



Coffee Diterpenes: before Harvesting the Bean to your Cup



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Abstract

Cafestol and kahweol are molecules that exist only in coffee beans, even though they are also available for each consumer of the coffee beverage. Endogenous coffee enzymes and the absence of these molecules in other matrices confer them the title of taxonomic markers of plants of the genus *Coffea*. The trajectory of these molecules initiates with their biosynthesis and accumulation in the coffee fruit, passes through transformations during the storage and roasting of beans, reaches their transference to the beverage and ends when the human organism absorbs and metabolizes them. The present work deals with the chemical transformations imposed on these molecules during their trajectory in the coffee commercial cycle, as well as aspects related to human health.

Keyword: Coffee diterpenes; Human consumption; Metabolism; Biological activities; Storage; Roasting degradation

Introduction

Coffee is one of the most consumed beverages in contemporary society. About 80% of the world's adult population appreciates the beverage, which is usually marketed in the form of blends between *Coffea arabica* L. and *C. canephora* P. [1]. Due to the great popular appreciation, coffee has been the object of studies within the Food Sciences, some directly related to its chemical composition [2-4].

In the last three decades, studies related to the diterpenic composition of coffee bean gained attention. Two main factors contributed to this interest. The first was related to the representative presence of cafestol and kahweol (C&K) derivatives (Figure 1) in the beans ($\leq 2.5\%$ w/w of its dry mass) and in its lipid fraction ($\leq 20\%$ w/w) [5,6], and the second their anti-carcinogenic, antioxidant, anti-inflammatory and hypercholesterolemic activities [7-13].

Biosynthesis and Concentration of Cafestol and Kahweol (C&K) in Coffee

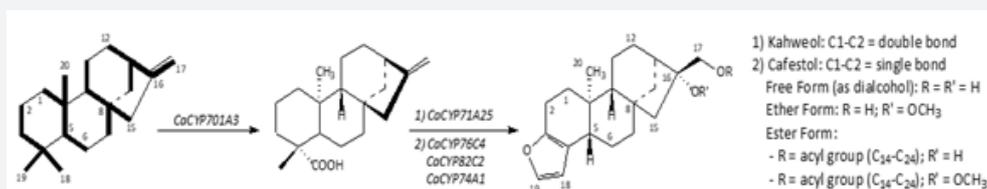


Figure 1: Ent-kaurane skeleton with bold form for isoprene units (left structure), biosynthetic intermediate (center) and primary structure of common diterpenes in *Coffea* (right) Adapted of [14].

The coffee tree biogenetically modifies the ent-kaurane skeleton to produce C&K and distributes them throughout the plant as dialcohols (free form), ethers or esters (Figure 1) [14]. They are found in all the main tissues of the shrub (roots, branches, leaves and fruits), but mainly in coffee fruits, where their amount is dependent on the fruit stage of maturity [14]. Cafestol is the most common coffee diterpene in not only the major commercial species, *C. arabica* and *C. robusta*, but also in wild coffee [15]. The Arabica coffee beans have kahweol:cafestol proportions between 1:2 and 2:1,

and this ratio is a coffee quality parameter for the beverage [2]. Kahweol may be absent in robusta coffee, or present in very low concentrations ($\leq 0.01\%$ w/w) [16]. Kahweol differs from cafestol by an unsaturation present in the ring A of the diterpene nucleus, between carbons 1 and 2 (Figure 1). The Robusta coffee has also ethers derived from C&K on carbon 16 (Figure 1) [5]. The presence and the ratio between Kahweol and 16-O-methyl-cafestol, when applied in a polynomial equation, can discriminate between different blend proportions of Arabica and Robusta beans in mixtures [17].

Commercial and wild coffee species have the esterified diterpenes in a proportion greater (250-fold) than their respective alcohols (Figure 1) [5-6]. However, according to SCOPUS database, there are few articles dealing with these compounds: only 16 papers compared to 362 for the free form of the dialcohol [18]. This is probably due to the dispersion of C&K into 24 esters of different chain lengths and degrees of unsaturation (Figure 1), and the absence of effective techniques to obtain them individually [3,19-21]. For this reason, the research is concentrated on the free form of C&K after hydrolysis of their respective esters, simplifying their determination in coffee matrices and increasing the bulk of these diterpenes for further studies.

Degradation of C&K due to green coffee bean storage and its roasting process

When the green (or raw) coffee beans are stored, there is an increase in the content of both free form of C&K and fatty acids. Endogenous lipases in the beans hydrolyze the ester forms of these diterpenes (Figure 1) and the acylglycerol derivatives [22,23]. When the green bean is submitted to the roasting conditions (180-265 °C / 2-21min), C&K lose water generating several dehydrocafestol and dehydrokahweol, respectively, as well as the ether and aldehyde derivatives [22,24]. The amounts of both compounds increase proportionally with raising roasting temperatures or time of exposition. The cafestol/dehydrocafestol ratio is a good indicator of the coffee roasting degree [25]. Values below 15 for this ratio signal dark roasted coffee and values between 15 and 25 indicate medium roasting. Values above 25 describe a light-roasted coffee [25,26].

C&K extraction in coffee beverage preparation and their absorption, metabolism and excretion

The C&K extraction from roasted and grounded beans happens during the coffee beverage preparation. However, the final C&K concentration in the beverage is dependent on the kind of extraction procedure employed. The boiled coffee beverage - Scandinavian-type - reaches up to 1.766mg L⁻¹ of C&K, whereas in beverages prepared with paper filter, C&K are widely retained, and their concentration reaches only 2.4mg L⁻¹ after the percolation of these compounds through the paper [27,28].

When ingested by humans, about 70% of the total coffee diterpenes are absorbed in the intestinal tract, whereas 24% are degraded in the stomach and only 1% is excreted in the urine after conjugation with glucuronic acid and sulfate salts [15,29]. Results in rats indicate the presence of C&K esters in the body for 5 to 10 days after its administration, whereas the hydrolyzed forms persist for less than 48h [30]. These findings show that the hydrocarbon chain of the esterified coffee diterpenes increases their liposolubility and the residence time in the tissues, which, therefore, increases their active

period in the organism. Therefore, the investigations should be directed to the esterified forms, unless these esters are hydrolyzed in the human organism, releasing the free form.

Conclusion

The present work discussed the trajectory of coffee diterpenes - cafestol and kahweol - on the molecular level in their environment/food/man relationship. It initiates with C&K biosynthesis in the plant, followed by their concentration in the coffee fruit, until their absorption in and elimination from the human organism. This multidisciplinary approach opens perspectives for several studies on these molecules and their derivatives along the coffee commercial path that ends with its consumption.

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