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Coffee silver skin as a source of polyphenols: High resolution mass spectrometric profiling of components and antioxidant activity

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ABSTRACT

Many beneficial effects of coffee have been ascribed to the presence of chlorogenic acids. For this reason, some green coffee bean decaffeinated extracts claiming several beneficial effects are actually on the market as either nutraceuticals or food supplements. Herein, we compared the polyphenol content of green coffee beans, roasted coffee, spent coffee and silver-skins. The phenolic fraction of all samples was assessed using both colorimetric and HPLC-UV approaches, performing a full detailed identification and quantification of the phenols by liquid chromatography high-resolution mass spectrometry. Furthermore, we also evaluated the antioxidant activity of the different extracts. Notably, silver-skin extract possesses a superimposable profile compared to green coffee beans extract, and such a profile was unaltered by silver-skin decaffeination. This study reveals the perspective of using decaffeinated silver-skins as a low-cost raw material for the preparation of caffeine-free, chlorogenic acid-based food supplements and nutraceuticals.

1. Introduction

Coffee is the third-most popular drink overall, after water and tea, as well as the second largest traded commodity after petroleum (www.globalexchange.org).

In the past, some retrospective studies suggested that coffee consumption was associated with cardiovascular morbidity and mortality while other studies suggested that coffee might cause pancreatic cancer. All these older studies have now been discredited, as pointed out by Alpert in an Editorial of the *American Journal of Medicine* in 2009 (Alpert, 2009).

Abbreviations: CGAs, chlorogenic acids; GCB, green coffee beans; RC, roasted coffee; SS, coffee silver-skins; dSS, silver-skins from decaffeinated green coffee beans; SC, spent coffee; SCe, spent coffee from espresso machines waste; DPPH, 2,2-diphenyl-1-picrylhydrazyl; ORAC, oxygen radical absorbance capacity; DCF, 2′,7′-dichlorofluorescein; TFA, trifluoroacetic acid; GAE, gallic acid equivalents; CAE, chlorogenic acid equivalents; CID, collision-induced dissociation; CQA, caffeoylquinic acids; CQAL, lactones of caffeoylquinic acids; diCQA, dicaffeoylquinic acids; p-CoQA, para-Coumaroylquinic acids; FQA, feruloylquinic acids; FQAL, lactones of feruloylquinic acids; FCQA, feruloyl-caffeoylquinic acids; CAF, caffeine; p-CoCQA, coumaroyl-caffeoylquinic acids

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Chemical compounds: 3-Caffeoylquinic acid (PubChem CID: 1794427); 2,2-Diphenyl-1-picrylhydrazyl (PubChem CID: 2735032); 2′,7′-Dichlorofluorescein (PubChem CID: 64944); 3,5-Dicaffeoylquinic acid (PubChem CID: 6474310); Caffeine (PubChem CID: 2519).

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Although there are still controversies concerning either the benefits or the risks of coffee consumption, reliable evidence is becoming available supporting its health promoting potential. In particular, epidemiological studies and meta-analyses on coffee consumption reveal its inverse correlation with all-cause mortality risk (Tamakoshi et al., 2011), including inflammatory and cardiovascular diseases (Andersen, Jacobs, Carlsen, & Blomhoff, 2006). Moreover, high coffee consumption has been associated with better glucose tolerance and a substantially lower risk of type 2 diabetes in different populations of Europe, Japan, China and US (Hjellvik, Tverdal, & Strom, 2011; Huxley et al., 2009; Lin et al., 2011; van Dam, 2006). Interestingly, several studies reported a dose-dependent relationship between coffee daily intake (i.e. number of cups) and a reduction of the risk of type 2 diabetes (DM). For instance, Huxley et al. (2009) reported that for every additional cup of coffee consumed in a day, a 7% reduction in the excess of DM was associated. The benefits of coffee consumption have also been tested in clinical trials. For instance, Kempf et al. reported that coffee consumption has beneficial effects both on HDL cholesterol and subclinical inflammation, which represents one important mechanism in the development of type 2 diabetes (Kempf et al., 2010). Coffee is a complex mixture of hundreds of chemicals (Spiller, 1984) and it is not yet clear which components are responsible for its properties. Caffeine has acutely reduced insulin sensitivity in short-term intervention studies (Greer, Hudson, Ross, & Graham, 2001; Keijzers, De Galan, Tack, & Smits, 2002; Thong et al., 2002). However, whether this effect pertains to long-term coffee consumption is unclear since other components of coffee may modify this effect and tolerance may develop. The inverse association between decaffeinated coffee consumption and risk of type 2 diabetes in different cohort studies supports the hypothesis that molecules other than caffeine may reduce risk of type 2 diabetes.

Many beneficial effects of coffee can be ascribed to chlorogenic acids (CGAs), which are phenolic compounds formed by the esterification of (-) quinic acids with cinnamic acids such as caffeic, ferulic or para-coumaric acid. Fig. 1 shows the structure of the main chlorogenic acids detected in either coffee fruit samples or coffee beverages.

Green coffee beans (GCB) can contain as much as 10% of dry weight CGAs and therefore coffee is the major dietary source of CGAs in humans (Wang & Ho, 2009). CGAs are highly bioavailable in humans (Williamson, Dionisi, & Renouf, 2011) and different biological effects have been reported for these molecules, which can partially explain the health effects of coffee. In details, CGAs may delay glucose absorption in the

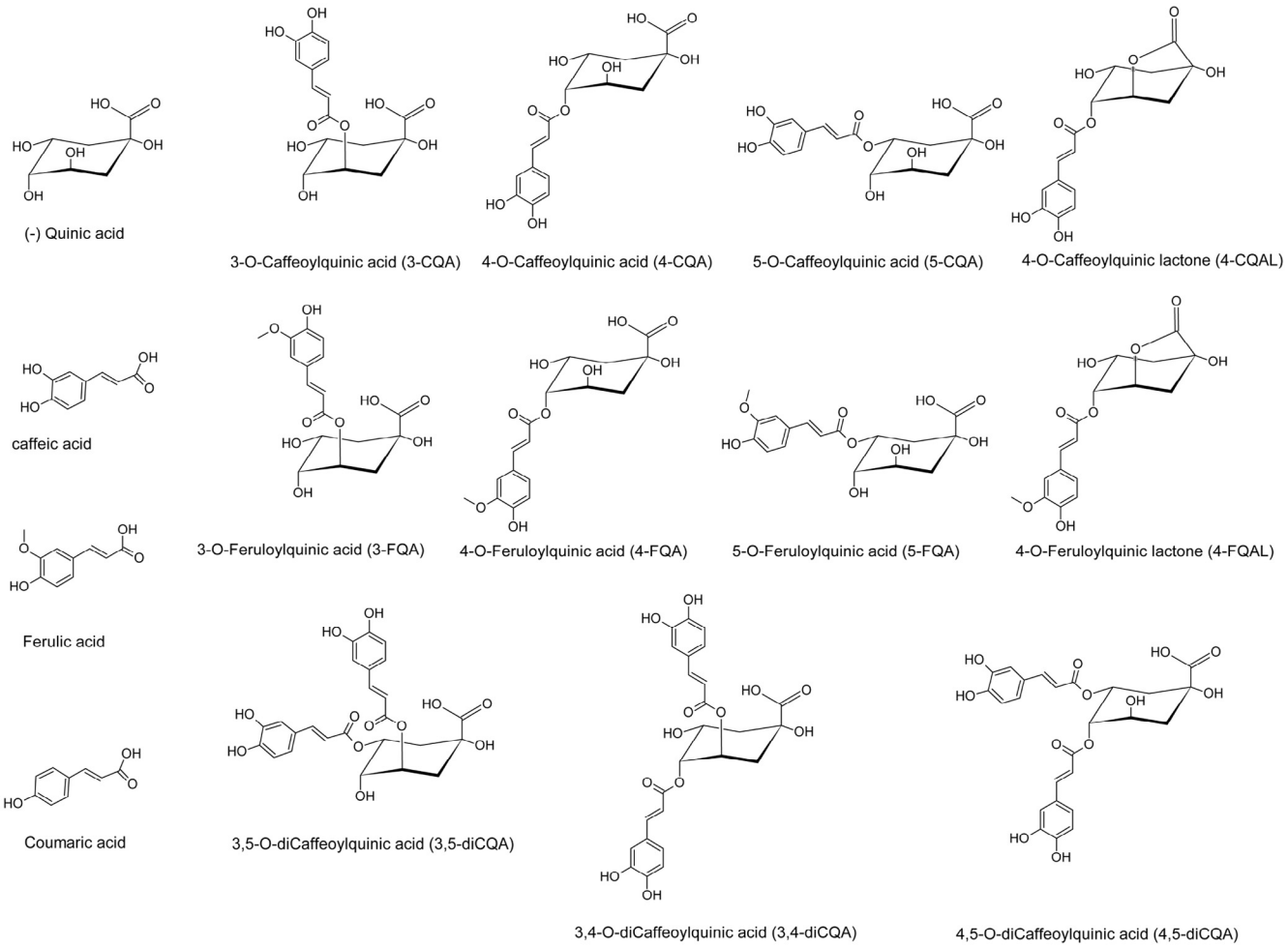

Fig. 1 – Structures of coffee's main chlorogenic acids.