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Functional properties of coffee and coffee by-products ☆

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ABSTRACT

Coffee, one of the most popular beverages, is consumed by millions of people every day. Traditionally, coffee beneficial effects have been attributed solely to its most intriguing and investigated ingredient, caffeine, but it is now known that other compounds also contribute to the valuable properties of this beverage. The role of coffee brew consumption in preventing some severe and prevalent diseases justifies its classification as a functional beverage. These properties are determined directly by the composition of the green beans and the changes that occur during roasting. On the other hand, by-products of coffee fruit and bean processing can also be considered as potential functional ingredients for the food industry. The coffee husks, peel and pulp, which comprises nearly 45% of the cherry, are one of the main by-products of coffee agro-industry and might be a valuable material for several purposes, including extraction of caffeine and polyphenols. Other by-products of coffee processing have been less studied, such as the mucilage and the parchment; however, they might have a high potential as a source of important ingredients as well. Furthermore, the use of the roasted coffee silverskin as a dietary fiber rich ingredient and for its antioxidative properties has also been evaluated. Finally, spent beans have been studied mainly for their antioxidative properties. The aim of this paper is to compile recent information on the functional properties of coffee, coffee beans and by-products in terms of the associated potential health benefits. The data in this review have been organized in sections according to the coffee product or by-product.

1. Introduction

Coffee is the most important food commodity worldwide and ranks second, after crude oil, among all commodities. About 60 tropical and subtropical countries produce coffee extensively, being for some of them the main agricultural export product (Lashermes, Andrade, & Etienne, 2008; Vieira, 2008). Economic importance of coffee is mainly due to the coffee brew or beverage, an infusion prepared from the roasted and ground beans. Most coffee beverage consumed around the world is produced by the species *Coffea arabica* (Arabica) and *Coffea canephora* (Robusta). The former one is considered to be superior due to its sensory properties (Bertrand, Guyot, Anthony, & Lashermes, 2003) and, therefore, reaches higher prices in the international market (Gielissen & Graafland, 2009).

Coffee brew is known as a stimulant, property mainly attributed to caffeine; however, the number of chemical compounds identified in this beverage is large and some of them have many beneficial attributes. In addition, by-products of the coffee industry, which are in many cases not properly handled and, therefore, an environmental concern, are also a potential source of compounds with functional properties. The aim of this review is to summarize the information related to the beneficial properties of coffee beverage and by-products of the coffee industry. To avoid repeating information already compiled and reviewed elsewhere, readers will be directed to other review papers when appropriate.

2. Coffee fruit, processing and by-products

The coffee fruit (also called berry or cherry) consists of a smooth, tough outer skin or pericarp, usually green in unripe fruits but that turns red-violet or deep red when ripe (even yellow or orange in particular genotypes). The pericarp covers the soft yellowish, fibrous and sweet pulp or outer mesocarp. This is followed by a translucent, colorless, thin, viscous and highly hydrated layer of mucilage (also called the pectin layer). Then, there is a thin endocarp yellowish in color, also called parchment. Finally, the silverskin covers each hemisphere of the coffee bean (endosperm) (Belitz, Grosch, & Schieberle, 2009; Berbert et al., 2001; Purseglove, 1974). Constitution of the coffee bean is depicted in Fig. 1.

Coffee is internationally traded as green coffee (the coffee bean covered or not with the silverskin), which is produced by either dry or wet processing. In the former process, harvested coffee fruits are dried in the sun and then mechanically hulled, being the dried husks (skin, pulp, mucilage and parchment) removed, together with, as much as possible, of the silverskin. In the wet process, flotation of damaged and

☆ This paper is dedicated to Prof. Dr. Dr. h.c. Reinhold Carle on the occasion of his 60th birthday and of 15 years professorship at the University of Hohenheim.

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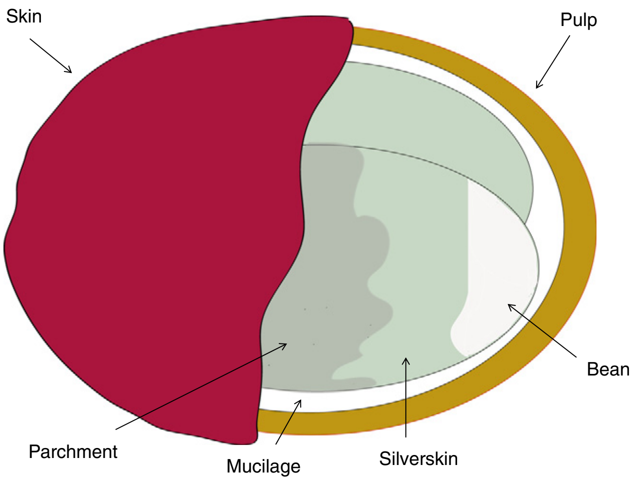

Fig. 1. Layers in a coffee fruit.

unripe berries in water allows their separation from the ripe ones, which sink (Belitz et al., 2009). Ochratoxin A (a nephrotoxic mycotoxin, associated to urinary tract tumors) contamination has been found to be higher in floating fruits (Batista et al., 2009). Then, the skin and most pulp of the sunken fruits are mechanically removed by pressing the fruit in water through a screen (by using a pulper). Pulp remnants and the mucilage layer have to be removed in a following step. This can be conducted through "controlled" fermentation (for 12–48 h) and wash in concrete tanks, or through mechanical scrubbing (aquapulping). In the fermentation step, the mucilage is hydrolyzed by enzymes from both the coffee tissues and from microorganisms found on the fruit skins (Belitz et al., 2009; Vaast, Bertrand, Perriot, Guyot, & Génard, 2006). The population of microorganisms has a direct influence on the final quality of the coffee beans (Avallone, Brillouet, Guyot, Olguin, & Guiraud, 2002; Avallone, Guyot, Brillouet, Olguin, & Guiraud, 2001). On the other side, mechanical removal of the pulp reduces the amount of water used and, in consequence, of waste polluted water, and allows recovering the mucilage fraction, which might be of interest. The resulting beans are still covered by the parchment, which is removed after drying and hulling steps. The silverskin can be optionally removed by a polishing machine to produce premium-priced coffee beans (Belitz et al., 2009; González-Ríos et al., 2007; Joët et al., 2010). The processing method to obtain the green coffee has an influence on the sensory properties of the coffee brew produced afterwards. Many of those differences can be backtracked to the chemical composition of the green beans, including the nonprotein aminoacid γ-aminobutyric acid and hexoses. It is generally assumed that wet-processed coffee has superior aroma and, therefore, higher acceptance (Bytof, Knopp, Schieberle, Teutsch, & Selmar, 2005; Knopp, Bytof, & Selmar, 2006). It has been also recently found that the wet method yielded higher contents of chlorogenic acids (CGA) and trigonelline and lower content of sucrose, whose importance is described below (Section 3.1), compared to the other method (Duarte, Pereira, & Farah, 2010).

Production of green tradable coffee beans renders thus several by-products depending on the processing method followed. The main by-product of the dry processing is composed by the skin, pulp, mucilage and parchment, all together in a single fraction (coffee husks) (Prata & Oliveira, 2007). Wet processing, in contrast, potentially allows recovery of the skin and pulp in one fraction (43.2% w/w from the whole fruit), mucilage and soluble sugars in a second fraction when fermentation is not used (11.8% w/w) and, finally, the parchment (6.1% w/w) (Bressani, 1978).

In the following sections, the composition and functional properties of each of the coffee products and by-products are summarized.

3. Composition and functional properties of green and roasted coffee beans and coffee beverage

Coffee beverage is, by far, the most important end-product obtained from the ground roasted coffee. Due to the importance of coffee beverage worldwide, extensive research has been conducted on the chemical composition, as well as on the potential beneficial and detrimental properties, of the green and roasted beans and the beverage (reviewed by Bisht & Sisodia, 2010; Dórea & da Costa, 2005; Hidgon & Frei, 2006; Meletis, 2006; Nkondjock, 2009; Serafini & Testa, 2009; Tao et al., 2008; Taylor & Antonio, 2007).

3.1. Green coffee beans, oil and extracts

As mentioned above (Section 2), the green coffee beans are composed of the seeds and the silverskin (when not removed in a polishing step). Being the green beans the raw material for coffee beverage preparation after roasting and grinding, they have been the subject of extensive analysis. Green coffee has a mild, green, bean-like aroma (Naidu, Sulochanamma, Sampathu, & Srinivas, 2008). Relevant is the fact that the composition and many characteristics of the beans, that later determine the properties and quality of the brewed coffee, are not only dependant on the species (e.g. *C. arabica* or *C. canephora*), cultivation conditions of the plants (shade, pruning, fertilization, soil, altitude, sun exposure, rainfall and temperature), degree of ripeness at harvest and harvesting method, but also on the processing method (dry or wet) described above (Section 2) and, particularly, in the case of the wet processing, on the fermentation step (Belay, Ture, Redi, & Asfaw, 2008; Stalmach, Mullen, Nagai, & Crozier, 2006). The latter is not so relevant when the mucilage is removed mechanically, without the participation of microorganisms.

As expected, green coffee beans are mainly composed, like most plant tissues, by insoluble polysaccharides like cellulose and hemicelluloses (ca. 50% w/w). They contain also soluble carbohydrates, such as the monosaccharides fructose, glucose, galactose and arabinose, the oligosaccharides sucrose (accounting for over 90% of the oligosaccharides), raffinose and stachyose, and polymers of galactose, mannose, arabinose and glucose. Soluble carbohydrates act by binding aroma, stabilizing foam, sedimenting and increasing viscosity of the extract. In addition, non-volatile aliphatic acids (such as citric, malic and quinic acids) and volatile acids are also present (such as acetic, propanoic, butanoic, isovaleric, hexanoic and decanoic acids). Oils and waxes are also important constituents, accounting for 8 to 18% of the dry mass, together with proteins and free amino acids (9–12% w/w) and minerals (3–5% w/w) (Arya & Rao, 2007; Belitz et al., 2009; Clifford, 1985a; González-Ríos et al., 2007).

The purine caffeine is the main alkaloid in coffee beans, accounting for 1 to 4% (dry basis), with large variation within cultivars and among them (Belitz et al., 2009; Dessalegn, Labuschagne, Osthoff, & Herselman, 2008; Mazzafera & Silvarolla, 2010). Caffeine contents are strongly related to the quality of coffee beverages, because it contributes to its bitterness (Farah, Monteiro, Calado, Franca, & Trugo, 2006). Caffeine is well-known for increasing alertness, through stimulation of the central nervous system, rising blood circulation and respiration, being probably the main reason for coffee popularity (Belitz et al., 2009; Reich, Dietrich, Finlayson, Fischer, & Martin, 2008). Other possible benefits of caffeine include mood enhancement, better exercise performance and reaction time, and reduction of symptoms associated with Parkinson's disease and tremors (Heckman, Weil, & González de Mejía, 2010). A concise review on positive effects of moderate consumption of caffeine has been recently published (Glade, 2010).

However, caffeine has also some negative effects such has sleeplessness and mild addiction, which has prompted development of a decaffeinated coffee industry (estimated for around 10–15% of the total amount of coffee consumed in the world) (DuFrene &

Rubinstein, 2010), which might also benefit from naturally decaffeinated coffee genotypes (Silvarolla, Mazzafera, & Fazuoli, 2004). High doses of caffeine also cause anxiety, restlessness, tension, nervousness, and psychomotor agitation (Daly & Fredholm, 1998), while long-term use of this alkaloid may increase the risk of cardiovascular diseases, with individual differences in caffeine response, probably related to genetic factors (Yang, Palmer, & de Wit, 2010). A more detailed report of concerns about coffee drinking can be found elsewhere (Dórea & da Costa, 2005).

Phenolic compounds are mainly found in green coffee beans as CGA (up to 12% of solids), which are esters of *trans* cinnamic acids and quinic acids. CGA found in green coffee beans include caffeoylquinic, feruloylquinic, p-coumaroylquinic, dimethoxycinnamoylquinic, dicaffeoylquinic, diferuloylquinic, di-p-coumaroylquinic, feruloylcaffeoyl quinic, dimethoxycinnamoylcaffeoylquinic, dimethoxycinnamoylferuloylquinic, p-coumaroylcaffeoylquinic, p-coumaroylferuloylquinic and p-coumaroyldimethoxycinnamoylquinic acids. Esterification at positions 3, 4, and 5, but not at position 1, renders several isomers, also found in coffee, together with free phenolic acids such as caffeic, ferulic and dimethoxycinnamic acids. Conjugation of hydroxycinnamic acids with amino acids (cinnamoyl amides) or glycosides (cinnamoyl glycosides) has also been reported in green coffee (Alonso-Salces, Guillou, & Berrueta, 2009; Alonso-Salces, Serra, Reniero, & Héberger, 2009; Belitz et al., 2009). Besides their potential as antioxidants (Iwai, Kishimoto, Kakino, Mochida, & Fujita, 2004), CGA have other valuable health properties, such as hepatoprotective, hypoglycemic, and antiviral activities. Other phenolic compounds, such as tannins, lignans and anthocyanins are found in lower contents in the coffee seeds (Farah & Donangelo, 2006).

The lipid fraction of green coffee beans is mainly composed of triacylglycerols, sterols, tocopherols, and diterpenes of the kaurene family, the latter comprising up to 20% of the total lipids (Speer & Kölling-Speer, 2006). Green coffee oil, usually obtained by mechanical cold-pressing and solvent extraction, is industrially used in cosmetics for its properties maintaining natural skin humidity (Ferrari, Ravera, De Angelis, Liverani, & Navarini, 2010) and might also have a potential as a sun protector due to the ultraviolet absorption property of the main fatty acid, linoleic acid (Wagemaker, Carvalho, Maia, Baggio, & Guerreiro Filho, 2011). The relatively large diterpene fraction impairs its use as an edible vegetable oil; however, fractionation by molecular distillation or supercritical CO_2 extraction allows employing it in nutritional, cosmetic and pharmaceutical applications (Araújo & Sandi, 2006). Molecular distillation, for instance, also permits purification of valuable products such as diterpene esters which have been reported to exhibit anticarcinogenic properties (de Azevedo et al., 2008; Durán, Maciel Filho, & Wolf-Maciel, 2010).

The roasting process causes a series of changes to the composition of the coffee beans, because some compounds are degraded or modified (Alves, Almeida, Casal, & Oliveira, 2010), resulting in the development of characteristic aroma, flavor and color (Buffo & Cardelli-Freire, 2004). To avoid loss of some compounds that could have health beneficial effects during this process, green coffee can be also used to obtain the so-called "green coffee extract", after extraction with either hot water (Suzuki, Kagawa, Ochiai, Tokimitsu, & Saito, 2002), alcohol (Thom, 2007) or their mixture (Naidu et al., 2008). Green coffee extracts have been investigated for their antioxidant potential (Naidu et al., 2008), body weight control properties (Shimoda, Seki, & Aitani, 2006), blood pressure-lowering effect (Watanabe et al., 2006), antibacterial activity (Arora, Kaur, & Kaur, 2009) and antihypertensive effect (Kozuma, Tsuchiya, Kohori, Hase, & Tokimitsu, 2005; Ochiai et al., 2004). Some green coffee extracts can be commercially found and contain most secondary metabolites from the green coffee beans, particularly CGA, but lower levels of caffeine, cafestol and kahweol. Cafestol and kahweol have been related to increased levels of serum cholesterol (Farah, Monteiro, Donangelo, & Lafay, 2008; Speer & Kölling-Speer, 2006; Thom, 2007) but, at the same time, might have some anticarcinogenic effects (Cavin et al., 2002). Concentrations of kahweol and another diterpene, 16-O-methylcafestol, are distinctive features between Arabica and Robusta coffees, because Arabica coffee has much higher levels of the first compound, while the second one has only been found in Robusta coffee beans (Rubayiza & Meurens, 2005; Speer & Kölling-Speer, 2006).

3.2. Roasted coffee

Characteristic properties of the coffee beverage, such as flavor and aroma, are developed during roasting, when the coffee beans experience a succession of reactions that cause modifications to their chemical composition (Buffo & Cardelli-Freire, 2004). For instance, polysaccharides are degraded during roasting to low molecular weight carbohydrates (Arya & Rao, 2007). The degree of roast, which has an influence on the above-mentioned characteristics, is reflected on the external color of the beans (from light to dark brown due to pyrolysis of organic compounds) (Belitz et al., 2009; Franca, Oliveira, Oliveira, Agresti, & Augusti, 2009). During roasting any silverskin remnants are removed from the beans (Belitz et al., 2009). Compounds built during roasting are also responsible for many positive biological activities of the coffee brew (Daglia et al., 2008). However, carcinogenic compounds, such as polycyclic aromatic hydrocarbons, can also be formed by the incomplete combustion of organic matter during roasting. Fortunately, they have been detected in coffee brew only in insignificant quantities (Orecchio, Ciotti, & Culotta, 2009). Acrylamide formation during coffee roasting has also been confirmed, especially during the first minutes of the roasting process. It was also observed that upon roasting Robusta coffee contained more acrylamide than Arabica coffee and, that acrylamide concentration diminished with the roasting time, probably as a consequence of the process (Bagdonaite, Derler, & Murkovic, 2008). Storage at ambient conditions reduces the acrylamide contents of roasted coffee (Lantz et al., 2006).

Roasted coffee is composed by carbohydrates (38–42% dry basis), melanoidins (23%), lipids (11–17%), protein (10%), minerals (4.5–4.7%), CGA (2.7–3.1%), aliphatic acids (2.4–2.5%), caffeine (1.3–2.4%), etc. From the ca. 850 volatile compounds identified until now in roasted coffee, only around 40 contribute to the aroma (Belitz et al., 2009).

CGA also contribute to the antioxidative properties of roasted coffee (Sato et al., 2011; Verzelloni, Tagliazucchi, Del Rio, Calani, & Conte, 2011). The high temperatures during coffee roasting cause a reduction in the total CGA, in accordance to the intensity of the roasting conditions (Moon, Yoo, & Shibamoto, 2009). The chemical transformations that occur to CGA are not completely clear. However, building of chlorogenic acid lactones as a consequence of this process and their influence on coffee brew bitterness were documented some years back (Ginz & Engelhardt, 2001).

There is also evidence that the building blocks of CGA, caffeic and quinic acids, are incorporated into melanoidins among other compounds (Delgado-Andrade & Morales, 2005; Farah & Donangelo, 2006). Melanoidins are high molecular weight compounds of unknown structure, due to the complexity of the molecules, with antioxidant activity. They result from the combination of sugars and amino acids through the Maillard reaction or caramelization of carbohydrates. Progressive reduction in the antioxidant activity of the coffee brew was observed with the degree of bean roasting, showing the medium roasted coffee the highest activity, due to the balance between the degradation of phenolic compounds and the generation of Maillard reaction products during this process (Bekedam et al., 2008; del Castillo, Ames, & Gordon, 2002; del Castillo, Gordon, & Ames, 2005; Sacchetti, Di Mattia, Pittia, & Mastrocola, 2009; Votavová et al., 2009). Budryn and Nebesny (2008) found that extracts of Robusta coffee had higher antioxidative efficacy than those from Arabica coffee beans and, also, that the most efficient method for extraction of antioxidants was boiling ground coffee beans in water under elevated pressure.

Serotonin, which acts as a neurotransmitter in the central nervous system, and its precursors, L-tryptophan and 5-hydroxytryptophan, have been detected in green and roasted coffee. Higher levels of serotonin, together with lower precursor levels, in the latter product suggest that serotonin could be formed by thermal degradation of its precursors (Martins & Gloria, 2010).

Roasting has also an impact on the amount of soluble dietary fiber present in the coffee beans. Silván, Morales, and Saura-Calixto (2010) found an increase from 39.4 mg/100 mg soluble dry matter in green coffee to 64.9 in severe roasted beans.

Oil can also be extracted from the roasted coffee. It conserves more or less the same composition and properties of the lipid fraction in the green beans since little effect of the roasting process has been observed over these compounds. However, during roasting, build-up of some volatile compounds, responsible for the roasted coffee flavor and aroma, occurs (Belitz et al., 2009; de Oliveira, Cruz, Eberlin, & Cabral, 2005). Moreover, it has been observed that roasted coffee extract has an antibacterial activity against several microorganisms, such as *Staphylococcus aureus* and *Streptococcus mutans* (Daglia et al., 2007, 2002) and several strains of enterobacteria (Almeida, Farah, Silva, Nunan, & Glória, 2006), probably due to the antibacterial activity of several coffee characteristic components, such as caffeic acid, trigonelline, caffeine, chlorogenic acid and protocatechuic acid (Almeida et al., 2006), as well as of melanoidins generated during the roasting process (Rufián-Henares & de la Cueva, 2009).

3.3. Coffee beverage (brew)

Coffee brew is prepared using several techniques, all of them basically involving boiling ground roasted coffee beans in water or, alternatively, pouring, dripping or spraying hot water through ground roasted coffee, and then filtering. Irrespectively of the brewing method, coffee brew and roasted coffee, share most compounds, with slight changes in aroma due to shifts in the concentration of the aroma substances during brewing (Belitz et al., 2009).

Coffee brew contains many of the most important functional ingredients known, like flavonoids (catechins and anthocyanins), caffeic and ferulic acid (Meletis, 2006). In addition, other biologically active compounds found in coffee are nicotinic acid, trigonelline, quinolinic acid, tannic acid, pyrogallic acid and caffeine (Minamisawa, Yoshida, & Takai, 2004). The beverage is also known for the antioxidant properties of its components caffeine, CGA, hydroxycinnamic acids and melanoidins (Rufián-Henares & Morales, 2007; Vignoli, Bassoli, & Benassi, 2011). Melanoidins from coffee showed higher antioxidant activity than those isolated from other sources, such as beer (Morales & Jiménez-Pérez, 2004). Thus, as mentioned above, the antioxidant capacity of coffee is associated to the presence of both natural compounds and substances developed during roasting (Vignoli et al., 2011). Antioxidants of the hydroxycinnamic acids group, such as combined or conjugated forms of caffeic, chlorogenic, coumaric, ferulic and sinapic acids, are also found in coffee beverage (Manach, Scalbert, Morand, Rémésy, & Jiménez, 2004). There is contrasting evidence regarding the contribution of caffeine to the antioxidant capacity of the coffee brew. While Brezová, Šlebodová, and Staško (2009) found a high antioxidant activity of caffeic acid but not of caffeine, others indicate that caffeine seriously contributes to the antioxidant properties of coffee brew (Vignoli et al., 2011). Additional data on antioxidant properties of coffee brew can be found elsewhere (Fujioka & Shibamoto, 2006; Wang & Ho, 2009).

Other beneficial physiological outcomes associated to coffee consumption are the stimulating effects observed on gastrointestinal tract and liver, probably from caffeine, chlorogenic and caffeic acids, inhibition of the onset of liver cirrhosis and alcohol-associated pancreatitis, reduction of the odds of having asthma symptoms and prevention of clinical manifestations of bronchial asthma. Furthermore, reduction in plasma glucose level, inverse association to prevalence of fasting hyperglycemia and lower risk of clinical type 2 diabetes have been associated to increased coffee consumption (reviewed by Dórea & da Costa, 2005). Moreover, decomposition of xenobiotica is accelerated through a higher glutathione S-transferase activity, as a consequence of cafestol, one of the coffee brew most abundant diterpenes. The method employed for coffee brewing has a direct influence on the amount of diterpenes, which is directly related to the total lipid contents in the brew (Speer & Kölling-Speer, 2006). While boiled coffee has the highest concentration of coffee oils due to the longer contact time between the ground roasted beans and water and the higher temperature, diterpenes are barely present in filtered coffee extract, due to the fact that the lipid fraction is not miscible with water and that it will tend to float on the surface of the water extract, thus being mostly retained in the filter (Bonita, Mandarano, Shuta, & Vinson, 2007). Tocopherols are also present in coffee brew (Alves, Casal, & Oliveira, 2010). Their contents allow discrimination between Arabica and Robusta coffees (González, Pablos, Martín, León-Camacho, & Valdenebro, 2001). Coffee has also shown antiviral activity in vitro, related, to a certain degree, to caffeine, but with participation of other, yet unidentified, components (Utsunomiya et al., 2008).

Regarding other compounds present in the brew, it has been observed that carbohydrates have various biological activities, such as diminishing colon cancer risk, in addition to improve the character of the final coffee brew (Arya & Rao, 2007). Moreover, some bioactive amines, also present in the coffee brew, seem to be required for normal development and growth, in responses to stress, inhibition of lipid peroxidation, stabilization of membranes, maturation of the gastrointestinal tract, as well as vasoactive or psychoactive effects (reviewed by da Silveira, Tavares, & Glória, 2007).

In addition to the phytochemicals present in the coffee brew, there is evidence that this beverage could also be a source of dietary fiber. Díaz-Rubio and Saura-Calixto (2007) found that the coffee brew contained higher amount of soluble dietary fiber (0.47–0.75 g/100 ml), with associated antioxidant phenolics, than other beverages. Furthermore, coffee consumption seems to increase the population of *Bifidobacterium* spp. and their metabolic activity, indicating that its consumption might have some prebiotic effects (Jaquet, Rochat, Moulin, Cavin, & Bibiloni, 2009).

Due to the considerable amount of information related to proved and possible effects of coffee beverage on different health issues, readers are encouraged to examine review papers published elsewhere for more details (e.g., Alves, Casal, & Oliveira, 2009; Bisht & Sisodia, 2010; Butt & Sultan, 2011; Dórea & da Costa, 2005; George, Ramalakshmi, & Rao, 2008; Taylor & Antonio, 2007).

3.4. Coffee by-products

Since more than 50% of the coffee fruit is not used for production of the commercialized green coffee and, therefore, is discarded during processing, it should be interesting to find applications for these by-products. Up to now, most progress has been achieved in their use for industrial purposes other than food industry, such has energy production (Kondamudi, Mohapatra, & Misra, 2008; Saenger, Hartge, Werther, Ogada, & Siagi, 2001), adsorption of compounds (Franca, Oliveira, & Ferreira, 2009; Franca, Oliveira, Nunes, & Alves, 2010; Oliveira, Franca, Alves, & Rocha, 2008; Oliveira, Franca, Oliveira, & Rocha, 2008) and manufacturing of industrial products, such as particleboards, ethanol, gibberellic acid and α-amylase (Bekalo & Reinhardt, 2010; Gouvea, Torres, Franca, Oliveira, & Oliveira, 2009; Machado, Soccol, de Oliveira, & Pandey, 2002; Murthy, Naidu, & Srinivas, 2009). Commercialized extracts from the coffee fruits, which contain CGA, condensed proanthocyanidins, quinic and ferulic acid, have shown interesting results for facial skin care (Farris, 2007). However, in spite of the known high phenolic antioxidant and phytonutrient levels of the coffee fruit, only limited progress has been achieved on its use as a functional ingredient (Heimbach et al., 2010).

3.4.1. Coffee husks, skin and pulp

As mentioned above (Section 2), coffee husks are composed by the coffee berry outer skin, the pulp and the parchment, mainly resulting from the coffee dry processing. They are rich in carbohydrates (35%), proteins (5.2%), fibers (30.8%) and minerals (10.7%) (Brand et al., 2001). The wet coffee processing produces a slightly different by-product, because pressing the fruit in water through a screen leaves part of the pulp, the mucilage and the parchment still attached to the seeds (Belitz et al., 2009). Coffee skin and pulp have a similar composition to that of the husks, viz., protein (7.5–15.0%), fat (2.0–7.0%) and carbohydrates (21–32%) (Ulloa-Rojas, Verreth, Amato, & Huisman, 2003).

Direct use of these by-products for animal feed has not been possible due to the antiphysiological and antinutritional factors (e.g., tannins and caffeine) present (Brand et al., 2001; Brand, Pandey, Roussos, & Soccol, 2000; Orozco et al., 2008; Pandey et al., 2000; Ulloa-Rojas, Verreth, van Weerd, & Huisman, 2002).

However, coffee husks, skin and pulp can be a source of phytochemicals for the food and pharmaceutical industries. Ramírez-Coronel et al. (2004) found four major classes of polyphenols (viz., flavan-3-ols, hydroxycinnamic acids, flavonols and anthocyanidins) in Arabica coffee pulp. For instance, the phenolic compounds tentatively identified by HPLC in fresh coffee pulp by Ramírez-Martínez (1988) are: chlorogenic acid (5-caffeoylquinic acid) (42.2% of the total of identified phenolic compounds), epicatechin (21.6%), 3,4-dicaffeoylquinic acid, (5.7%), 3,5-dicaffeoylquinic acid (19.3%), 4,5-dicaffeoylquinic acid (4.4%), catechin (2.2%), rutin (2.1%), protocatechuic acid (1.6%) and ferulic acid (1.0%). Later on, Clifford and Ramírez-Martínez (1991a) additionally identified 5-feruloylquinic acid in coffee pulp. More recently, Prata and Oliveira (2007) described the use of fresh coffee husks as a potential source of the anthocyanin cyanidin-3-rutinoside. In a similar study, but using peels and pulp derived from wet-processed fruits, Esquivel, Kramer, Carle, and Jiménez (2010) identified cyanidin-3-rutinoside, cyanidin-3-glucoside and its aglycone as the major anthocyanins present before and after tissue browning. Moreover, they also found important levels of caffeine in these coffee by-products. Caffeine contents are two to ten times lower in the pericarp than in the seed, depending on the developmental stage of the fruit and the genotype. Since this alkaloid is no longer synthesized in the late stages of fruit development, the caffeine synthesized in the earlier stages is the only one present at full ripeness (Koshiro, Zheng, Wang, Nagai, & Ashihara, 2006).

Condensed tannins (proanthocyanidins) are also important constituents of the fresh coffee pulp (Clifford, 1985b; Clifford & Ramírez-Martínez, 1991b). Their concentration increases along pulp drying and is greater in yellow coffee varieties than in red ones (González-de-Colmenares, Ramírez-Martínez, Aldana, & Clifford, 1994).

3.4.2. Coffee mucilage

The coffee mucilage fraction remains adhered to the coffee bean in the wet processing after depulping without enzymatic degradation. This method allows separation and concentration of this fraction. The mucilage is composed of water (84.2%), protein (8.9%), sugar (4.1%), pectic substances (0.91%) and ash (0.7%) (Belitz et al., 2009). The composition analysis of the alcohol-insoluble residues showed the presence of pectic substances (ca. 30%), cellulose (ca. 8%) and neutral noncellulosic polysaccharides (ca. 18%). Pectins contained uronic acids (ca. 60%) with a high degree of methyl esterification and a moderate degree of acetylation (Avallone, Guiraud, Guyot, Olguin, & Brillouet, 2000; Avallone, Guiraud, Guyot, Olguin, & Brillouet, 2001). However, so far as the authors are aware, a detailed study on the functional properties of this fraction has not been conducted yet.

3.4.3. Coffee parchment

As previously mentioned (Section 2), the strong fibrous endocarp that covers both hemispheres of the coffee seed and separates them from each other is called the parchment. In the dry processing, the parchment is separated from the green coffee beans together with the peel and pulp, in a single step. However, in the wet processing, the parchment is removed after drying and hulling separate steps (Belitz et al., 2009). The latter process permits collection and use of parchment separately from other by-products.

Coffee parchment is composed by (α-) cellulose (40–49%), hemicellulose (25–32%), lignin (33–35%) and ash (0.5–1%) (Bekalo & Reinhardt, 2010). Similar to the mucilage, authors do not know any study on the functional characteristics of coffee parchment.

3.4.4. Coffee silverskin

As mentioned above (Section 2), silverskin remnants still attached to the green coffee beans are removed during roasting (Belitz et al., 2009). They can be easily found as a coffee processing by-product in coffee roasting plants and are presently used as fuel or for composting (Menéndez, Domínguez, Fernández, & Pis, 2007; Saenger et al., 2001). Borrelli, Esposito, Napolitano, Ritieni, and Fogliano (2004) and Napolitano, Fogliano, Tafuri, and Ritieni (2007) recommended the use of silverskins as functional ingredient, based on the low amount of fats and reducing carbohydrates, high contents of soluble dietary fiber (60%) and marked antioxidant activity. The latter is probably a consequence of the high contents of melanoidins generated during roasting, because silverskin has low contents of free phenol compounds. Additionally, silverskin supports growth of bifidobacteria in vitro, which might have some beneficial effects, has mentioned in Section 3.3 (Borrelli et al., 2004).

3.4.5. Low-grade green coffee and spent coffee

Coffee with imperfections, such as black or dark brown color, insect damage, spots, bits, from immature fruits, etc., is graded during processing and termed as low-grade coffee beans. These beans comprise about 15–20% of coffee production. On the other side, spent coffee, viz. residues from the instant (soluble) coffee production after extraction and concentration of water solubles, is also an important by-product of the coffee industry, considering that almost 50% of the world coffee production is processed for soluble coffee. Disposal of both by-products is an environmental concern; therefore, they have attracted attention as a source of bioactive compounds (Ramalakshmi, Rao, Takano-Ishikawa, & Goto, 2009). Extracts from both sources have been evaluated for biological activity. They have shown strong radical-scavenging, antioxidant and anti-tumor activity, although only limited anti-inflammatory and anti-allergic action (Ramalakshmi, Kubra, & Rao, 2008; Ramalakshmi et al., 2009). Their antioxidative properties could be the consequence of the presence of caffeine, trigonelline and chlorogenic acids (Franca, Oliveira, Mendonça, & Silva, 2005; Ramalakshmi, Kubra, & Rao, 2007).

4. Conclusions

Proven health benefits of coffee brew plenty justifies the inclusion of this infusion as a functional food. Bisht and Sisodia (2010) recently mentioned that coffee is the most frequently consumed functional food worldwide. The wide distribution of coffee drinking impacts a broader demographic population than other functional foods that act on a more defined population (Dórea & da Costa, 2005). New beneficial properties of the coffee beverage are being continuously discovered. Properties of coffee by-products are less known and considerably less research has been conducted on the subject. Newly developed techniques for biochemical analysis will help identifying proven and potentially beneficial compounds and will certainly increase the value of several coffee by-products, whose disposal is currently an environmental concern, because they have at present few uses.

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