Cafestol	0.8%	-	Acevedo et al., 2013
Kahweol	0.4%	-	Acevedo et al., 2013
Ashes	1.30%	5.36%	Ballesteros et al., 2014
Protein	17%	18%	Ballesteros et al., 2014

(Continues)

TABLE 1 (Continued)

Chemical components	SCG	CS	References
Nitrogen	2%–3%	3%	Ballesteros et al., 2014
Carbon/nitrogen ratio	17%	14%–15%	Ballesteros et al., 2014

[a]Referred to total carbohydrates.

melanoidins. During this process, the relaxation and swelling of the cell-wall and the polysaccharide depolymerization, improves the solubility of mannans and of arabinogalactan too (Nunes & Coimbra, 2010). Coffee arabinogalactans are extremely susceptible to degradation even after a light roast, in contrast to cellulose, which is the polysaccharide that is less impacted by roasting. Galactomannans and arabinogalactans can increase the viscosity giving the characteristic "body", smooth sensation, and high foam stability to the extracted beverage (Nunes & Coimbra, 2010). At the same time, they can have an adverse impact on the procedures required to produce instant soluble coffee (Ishwarya & Nisha, 2021; Wei et al., 2012).

In coffee roasting and extraction by-products, SCG and CS respectively, the carbohydrate fraction is constituted by insoluble polysaccharides such as cellulose and hemicellulose. From a nutritional point of view, these molecules are considered dietary fibers as they cannot be digested in gastro-intestinal apparatus, but they can have beneficial impacts in improving the formation and correct expulsion of feces and decreasing the absorption of nutrients, benefits mainly related to pathological situations of obesity or diabetes. Among dietary fibers in coffee by-products also lignin must be considered even if it does not present a polysaccharidic structure. Total dietary fibers content in SGC is around 58% while the crude fibers of untreated CS were quantified as around 28% (Ateş & Elmacı, 2019; Vázquez-Sánchez et al., 2018). Differences in carbohydrate and dietary fibers composition of SCG and CS can occur due to geographical origin, genotype, harvest season, as well as various production factors such as roasting temperature and soil (Iriondo-De Hond, 2019). Several studies have reported the possibility of use the coffee by-product as source of fibers for further functional food formulations (Ateş & Elmacı, 2019; Pourfarzad, Mahdavian-Mehr & Sedaghat, 2013; Rios et al., 2020; Vázquez-Sánchez et al., 2018).

2.1 | Carbohydrate and fiber composition of SCG

The majority (more than the 80%) of the polysaccharides present in roasted coffee powder is not extracted during the coffee cup preparation and persists in the SCG as water-insoluble material. The resulting SCG matrix is, therefore, rich in polymerized sugar, mainly forming galactomannans (mannose and galactose), cellulose (glucose) and hemicellulose (arabinose, mannose, and galactose) structures. These correspond to almost half (45.3%, w/w) of the SCG material (Simões et al., 2013). Galactomannans resulted in the major polysaccharide in Arabica SCG (approximately 50% of the total carbohydrates) constituted of mannose (46%) and galactose (27%) (Simões et al., 2013). The main constituent of SCG galactomannans is mannose. It is frequently exploited as a nutritional supplement in food and pharmaceutical sectors to produce drug forms. Mannose can speed up the healing of wounds, reduce the obesity deriving from a high-fat diet and it may help prevent diabetes too (Cavanagh et al., 2023). The other component of SCG galactomannans is the galactose. Monosaccharides analysis of SCG reported contents in the range of 21%–37% of mannose, 15%–32% of galactose, 10%–20% of glucose, and 1%–7% of arabinose (Ballesteros et al., 2014; Bijla et al., 2022; Mussatto et al., 2011; Simões et al., 2013). The differences in chemical composition found in scientific literature on SCG carbohydrate fraction characterization probably are results of different varieties of beans, different roasting processes, and a different extraction method that can lead to a significant difference in unextracted material.

Polysaccharides constituted of glucose (20%), and arabinose (7%) were found in SCG as products of cellulose, hemicellulose and arabinogalactans degradation. In coffee, after the extraction, only the water-insoluble fraction of the total glucose remains in SCG as part of cellulose and hemicellulose or other insoluble polysaccharidic structures (Simões et al., 2013).

Regarding fiber content, SCG contains 43% total fiber (8% and 35% soluble and insoluble, respectively) (Murthy & Naidu, 2012). Furthermore, during the Maillard reaction, melanoidins are formed from the combination of sugars and amino acids. Melanoidins are brown, high molecular weight heterogeneous polymers produced in food matrices with low water activity during non-enzymatic high temperatures processes (Moreira et al., 2012). In coffee beverages, melanoidins were estimated to account for up to around 29% (w/w) of the dry matter positioning coffee as one of the main sources of melanoidins in the human diet. also because it is widely and daily consumed. The intake of these molecules is associated with some health benefits, such as antimicrobial activity, modulation of colon bacterial population, anti-inflammatory, antihypertensive, and anti-glycative action (Delgado-Andrade et al., 2005; Reichardt et al., 2009; Rufián-Henares & de la Cueva, 2009; Verzelloni et al., 2011; Vitaglione et al., 2010). SCG contains substantial amounts of lignin 23.90% (w/w), a non-polysaccharidic dietary fiber. The most important lignin constituents in SCG are chlorogenic, caffeic, and coumaric acids, and these substances have a significant impact on health

because of its antioxidant characteristics that are covered in Section 4 of this review.

2.2 | Carbohydrate and fiber composition of CS

In coffee production, previous steps are necessary to obtain roasted coffee beans; during these processes several by-products are generated. In scientific literature, some beneficial effects of CS have already been described (Borrelli et al., 2004; Murthy & Naidu, 2012; Ballesteros et al., 2014; Iriondo-De Hond, 2019). CS was valued especially for its high content of dietary fibers, which is in the range of 60%–80%, polysaccharides components (60%–70%) and total sugar content (1.6%–12%) (Pourfarzad et al., 2013). The first attempts to define the dietary fiber composition of CS point to a potential use of CS as a functional component for the dietary fiber enrichment of foods. However, current knowledge does not provide an in-depth description of CS fiber architectures, including specifics on lignin and polysaccharide interunit connections (Gottstein et al., 2021). Cellulosic structures are more abundant in CS than in SCG, resulting thus in a higher concentration of glucose. Regarding hemicellulose, the main difference between SCG and CS is represented by the presence of xylose, that is the main sugar in CS hemicellulose, but it is not present in the SCG (Ballesteros et al., 2014). The high glucose content is given by the cell wall polysaccharide cellulose and the xylose is related to the dicotyledonous type of coffee plants (Hall et al., 2022; Oosterveld et al., 2003). Moreover, Borrelli et al. (2002) studied CS from several Italian coffee plants and underlined the high amount of soluble dietary fiber (about 14% of the total fiber) and the very high antioxidant activity. In terms of monosaccharides composition, Mussatto et al. (2011) reported that CS contains 58.76% glucose, 18.81% xylose, 9.29% galactose, 8.75% arabinose, and 4.37% mannose. Lignin is also a significant fraction of CS fibers, reported with percentages around 28%–30% (Ateş & Elmacı, 2019; Borrelli et al., 2004; Gottstein et al., 2021). Nowadays, the food application of CS seems to be attractive due to its composition in terms of fibers, antioxidants and proteins (Iriondo-De Hond, 2019). Several authors have suggested the usage of CS as fiber-enriching ingredient to be incorporated in several food formulations, according also with other properties as the antioxidant activity, protein and ash content (Ballesteros et al., 2014; Bresciani et al., 2014; Jiménez-Zamora et al., 2015; Murthy & Naidu, 2012). For example, a recent study by Bertolino et al. (2019) proposed the addition of CS to yogurt formulations to increase the dietary fibers, phenolic compounds, and caffeine values.

2.3 | Carbohydrates and fibers extraction methods from SCG and CS

2.3.1 | Determination of polysaccharides and sugars

Soluble fraction of polysaccharides in coffee is extracted during coffee cup preparation, so in SCG there would be only the insoluble sugars, implicating specific efforts to extract and characterize its polysaccharidic fraction. In fact, the main problem for the SCG and CS utilization as a source of polysaccharides is the low yield of extraction. Several research works have described the polysaccharides extraction from SCG using different methods such as the solid–liquid extraction through organic solvents (Simões et al., 2010), dilute acidic and alkaline hydrolysis (Mussatto et al., 2011), and microwave-assisted extraction (Passos & Coimbra, 2013). Also, some pretreatment strategies were proposed to improve the extractability of galactomannans without degradation. For example, Ballesteros et al. (2015) tested an alkali pretreatment with NaOH 4 M at 25°C reaching the 6.05% of extraction yield. The extractability of SCG galactomannans was improved without degradation in Simões et al. (2013) investigation. In their study, SCG undergoes to a roasting pre-treatment followed by extractions with hot water and with alkaline solutions at different temperatures. The extracted galactomannans were then submitted to an enzymatic hydrolysis and the obtained oligosaccharides were separated through size exclusion chromatography. Finally, electrospray tandem mass spectrometry (ESI-MS/MS) technique was used to characterize their structures. They assessed that a preventive roasting SCG at 160°C can implement the extraction of galactomannans without any improvement in arabinogalactans yield. According to the investigated literature, the main problem for the SCG and CS utilization as a source of polysaccharides is the low yield of extraction. For example, Zhang et al. (2021) investigated the extraction of polysaccharides from SCG using water with ultrasound-assisted extraction (UAE) maximizing the yields through a central composite design. Under optimal conditions, polysaccharide yields were 1.1%. The mainly used method is the hydrolyzation of SCG and CS polysaccharides using acid, alkaline or enzymatic procedures (Gottstein et al., 2021; Nolasco et al., 2022). Typically, reducing sugars, as galactose and mannose, are the main constituents of hydrolyzed SCG and CS. Reducing sugars can act as reducing agents because they have a free aldehyde or ketone group (Mussatto et al., 2011). Total carbohydrates in CS were extracted using UAE with acetonitrile/water solution as solvent and determined through HPLC-UV system by Nolasco et al. (2022). Their results, including the entire nutritional profile monitoring, reported carbohydrates as the main constituent of CS with 42% of value. Furthermore, the enzyme-based hydrolyzation of SCG and CS carbohydrates into reducing sugars was proposed as a practical and green technique for sugars extraction into food-applicable ingredients (Bhaturiwala & Modi, 2020). In addition, the transformation of insoluble fractions into soluble molecules, thereby reducing the particle size of samples, is another plus of enzyme hydrolysis as it can help in SCG and CS polysaccharide characterization (Cavanagh et al., 2023; Franca & Oliveira, 2022). An alkali treatment-mannanase digestion combined technique was applied by Wongsiridetchai et al. (2021) to characterize mannooligosaccharides obtained from SCG and evaluate their prebiotic activity. Results showed that the mainly present sugars were mannose, mannobiose, mannotriose, and mannopentose, and that the obtained extract had prebiotic properties. An oligosaccharides extraction from SCG procedure was

proposed by Bhaturiwala and Modi (2020) involving a series of sequential treatments. The best yield of polysaccharides (33.25%) was obtained using the central composite design, applying a roasting step at 160°C for 10 min with a liquid/solid ratio of 15 mL/g and a β-mannanase enzymatic hydrolysis of the treated materials. Further characterization through FTIR (Fourier-transform infrared spectroscopy) highlighted the β-glycosidic bonds breaking, verifying the efficiency of the extraction processes. Moreover, the microwave-assisted extraction (MAE) using superheated water to obtain polysaccharides and oligosaccharides was presented as a possible method to increase the extraction yield. Passos & Coimbra (2013) applied a two-steps MAE extraction to obtain both galactomannans and arabinogalactans reaching the extraction of the 74% of the total galactose and the 66% of the total mannose.

2.3.2 | Determination of total, soluble, and insoluble fiber

The extraction of dietary fiber from plant by-products can be related to the recovery of other constituents like antioxidants or proteins (Murthy & Naidu, 2012). In dietary fiber extractions, the gravimetric enzymatic method optimized by Prosky et al. (1988) is still the main applied technique. The method involves two main steps: enzymatic digestion, common to all fiber types, and filtration, that is different for each kind of investigating fiber (Borrelli et al., 2004). In enzymatic digestion step, the main used enzymes are mannanase, cellulase, and glucanase as they were proved to be effective to produce hydrolysates suitable for food purposes (Franca & Oliveira, 2022). After this step, a specific filtration is applied to determine the total, soluble, and insoluble fibers content respectively. Total dietary fiber fraction is usually obtained through ethanol solution filtration with a Celite filter. For this analysis, an assay kit is available called Megazyme Integrated Total Dietary Fiber Assay kit, and it is accepted as AOAC method consistent with the CODEX Alimentarius definition of dietary fiber (Cunniff & Washington, 1997). This involves an enzymatic digestion with amylase, protease, and amyloglucosidase, to cut off protein and starch, followed by precipitation with ethanol, filtration, and drying of the extract. The total dietary fibers are then calculated by difference of ash and protein on the final weight (Martuscelli et al., 2021). Insoluble dietary fibers fraction determination involves the same procedure but with an additional warm water washing of the digested solution and analysis of the residue. The soluble dietary fibers fraction is obtained from the liquid part of insoluble fibers filtration with consequent precipitation with ethanol.

Lignin contents of SCG and CS are mainly investigated as Klason lignin and/or as acetyl bromide soluble lignin (ABSL) (Schäfer et al., 2019). The determination of Klason lignin involves a two-step sulfuric acid hydrolysis and a gravimetric precipitation. In ABSL lignin extraction, polysaccharides are partially degraded using a cell wall degrading enzyme, called driselase, to improve the lignin extraction and minimize estimation mistakes due to the interference of polysaccharides degradation products. Then a derivatization step with acetyl bromide solution and a following alkalinization allow the spectrophotometric determination of lignin by measuring the absorbance at 280 nm (Gottstein et al., 2021). Both these lignin determining methods are non-specific, although they differ in the co-analyzed substances. In SCG and CS, Klason lignin concentrations may be significantly influenced by Maillard reaction products such melanoidins, which are not entirely broken by hydrolysis (Bunzel et al., 2011).

3 | LIPIDS

The storage of lipids in coffee beans, as for the other fruit, occurs during the ripening stage and most often coffee cherries are picking prior to their maturation, hence beans present low lipids content (Quijote et al., 2021). Another important aspect to be taken into consideration is the coffee beans species respectively Arabica 15%–18% (w/w) and Robusta 8%–12% (w/w) (Belitz et al., 2009). SCG and CS, which are both produced as waste products of the coffee manufacture, are good sources of lipids particularly 18%–30% (w/w) for industrial generation of SCG and 9%–17% (w/w) for those produced by espresso machine (Couto et al., 2009; Efthymiopoulos et al., 2018; Quijote et al., 2021), while CS accounts 2%–3% (w/w) (Angeloni, Scortichini, et al., 2020). The oil yield and the lipid composition of SCG and CS are strongly influenced by the different extraction methods. The lipid recovery from plant-based sources is commonly achieved either through mechanical or solvent extraction like the Soxhlet extraction or Folch method (Loyao et al., 2018). However, valuable and promising solutions such as supercritical CO_2 extraction and enzymatic hydrolysis have been investigated in order to address the selectivity, the safety and the efficiency of the extraction method (Couto et al., 2009; Mota et al., 2020; Quijote et al., 2021).

3.1 | Lipids composition of SCG

SCG is particularly rich in lipids since they are mainly retained in the coffee ground and not leaching to the brew. Several extraction methods have been implemented for the recovery of fat from SCG. An increased yield of SCG oil has been observed by the used solvents in the order ethanol with petroleum ether > hexane > heptane respectively 25.6% > 15.3% > 7–13% (Quijote et al., 2021). Moreover, the SCG oil yield is affected by the extraction conditions using in the Soxhlet apparatus as well as the duration of extraction, in this regard pentane, hexane, toluene, chloroform, acetone, isopropanol, and ethanol were used for 15–70 min and the highest oil recovery was reported with hexane 15.28% (w/w) while the lowest 8.6% (w/w) with chloroform (Al-Hamamre et al., 2012). In general, the most suitable solvents are nonpolar due to their free charges which makes the SCG penetration easier. However, the conventional solvent-liquid extraction with organic solvents presented several limitations including undesirable residues in the extract, thermal

degradation, and oxidation of the target compounds as well as legal restriction for what concern food and pharmaceutical applications. For this reason, supercritical CO_2 extraction has been widely investigated aimed at selective extraction thus guaranteeing the preservation of thermolabile compounds as well as allowing an environmentally friendly operation (Essien et al., 2020). To achieve this goal, supercritical CO_2 was carried out on SCG in the pressure range of 15–30 MPa and at temperature of 313–333 K for 50, 120, and 180 min. The oil yield increased with pressure at fixed temperature, this means that higher pressure caused an increased CO_2 density and thus its ability to solubilize the SCG lipids. Differently, the effect of temperature in the oil extraction showed different behaviors as a function of the applied pressure. Higher pressure (25 and 30 MPa) promoted an increased oil yield by increasing temperature, while at 20 MPa a decrease in oil extraction was reported with high temperature. This behavior was explained by the influence of increased temperature which determining a decrease of CO_2 density and thus its solvation capacity (Couto et al., 2009). Regarding the application of SCG for biodiesel production, interesting is the employment of dilute acid hydrolysis as pre-treatment to produce wet residues with 1.4 times more of the lipid content 23% (w/w) (Quijote et al., 2021). The extracted SCG oil in general presented mainly triacylglycerol (84.4%), diterpene (12.3%), alcohol esters (1.9%), sterols (1.9%), polar material (1.3%), and sterol esters (0.1%) (Campos-Vega et al., 2015). However, the lipid matter composition varied according to the different methods applied. The fatty acid methyl esters (FAMEs) composition of the SCG oil extracts available in the literature range from 3.7 to 4.9 g/100 g (Al-Hamamre et al., 2012; Loyao et al., 2018), except for the application of acid hydrolysis as pre-treatment in the extraction process where the yield reached around 19.5 g FAMEs/100 g (Quijote et al., 2021). In more details, the most representative were palmitic (C16:0) (32%), linoleic (C18:2) (36%–42%), oleic (C18:1) (10%–12%), stearic (C18:0) (7%–10%) and arachidic (C20:0) (2%–5%) acids, whereas lauric (C12:0) and myristic (C14:0) acids were scarcely detected depending on the method, parameters of extraction and origin (Campos-Vega et al., 2015; Mota et al., 2020; Quijote et al., 2021). Based on the FAMEs profile, oil can be classified into two main clusters; one with low palmitic and high linoleic (>40%) acids and the other account the contrary. Thus, resulting in different oil quality, prevention, and treatment of diseases as a function of the polyunsaturated/saturated fatty acid ratio. For what concern the unsaponifiable matter which account for 10%–20% of the SCG total lipid it is mainly characterized by sterols, terpenes, and tocopherols, compounds particularly appreciated in cosmetic and pharmaceutical industries as well as in biofuels storage (Cholakov et al., 2013).

Among the sterols sitosterol (48%–52%), stigmasterol (21%–22%) and campesterol (16%–18%) were the most abundant (Campos-Vega et al., 2015). Whereas diterpenes like cafestol and kahweol were detected in SCG oil extracted by supercritical CO_2 and their concentration varied according to the process conditions. In detail, an increase was observed at 80°C and 98 bar 0.8 and 0.4 mg/g for cafestol and kahweol respectively (Acevedo et al., 2013).

3.2 | Lipids composition of CS

According to the literature review, the lipid content of CS presented lower oil yield recovery (around 3%) compared to SCG, however their FAMEs composition was similar. The different CS extraction methods allowed us to obtain different lipid profiles. The highest amount of the extracted lipids was observed with the Folch's method using chloroform/methanol, while the UAE with hexane resulted in the lowest fat yield. However, the lipid composition of CS extract obtained by the UAE led to an enhanced release of free fatty acids (58%) and lower content of triacylglycerols (9%) compared to Soxhlet method (21% and 48% respectively) (Mota et al., 2020).

Hence, in CS oil C16:0 (34%–35%), C18:2 (27%–36%), C18:0 (6%–9%) and C18:1 (5%–8%) have been detected as well as for SCG oil, in addition behenic acid (C22:0) (8%–10%) has been found (Angeloni, Scortichini, et al., 2020; Mota et al., 2020; Toschi et al., 2014). In general, CS contained mainly saturated fatty acids (55%–64%) followed by polyunsaturated (28%–36%) and finally monounsaturated fatty acids (6%–8%) (Angeloni, Scortichini, et al., 2020; Mota et al., 2020). Since CS oil was mainly composed of triacylglycerols, interesting was the application of lipase which provided a selective hydrolysis promoting oil enriched in polyunsaturated fatty acids by the production of acylglycerols thanks to its mild reaction able to guarantee quality oil deterioration (Barbosa et al., 2019). In addition, CS oil is a valuable source of phytosterols that can help to reduce low density lipoprotein (LDL) cholesterol level (Santanatoglia et al., 2023f), however, as sensitive bioactive compounds, they are susceptible to oxidative degradation. Concerning the unsaponifiable matter, 0.2%–0.4% of CS was mainly composed by β-sitosterol (71%), campesterol (14%), stigmasterol (11%), and 5-avenasterol (4%), observing lower amount compared to those from green coffee. Thus, could be probably ascribed to the degradation process occurring during the roasting process, which leading to their reduction (Toschi et al., 2014).

4 | BIOACTIVE COMPOUNDS

Considerable attention has been paid to polyphenolic compounds in recent years due to the growing evidence suggesting that their consumption may provide a multitude of health benefits. They showed anti-inflammatory, antimicrobial, and antithrombotic properties but also antihyperglycemic, anti-carcinogenic, anti-obesity, and anti-diabetic effects. All these biological properties are closely linked to their antioxidant capacities because, thanks to their chemical structure, they can work through a ROS elimination mechanism (Perron & Brumaghim, 2009). The main important classes of phenolic

compounds are phenolic acids and flavonoids and among these, there are further subclasses (Quideau et al., 2011). Phenolics are predominantly present in nature as bound forms, often combined with sugars, organic acids, and esters. There are some instances where phenolics occur as aglycones (Parus, 2012). Flavonoids, instead, are present in plants in two distinct forms: free aglycones and bound forms as O- and C-glycosides—and are classified into different subclasses based on their chemical structure, such as flavanones, flavanols, flavones, isoflavones, flavonols, and anthocyanins (Falcone Ferreyra et al., 2012; Quideau et al., 2011). Coffee is a rich source of bioactive molecules as phenolic compounds, but the main ingredients are caffeine, chlorogenic acids (comprising different groups of compounds and related isomers such as caffeoylquinic acids, feruloylquinic acids, *p*-coumaroylquinic acids, among others), caffeic acid, coumaric acid, protocatechuic acid, ferulic acid, vanillic acid, gallic acid, vanillin, flavonoids (such as kaempferol, quercetin, catechin, epicatechin, and others), and these compounds are still present in coffee by-products (LIczbiński & Bukowska, 2022). The large quantities of these residues generated in industrial activities make this matrix a substrate with a high potential to serve as raw materials to obtain bioactive compounds. Generally, it was seen that phenolic compounds in spent coffee represent approximately 16–19 mg gallic acid equivalents (GAE)/g SCG, instead in CS are about 13 mg GAE/g (Ballesteros et al., 2014; Mussatto et al., 2011).

The processes that the two matrices undergo negatively influence the content of bioactive compounds, in fact, the roasting degree, the procedure and conditions used for coffee brewing (as the water temperature or coffee/water ratio and the time that coffee is in contact with water) could change the concentration of these compounds in spent coffee. Moreover, the high temperature applied to CS during roasting can lead to the degradation of these compounds (Murthy & Naidu, 2012). In the meantime, also the amount of alkaloid is high in the by-products derived from coffee, in fact the level of caffeine in SCG varies from 3.59 to 5.20 mg/g (Bravo et al., 2012) and in CS range from 8.3 to 13.7 mg/g (Napolitano et al., 2007). These levels are also high when compared to coffee (from 10.7 to 15.64 mg/g) a drink considered very rich in caffeine (Bravo et al., 2012). A total of 43 compounds are reported in Table 2 between alkaloids and polyphenols belonging to different classes, namely alkaloids (5 compounds), phenolic acids (25 compounds), flavonoids (11 compounds), xanthone (1 compound), and secoiridoids (1 compound).

4.1 | Alkaloids

Coffee beans contain two types of alkaloids, caffeine and trigonelline, as major components. Caffeine, 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione, belongs to methylxanthine-class and it is synthesized from xanthosine. It is one of the few alkaloids legal throughout the world despite it is a psychoactive and central nervous system stimulant in fact it is a widely used as psychotropic drug and seems to have a positive effect on long-term memory reducing the risk of neurodegenerative diseases such as Alzheimer's disease and Parkinson's disease (Boppana et al., 2022). Another important molecule belonging to the alkaloids family is trigonelline (Saud & Salamatullah, 2021), which will be discussed in detail in Section 4.1.2.

4.1.1 | Alkaloids composition of SCG

In SCG the content of caffeine varies from 400 to 54,440.2 μg/g of dry weight extract (dw). The lower levels of caffeine were detected in freeze-dried samples by López-Barrera et al. (2016) using a Soxhlet extraction with petroleum ether for 6 h. Instead, the highest level found in the literature was reported by Zengin et al. (2020), which compared 5 different extraction methods and selected EtOH/H2O 70% as the best one. Quinine, another alkaloid isolated for the first time from the bark of cinchona tree and known as a potent antimalarial agent (Jones et al., 2015), was found in SCG only by Zengin et al. (2020) and the higher concentration of 3.65 μg/g of dw was obtained using EtOH/H_2O 70% as extraction solvent. Within all the chosen articles, only caffeine and quinine were reported as the alkaloids present in SCG.

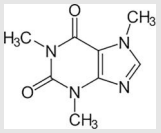
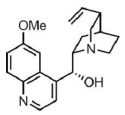
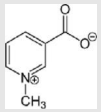
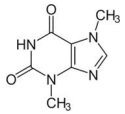
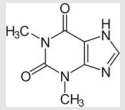
4.1.2 | Alkaloids composition of CS

Caffeine was found in CS with values like those reported in spent coffee. Considering all the articles found, caffeine concentrations range from 845.5 to 41,877.13 μg/g of silver skin extracts, obtained respectively by Angeloni, Scortichini, et al. (2020) and by Zengin et al. (2020). The polar solvent, EtOH/H_2O 70% combined with UAE, was the most efficient extraction method for caffeine at low pressure. Moreover, CS extract has other and different alkaloids than spent coffee extract such as trigonelline, theobromine, and theophylline. Trigonelline, which is present in CS extract in a concentration of 23.7 μg/g, is a pyridine alkaloid compound and a methylation product of vitamin B3 (niacin) (Zhou et al., 2012). This alkaloid has been shown to provide evidence of therapeutic effects, such as the enhancement of distinct neuron function and memory in mice with Alzheimer's disease. Additionally, it has been found to mitigate oxidative stress and inflammation in the brain, as well as improve blood glucose levels and lipid metabolism in animals with metabolic disorders (Bevilacqua et al., 2023). Theobromine and theophylline are present in CS extract in concentrations of 23,700 and 300 μg/g, respectively. These alkaloids were quantified by UHPLC-Q-Orbitrap (Castaldo et al., 2020). Furthermore, Nzekoue et al. (2020a, 2020b) and Zengin et al. (2020) found quinine in low concentration (from 0.61 to 0.93 μg/g) by the HPLC-MS/MS method.

4.2 | Polyphenols

Most abundant phenolic compounds are mainly found in coffee beans and consequently in coffee by-products are the chlorogenic acids (CGAs) (Esquivel & Jiménez, 2012). These CGAs are water-soluble

TABLE 2 Bioactive compounds identified in SCG and CS.

No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
	Alkaloids								
1	Caffeine	$C_8H_{10}N_4O_2$		400–54440.2	845.5–41877.13	HPLC-MS/MS; cLC-DAD; UHPLC-PDA; HPLC-DAD	HPLC-MS/MS; UHPLC-Q-Orbitrap; HPCE-DAD	Andrade et al., 2022; Angeloni, Nzekoue, et al., 2020; López-Barrera et al., 2016; Ramón-Gonçalves et al., 2019; Torres-Valenzuela et al., 2019; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Castaldo et al., 2020; Mesías et al., 2014; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
2	Quinine	$C_{20}H_{24}N_2O_2$		3.65	0.61–0.93	HPLC-MS/MS	HPLC-MS/MS	Zengin et al., 2020	Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
3	Trigonelline	$C_7H_7NO_2$		-	23,700	-	UHPLC-Q-Orbitrap	-	Castaldo et al., 2020
4	Theobromine	$C_7H_8N_4O_2$		-	300	-	UHPLC-Q-Orbitrap	-	Castaldo et al., 2020
5	Theophylline	$C_7H_8N_4O_2$		-	100	-	UHPLC-Q-Orbitrap	-	Castaldo et al., 2020

(Continues)

TABLE 2 (Continued)

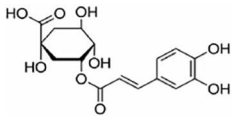
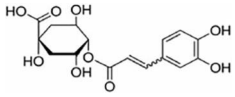
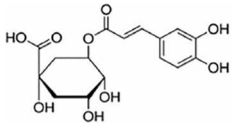
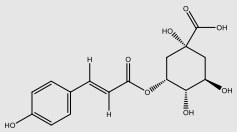
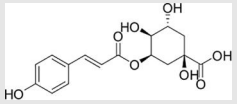
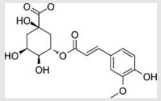
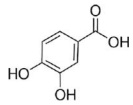
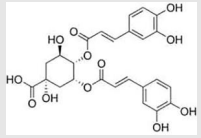
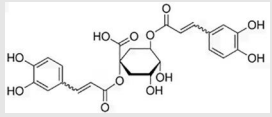
No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
	Polyphenols								
	Phenolic acids								
6	3-caffeoylquinic acid	$C_{16}H_{18}O_9$		3.9–5600	128.51–8202	HPLC-MS/MS; cLC-DAD; UHPLC-PDA; HPLC-DAD	HPLC-MS/MS; UHPLC-Q-Orbitrap; HPCE-DAD; UHPC-LITMS	Andrade et al., 2022; Angeloni, Nzekoue, et al., 2020; García-Roldán et al., 2023; Ho et al., 2020; López-Barrera et al., 2016; Ramón-Gonçalves et al., 2019; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Bresciani et al., 2014; Castaldo et al., 2020; Mesías et al., 2014; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
7	4-Caffeoylquinic acid			-	849–9099	-	UHPLC-Q-Orbitrap; HPCE-DAD; UHPC-LITMS	-	Bresciani et al., 2014; Castaldo et al., 2020; Mesías et al., 2014
8	5-caffeoylquinic acid			338.1 10,613.6	985.7–26346	HPLC-MS/MS; UHPLC-PDA; HPLC-DAD	HPLC-MS/MS; UHPLC-Q-Orbitrap; HPCE-DAD; UHPC-LITMS	Andrade et al., 2022; Angeloni, Nzekoue, et al., 2020; Ho et al., 2020; Torres-Valenzuela et al., 2019; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Bresciani et al., 2014; Castaldo et al., 2020; Mesías et al., 2014; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020

TABLE 2 (Continued)

No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
9	3-p-coumaroylquinic acid	$C_{16}H_{18}O_8$		-	24–4300	-	UHPLC-Q-Orbitrap; UHPC-LITMS	-	Bresciani et al., 2014; Castaldo et al., 2020
10	5-p-coumaroylquinic acid			-	57–2670	-	UHPLC-Q-Orbitrap; UHPC-LITMS	-	Bresciani et al., 2014; Castaldo et al., 2020
11	3-feruloylquinic acid	$C_{17}H_{20}O_9$		-	212–1510	-	UHPLC-Q-Orbitrap; UHPC-LITMS	-	Bresciani et al., 2014; Castaldo et al., 2020
12	3,4-dihydroxybenzoic acid	$C_7H_6O_4$		50	-	cLC-DAD	-	Ramón-Gonçalves et al., 2019	-
13	3,4-dicaffeoylquinic acid	$C_{25}H_{24}O_{12}$		70	50	UHPLC-PDA	UHPLC-Q-Orbitrap	Andrade et al., 2022	Castaldo et al., 2020
14	1,5-dicaffeoylquinic acid			23	-	UHPLC-PDA	-	Andrade et al., 2022	-

(Continues)

TABLE 2 (Continued)

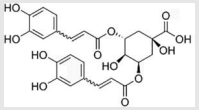
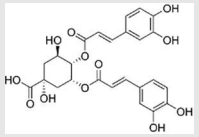
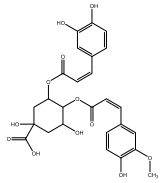
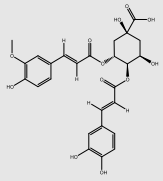
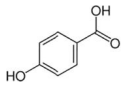
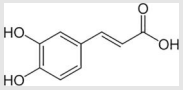
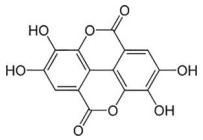
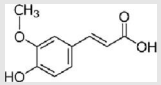
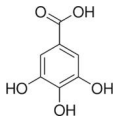
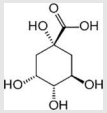
No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
15	3,5-dicaffeoylquinic acid			147.9–1194.62	41.48–1400	HPLC-MS/MS	UHPLC-Q-Orbitrap; HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Castaldo et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
16	4,5-dicaffeoylquinic acid			110	-	UHPLC-PDA	-	Andrade et al., 2022	-
17	3,4-caffeoyl-feruloylquinic acid	$C_{26}H_{26}O_{12}$		-	250	-	UHPLC-Q-Orbitrap	-	Castaldo et al., 2020
18	4,5-caffeoyl-feruloylquinic acid	$C_{26}H_{26}O_{12}$		-	70	-	UHPLC-Q-Orbitrap	-	Castaldo et al., 2020
19	*p*-hydroxybenzoic acid	$C_7H_6O_3$		27.9	-	HPLC-MS/MS	-	Ho et al., 2020	-

TABLE 2 (Continued)

No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
20	Caffeic acid	$C_9H_8O_4$		8.49–204.95	1.42–212.38	HPLC-MS/MS; UHPLC-PDA; HPLC-DAD	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Andrade et al., 2022; García-Roldán et al., 2023; Ho et al., 2020; López-Barrera et al., 2016; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
21	Ellagic acid	$C_{14}H_6O_8$		100	-	HPLC-DAD	-	López-Barrera et al., 2016	-
22	Ferulic acid	$C_{10}H_{10}O_4$		0.97–136.98	0.20–226.23	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Ho et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
23	Gallic acid	$C_7H_6O_5$		2.31–2500	0.31–44.21	HPLC-MS/MS; HPLC-PDA; HPLC-DAD	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; García-Roldán et al., 2023; Ho et al., 2020; López-Barrera et al., 2016; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
24	Quinic acid	$C_7H_{12}O_6$		238.3	-	HPLC-MS/MS	-	Ho et al., 2020	-

(Continues)

TABLE 2 (Continued)

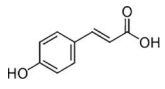
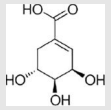
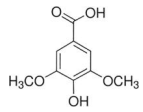
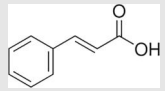
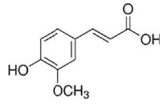
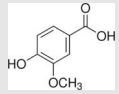
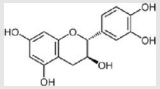
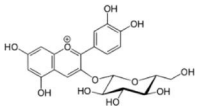
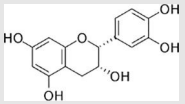
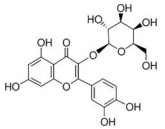
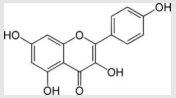
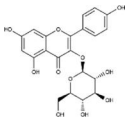
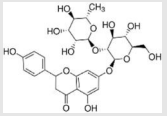
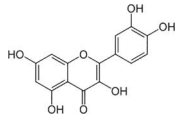
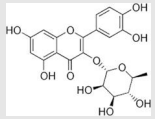
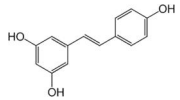
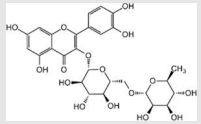
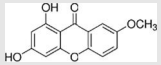
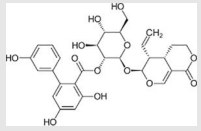
No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
25	*p*-Coumaric acid	$C_9H_8O_3$		0.25–500	0.22–18.18	HPLC-MS/MS; cLC-DAD; HPLC-DAD	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Ho et al., 2020; López-Barrera et al., 2016; Ramón-Gonçalves et al., 2019; Zengin et al., 2020	Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
26	Shikimic acid	$C_7H_{10}O_5$		5.60	0.520	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020	Angeloni, Nzekoue, et al., 2020
27	Syringic acid	$C_9H_{10}O_5$		0.21–94.20	0.35–85.64	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
28	*trans*-Cinnamic acid	$C_9H_8O_2$		0.149–4.95	0.08–4.87	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
29	*trans*-Ferulic acid	$C_{10}H_{10}O_4$		4–160	-	cLC-DAD; HPLC-DAD	-	López-Barrera et al., 2016; Ramón-Gonçalves et al., 2019	-
30	Vanillic acid	$C_8H_8O_4$		1.31–140.38	1.47–345.13	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Ho et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
	Flavonoids								

TABLE 2 (Continued)

No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
31	Catechin	$C_{15}H_{14}O_6$		1.34–600	-	HPLC-MS/MS	-	Angeloni, Nzekoue, et al., 2020; Ho et al., 2020; López-Barrera et al., 2016; Zengin et al., 2020	-
32	Cyanidin 3-glucoside	$C_{21}H_{21}ClO_{11}$		0.012–1.89	-	HPLC-MS/MS	-	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	-
33	Epicatechin	$C_{15}H_{14}O_6$		0.38–37.2	123.65–151.07	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
34	Hyperoside	$C_{21}H_{20}O_{12}$		0.37–0.87	0.012–0.56	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
35	Kaempferol	$C_{15}H_{10}O_6$		-	1.66	-	HPLC-MS/MS	-	Nzekoue et al., 2020a, 2020b
36	Kaempferol 3-glucoside	$C_{21}H_{20}O_{11}$		0.05–1.89	0.06–1.26	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020
37	Naringin	$C_{27}H_{32}O_{14}$		0.22–300	0.034–0.45	HPLC-MS/MS; cLC-DAD	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Ramón-Gonçalves et al., 2019; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020

(Continues)

TABLE 2 (Continued)

No.	Compounds name and class	Molecular formula	Structure	Reported amount		Detecting system		References	
				Spent coffee grounds	Coffee silverskin	Spent coffee grounds	Coffee silverskin	Spent coffee	Coffee silverskin
38	Quercetin	$C_{15}H_{10}O_7$		0.23–960	2.46–3.56	HPLC-MS/MS; HPLC-DAD	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; López-Barrera et al., 2016; Zengin et al., 2020	Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
39	Quercitrin	$C_{21}H_{20}O_{11}$		0.25–0.83	0.03–0.59	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
40	Resveratrol	$C_{14}H_{12}O_3$		0.10–140	-	HPLC-MS/MS; cLC-DAD	-	Angeloni, Nzekoue, et al., 2020; Ramón-Gonçalves et al., 2019	--
41	Rutin	$C_{27}H_{30}O_{16}$		0.015–360	0.05–10.65	HPLC-MS/MS; cLC-DAD; HPLC-DAD	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; López-Barrera et al., 2016; Ramón-Gonçalves et al., 2019; Zengin et al., 2020	Angeloni, Nzekoue, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
	Xanthone								
42	Isogentisin	$C_{14}H_{10}O_5$		0.07–2.54	0.50–1.36	HPLC-MS/MS	HPLC-MS/MS	Angeloni, Nzekoue, et al., 2020; Zengin et al., 2020	Nzekoue et al., 2020a, 2020b; Zengin et al., 2020
	Secoiridoids								
43	Amarogentin	$C_{29}H_{30}O_{13}$		0.02	-	HPLC-MS/MS	-	Angeloni, Nzekoue, et al., 2020	-

Note: The reported data was expressed in μg/g in according to literature. – not found literature.

esters formed between quinic acid and one or two moieties of caffeic acid, a trans-cinnamic acid. The phenolic acid in CS has a broad range of biological effects, such as being hypoglycemic, hepatoprotective, antiviral, antibacterial, anticarcinogenic, and anti-inflammatory, most of which stem from its potent antioxidant properties (Mussatto, 2015).

4.2.1 | Polyphenols composition of SCG

Mono caffeoylquinic acids (3-CQA, 5-CQA) and Di caffeoylquinic acids (1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA) represent the most abundant phenolic acids in SCG and the content goes from 3.9 to 5600 μg/g for 3-CQA, from 338.1 to 10,613.6 μg/g for 5-CQA and from 147.9 to 1194.62 μg/g for 3,5-diCQA. Instead, few authors have quantified 1,5-diCQA, 3,4-diCQA, and 4,5-diCQA with values respectively of 23 μg/g, 70 μg/g, and 110 μg/g. The most used solvent for these compounds is a mixture of EtOH/H_2O and the most efficient is Soxhlet extraction with petroleum ether for 6 h.

However today the growing attention to sustainability has led to the extraction of SCG with new solvents: natural deep eutectic solvents (NADEs), a green and nontoxic alternative to hydroalcoholic extraction methods increasingly used especially for the recovery of bioactive compounds for food and/or nutraceuticals ingredients (García-Roldán et al., 2023). These authors quantified 3-CQA (131.34 μg/g of SCG) but also gallic (154.73 μg/g of SCG) and caffeic acid (63.17 μg/g of SCG) and obtained similar values with respect to other authors. In fact, according to many authors, gallic acid is one of the most present compounds in coffee and in SCG after chlorogenic acids (2.31–2500 μg/g). In summary, the analysis of SCG reveals its remarkable richness also in a wide array of phenolic compounds as: *p*-coumaric acid, caffeic acid, vanillic acid, ferulic acid, quercetin, catechin, and other minor constituents.

4.2.2 | Polyphenols composition of CS

Among phenolic acids, CQAs are the most abundant polyphenolic compounds primarily found in silverskin: 5-CQA (from 985.7 to 26,346 μg/g), 4-CQA (from 849 to 9099 μg/g), and 3-CQA (from 128.51 to 8202 μg/g). In silver skin, only two diCQAs were quantified: 3,5-diCQA (from 41.48 to 1400 μg/g) and 3,4-diCQA (50 μg/g) acid. Like SCG, one of the most used solvent extractions is the mixture of EtOH/H_2O (Angeloni, Scortichini, et al., 2020; Nzekoue et al., 2020a, 2020b; Zengin et al., 2020) but it is reported also the use of hot water (Bresciani et al., 2014; Castaldo et al., 2020; Mesías et al., 2014) to obtain a good level of these molecules. Unlike SCG, some authors (Bresciani et al., 2014; Castaldo et al., 2020), studying CS, have reported the presence of 3-*p*-coumaroylquinic (from 24 to 4300 μg/g), 5-*p*-coumaroylquinic (from 57 to 2670 μg/g) and 3-feruloylquinic acid (from 212 to 1510 μg/g). Besides chlorogenic acid, other phenolic compounds including flavonoids, ferulic acid, quinic acid, gallic acid, *p*-hydroxybenzoic acid and other constituents, have also been found in CS.

4.3 | Other bioactive compounds of SCG and CS

A xanthone of a Gentian plant (Mustafa et al., 2015) namely isogentisin was found in all by-products of coffee studied in this review. The molecule was detected in small quantities: 0.07–2.54 μg/g in SCG and 0.50–1.36 μg/g in CS. The secoiridoid amarogentin was instead detected in small quantities only in SCG by Angeloni, Scortichini, et al., 2020 (0.02 μg/g). Isogentisin and amarogentin are not major or well-known components of coffee; however, trace amounts of these compounds have been reported in coffee by-products due to the complex chemical composition of coffee beans.

5 | CONCLUSIONS

This work provided a comprehensive characterization of the chemical profile of two coffee by-products being SCG and CS. In addition, a focused study of the valorization of main nutrients, being carbohydrates, dietary fibers, lipids and bioactive compounds and the most common extraction methods to obtain them from SCG and CS, was conducted. The present research work has helped to expand the knowledge of coffee by-products with the hope that further innovative applications of SCG and CS can be developed. In terms of a more sustainable economy, the reuse of coffee by-products could lead to a decrease in waste released into the environment. The variety of compounds present in coffee by-products could be valuable for different kinds of industrial applications, fostering a greener and economically circular viable utilization of this food waste. In conclusion, the optimization of extraction methods and the yield improvement for the discussed compounds from SCG and CS can encourage the reuse of these waste matrices at industrial level.

AUTHOR CONTRIBUTIONS

Agnese Santanatoglia: Conceptualization, investigation, formal analysis, methodology, writing – original draft; **Laura Alessandroni:** Formal analysis, writing – original draft; **Cinzia Mannozzi:** Data curation, methodology; **Riccardo Marconi:** Investigation, formal analysis; **Diletta Piatti:** Investigation, formal analysis, methodology; **Gianni Sagratini:** Funding acquisition, supervision; **Sauro Vittori:** Funding acquisition, supervision; **Giovanni Caprioli:** Resources, funding acquisition, supervision, writing – review & editing.

ACKNOWLEDGMENTS

This work has been partially funded by the European Union—NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 - VITALITY - CUP J13C22000430001.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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REFERENCES

Acevedo, F., Rubilar, M., Scheuermann, E., Cancino, B., Uquiche, E., Garcés, M., Inostroza, K., & Shene, C. (2013). Spent coffee grounds as a renewable source of bioactive compounds. *Journal of Biobased Materials and Bioenergy*, *7*(3), 420–428. https://doi.org/10.1166/jbmb.2013.1369

Al-Hamamre, Z., Foerster, S., Hartmann, F., Kröger, M., & Kaltschmitt, M. (2012). Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing. *Fuel*, *96*, 70–76. https://doi.org/10.1016/j.fuel.2012.01.023

Andrade, C., Perestrelo, R., & Câmara, J. S. (2022). Bioactive compounds and antioxidant activity from spent coffee grounds as a powerful approach for its valorization. *Molecules*, *27*(21), 7504. https://doi.org/10.3390/molecules27217504

Angeloni, S., Mustafa, A. M., Abouelenein, D., Alessandroni, L., Acquaticci, L., Nzekoue, F. K., Petrelli, R., Sagratini, G., Vittori, S., Torregiani, E., & Caprioli, G. (2021). Characterization of the aroma profile and main key odorants of espresso coffee. *Molecules*, *26*(13), 3856. https://doi.org/10.3390/molecules26133856

Angeloni, S., Nzekoue, F. K., Navarini, L., Sagratini, G., Torregiani, E., Vittori, S., & Caprioli, G. (2020). An analytical method for the simultaneous quantification of 30 bioactive compounds in spent coffee ground by HPLC-MS/MS. *Journal of Mass Spectrometry*, *55*(11), e4519. https://doi.org/10.1002/jms.4519

Angeloni, S., Scortichini, S., Fiorini, D., Sagratini, G., Vittori, S., Neiens, S. D., Steinhaus, M., Zheljazkov, V. D., Maggi, F., & Caprioli, G. (2020). Characterization of odor-active compounds, polyphenols, and fatty acids in coffee silverskin. *Molecules*, *25*(13), 2993. https://doi.org/10.3390/molecules25132993

Ateş, G., & Elmacı, Y. (2019). Physical, chemical and sensory characteristics of fiber-enriched cakes prepared with coffee silverskin as wheat flour substitution. *Journal of Food Measurement and Characterization*, *13*(1), 755–763. https://doi.org/10.1007/s11694-018-9988-9

Ballesteros, L. F., Cerqueira, M. A., Teixeira, J. A., & Mussatto, S. I. (2015). Characterization of polysaccharides extracted from spent coffee grounds by alkali pretreatment. *Carbohydrate Polymers*, *127*, 347–354. https://doi.org/10.1016/j.carbpol.2015.03.047

Ballesteros, L. F., Teixeira, J. A., & Mussatto, S. I. (2014). Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. *Food and Bioprocess Technology*, *7*(12), 3493–3503. https://doi.org/10.1007/s11947-014-1349-z

Barbosa, M. D. S. G., dos Santos Scholz, M. B., Kitzberger, C. S. G., & de Toledo Benassi, M. (2019). Correlation between the composition of green Arabica coffee beans and the sensory quality of coffee brews. *Food Chemistry*, *292*, 275–280. https://doi.org/10.1016/j.foodchem.2019.04.072

Belitz, H. D., Grosch, W., & Schieberle, P. (2009). Coffee, tea, cocoa. *Food Chemistry*, 938–970.

Bertolino, M., Barbosa-Pereira, L., Ghirardello, D., Botta, C., Rolle, L., Guglielmetti, A., Borotto Dalla Vecchia, S., & Zeppa, G. (2019). Coffee silverskin as nutraceutical ingredient in yogurt: Its effect on functional properties and its bioaccessibility. *Journal of the Science of Food and Agriculture*, *99*(9), 4267–4275. https://doi.org/10.1002/jsfa.9659

Bessada, S. M., Alves, R. C., & Pp Oliveira, M. B. (2018). Coffee silverskin: A review on potential cosmetic applications. *Cosmetics*, *5*(1), 5. https://doi.org/10.3390/cosmetics5010005

Bevilacqua, E., Cruzat, V., Singh, I., Rose'Meyer, R. B., Panchal, S. K., & Brown, L. (2023). The potential of spent coffee grounds in functional food development. *Nutrients*, *15*(4), 994. https://doi.org/10.3390/nu15040994

Bhaturiwala, R. A., & Modi, H. A. (2020). Extraction of oligosaccharides and phenolic compounds by roasting pretreatment and enzymatic hydrolysis from spent coffee ground. *Journal of Applied Biology & Biotechnology*, *8*(4), 75–81. https://doi.org/10.7324/jabb.2020.80412

Bijla, L., Aissa, R., Laknifli, A., Bouyahya, A., Harhar, H., & Gharby, S. (2022). Spent coffee grounds: A sustainable approach toward novel perspectives of valorization. *Journal of Food Biochemistry*, *46*(8), e14190. https://doi.org/10.1111/jfbc.14190

Boppana, S. H., Peterson, M., Du, A. L., Kutikuppala, L. S., Gabriel, R. A., Du, A., & Kutikuppala, L. V. S. (2022). Caffeine: What is its role in pain medicine? *Cureus*, *14*(6). https://doi.org/10.7759/cureus.25603

Borrelli, R. C., Esposito, F., Napolitano, A., Ritieni, A., & Fogliano, V. (2004). Characterization of a new potential functional ingredient: Coffee silverskin. *Journal of Agricultural and Food Chemistry*, *52*(5), 1338–1343. https://doi.org/10.1021/jf034974x

Borrelli, R. C., Visconti, A., Mennella, C., Anese, M., & Fogliano, V. (2002). Chemical characterization and antioxidant properties of coffee melanoidins. *Journal of Agricultural and Food Chemistry*, *50*(22), 6527–6533. https://doi.org/10.1021/jf025686o

Bravo, J., Juaniz, I., Monente, C., Caemmerer, B., Kroh, L. W., De Peña, M. P., & Cid, C. (2012). Evaluation of spent coffee obtained from the most common coffeemakers as a source of hydrophilic bioactive compounds. *Journal of Agricultural and Food Chemistry*, *60*(51), 12565–12573. https://doi.org/10.1021/jf3040594

Bresciani, L., Calani, L., Bruni, R., Brighenti, F., & Del Rio, D. (2014). Phenolic composition, caffeine content and antioxidant capacity of coffee silverskin. *Food Research International*, *61*, 196–201. https://doi.org/10.1016/j.foodres.2013.10.047

Bunzel, M., Schüßler, A., & Tchetseubu Saha, G. (2011). Chemical characterization of Klason lignin preparations from plant-based foods. *Journal of Agricultural and Food Chemistry*, *59*(23), 12506–12513. https://doi.org/10.1021/jf2031378

Campos-Vega, R., Loarca-Pina, G., Vergara-Castañeda, H. A., & Oomah, B. D. (2015). Spent coffee grounds: A review on current research and future prospects. *Trends in Food Science & Technology*, *45*(1), 24–36. https://doi.org/10.1016/j.tifs.2015.04.012

Castaldo, L., Narváez, A., Izzo, L., Graziani, G., & Ritieni, A. (2020). In vitro bioaccessibility and antioxidant activity of coffee silverskin polyphenolic extract and characterization of bioactive compounds using UHPLC-Q-Orbitrap HRMS. *Molecules*, *25*(9), 2132. https://doi.org/10.3390/molecules25092132

Cavanagh, Q., Brooks, M. S. L., & Rupasinghe, H. V. (2023). Innovative technologies used to convert spent coffee grounds into new food ingredients: Opportunities, challenges, and prospects. *Future Foods*, *8*, 100255. https://doi.org/10.1016/j.fufo.2023.100255

Cholakov, G., Toteva, V., Nikolov, R., Uzunova, S., & Yanev, S. (2013). Extracts from coffee by-products as potential raw materials for fuel additives and carbon adsorbents. *Journal of Chemical Technology and Metallurgy*, *48*(5), 497–504.

Couto, R. M., Fernandes, J., Da Silva, M. G., & Simoes, P. C. (2009). Supercritical fluid extraction of lipids from spent coffee grounds. *The Journal of Supercritical Fluids*, *51*(2), 159–166. https://doi.org/10.1016/j.supflu.2009.09.009

Cunniff, P., & Washington, D. (1997). Official methods of analysis of AOAC international. *Journal of AOAC International*, *80*(6), 127A.

Delgado-Andrade, C., Rufián-Henares, J. A., & Morales, F. J. (2005). Assessing the antioxidant activity of melanoidins from coffee brews by different antioxidant methods. *Journal of Agricultural and Food Chemistry*, *53*(20), 7832–7836. https://doi.org/10.1021/jf0512353

Dos Santos Polidoro, A., Scapin, E., Lazzari, E., Silva, A. N., dos Santos, A. L., Caramao, E. B., & Jacques, R. A. (2018). Valorization of coffee silverskin industrial waste by pyrolysis: From optimization of bio-oil production to chemical characterization by GC× GC/qMS. *Journal of Analytical and Applied Pyrolysis*, *129*, 43–52. https://doi.org/10.1016/j.jaap.2017.12.005

Efthymiopoulos, I., Hellier, P., Ladommatos, N., Kay, A., & Mills-Lamptey, B. (2018). Integrated strategies for water removal and lipid extraction from coffee industry residues. *Sustainable Energy Technologies and Assessments*, *29*, 26–35. https://doi.org/10.1016/j.seta.2018.06.016

Esquivel, P., & Jiménez, V. M. (2012). Functional properties of coffee and coffee by-products. *Food Research International*, *46*(2), 488–495. https://doi.org/10.1016/j.foodres.2011.05.028

Essien, S. O., Young, B., & Baroutian, S. (2020). Recent advances in subcritical water and supercritical carbon dioxide extraction of bioactive compounds from plant materials. *Trends in Food Science & Technology*, *97*, 156–169. https://doi.org/10.1016/j.tifs.2020.01.014

Falcone Ferreyra, M. L., Rius, S. P., & Casati, P. (2012). Flavonoids: Biosynthesis, biological functions, and biotechnological applications. *Frontiers in Plant Science*, *3*, 222. https://doi.org/10.3389/fpls.2012.00222

Franca, A. S., & Oliveira, L. S. (2022). Potential uses of spent coffee grounds in the food industry. *Foods*, *11*(14), 2064. https://doi.org/10.3390/foods11142064

García-Roldán, A., Piriou, L., & Jauregi, P. (2023). Natural deep eutectic solvents as a green extraction of polyphenols from spent coffee ground with enhanced bioactivities. *Frontiers in Plant Science*, *13*, 1072592. https://doi.org/10.3389/fpls.2022.1072592

Gottstein, V., Bernhardt, M., Dilger, E., Keller, J., Breitling-Utzmann, C. M., Schwarz, S., Kuballa, T., Lachenmeier, D. W., & Bunzel, M. (2021). Coffee silver skin: Chemical characterization with special consideration of dietary fiber and heat-induced contaminants. *Foods*, *10*(8), 1705. https://doi.org/10.3390/foods10081705

Hall, R. D., Trevisan, F., & de Vos, R. C. (2022). Coffee berry and green bean chemistry–Opportunities for improving cup quality and crop circularity. *Food Research International*, *151*, 110825. https://doi.org/10.1016/j.foodres.2021.110825

Ho, K. V., Schreiber, K. L., Park, J., Vo, P. H., Lei, Z., Sumner, L. W., Brown, C. R., & Lin, C. H. (2020). Identification and quantification of bioactive molecules inhibiting pro-inflammatory cytokine production in spent coffee grounds using metabolomics analyses. *Frontiers in Pharmacology*, *11*, 229. https://doi.org/10.3389/fphar.2020.00229

ICO. (2023). https://www.ico.org/Market-Report-22-23-e.asp. Accessed 7 September 2023.

Iriondo-De Hond (2019). *Development of novel functional dairy foods using byproducts from the coffee and wine industries for sustainable nutrition and health*. Doctoral dissertation. Universidad Autónoma de Madrid.

Iriondo-De Hond, A., Martorell, P., Genovés, S., Ramón, D., Stamatakis, K., Fresno, M., Molina, A., & Del Castillo, M. D. (2016). Coffee silverskin extract protects against accelerated aging caused by oxidative agents. *Molecules*, *21*(6), 721. https://doi.org/10.3390/molecules21060721

Ishwarya, S. P., & Nisha, P. (2021). Unraveling the science of coffee foam–a comprehensive review. *Critical Reviews in Food Science and Nutrition*, *61*(10), 1704–1724. https://doi.org/10.1080/10408398.2020.1765136

Ishwarya, S. P., & Nisha, P. (2022). Insights into the composition, structure-function relationship, and molecular organization of surfactants from spent coffee grounds. *Food Hydrocolloids*, *124*(A), 107204. https://doi.org/10.1016/j.foodhyd.2021.107204

Jiménez-Zamora, A., Pastoriza, S., & Rufián-Henares, J. A. (2015). Revalorization of coffee by-products. Prebiotic, antimicrobial and antioxidant properties. *LWT-Food Science and Technology*, *61*(1), 12–18. https://doi.org/10.1016/j.lwt.2014.11.031

Jones, R. A., Panda, S. S., & Hall, C. D. (2015). Quinine conjugates and quinine analogues as potential antimalarial agents. *European Journal of Medicinal Chemistry*, *97*, 335–355. https://doi.org/10.1016/j.ejmech.2015.02.002

LIczbiński, P., & Bukowska, B. (2022). Tea and coffee polyphenols and their biological properties based on the latest in vitro investigations. *Industrial Crops and Products*, *175*, 114265. https://doi.org/10.1016/j.indcrop.2021.114265

López-Barrera, D. M., Vázquez-Sánchez, K., Loarca-Piña, M. G. F., & Campos-Vega, R. (2016). Spent coffee grounds, an innovative source of colonic fermentable compounds, inhibit inflammatory mediators in vitro. *Food Chemistry*, *212*, 282–290. https://doi.org/10.1016/j.foodchem.2016.05.175

Loyao, A. S., Jr, Villasica, S. L. G., Peña, P. L. L. D., & Go, A. W. (2018). Extraction of lipids from spent coffee grounds with non-polar renewable solvents as alternative. *Industrial Crops and Products*, *119*, 152–161. https://doi.org/10.1016/j.indcrop.2018.04.017

Malara, A., Paone, E., Frontera, P., Bonaccorsi, L., Panzera, G., & Mauriello, F. (2018). Sustainable exploitation of coffee silverskin in water remediation. *Sustainability*, *10*, 3547. https://doi.org/10.3390/su10103547

Martuscelli, M., Esposito, L., Di Mattia, C. D., Ricci, A., & Mastrocola, D. (2021). Characterization of coffee silver skin as potential food-safe ingredient. *Foods*, *10*(6), 1367. https://doi.org/10.3390/foods10061367

Mesías, M., Navarro, M., Martínez-Saez, N., Ullate, M., Del Castillo, M. D., & Morales, F. J. (2014). Antiglycative and carbonyl trapping properties of the watersoluble fraction of coffee silverskin. *Food Research International*, *62*, 1120–1126. https://doi.org/10.1016/j.foodres.2014.05.058

Moreira, A. S., Nunes, F. M., Domingues, M. R., & Coimbra, M. A. (2012). Coffee melanoidins: Structures, mechanisms of formation and potential health impacts. *Food & Function*, *3*(9), 903–915. https://doi.org/10.1039/c2fo30048f

Mota, D. A., Santos, J. C., Faria, D., Lima, Á. S., Krause, L. C., Soares, C. M., & Ferreira-Dias, S. (2020). Synthesis of dietetic structured lipids from spent coffee grounds crude oil catalyzed by commercial immobilized lipases and immobilized Rhizopus oryzae lipase on biochar and hybrid support. *Processes*, *8*(12), 1542. https://doi.org/10.3390/pr8121542

Murthy, P. S., & Naidu, M. M. (2012). Sustainable management of coffee industry by-products and value addition—A review. *Resources, Conservation and Recycling*, *66*, 45–58. https://doi.org/10.1016/j.resconrec.2012.06.005

Mussatto, S. I. (2015). Generating biomedical polyphenolic compounds from spent coffee or silverskin. In *Coffee in health and disease prevention* (pp. 93–106). Academic Press.

Mussatto, S. I., Ballesteros, L. F., Martins, S., & Teixeira, J. A. (2012). Use of agro-industrial wastes in solid-state fermentation processes. *Industrial Waste*, *274*. https://doi.org/10.5772/36310

Mussatto, S. I., Machado, E. M., Martins, S., & Teixeira, J. A. (2011). Production, composition, and application of coffee and its industrial residues. *Food and Bioprocess Technology*, *4*(5), 661–672. https://doi.org/10.1007/s11947-011-0565-z

Mustafa, A. M., Abouelenein, D., Angeloni, S., Maggi, F., Navarini, L., Sagratini, G., Santanatoglia, A., Torregiani, E., Vittori, S., & Caprioli, G. (2022). A new HPLC-MS/MS method for the simultaneous determination of quercetin and its derivatives in green coffee beans. *Foods*, *11*(19), 3033. https://doi.org/10.3390/foods11193033

Mustafa, A. M., Caprioli, G., Ricciutelli, M., Maggi, F., Marín, R., Vittori, S., & Sagratini, G. (2015). Comparative HPLC/ESI-MS and HPLC/DAD

study of different populations of cultivated, wild and commercial Gentiana lutea L. *Food Chemistry*, *174*, 426–433. https://doi.org/10.1016/j.foodchem.2014.11.089

Napolitano, A., Fogliano, V., Tafuri, A., & Ritieni, A. (2007). Natural occurrence of ochratoxin A and antioxidant activities of green and roasted coffees and corresponding byproducts. *Journal of Agricultural and Food Chemistry*, *55*(25), 10499–10504. https://doi.org/10.1021/jf071959+

Nolasco, A., Squillante, J., Velotto, S., D'Auria, G., Ferranti, P., Mamone, G., Errico, M. E., Avolio, R., Castaldo, R., Cirillo, T., & Esposito, F. (2022). Valorization of coffee industry wastes: Comprehensive physicochemical characterization of coffee silverskin and multipurpose recycling applications. *Journal of Cleaner Production*, *370*, 133520. https://doi.org/10.1016/j.jclepro.2022.133520

Nunes, F. M., & Coimbra, M. A. (2010). Role of hydroxycinnamates in coffee melanoidin formation. *Phytochemistry Reviews*, *9*(1), 171–185. https://doi.org/10.1007/s11101-009-9151-7

Nzekoue, F., Khamitova, G., Angeloni, S., Sempere, A. N., Tao, J., Maggi, F., Xiao, J., Sagratini, G., Vittori, S., & Caprioli, G. (2020). Spent coffee grounds: A potential commercial source of phytosterols. *Food Chemistry*, *325*, 126836. https://doi.org/10.1016/j.foodchem.2020.126836

Nzekoue, F. K., Angeloni, S., Navarini, L., Angeloni, C., Freschi, M., Hrelia, S., Vitali, L. A., Sagratini, G., Vittori, S., & Caprioli, G. (2020b). Coffee silverskin extracts: Quantification of 30 bioactive compounds by a new HPLC-MS/MS method and evaluation of their antioxidant and antibacterial activities. *Food Research International*, *133*, 109128. https://doi.org/10.1016/j.foodres.2020.109128

Oosterveld, A., Harmsen, J. S., Voragen, A. G. J., & Schols, H. A. (2003). Extraction and characterization of polysaccharides from green and roasted Coffea arabica beans. *Carbohydrate Polymers*, *52*(3), 285–296. https://doi.org/10.1016/s0144-8617(02)00296-5

Parus, A. (2012). Antioxidant and pharmacological properties of phenolic acids. *Postępy Fitoterapii*.

Passos, C. P., & Coimbra, M. A. (2013). Microwave superheated water extraction of polysaccharides from spent coffee grounds. *Carbohydrate Polymers*, *94*(1), 626–633. https://doi.org/10.1016/j.carbpol.2013.01.088

Pavlić, B., Aćimović, M., Sknepnek, A., Miletić, D., Mrkonjić, Ž., Kljakić, A. C., Jerković, J., Mišan, A., Pojić, M., Stupar, A., Zeković, Z., Teslić, N., & Teslić, N. (2023). Sustainable raw materials for efficient valorization and recovery of bioactive compounds. *Industrial Crops and Products*, *193*, 116167. https://doi.org/10.1016/j.indcrop.2022.116167

Perron, N. R., & Brumaghim, J. L. (2009). A review of the antioxidant mechanisms of polyphenol compounds related to iron binding. *Cell Biochemistry and Biophysics*, *53*(2), 75–100. https://doi.org/10.1007/s12013-009-9043-x

Pourfarzad, A., Mahdavian-Mehr, H., & Sedaghat, N. (2013). Coffee silverskin as a source of dietary fiber in bread-making: Optimization of chemical treatment using response surface methodology. *LWT-Food Science and Technology*, *50*(2), 599–606. https://doi.org/10.1016/j.lwt.2012.08.001

Prosky, L., Asp, N. G., Schweizer, T. F., Devries, J. W., & Furda, I. (1988). Determination of insoluble, soluble, and total dietary fiber in foods and food products: Interlaboratory study. *Journal of the Association of Official Analytical Chemists*, *71*(5), 1017–1023. https://doi.org/10.1093/jaoac/71.5.1017

Quideau, S., Deffieux, D., Douat-Casassus, C., & Pouységu, L. (2011). Plant polyphenols: Chemical properties, biological activities, and synthesis. *Angewandte Chemie International Edition*, *50*(3), 586–621. https://doi.org/10.1002/anie.201000044

Quijote, K. L., Go, A. W., Agapay, R. C., Ju, Y. H., Angkawijaya, A. E., & Santoso, S. P. (2021). Lipid-dense and pre-functionalized post-hydrolysis spent coffee grounds as raw material for the production of fatty acid methyl ester. *Energy Conversion and Management*, *240*, 114216. https://doi.org/10.1016/j.enconman.2021.114216

Ramón-Gonçalves, M., Gómez-Mejía, E., Rosales-Conrado, N., León-González, M. E., & Madrid, Y. (2019). Extraction, identification and quantification of polyphenols from spent coffee grounds by chromatographic methods and chemometric analyses. *Waste Management*, *96*, 15–24. https://doi.org/10.1016/j.wasman.2019.07.009

Reichardt, N., Gniechwitz, D., Steinhart, H., Bunzel, M., & Blaut, M. (2009). Characterization of high molecular weight coffee fractions and their fermentation by human intestinal microbiota. *Molecular Nutrition & Food Research*, *53*(2), 287–299. https://doi.org/10.1002/mnfr.200700509

Rios, M. B., Iriondo-De Hond, A., Iriondo-De Hond, M., Herrera, T., Velasco, D., Gómez-Alonso, S., Callejo, M. J., & Del Castillo, M. D. (2020). Effect of coffee cascara dietary fiber on the physicochemical, nutritional and sensory properties of a gluten-free bread formulation. *Molecules*, *25*(6), 1358. https://doi.org/10.3390/molecules25061358

Rufián-Henares, J. A., & de la Cueva, S. P. (2009). Antimicrobial activity of coffee melanoidins, A study of their metal-chelating properties. *Journal of Agricultural and Food Chemistry*, *57*(2), 432–438. https://doi.org/10.1021/jf8027842

Santanatoglia, A., Alessandroni, L., Fioretti, L., Sagratini, G., Vittori, S., Maggi, F., & Caprioli, G. (2023a). Discrimination of filter coffee extraction methods of a medium roasted specialty coffee based on volatile profiles and sensorial traits. *Foods*, *12*(17), 3199. https://doi.org/10.3390/foods12173199

Santanatoglia, A., Angeloni, S., Bartolucci, D., Fioretti, L., Sagratini, G., Vittori, S., & Caprioli, G. (2023d). Effect of brewing methods on acrylamide content and antioxidant activity studying eight different filter coffee preparation. *Antioxidants*, *12*(10), 1888. https://doi.org/10.3390/antiox12101888

Santanatoglia, A., Angeloni, S., Fiorito, M., Fioretti, L., Ricciutelli, M., Sagratini, G., Vittori, S., & Caprioli, G. (2024). Development of new analytical methods for the quantification of organic acids, chlorogenic acids and caffeine in espresso coffee by using solid-phase extraction (SPE) and high-performance liquid chromatography-diode array detector (HPLC-DAD). *Journal of Food Composition and Analysis*, *125*, 105732. https://doi.org/10.1016/j.jfca.2023.105732

Santanatoglia, A., Caprioli, G., Cespi, M., Ciarlantini, D., Cognigni, L., Fioretti, L., Maggi, F., Mustafa, A. M., Nzekoue, F., & Vittori, S. (2023b). A comprehensive comparative study among the newly developed Pure Brew method and classical ones for filter coffee production. *LWT-Food Science and Technology*, *175*, 114471. https://doi.org/10.1016/j.lwt.2023.114471

Santanatoglia, A., Cespi, M., Perinelli, D. R., Fioretti, L., Sagratini, G., Vittori, S., & Caprioli, G. (2023c). Impact of the human factor on the reproducibility of different coffee brewing methods. *Journal of Food Composition and Analysis*, *124*, 105698. https://doi.org/10.1016/j.jfca.2023.105698

Santanatoglia, A., Nzekoue, F. K., Sagratini, G., Ricciutelli, M., Vittori, S., & Caprioli, G. (2023f). Development and application of a novel analytical method for the determination of 8 plant sterols/stanols in 22 legumes samples. *Journal of Food Composition and Analysis*, *118*, 105195. https://doi.org/10.1016/j.jfca.2023.105195

Saud, S., & Salamatullah, A. M. (2021). Relationship between the chemical composition and the biological functions of coffee. *Molecules*, *26*(24), 7634. https://doi.org/10.3390/molecules26247634

Schäfer, J., Sattler, M., Iqbal, Y., Lewandowski, I., & Bunzel, M. (2019). Characterization of Miscanthus cell wall polymers. *Gcb Bioenergy*, *11*(1), 191–205. https://doi.org/10.1111/gcbb.12538

Severini, C., Caporizzi, R., Fiore, A. G., Ricci, I., Onur, O. M., & Derossi, A. (2020). Reuse of spent espresso coffee as sustainable source of fibre and antioxidants. A map on functional, microstructure and sensory effects of novel enriched muffins. *Lwt*, *119*, 108877. https://doi.org/10.1016/j.lwt.2019.108877

Simões, J., Nunes, F. M., Domingues, M. R., & Coimbra, M. A. (2013). Extractability and structure of spent coffee ground polysaccharides

by roasting pre-treatments. *Carbohydrate Polymers*, *97*(1), 81–89. https://doi.org/10.1016/j.carbpol.2013.04.067

Simões, J., Nunes, F. M., Maria do Rosário, M. D., & Coimbra, M. A. (2010). Structural features of partially acetylated coffee galactomannans presenting immunostimulatory activity. *Carbohydrate Polymers*, *79*(2), 397–402. https://doi.org/10.1016/j.carbpol.2009.08.020

Tea and Coffee. (2023). https://www.teaandcoffee.net/news/32564/ico-reports-coffee-prices-recover-in-july-after-first-falling/#:~:text=Production%20and%20Consumption&text=World%20coffee%20production%20decreased%20by,million%20bags%20in%202022%2F23. Accessed 4 August 2023.

Torres-Valenzuela, L. S., Ballesteros-Gomez, A., Sanin, A., & Rubio, S. (2019). Valorization of spent coffee grounds by supramolecular solvent extraction. *Separation and Purification Technology*, *228*, 115759. https://doi.org/10.1016/j.seppur.2019.115759

Toschi, T. G., Cardenia, V., Bonaga, G., Mandrioli, M., & Rodriguez-Estrada, M. T. (2014). Coffee silverskin: Characterization, possible uses, and safety aspects. *Journal of Agricultural and Food Chemistry*, *62*(44), 10836–10844. https://doi.org/10.1021/jf503200z

Vázquez-Sánchez, K., Martinez-Saez, N., Rebollo-Hernanz, M., Del Castillo, M. D., Gaytán-Martínez, M., & Campos-Vega, R. (2018). In vitro health promoting properties of antioxidant dietary fiber extracted from spent coffee (Coffee arabica L.) grounds. *Food Chemistry*, *261*, 253–259. https://doi.org/10.1016/j.foodchem.2018.04.064

Verzelloni, E., Tagliazucchi, D., Del Rio, D., Calani, L., & Conte, A. (2011). Antiglycative and antioxidative properties of coffee fractions. *Food Chemistry*, *124*(4), 1430–1435. https://doi.org/10.1016/j.foodchem.2010.07.103

Vitaglione, P., Morisco, F., Mazzone, G., Amoruso, D. C., Ribecco, M. T., Romano, A., Fogliano, V., Caporaso, N., & D'Argenio, G. (2010). Coffee reduces liver damage in a rat model of steatohepatitis: The underlying mechanisms and the role of polyphenols and melanoidins. *Hepatology*, *52*(5), 1652–1661. https://doi.org/10.1002/hep.23902

Wei, F., Furihata, K., Koda, M., Hu, F., Miyakawa, T., & Tanokura, M. (2012). Roasting process of coffee beans as studied by nuclear magnetic resonance: Time course of changes in composition. *Journal of Agricultural and Food Chemistry*, *60*(4), 1005–1012. https://doi.org/10.1021/jf205315r

Wongsiridetchai, C., Jonjaroen, V., Sawangwan, T., Charoenrat, T., & Chantorn, S. (2021). Evaluation of prebiotic mannooligosaccharides obtained from spent coffee grounds for nutraceutical application. *LWT-Food Science and Technology*, *148*, 111717. https://doi.org/10.1016/j.lwt.2021.111717

Zengin, G., Sinan, K. I., Mahomoodally, M. F., Angeloni, S., Mustafa, A. M., Vittori, S., Maggi, F., & Caprioli, G. (2020). Chemical composition, antioxidant and enzyme inhibitory properties of different extracts obtained from spent coffee ground and coffee silverskin. *Foods*, *9*(6), 713. https://doi.org/10.3390/foods9060713

Zhang, S., Yang, J., Wang, S., Rupasinghe, H. V., & He, Q. S. (2021). Experimental exploration of processes for deriving multiple products from spent coffee grounds. *Food and Bioproducts Processing*, *128*, 21–29. https://doi.org/10.1016/j.fbp.2021.04.012

Zhou, J., Chan, L., & Zhou, S. (2012). Trigonelline: A plant alkaloid with therapeutic potential for diabetes and central nervous system disease. *Current Medicinal Chemistry*, *19*(21), 3523–3531. https://doi.org/10.2174/092986712801323171

How to cite this article: Santanatoglia, A., Alessandroni, L., Mannozzi, C., Marconi, R., Piatti, D., Sagratini, G., Vittori, S., & Caprioli, G. (2024). Valorization of spent coffee ground and coffee silverskin as a source of nutrients and bioactive compounds. *Future Postharvest and Food*, 1–21. https://doi.org/10.1002/fpf2.12007