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Review

The Impact of Brewing Methods on the Quality of a Cup of Coffee

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Abstract

A comprehensive overview is provided on factors and processes influencing the final quality of a cup of coffee, with an emphasis on the brewing method's central role. Coffee quality assessment, both at the bean and cup level, combines objective parameters (color, moisture, bean defects, density) with a notable degree of subjectivity, as consumer sensory perception is ultimately decisive. The brewing technique is described as a critical determinant of the final chemical, physical, and sensory attributes. Key parameters such as aroma profile, pH, titratable acidity, total and filtered solids, lipid and fatty acid content, viscosity, foam (crema), and colorimetric indices are detailed as essential metrics in coffee quality evaluation. Roasting creates most of coffee's key aroma compounds. The brewing method further shapes the extraction of both volatile and other bioactive compounds like caffeine, chlorogenic acids, and lipids. Brewing methods significantly affect acidity, "body," and crema stability, while water quality, temperature, and pressure are shown to impact extraction results and sensory properties. Attention is paid to how methods such as Espresso, filter, French press, and cold brew yield distinct physicochemical and sensory profiles in the cup. Overall, the review highlights the multifaceted nature of coffee cup quality and the interplay between raw material, processing, and preparation, ultimately shaping the coffee sensory experience and market value.

Keywords: aroma; caffeine; coffee brewing; Espresso; furans; melanoidin; phenolic compounds; pyrazines; quality; volatile compounds

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1. Introduction

Coffee is the world's most traded commodity, with an increasing amount and value over years, with a production from approximately 70 countries [1]. The definition of coffee brew quality is fundamentally related to the customer' expectations, therefore its sensory characteristics are of paramount importance [2,3]. Excluding minor species traded in limited contexts, such as *Coffea iberica* and *Coffea excelsa*, the two species that are commonly found on the trade markets are *Coffea arabica* and *Coffea robusta*, with the latter representing the majority [1].

A common way of grading coffee commercially is to use four categories, namely, exemplary quality, high quality, mainstream quality, and undergrads or low grades. These categories are mostly based on the number of defective beans and on the cup quality evaluation. As the international regulations related to coffee imply some minimum export

standard, there might be a high amount of coffee that is below the minimum quality standard in producing countries and thus cannot be exported. Also, coffee quality evaluation, as carried out by the industry, has a certain degree of subjectivity [1]. Regarding the quality parameters of coffee beans, the most common ones evaluated are color, moisture content, absence of visible defects, presence of insect infestation, and bean size and density. As coffee is consumed in a liquid form, the brewing process strongly affects the physicochemical and sensory properties of the final product. The quality evaluation of the coffee brew is more complex, as the number of parameters to be evaluated might be larger and not well defined with strict limits and mostly related to the consumer's appreciation of a particular brew. The quality of the coffee brew is affected by the origin of the coffee beans, their post-harvest processing, roasting degree, and grinding process. However, these factors will not be extensively reported in the current review, which focuses on the changes due to the brewing process.

Before describing individual types of coffee brews, which differ significantly from a physicochemical point of view as well as sensory point of view, the reader should always keep in mind that the final "judge" will be the consumer; therefore, consumer's liking for a particular type of coffee, and for a particular characteristic for which this coffee brew is popular, is of critical importance for the coffee industry. For example, Espresso coffee has become popular for its peculiarities among all coffee brews.

Coffee composition and quality characteristics, including its aroma profile, can vary greatly, depending on factors such as the coffee origin—e.g., coffee species, geographical origin, post-harvest processing, roasting conditions, etc.—but also on the brewing process. The current review reports these changes by describing different brewing techniques and their impact on the coffee brew composition and flavor.

2. Sensory Characteristics of Coffee Brews and Their Evaluation

As stated at the beginning of this review, the sensory characteristics of a cup of coffee are of paramount importance in defining its price and customer. Consumers are becoming more and more interested in coffee quality, which is often one of the greatest commercial drivers. As quality is defined as the ensemble of characteristics that meet the consumer's expectations, it is important to understand how consumers perceive it for the coffee beverage, in terms of intrinsic properties.

Brewing methods are known to affect the physicochemical properties of coffee beverages. Coffee is often consumed for its stimulating effect due to caffeine, but also—or perhaps mainly—because of its characteristic and pleasant aroma. This factor is strongly linked to consumer preference and is investigated by sensory science to describe coffee brews. Thus, parameters such as colorimetric indices, foam index (ratio between foam and liquid volumes and persistence, density and viscosity, turbidity, pH and titratable acidity, total and filtered solids, lipid content, and fatty acid composition should be considered in the evaluation of the overall acceptability of coffee brews, together with flavor and taste components [4].

Foam is responsible for the coffee "crema", which is a characteristic mostly of Espresso coffees. It is produced by the release of CO_2 entrapped in the ground coffee, and its amount and stability depend on the time between grinding and coffee brewing, which for Espresso coffee should not be longer than 30 min to avoid carbon dioxide loss [5]. Coffee acidity mainly depends on the carboxylic acids (acetic, malic, and citric acids) contained in the brew, but phosphoric acid and chlorogenic acids also contribute to this parameter. Viscosity is affected by the quantity of liquid droplets in the emulsion. Turbidity, which is due to the presence of suspended particles, is directly related to total solids, filtered solids, and viscosity [6], which are, in turn, related to the coffee "body". The amount of lipids depends

on coffee variety, roasting, grinding, water quality, pressure, temperature, and extraction time. They play an important role in the retention of aroma and in foam amount and stability [7,8].

The typical odor of coffee brews is given by the large quantity of volatile compounds, the majority of which are generated through roasting. In the coffee brews, there are only very limited amounts of some sweet compounds as they degrade during the roasting, e.g., sucrose completely disappears from the green to the roasted coffee beans. Coffee sensory aroma attributes vary dramatically over each step of the coffee production chain, i.e., from the coffee bean roasting to the coffee brew. The typical smoky, roasted, nutty notes that are so appreciated in coffee brew originate from the Maillard reaction that occurs during the roasting process, in which the green coffee beans' volatile compounds precursors break into a large number of smaller volatile molecules, many of which are odor-active. The following aroma descriptors are commonly used to describe coffees in sensory assessment, according to Bhumiratana et al. [9]: coffee, roasted, burnt-acrid, brown, beany, nutty, cocoa, musty/earthy, floral, fruity, green, ashy/sooty, sweet aromatic, sour aromatic, and pungent. Coffee roasting causes the formation of typical roasted notes, as well as nutty, cocoa, and some other sweet notes. The level of roasting influences the complexity of these notes, reaching even burnt, tobacco, and chocolate notes.

Consumer tests are used when the aim is to study flavor in terms of consumer appreciation of a particular preparation or blend. These involve a large number of untrained consumers who are usual coffee drinkers, and it is mostly a preference test in which they are asked to state which product they prefer. We are not going to extensively report on the methods for food sensory analysis, e.g., quantitative descriptive analysis, as other books or scientific reviews are already available for this scope.

In the coffee sector, however, expert reviews are preferred over customer surveys. This is based on one expert assessment, who is often the roaster themselves, evaluating the roasting degree by taking samples from time to time to decide whether to stop the roasting on the basis of its appearance and odor. This method is applied to the coffee beans, while a universally applied method to assess the flavor of coffee brews is based on the so-called "cupping test" or "cupping method". This method is widely used by the coffee industry, and it is based on the assessment of the coffee beverage carried out by professional tasters. There is, however, a distinction between coffee cupping and coffee tasting, the latter being referred to as a larger variety of coffee types, for example, Espresso, single-serve coffees, etc. This is because coffee cupping uses a protocol that tries to reduce any possible external variable, make it consistent, and evaluate the drink for its intrinsic quality.

While there have been efforts to standardize this method, aiming to create a universally accepted one, e.g., Specialty Coffee Association (SCA) released guidelines for cupping, there is currently no international agreement. An ISO standard for coffee sample preparation exists [10], as well as a vocabulary for its sensory analysis [11]. The cupping method differs from a proper sensory analysis as it is carried out for other food products, for instance, for some of them, there are rigorously established international regulations, such as for virgin olive oils. In particular, the "cupper" is suggested to taste the coffee at least three times at different temperatures while the sample cools down, and then, they will discuss with other cuppers to compare or align scores. In practice, the cupper is often a single person instead of a panel of tasters. This section will not describe in detail the cupping method, for which the reader can refer to the book chapter by Revi [12] and a chapter by Lingle and Menon [13].

Several conditions are common to all food sensory analysis protocols, for example, the presence of standardized environmental conditions, while others are specific. As an example, the water should ideally have between 125 and 175 ppm of total dissolved solids,

so distilled or softened water should not be used. The water temperature should be at 93 °C. Additionally, a 5-cup setup is often used; therefore, the cupper needs to taste them consecutively in a relatively fast manner. Scoring uses descriptive language or a scale from 0 to 10, in which 6 corresponds to "good" and 9 to "outstanding", and only quartile decimals can be used. It should also be highlighted that the cupping protocol differs for Arabica and Robusta coffees and that the cupping method has obviously evolved since the traditional informal one was carried out by traders. A promotion program carried out by the International Coffee Organization (ICO) fostered the creation of the formal Specialty Coffee Association of America (SCAA) protocol for coffee cupping, which was initially developed for Brazilian Arabica coffees. The protocol is based on a scale of 100 total points and evaluates the following 10 attributes: (1) fragrance/aroma; (2) flavor; (3) aftertaste; (4) acidity; (5) body; (6) uniformity; (7) balance; (8) clean cup; (9) sweetness; and (10) overall. For details on the method, the reader can refer to Lingle and Menon [13].

In order to help producers and better define quality parameters, the SCAA created the Specialty Coffee Institute (SCI), which then became the Coffee Quality Institute (CQI), which developed the Q Coffee System, based on the SCAA cupping method. Efforts have also been made to create a similar method for the evaluation of Robusta coffees, especially in Uganda. Given its wide training program and its use in several countries, this system can be regarded as the closest to an international standardized method.

It should also be noted that recently, some researchers developed a coffee taster flavor wheel in an extensive work involving above 70 experts, in collaboration with the SCAA. This way, these descriptors can hopefully be used in a standardized manner by the coffee experts, industry, and even in marketing when communicating with the consumers [14]. Serving temperature has also been shown to exert a significant sensory impact on the flavor perception of coffee brews. This topic is extensively discussed in the final section of this review.

3. Coffee Brewing Methods

3.1. Description of the Beverage Preparation

Coffee brewing is substantially a solid–liquid extraction, sometimes referred to as 'leaching', which is the removal of a soluble fraction from a solid material. While coffee brewing is based on extracting coffee compounds using hot water, the methods used can be different. There are methods based on decoction, in which the ground coffee remains in contact with hot water for a considerable period of time; infusion methods, in which the contact time is shorter; percolation, based on continuous recirculation of the hot water; filtration, in which the hot water passes through a filter (either a paper one, a metal one, etc.); some authors also report pressure methods, based on the application of a pressure higher than the atmospheric one to the coffee, even if they can be considered as filtration as well. A summary of the main parameters characterizing each type of coffee brew, with indication of the typical values, is reported in Figure 1.

- *Cold drip and cold brew*: These types of preparation involve the use of cold water. In the first case, the water passes through a bed of ground coffee, typically using a very slow flow rate, such as 1 drip per second. In the latter type, the extraction water is left in contact with the ground coffee for a long time, usually 8–24 h. The difference between the two preparations is that cold drip requires a shorter time, e.g., 2 h, as the extraction is based on a continuous 'washing out' of the bioactive constituents over time instead of slowly reaching an equilibrium between the solid and liquid phase. Cold brews have lower content of total titratable acids and lower antioxidant activity compared to hot brews, as well as lower content of total solids and caffeine. The equilibrium for some compounds is reached after several hours. For example, when comparing

the content of 3-chlorogenic acid in cold brew and French press, it was shown that the equilibrium is reached between 6 and 7 h, reaching a concentration similar to the French press coffee [15]. In terms of sensory description, coffee brews have stronger intensity of 'sweet', 'fruity', and 'floral' aroma attributes, and a creamy body [16]. This brewing method leads to an aromatic coffee that retains some volatile compounds, which are typically lost at high temperatures.



Paramiters	Filtered (Americano)	Espresso	Turkish/ Greek	French press	Moka	Napoletana	Cold drip/ cold brew
Temperature (°C)	~90-96	88-95	~100	~90	~110	<100	4-25
Pressure (bar)	0	8-19	0	~0	1-2	0	~0
Water to coffee ratio	~13-20	3.5-6	~20	~15-20	~9-15	~10-15	~4-15
Particle size	Coarse	Medium	Fine	Coarse	Medium	Coarse	Medium
Compactation	No	Yes	No	No	Yes	Yes	No
Brewing time	3-10'	25-40''	5-10'	2-5'	3-5'	5-8'	2-24 h

Figure 1. The main parameters characterizing each type of coffee brew ' = minute, '' = second.

- *Boiled coffee*: This method involves boiling water and ground coffee for relatively long times, even up to 10 min. It has been reported to have higher concentrations of cafestol and kahweol.
- *Turkish/Greek coffee*: It is prepared using a special pot called ibrik, in which the brew is prepared by using very finely ground coffee. This is necessary so that coffee can sediment easily, but still part of the coffee powder ends up in the coffee cup; therefore, the customer has to be careful not to drink the whole cup. Also, the customer has to request whether they prefer sweet coffee as sugar is added together with the ground coffee to the water before boiling it. The maximum brewing time should not exceed 3 min; however, after a first boiling phase, the pot is put back to boil so that a thick foam is obtained. Traditionally, for Turkish coffee, there are four levels of sweetness to define the brew, and sometimes, milk is added [17].
- *Plunger coffee/French press*: Ground coffee and hot water are added to a cylindrical container, then left to rest for a few minutes, and finally, the top of the container holding a metal filter is pressed so that it retains the solid particles. The plunger is pushed down manually; therefore, the pressure applied is typically 0.5 bar, and the contact time is typically 2–5 min, depending on the consumer's preference.
- *Filter coffee/Americano*: It is basically a filtration process in which hot water is added to a filter containing ground coffee. The paper filter allows water to pass through the ground coffee only once, and this process is important in retaining some compounds, such as lipids, together with the solids. The coffee maker adds water at the correct temperature, then waits about a minute or two so that some foam is produced due to the retained CO_2 in the ground coffee, and then, the final amount of water is added until the desired final volume.
- *Percolator coffee*: It uses a device designed to allow recirculation of the hot water through a bed of ground coffee held in a percolated chamber. Given the recirculation

of water, the extraction is very intense, giving even a strong astringent sensation to the over-extraction, together with the loss of many volatile compounds.

- *Soluble coffee*: The powder of soluble coffee is dissolved in hot water. This review will not extensively report on this kind of preparation due to its strong differences.
- *Single-serving coffees*: This method uses pods or capsules, which can be made of different materials and contain defined amounts of ground coffee. The basic process, however, does not differ dramatically from the Espresso coffee concept.
- *Special coffees with additional ingredients*: There is a wide range of niche products or specialty coffees that make this part complicated for comprehensive reporting. Suffice to say that the most common additional ingredients or 'additives' to coffees are milk or cream; however, many more can be used to add special flavors.
- *Moka*: A lower part of the coffee pod contains water, which, when it reaches the boiling point, passes through a bed of compressed ground coffee into the upper part of the moka machine, where it is stored until consumed. For the extraction process, the water typically must reach 110 °C, which corresponds to about 0.5 bar of pressure. Excessive temperatures or extraction times can, however, leave an unpleasant "burnt" flavor. It is normally suggested not to leave the pod too much on the heat source at the end of the extraction process, to avoid this burnt flavor. An additional variable might arise from the amount of ground coffee added to the pod, which influences the level of compression and then the hydraulic resistance.
- *Napoletana/Neapolitan coffee*: It is also known as "flip drip pot" because of its design. It is an ancient pod, already used commonly in Naples (Italy) before 1800. It produces a brew stronger than filter coffee but not as strong as Espresso. It is based on heating the lower part of the pod containing water, then flipping it when it is boiling, such that hot water can percolate through a beam of coffee powder entrapped between the upper and lower parts of the pod. The coffee is somehow similar to filter coffee but stronger, due to the wetting of the ground coffee during the water heating and a slightly higher water temperature during the extraction.
- *Espresso*: Espresso coffee is a relatively new coffee brew, born from an Italian innovation. It is based on an extraction at high pressure, in a rapid manner, which is also one of the meanings of the word "Espresso" (the other being "made at the moment", "made explicitly at the customer's request"). In addition to this, the final coffee of the Espresso brew is typically smaller compared to other preparations. This is particularly true for the Italian Espresso and for the "ristretto" type. The percolation time is considered ideal at about 30 s, with typically 9 bar of pressure and 90 °C for water temperature. The Espresso machine is quite complicated when compared to all other coffee brewing techniques, and the reader can refer elsewhere for details on its engineering properties [2]. Espresso coffee also differs significantly from other coffee brews from a physical point of view, as its viscosity is about double that of other coffees and it has a stronger "body". Espresso is also characterized by its "crema", which is a thick and quite stable foam. This is influenced by polysaccharides, while its persistence depends on the protein fraction. Soluble carbohydrates are usually 8 g/L in Espresso, which is approximately 15% of the total solids. Caffeine ranges between 1.2 and 4 mg/mL, depending on the coffee and the cup size. For in-depth information about foam formation, stability, and the chemistry behind these processes, the reader can refer to a chapter by Folmer, Blank, and Hofmann [18]. The type of ground coffee is coarse or medium-coarse and typically has a bimodal distribution of the particle size so that the larger ones will entrap smaller ones and "self-filtrate" during the percolation process.

Mouthfeel sensations that are particularly important for Espresso coffee perception are the so-called "body", which is described as the physical sensation when moving the tongue against the palate or gum, and the astringency. The latter is caused by the precipitation of salivary proteins that cause a lack of smooth sensations [19].

Petracco defined a fine Espresso as a product that "tastes bittersweet with an initial slightly acidic note, should display strong body and intense aroma and should be pleasantly persistent" [2]. Extraction times are short compared to all other preparations, and they should not exceed 30 s, the optimal usually considered 25–30 s, and the minimum 15 s, for example, for "ristretto". The water temperature during extraction ranges between 88 °C and 93 °C, even if other authors reported water temperatures of 92 to 95 °C, and optimal pressure ranges between 9 and 10 atmospheres (others describing pressures up to 12 bar, and several manufacturers of Espresso coffee machines [2]. A portion of ground coffee for Espresso coffee making is typically 5–8 g. The larger amount is, however, not ideal because it can create a compact cake, which disturbs the percolation. The amount of 6.5 g is often regarded as ideal for Arabica coffee, while a smaller amount is required for Robusta. In a coffee cup, especially Espresso, the emulsion of coffee lipids and the suspension of solid particles and the gas bubbles that evolve into a foam coexist and make this coffee brew particularly different from the others.

3.2. Influence of Key Parameters

When analyzing the differences in composition of coffee brews, one must consider that each coffee brewing method has peculiarities related not only to the optimal water temperature, ground coffee-to-water ratio, and coffee grinding size but also to the final volume of the coffee cup (Table 1). Regarding the latter, this also varies in relation to the individual consumer preferences, and therefore, it will affect the concentration of coffee compounds.

Table 1. Summary of the parameters affecting the coffee cup quality and composition.

Water	Ground Coffee	Extraction	Cup
Temperature	Amount	Pressure	Cup size (volume)
Volume	Particle size distribution	Flow rate	Ratio of water/ground coffee
Quality (hardness)	Compaction	Flow time	
	Shape of the coffee bed		

(Modified from Mestdagh et al. [20]).

Each coffee preparation requires a particular coffee grinding size, as the extraction would not be optimal if too fine or too coarse particles are used. Additionally, Espresso coffee requires a bimodal or multimodal distribution of the particle size in order for the finer particles to cover the empty spaces among the larger ones and, therefore, obtain an optimal extraction while retaining the smaller solids [20]. Larger particle sizes allow water to flow at a larger velocity, while an excessively small particle size can lead to filter clogging and over-extraction due to the larger surface exposure. The initial wetting of the ground coffee is thought to influence the hydrodynamic processes and, therefore, the type of extraction; however, limited information is available in the scientific literature in this regard.

Coffee particle size affects the aroma composition and the chemical properties of Espresso coffee [21–23]. Particularly, it has been reported that volatile compound extraction follows a monotonic law compared to granulometric size, i.e., the finer grinding leads to the greater extraction of volatile compounds. Another work reported that Espresso

coffee prepared using a particle size distribution of 300 µm for Arabica coffee exhibited the highest extraction of the largest number of volatile compounds, among the different grinding sizes studied (150–850 µm) [24]. The authors explained these results as possibly due to the different internal distribution of precursors and to the different non-isotropic roasting grades of the beans that could affect the kinetics of aroma compound formation based on the way the bean is crushed during the grinding phase.

The presence of coffee compounds in the coffee brew depends on the solubility of coffee constituents, which, in turn, depends on their polarity and their molecular structure. Compounds with a very strong hydrophilicity are extracted within the first few seconds of brewing, e.g., caffeine, sugars, and organic acids. Longer extraction times lead to the solubilization of compounds such as phenyl-indanes, which impact the bitterness of the brew by conferring harsh bitterness, as opposed to the pleasant bitterness given by chlorogenic acid lactones. This is also valid for volatile compounds, whose release into the brew is affected by their polarity and their interaction with Maillard reaction products. Over-extraction can also happen for odor compounds, e.g., guaiacol, 4-ethylguaiacol, and 4-vinylguaiacol, whose extraction time seems correlated with the extraction time, but can produce off-flavors when found in excessive concentration in the brew.

The major parameters that often change among the different types of coffee brews can be the following: infusion temperature and time, ground coffee-to-water ratio, and coffee granulometry.

Farah [25] reported that there is a general agreement among coffee specialists that water temperature for coffee brewing should not exceed 90–95 °C. More in depth, a temperature near 93 °C is described as optimal so that drip brewers that do not reach at least 92 °C within a prescribed time fail their certification [26]. However, the ideal temperature is characteristic of each coffee brew type. For example, changes in the profiles of the Espresso coffee machine have been reported to exert a significant impact on the sensory profile of the coffee cup. In particular, Salamanca et al. [4] compared increasing gradient from 88 to 93 °C, decreasing gradient from 93 to 88 °C, and a fixed temperature of 90 °C. The study used both Arabica and Robusta coffees. Decreasing the temperature gradient resulted in a lower foam index compared to the other two profiles, as well as lower density. The lowest total solids, however, were found for the decreasing gradient (except for washed Arabica), together with the lowest total phenolic content, total lipids (again, an opposite trend was found for washed Arabica), and chlorogenic acid content. Generally, lower temperatures are associated with lower extractions and lower total solids, together with lower caffeine content [8,16]. However, Batali et al. [26] have downplayed the role of temperature as a key factor in the quality of a cup of coffee. In fact, they found that brew strengths (expressed as total soluble solids) and extraction yield (expressed as percentage yield) are the real key parameters since they affect the coffee sensory profile. This implies that it is possible to brew at different temperatures (87, 90, or 93 °C) without detriment to quality, if the pre-established values of total soluble solids and extraction yield are achieved by adjusting the grind size and overall brew time. These quantities are linked to the water-to-coffee ratio and are displayed in the "Coffee Brewing Control Chart" by Lockart [27]. Looking at the total solid content, this parameter is influenced by the ratio between the amount of ground coffee used to the extraction water, but also by the pressure applied to it during the extraction. The quantity of soluble solids extracted during the coffee brewing process is a useful parameter to evaluate the yield. Generally, extraction yields of 18–22% are considered as adequate; below 16% means that not all the useful soluble solids have been extracted; and values above 25% are considered excessive, leading to over-extraction (except for the "torrefacto" coffee in which the added sugar allows extracting larger amounts without bringing a negative sensory impact). According to Andueza et al. [23], the ideal

water temperature for Espresso coffee was reported to be 92 °C for Arabica and Robusta, but 88 °C for Robusta "torrefacto", at which temperatures the overall acceptability reaches its maximum.

Pressure is another critical parameter to define the type of coffee brew as it affects the composition and sensory impact of the brew. Higher pressure leads to different vaporization of volatile compounds from the coffee bed, as well as higher formation of 'crema'. This is because the CO_2 entrapped in the ground coffee is forced by the water, causing a larger foam formation. For Espresso coffees, the amount and stability of the foam are critical, and it is strongly influenced by the pressure applied. The pressure for an Espresso machine commonly ranges from 7 to 9 bar, with stronger pressures leading to better foam consistency and aroma intensity. However, very high pressures, for example 11 bar, allow a higher lipid extraction and diterpene content but can lead to lower consumers' acceptance [16].

This effect might be due to over-extraction of the coffee. However, over-extraction can also arise from excessive extraction time or from an incorrect ground coffee-to-water ratio if the amount of ground coffee is excessive or the amount of water is not enough for an adequate ratio. For some preparations such as Espresso coffee, this ratio will also impact other mechanical properties of the extraction as it will influence the compactness of the coffee bed, thus impacting the bed permeability, and, consequently, a different flow rate. Andueza et al. [23] investigated the effect of water pressure on Arabica Espresso coffee, comparing 7, 9, and 11 atm. They reported that the coffees obtained at 9 atm had better crema and more key odorants related to freshness and fruity, malty, and buttery flavors [28]. Pressure values in the 7–11 bar range increase the coffee diterpene content, while pressures up to 14 bar determine the reduction of the concentration of these molecules [29]. Pressures around 12 bar maximize the extraction of total lipids [8]. A good extraction is particularly important for Espresso preparation, in which the high pressure applied allows for extracting the lipid fraction of the coffee bean and producing, at the same time, an emulsion and foam, which needs to be stable for at least 2 min after the coffee-making process. The foam is often called "crema" and it is of crucial importance in defining the Espresso coffee quality. Its stability is influenced by the protein content and the presence of melanoidins, products of the Maillard reaction. Also, water hardness is known to reduce the stability of the crema. The emulsified lipid droplets cause an increase in dynamic viscosity of the coffee, which is typically 1.14–1.34 mPa · s [20,30].

Water hardness is known to influence the quality of the coffee brew, as calcium and magnesium cations can lead to the formation of insoluble salts that can affect the heat exchange coefficient. Additionally, water pH affects the extraction of coffee constituents, thus reflecting differences in the sensory properties of the coffee. In this regard, it is known that both Ca^{2+} and Mg^{2+} are needed for a good extraction, but the flavor of the coffee brew depends on the balance between cations and bicarbonate, which acts as a buffer [31]. The common practice in home brewing and cafés is to use tap water, which is sometimes filtered. While there are a few studies regarding the impact of water quality on Espresso coffee brew, there is a lack of knowledge regarding other coffee brews.

Coffee brewing causes the acidification of the water solution due to the solubilization of coffee constituents, typically to pH values of 4.85–5.15 in Arabica and 5.25–5.40 in Robusta coffees. Gloess et al. [32] compared pH, titratable acidity, fatty acid content, and total solid of coffee brews obtained through the following 9 extraction methods: Espresso from semi-automatic machine (DE); Lungo from semi-automatic machine (DL); Espresso from fully automatic machine (SE); Lungo from fully automatic machine (SL); Espresso—NEspresso (NE); Espresso—Bialetti (Bia); Lungo—French press (Bo); Lungo—Karlsbader Kanne (KK); and Lungo—filter coffee (F). The same coffee was used for all extractions except for the single-serve capsules NEspresso. Green beans were roasted at two different degrees for

Espresso and Lungo coffees. The Espresso coffees DE, SE and NE had total solid contents of above 4% while total solids in the Lunghi were slightly more than one percent, with the highest value found for the French press (1.43 ± 0.01) and the lowest one for the filter coffee extract (1.03 ± 0.01%). NE and French press had the lowest and highest pH (5.51 and 5.92), respectively. There was no difference between the acidity of Espresso and Lungo extract, probably because the lower roasting degree of Lunghi (which may preserve acids) might have compensated for the higher dilutions. The content of esterified fatty acids was lower than 0.2% in all cases. The French press extraction showed the highest fatty acid content as a consequence of the long contact between ground coffee and hot water. It was perceivable as a film of fat covering the walls of the glass jar. Filter coffee showed the lowest content of fatty acids, since the paper filter appeared to hold them.

Asiah et al. [33] evaluated the pH, refractive index, and total dissolved solids of cold and hot brew Arabica coffee at various resting times. Hot coffees showed lower pH, higher refractive index, and higher total dissolved solids (4.70–4.85, 4.06–4.50, and 113–114, respectively) than cold brews (5.13–5.20, 3.97–4.13, and 106–111). At increasing resting times, pH and refractive index increased, independently of the brewing methods. Total dissolved solids remained unchanged with the hot coffee procedures and decreased as the resting time increased with the cold coffee procedures.

4. Effects of the Brewing Methods on Contents of Key Compounds in Coffee Brews

4.1. Caffeine and Other Methylxanthines

Caffeine (1,3,7 trimethylxanthine) (Figure 2a) is one of the most important bioactive compounds in coffee [34]. Traces of other methylxanthines, such as theophylline (1,3-dimethylxanthine) and theobromine (3,7-dimethylxanthine) (Figure 2b,c), which are caffeine metabolites, can be detected in coffee seeds [35]. But, their amounts is considerably lower than that of caffeine [36]. Methylxanthines are classified as purine alkaloids, which are secondary metabolites derived from purine nucleotides [37]. The main biosynthetic pathway contributing to the conversion of xanthosine to caffeine is a four-step sequence consisting of a first methylation to 7-methylxanthosine, a nucleosidase reaction to 7-methylxanthine, and two other methylation reactions leading to theobromine and, finally, to caffeine [38]. The major catabolic pathway is caffeine → theophylline → 3-methyxanthine → xanthine (further degraded by the conventional purine catabolism pathway to CO_2 and NH_3 via uric acid, allantoin, and allantoate). The conversion of caffeine to theophylline is the rate-limiting step in purine alkaloid catabolism and provides an explanation for the accumulation of caffeine [39].

Caffeine contributes to no more than 10% of the perceived bitterness of the coffee beverage [40] but strongly contributes to its antioxidant activity. Arabica (*Coffea arabica*) and Robusta (*Coffea canephora*) coffees differ greatly in their caffeine contents, which reach about 1.45 and 2.38 g/100 g, respectively [41]. In addition to wild coffee species of Madagascar, a caffeine-free *Coffea arabica* variety able to accumulate theobromine, the immediate precursor of caffeine, because of a deficiency in the enzyme caffeine synthase, has been discovered in Ethiopia [42]. Decaffeination is able to decrease the coffee caffeine content until it reaches one of two standards: the international standard of removing 97% of the original methylxanthine content or the EU standard requiring that decaffeinated coffee must be 99.9% alkaloid-free [43]. Instead, the term "decaffito" concerns decaffeinated coffee derived from Arabica plants with beans naturally low in or almost devoid of caffeine, and 'decaffito™' is a trademark of Brazil [35].

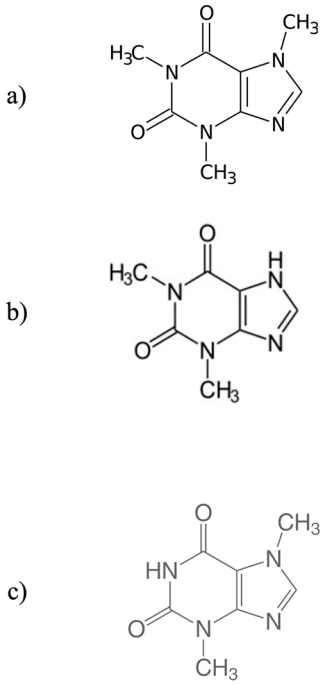


Figure 2. (**a**) Caffeine; (**b**) theophylline; (**c**) theobromine.

Since caffeine is a heat-stable alkaloid, its concentration in the green coffee is not significantly altered by roasting. Small losses can occur due to sublimation, but the loss of other compounds during roasting can result in an increase in caffeine content [25].

Caffeine stimulates the central nervous system as an adenosine receptor antagonist, and its effects on health are controversial. Low to moderate doses of caffeine are associated with higher alertness, learning capacity, exercise performance, and better mood. Its physiological effects also include diuresis, coronary vessel dilation, and gastric acid secretion stimulation. High intakes can be responsible for anxiety, tachycardia, insomnia, an increase in the urinary excretion of minerals such as calcium, negative effects on glucose tolerance, glucose disposal, insulin sensitivity, high blood cholesterol, coronary diseases, and cancer. However, most negative effects have a duration limited to the coffee half-life (2–6 h after intake) and disappear because of metabolic adaptations in the body [25]. Caffeine also exhibits antioxidant and antimicrobial activities as demonstrated by the lower effects exerted by decaffeinated coffee [44,45].

Jeszka-Skowron et al. [46] published a comprehensive review on the most important analytical methods applied to quantify the major bioactive compounds in coffee. Based on this paper, caffeine is usually determined in coffee samples by high-performance liquid chromatography ultra-violet (HPLC-UV) detector at 270–280 nm with a preliminary simple preparation that consists of operations such as filtration, clarification, water dilution, and water or solid phase extraction. The HPLC procedure is then carried out in a reverse phase elution mode with an octadecylsilica-packed column. HPLC coupled with mass spectrometry can be alternatively used to determine theobromine and theophylline. Other rarely used chromatographic techniques include gas chromatography–mass spectrometry (GC–MS), preceded by drop-to-drop microextraction with chloroform, and micellar electrokinetic chromatography (MEKC) with ultraviolet absorbance detection, preceded by chloroform extraction, evaporation, and reconstitution into water. Among the non-chromatographic methods, the following deserve mention: direct analysis in real-time ionization (DART)—high-resolution mass spectrometry; Fourier transform infrared (FTIR) spectroscopy of the chloroform extracts in combination with attenuated total reflectance

(ATR) techniques; ultra-violet (UV) spectrometry; voltammetry; gravimetric analysis; and paper substrate phosphorescence.

The amount of caffeine extracted from coffee powder is strongly affected by the brewing method used since each brewing method involves a specific ground coffee-to-water ratio, time–temperature profile, filtration/boiling step, and volume of the final beverages. Since the topic has been investigated by many researchers, this section can be intended as a comprehensive overview of the literature concerning the influence of different coffee drink preparations on the amount of caffeine detectable in a cup of coffee. Contrasting results have been reported on this matter. Some research papers indicated that moka leads to the highest caffeine extraction, with almost no caffeine found in the spent coffee [30]. Others indicated that this happens for filter coffee makers, with 75 to 85% of caffeine extraction observed for Espresso [2] and 66–75% for plunger coffee makers [47]. A good coffee maker should avoid over-extraction and under-extraction to obtain the best coffee brew for each type of preparation. Under-extraction will lead to an acidic-sweet coffee, while an over-extracted brew will have unpleasant bitter and astringent notes.

A quantitative study of caffeine in five different coffee (100% Arabica) preparations, namely, Americano, moka, Italian Espresso, Neapolitan, and Turkish, was performed by Santini et al. [48]. They extracted caffeine with chloroform and spectrophotometrically determined its content at 270 nm. The average caffeine contents were detected in the considered samples in the following decreasing order (Figure 3): moka, Italian Espresso, Turkish, Neapolitan, and Americano. To express the amount of caffeine per served cup, the following drinks' average volumes were considered: espresso 25 mL, Neapolitan and moka 30 mL, Turkish 50 mL, and Americano 150 mL, and the calculated caffeine intakes per served cup are reported in Figure 3.

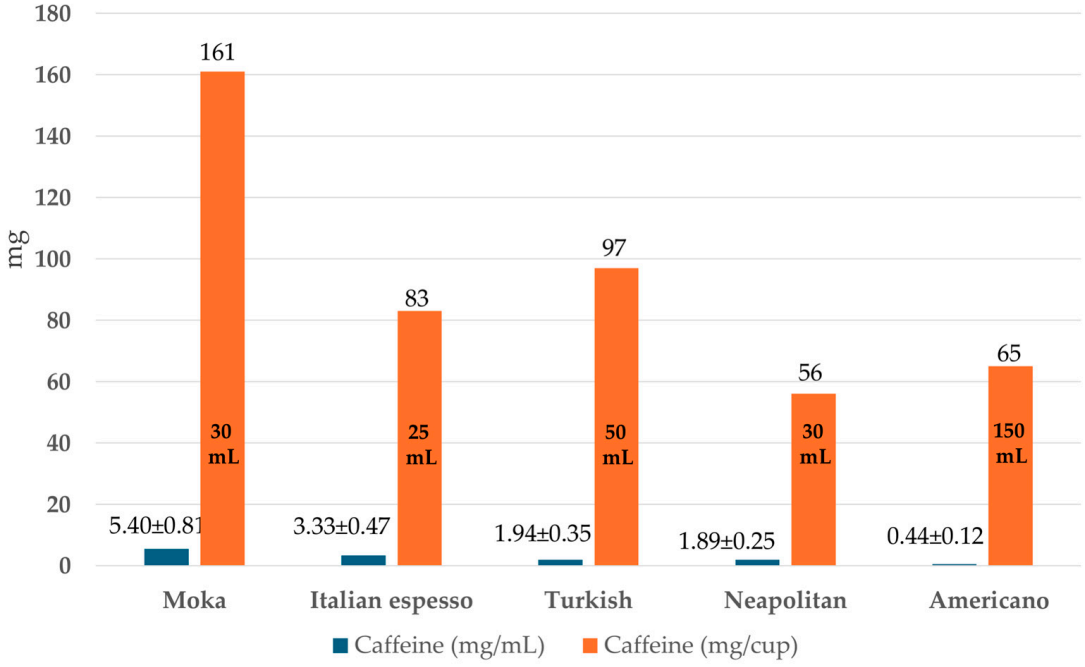


Figure 3. Concentrations of caffeine in coffee brews produced according to several methods (elaboration of data of Santini et al. [48]). The volumes of served cups are reported in the corresponding bars.

Santini et al. [48] also measured the hydrophilic and lipophilic antioxidant activity and detected the highest antioxidant activity values in Neapolitan and Turkish coffees, regardless of their relatively low amount of caffeine. The lowest lipophilic and hydrophilic antioxidant activity was observed in the Americano coffee, while the moka preparations showed hydrophilic antioxidant activity similar to that detected in the Neapolitan and

Turkish coffees, but low lipophilic antioxidant activity. The absence of correlations between caffeine content and antioxidant activity is related to the presence of other antioxidant compounds, such as melanoidins and phenolics.

Evaluations of the effects of roasting level (light, medium, and dark), grinding degree (fine, fine-coarse, and coarse), and brewing methods (espresso, Americano, and Turkish) on the caffeine contents were performed by Severini et al. [49]. The content of caffeine, quantified by HPLC, exhibited the highest value for dark coffee, confirming the results of Farah [25], and for the fine grinding level, which affected the kinetics of extraction by increasing the percolation rate. Concerning the brewing method, the highest caffeine content per mL of beverage was detected in Italian espresso, followed by Turkish coffee and Americano. But, due to the different volumes of the final beverages, a regular cup of Espresso (25 mL) contained from 80 to 120 mg of caffeine, while a regular cup (200 mL) of Americano coffee supplied from 280 to 350 mg of caffeine.

The already cited research of Gloess et al. [32] compared the caffeine contents of coffee brews obtained through 9 extraction methods. Caffeine was previously extracted with methanol and the Carrez reagents and then analyzed by high-performance liquid chromatography with diode array detection (HPLC-DAD) at 272 nm. The results were expressed as mg per 10 mL of coffee extract, which corresponds to the amount of coffee brewed in one sip. The highest concentration of caffeine per sip of coffee was measured in the Espresso coffees. The highest caffeine concentrations (21.0 $\pm$ 0.4 mg) were detected in DE, then the contents decreased from SE, NE, Bia to Lunghi DL, SL, Bo, KK, and FF (4.7 $\pm$ 0.1 mg).

Caporaso et al. [50] compared the caffeine contents of coffee brews produced according to 4 brewing procedures, namely, Americano, Neapolitan, moka, and espresso, starting from a batch of Arabica 100% coffee, having a medium-high level of roasting and particle size of 0.35 mm. Quantification of caffeine was performed by HPLC-DAD at 278 nm. The caffeine concentration ranged from 2.44 mg/mL of Espresso (this high value was explained by the low volume of water and the higher operating pressure) to 1.30 mg/mL of Neapolitan. Americano (1.39 mg/mL) and moka (1.68 mg/mL) coffee brews showed caffeine contents comparable to those of the Neapolitan one. The Americano brewing procedure showed the highest caffeine extraction efficiency (12.75 mg/g ground coffee). Besides the similarities between Americano and Neapolitan brewing procedures, the caffeine yield of the Americano brew was almost double with respect to the Neapolitan brew, due to the time of contact between coffee and hot plate and the higher temperature reached.

Some researchers focused their attention on the caffeine content of decaffeinated coffee drinks. McCusker et al. [51] published the results of the caffeine analyses of 10 decaffeinated samples purchased from coffee shops and eating establishments in Maryland (USA). Caffeine contents, isolated from the coffee by liquid–liquid extraction and analyzed through a gas chromatography (GC) system equipped with a nitrogen–phosphorus detector, were in the range of 0–13.9 mg per 16 oz serving (equal to ~573 mL). The researchers also analyzed 6 decaffeinated espresso coffee beverages, detecting from 3.0 to 15.8 mg of caffeine per shot. The variability in the Espresso was attributed to the human manipulation involved in its preparation.

Specialty coffees deserve a separate discussion. McCusker et al. [52] performed a survey on the caffeine contents of 20 caffeinated (6 espresso and 14 brewed coffees) and 7 decaffeinated specialty coffee samples obtained from coffee shops in Maryland (USA). The analysis of caffeine was performed as in McCusker et al. [51]. The coffees sold as decaffeinated were found to have caffeine contents lower than 17.7 mg/dose. A wide range of caffeine content was detected in caffeinated coffees (58–259 mg/dose). The mean caffeine content of the brewed specialty coffees was 188 $\pm$ 36 mg per 16 oz serving.

Some researchers devoted their studies to the analysis of caffeine content in coffee brands sold in a specific country market. Phan et al. [53] focused their attention on 5 brands (Dak Tin, Di Linh, Nam Nguyen, Origin and Vinacafe) of ground roasted coffee purchased in the Vietnamese market and investigated the influence of temperature (80, 90, and 100 °C), water volume (30, 70, and 150 mL), and extraction time (1, 3, and 5 min) on the coffee brew caffeine. Caffeine was spectrophotometrically quantified at 273 nm. According to their results, caffeine content was strongly dependent on the temperature of water and brewing lengths but independent of water volume. The highest amount of caffeine was found in Vinacafe (54.30 ± 0.470 μg/mL) at 90 °C for 5 min, while the lowest was found in Dak Tin (19.40 ± 0.232 μg/mL) at 90 °C for 1 min. The order of caffeine contents in coffee samples was Dak Tin, Di Linh, Nam Nguyen, Origin, and Vinacafe. Crozier et al. [54] analyzed the caffeine contents of single-shot Espresso coffees purchased from 20 different outlets in Glasgow. Analyses were performed through high-performance liquid chromatography with photodiode array detection (HPLC-PDA) at 280 nm. According to the results, the amount of caffeine per serving ranged from 51 to 322 mg. In particular, three samples contained more than 200 mg, exceeding the 200 mg day upper limit recommended during pregnancy by the UK Food Standards Agency. This large variability in caffeine content could be due to several factors, such as the amount of coffee used to prepare a serving of Espresso, batch-to-batch differences, roasting procedures, grinding conditions, and the coffee-making/barista process (temperature of water/steam in the extraction vessel, its duration, coffee/water/steam ratio, etc.).

In recent times, coffee brews can be produced according to new brewing procedures known as cold extraction methods, which involve longer extraction times at room or colder temperatures instead of the traditional rapid exposure to high temperatures. However, few studies have investigated these extraction methods despite their increasing popularity. Angeloni et al. [55] investigated the coffee beverages obtained by cold brewing and cold drip. Starting from the same batch of 100% Arabica, two temperatures (5 and 22 °C) and two powder–water contact times (3 and 6 h for cold brew; 1 drop/5 s and 1 drop/10 s for cold drip) were tested. The French press extraction was used as a benchmark. Caffeine was analyzed by HPLC-DAD at 278 nm and a high-performance liquid chromatography time of flight (HPLC-TOF) mass spectrometer. The highest caffeine contents were found for the slow cold drip at 22 °C (1.267 ± 0.152 mg/mL). This result was due to the continuous renewal of the extraction solvent that, while allowing for maintaining a high concentration gradient, facilitated the matter transfer from the solid to the liquid phase. Among the cold brew experiments, the best results were obtained at 22 °C for 10 h (0.973 ± 0.124 mg/mL), but no significant differences in caffeine content were found between the two contact times. French press coffees contained 1.09 ± 0.11 mg/mL of caffeine.

Olechno et al. [56] performed a complete review of the studies published from 2010 to 2020, with the aim of summarizing the effects of various factors (species, geographical origin, brewing time, water temperature and type, pressure, roasting degree, grinding degree, and water/coffee ratio) on caffeine contents of coffee brews prepared using different methods. Water pressure and type of water do not seem to be a decisive factor for caffeine extraction. Concerning the methods of growing, nitrogen fertilization can increase the amount of caffeine. Regarding the place of cultivation, altitude exerts a positive effect on the caffeine content of Arabica beans. The same authors also observed that the influence of species depends on the brewing methods. Although Robusta coffee genetically has more caffeine than Arabica, a brew of Arabica contains more caffeine (from 0.330 ± 0.020 to 0.410 ± 0.020 g/L) than a brew of Robusta (0.150 ± 0.010 g/L) when prepared in a coffee machine. Instead, Robusta contains more caffeine than Arabica brews if made by pouring hot water and in a percolator [57]. Caprioli et al. [58] showed that the content

of caffeine decreased with the extension of extraction time due to a dilution effect. Water temperature significantly affects the caffeine content due to the increase in solubility that is equal to 1.46 mg/mL at 20 °C, increases to 180 mg/L at 80 °C, and reaches its maximum at 100 °C (670 mg/mL) [59].

4.2. Phenolic Compounds

The most representative phenolics in coffee bean are chlorogenic acids (Figure 4), which include the following compounds: 3 isomers (3-, 4- and 5-) of caffeoylquinic acid (CQA); 3 isomers (3,4-, 3,5-, 4,5-) of dicaffeoylquinic aci (diCQA); 3 isomers (3-, 4-, and 5-) of feruloylquinic acid (FQA); 3 isomers (3-, 4-, and 5-) of *p*-Coumaroylquinic Acid (*p*CoQA); and mixed diesters of caffeoylferuloylquinic acid (CFQA). CGAs are known to influence flavor since they contribute to acidity and confer astringency and bitterness [60].

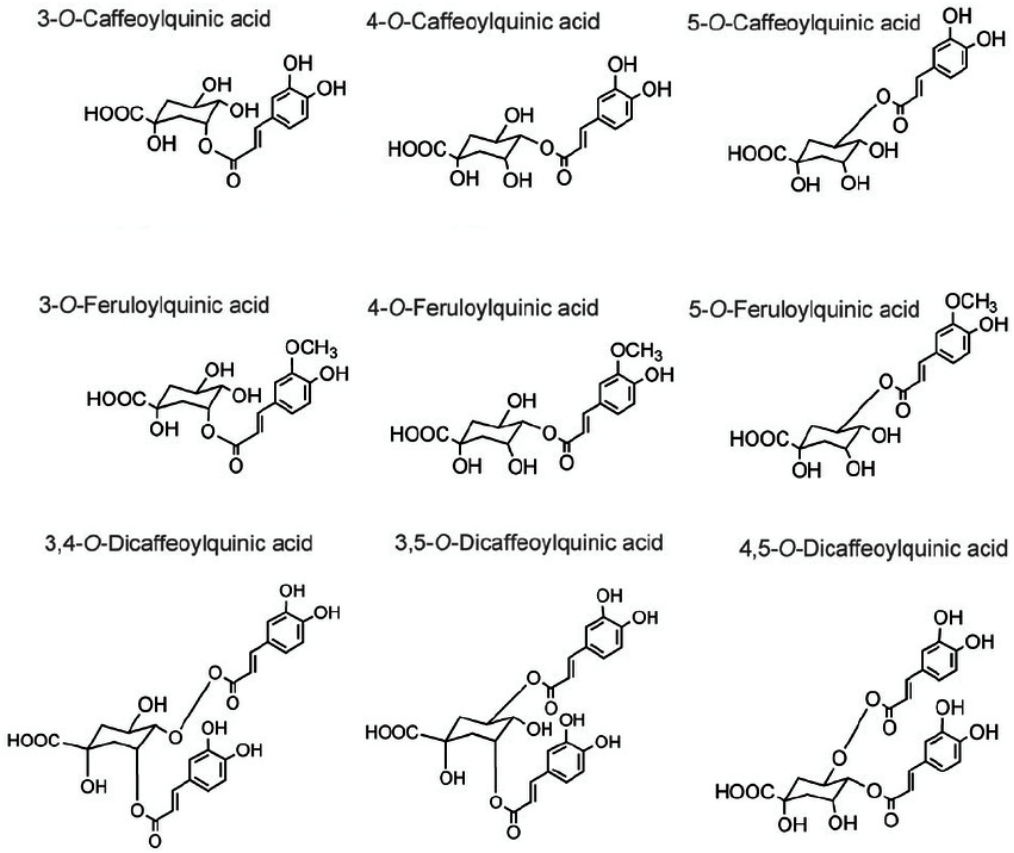


Figure 4. Chlorogenic acids.

The initial steps in the biosynthesis of CQAs are via the phenylpropanoid pathway, and the enzymes catalyzing the conversions that produce 5-CQA are known. The conversion of phenylalanine to *p*-coumaroyl-coenzyme A (*p*-coumaroyl-CoA), with cinnamic acid and *p*-coumaric acid acting as intermediates, is catalyzed by phenylalanine ammonia lyase, cinnamate 4′-hydroxylase, and 4-cinnamoyl-CoA ligase [61]. From the *p*-coumaroyl-CoA, three possible pathways are proposed, and each involves the same types of enzymatic reactions: esterification and hydroxylation. In detail, the conversion of *p*-coumaroyl-CoA to 5-CQA involves the enzymes hydroxycinnamoyl CoA:quinate hydroxycinnamoyl transferase and a cytochrome P450 oxidase *p*-coumaroyl-3′-hydroxylase. There is less clarity about the later stages of the pathway leading from 5-CQA to other acyl-quinic acids.

The total content of chlorogenic acids in green coffee beans depends on species, degree of maturation, agricultural practices, climate, and soil. Organic coffee beans seem to show higher content of bioactive compounds (total phenolic, phenolic acids, and flavonoids) than

conventional coffee beans [62]. Concerning the effect of roasting, the 'native' polyphenols of the green beans are significantly lost, especially at high temperature (reduction by ~60% for light, 67% for medium, 88% for dark, and 96.5% for very dark roast in Arabica coffee, while melanoidin contents increased [49,63].

From an analytical point of view, chlorogenic acids can be easily extracted with a methanol/water mixture, filtered, and directly injected into an HPLC apparatus [64] equipped with a UV or a DAD detector or in a high-performance liquid chromatography mass spectrometry (HPLC-MS) system. Alternative extraction techniques include microwave-assisted extraction and extraction using boiling water under elevated pressure [65,66]. Other alternative techniques include electroanalytical methods, especially voltammetry (differential pulse voltammetry, square-wave voltammetry, and adsorptive stripping voltammetry). These methods are simple, fast, and inexpensive but not selective [46].

The already cited research of Gloess et al. [32] compared the chlorogenic acid contents of the 9 extraction methods. Chlorogenic acid was extracted from the sample using the same procedure described for caffeine and quantified by the same HPLC-DAD method at 323 nm. The differences in the roasting degree between Espresso and Lungo coffees affected the chlorogenic acid contents of the starting coffee beans, but they were closer to a typical consumer's situation. Espresso coffees showed the highest concentrations. The amounts of 3-CQA per sip ranged from 1.83 ± 0.05 mg of F sample to 5.8 ± 0.2 mg per DE coffee, while the amounts of 5-CQA ranged from 0.78 ± 0.04 mg of KK to 2.8 ± 0.2 mg of DE coffee.

In the research of Angeloni et al. [55] on the comparison of cold brew and cold drip extraction, CGAs were analyzed by HPLC-DAD at 330 nm and HPLC-TOF mass spectrometer. Fourteen CGAs were detected in coffee samples. Concentrations increased with temperature, regardless of the extraction method and contact time. The highest concentrations were found in coffees obtained by drip extraction at ambient temperature. More specifically, the highest concentration of 5-CQA was 0.37 ± 0.07 mg/mL, while that of the sum of the other CQAs was 0.51 ± 0.08 mg/mL. Such concentrations were similar to those obtained with the French press extraction (0.39 ± 0.03 mg/mL for 5-CQA and 0.51 ± 0.12 mg/mL for the sum of other CQAs).

The already cited research of Crozier et al. [54] also considered the CQA contents of the Espresso coffees sold in Glasgow. The CQA content varied from 24 to 422 mg per serving. The main chlorogenic acid in all the coffees was 5-CQA (41–58% of the total CQA), with smaller amounts of 3-CQA (13–36%) and 4-CQA (23–33%).

Tfouni et al. [67] evaluated the effects of coffee cultivar (*Coffea arabica* cv. Catuaí Amarelo and *Coffea canephora* cv. Apoatã), roasting degree (light, medium, and dark), and brewing procedure (filtered coffee and boiled coffee) in the presence and transfer of caffeoylquinic acids (CQAs) from ground roasted coffee to the brews. The sum of CQA isomers ranged from 24.2 mg/100 mL to 295.6 mg/100 mL for *Coffea arabica* and from 30.4 to 253.8 for *Coffea canephora*. The percentages of 5-CQA ranged from 33 to 43% and from 34 to 41% of the sum, respectively. Brews prepared with dark-roasted coffees showed that CQA levels reduced up to 91%. Concerning brewing procedures, boiled coffees showed higher content of CQAs than the corresponding filtered ones. Boiled brews prepared with light-roasted coffee greatly contribute to the CQA intake, with 671.0 mg per day for *Coffea arabica* and 576.1 mg per day for *Coffea canephora*.

Rao and Fuller [68] investigated the concentrations of three caffeoylquinic acid isomers in cold and hot brew coffees prepared with light roast coffees from Brazil, Ethiopia, Colombia, Myanmar, and Mexico. Analyses were performed by HPLC-DAD at 325 nm. The total CQA contents ranged from 2503 ± 103 to 3270 ± 90 mg/L in hot brew coffees

and from 1616 ± 111 to 2201 ± 53 in the cold ones. In both types of brews, 5-CQA was the most representative isomer, accounting for over 50% of the total CQA. Although cold brew coffee is often preferred by consumers suffering from gastrointestinal symptoms due to its lower acidity, it shows a lower chemoprotective effect (against oxidation) than the hot brew ones.

Moeenfard et al. [69] used HPLC-DAD at 325 nm to analyze the concentrations of the main caffeoylquinic acids in 24 coffee brews. The major isomer was 3-CQA (about 50% of the total CQAs), while 5-CQA and 4-CQA accounted for about 24–36% of each one. The total content of CQAs was in the range of 45.79 (iced cappuccino) to 1662.01 mg/L (pod Espresso), and in general, coffee brews prepared using pressurized methods were the greater sources of CQAs (Figure 5).

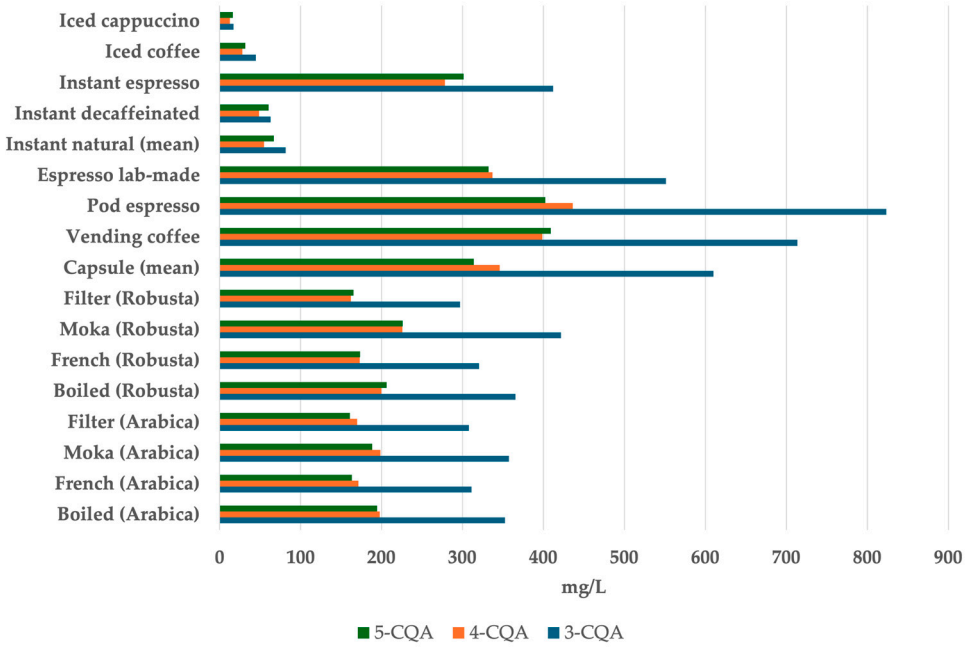


Figure 5. Concentrations of 3-, 4-, and 5-caffeoylquinic acids in different coffee brews (elaboration of data of Moeenfard et al. [69]).

Many papers concerning the coffee antioxidant compounds use synthetic indices such as total phenolic content, total flavonoids, and condensed tannins since their spectrophotometric determination requires faster and less expensive analyses than the chromatographic methods.

Beder-Belkhiri et al. [70] investigated both the hydroxycinnamic acid profiles by ultra-high-performance liquid chromatography coupled with diode array detection and electrospray ionization mass spectrometry (UHPLC-DAD-ESI-MS) and the total phenolic profile according to the Folin–Ciocalteu method of green dark-roasted coffee beans and coffee brews prepared from a blend of Arabica and Robusta 20:80 using moka, Turk, and filter procedures. Arabica and Robusta dark-roasted beans had similar chromatographic profiles, rich in caffeoylquinic acid and feruloylquinic acid isomers. Green beans showed the total phenolic content (TPC) (4.59 ± 0.03 for Arabica and 3.88 ± 0.15 g/100 g of dry matter for Robusta) lower than that of roasted coffee beans (5.68 ± 0.04 and 5.43 ± 0.09, respectively). Concerning the effects of the brewing procedures, filter and moka coffees showed higher levels of TPC (0.69 ± 0.05 and 0.70 ± 0.04 g/100 g of dry matter) than the Turkish brew (0.47 ± 0.01 g/100 g of dry matter).

In a work of Kaur et al. [71], the effects of 11 brewing methods on total flavonoid and phenolic content, expressed as mg of quercetin equivalent per g of coffee, of green coffee *Coffea arabica* and *Coffea canephora* were evaluated. The brewing methods were as follows:

soft infusion, hard infusion, ambient infusion, cold infusion, decoction method, chilled green coffee, cold cocktail, hot cocktail, pour-over method, overnight brewing, and French press. The coffee species showed different behavior when subjected to the same brewing methods. Concerning Arabica coffee, the flavonoid content ranged between 7.53 mg/g (pour-over method) and 69.24 mg/g (decoction method) and the total phenolic content ranged between 72.78 mg/g (pour-over method) and 108.67 mg/g. Concerning Robusta coffee, the highest (57 mg/g) and the lowest (10.35 mg/g) flavonoid contents were detected for cold cocktail and overnight brewing, respectively, while the highest (93.33 mg/g) and the lowest (71 mg/g) total phenolic contents were detected in overnight brewing/chilled green coffee and pour-over method.

Ormaza-Zapata et al. [72] studied the antioxidant metabolites of coffee beverages prepared from *Coffea arabica* using five methods of pressure filtration, namely, Aeropress, Presso, Staresso, espresso, moka, or home espresso. The authors found the highest total phenol concentration in Espresso coffee (5306.2 mg of gallic acid/100 g), followed by Moka (2929.3), and Staresso (2170.3). The lowest phenolic concentrations detected in Aeropress and Presso coffee brews can be explained by the dilution effect of these methods. The flavonoid concentrations, expressed as mg of catechin equivalent/100 g sample, followed the same order: espresso, moka, and Staresso methods, with values of 10,705.2, 3003.1, and 2352.6 mg, respectively. The concentrations of condensed tannins were the highest in Espresso brews (197.4 mg of catechin eq./100 g sample), followed by Staresso (129.5 mg) and Presso (118.1 mg). The Aeropress coffee brew showed the lowest tannin content. Concerning hydroxycinnamic phenolic acid, chlorogenic acid content was the highest for the Staresso brews, which also contained caffeic acid. The highest *p*-coumaric acid contents were detected in espresso and moka brews, which also showed the highest ferulic acid content, together with Staresso coffee.

An interesting work of Ludwig et al. [73] explored the extraction behavior of the main coffee antioxidants during brewing time in filter and espresso coffee brews. In Espresso coffee, more than 70% of the antioxidants of a coffee brew were extracted at the beginning of the brewing process (during the first 8 s), while the last fraction (16–24 s) only accounted for 1–2%. In filter coffee, a U-shape antioxidant extraction profile was observed, with the highest antioxidant concentrations detected in the first and last fractions, and the lowest found in the intermediate fraction.

Olechno et al. [74] investigated the effect of various types of starting materials (instant Arabica and Robusta, freshly ground Arabica and Robusta, ground Arabica and Robusta, decaffeinated Arabica, and green Arabica and Robusta) and various brewing methods (pouring hot water over, percolator, coffee machine) on the total phenolic content (TPC) of the coffee brews. The highest TPC (657.3 $\pm$ 23 mg/100 g infusion) was obtained for 100% Arabica ground coffee prepared in a percolator with unfiltered water at 100 °C. According to Nosal et al. [75], the capsule has higher total phenolic content than French press, and the corresponding brew leads to a higher body's antioxidant status.

4.3. Melanoidins

Melanoidins are macromolecular, nitrogenous, brown-colored Maillard reaction end-products, formed by cyclizations, dehydrations, retroaldolizations, rearrangements, isomerizations, and condensations of initial Maillard reaction products [76]. Although their chemical structures are not clarified, it was suggested that coffee melanoidins incorporate chlorogenic acids, protein fragments and that polysaccharides or their fragments are likely involved in melanoidin formation [77,78].

The interest in these compounds is related to their numerous properties: contribution to color formation; ability to bind flavors; ability to exert antioxidant, anti-inflammatory,

antihypertensive, and antiglycative activities; metal-chelating properties; and the related antimicrobial activity [79–82].

The most applied approach to coffee melanoidin isolation is based on their high molecular weight and consists of applying dialysis tubing, ultrafiltration with 10 kDa cut-off membranes, and column gel permeation for molecular exclusion separation of melanoidins and subsequent gravimetric estimation. Other rapid procedures are based on the color potency of melanoidins and on the measure of the absorption at wavelengths higher than 400 nm [83].

The amount of melanoidin in the cup varies with the roasting degree and coffee brew preparation (type of extraction, powder/water ratio, pressure, and serving size).

Vignoli et al. [84] investigated the effect of raw materials (*Coffea arabica* and *Coffea canephora* species), roasting degree (light, medium, dark), and extraction system of the soluble powder (conventional and double-extraction) on the melanoidin content of soluble coffee isolated by dialysis membrane separation system. The melanoidin content, expressed as g per 100 g of sample, ranged from 19.66 ± 2.04 to 30.44 ± 1.84. The soluble coffees produced from *Coffea canephora* showed significantly higher melanoidin contents than *Coffea arabica*, and the double-extraction system was more effective in extracting melanoidins. Concerning the effects of roasting, the concentrations of melanoidins were in the following decreasing order: dark > light > medium.

Fogliano and Morales [83] investigated the melanoidin contents of coffee brews prepared from roasted Arabica coffee powder according to the following procedure: Italian (moka coffee pot), filter (drip electric coffee maker), and espresso (food service industry coffee maker). To isolate melanoidins, the coffee brews were filtered, defatted with dichloromethane, and subjected to ultrafiltration using a 10 kDa nominal molecular mass cut-off membrane. The retentate was washed, and the high molecular weight fraction corresponded to melanoidins. The amounts per serving cup were in the following decreasing order: filter (233.9 mg), espresso (111.6 mg), Italian (99.3 mg); while if expressed per mL, the order became as follows: espresso (2.2 mg), filter (1.8 mg), Italian (1.6 mg). Generally, instant coffee showed higher melanoidin contents than other types of coffees due to the process that concentrates the components found in roasted coffee [85].

Melanoidins have an active role in reducing the perception of the typical aroma of freshly brewed coffee. Unfortunately, significant molecular alterations able to reduce the olfactory quality of coffee brews can be traced back to the binding of aroma active compounds to non-volatile coffee constituents, such as low and high-molecular-weight coffee constituents. More in depth, aldehydes and non-aromatic thiols covalently react with melanoidins; pyrazines and methoxyphenols form non-covalent interactions, most likely in the form of π-π stacking; and the aromatic components interact both in covalent and non-covalent ways [86].

Machado et al. [87] performed an in vitro study of human colonic fermentation of fractions isolated from coffee, rich in arabinogalactans or melanoidins. They observed a higher fermentability of the carbohydrate fraction of arabinogalactans than that of melanoidins, which resulted in short-chain fatty acid content of 63 mM and 22 mM, respectively. The presence of melanoidins reduced the production of bile acids, whose high content is associated with neurodegenerative and cardiovascular diseases and colorectal cancer. Moreover, the fermentation of coffee fractions resulted in the release of di-hydroferulic and di-hydrocaffeic acids, both known for their antioxidant activity.

4.4. Minor Compounds

Among the bioactive compounds detectable in coffee, the alkaloids trigonelline and β-carbolines and the diterpens cafestol and kahweol deserve a separate discussion.

4.4.1. Trigonelline

Trigonelline (N-methyl nicotinic acid) (Figure 6) is a nitrogenous compound derived from the methylation of the nitrogen atom of nicotinic acid (niacin) and represents the second main alkaloid found in green coffee beans.

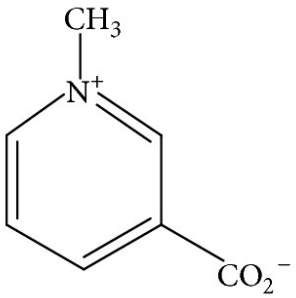


Figure 6. Trigonelline.

During the roasting process, trigonelline undergoes a strong thermal degradation, thus generating most of the volatile compounds responsible for coffee flavor and aroma [36]. Its concentrations are also used to discriminate the coffee roasting level [88]. During roasting, trigonelline demethylation results in nicotinic acid, i.e., a form of niacin or vitamin B3 [89]. The contents of trigonelline and nicotinic acid in coffee brews are highly influenced by coffee species (Arabica shows slightly higher trigonelline content than Robusta coffee beans), variety, geographical origin, and roasting conditions [88,90], while it does not seem to be affected by the brewing method [91].

Trigonelline is supposed to impart bitterness to coffee brew, and its derivative compounds formed during roasting, such as pyridines and pyrroles, contribute to the global coffee aroma and flavor.

Fast liquid chromatography–mass spectrometry (LC–MS) method for the simultaneous analysis of caffeine, trigonelline, nicotinic acid, and sucrose are available, as well as the proton nuclear magnetic resonance (^{1}H NMR) technique, which is useful for the quantitative and simultaneous determination of trigonelline, caffeine, formic acid, and 5-(hydroxymethyl)-2-furaldehyde [92].

Poerner, Rodriguez, and Bragagnolo [93] performed a study on the trigonelline content of regular and decaffeinated roasted ground coffee brews and regular and decaffeinated soluble coffee brews. Trigonelline was measured by HPLC-DAD at 262 nm. The trigonelline contents of coffee brews (expressed as mg/100 g of dry matter) were in the following decreasing order: decaffeinated roasted ground coffee, 2985.3 $\pm$ 245.4; regular roasted ground coffee, 2043.7 $\pm$ 710.7; decaffeinated soluble coffee, 1247.6 $\pm$ 77.7; regular soluble coffee, 631.3 $\pm$ 98.5. The lowest levels of trigonelline in soluble coffee brews were attributed to the use of greater proportions of *Coffea canephora* in the blend formulation.

Using ultra-high-performance liquid chromatography–tandem mass spectrometry (UHPLC-MS/MS), Angelino et al. [94] analyzed the trigonelline contents of 65 capsule-brewed coffees representative of 5 brands commercialized in Italy. Lungo coffees showed higher trigonelline levels (15.32–47.32 mg per serving) than decaffeinated (8.38–33.74 mg) and regular Espresso coffees (6.78–17.88 mg). However, data were expressed as mg/mL, and the regular Espresso coffees showed concentrations almost double that of the other two types of coffee, with average values of 0.52 mg/mL.

Plasma trigonelline can be used profitably as a marker of coffee intake [95]. Antimicrobial, anticarcinogenic, and antihyperglycemic effects are recognized in trigonelline, as well as anti-degranulation properties against the development of allergic diseases [96].

4.4.2. β-Carbolines

β-carbolines are a group of biologically active alkaloids that are derivatives of indole. They naturally occur in and are present in several plants but are also detectable in many thermally processed foods [97]. In fact, the chemical structures of the two main compounds of this group, harman and norharman (Figures 7a and 7b, respectively), are related to the nonpolar heterocyclic aromatic amines produced with pyrolysis.

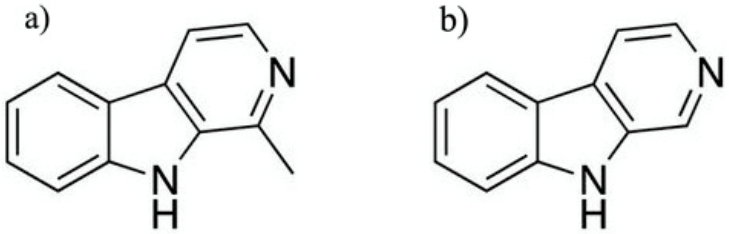


Figure 7. (**a**) Harman and (**b**) norharman.

During coffee roasting, they are formed through a Pictet–Spengler condensation of indolethylamines and carbonylic compounds, followed by oxidation and decarboxylation [25]. Studies performed on the effects of these compounds on human health gave contradictory results. The interest in β-carbolines is related to their pharmacological (antitumor, antiviral, and antimicrobial activity) and psychopharmacological properties [98,99]. The β-carbolines harman and norharman seem to exert a protective effect against aging processes and neurodegenerative disease [100]. Coffee seems to be the main exogenous dietary source of β-carbolines.

Alves et al. [101] performed a study on the β-carboline content in Espresso coffee, analyzing the effects of coffee species, roasting degree, and brew length. The quantification of norharman and harman by reverse phase high-performance liquid chromatography (RP-HPLC) coupled with fluorescence detection highlighted the significant influence of species and brew length and the limited contribution of roasting to the final concentration of these compounds. A serving cup (30 mL) of Espresso obtained by 100% Arabica coffee contains 4.08 μg of norharman and 1.54 μg of harman, and the addition of Robusta (commercial blends are usually produced with a maximum of 30% Robusta) increased the amounts of both compounds up to 10.37 μg of norharman and 4.35 μg of harman. In a successive work, Alves and Mendes et al. [102] evaluated the β-carboline amounts in commercial instant coffee-based beverages. The researchers highlighted a high variability among samples, with amounts ranging from 1.06 to 5.59 μg/g for norharman and from 0.28 to 2.11 μg/g for harman. The lower concentrations were detected in 100% Arabica coffee. Considering that the use of 2–6 g of powder is recommended in the preparation of instant coffee brews, the amounts of β-carbolines provided by these beverages are within those reported for standard Espresso coffees [101].

In a work of Herraiz [103] on the effects of brewing on the β-carboline contents of coffee beverages, the analyses highlighted that filtered coffees had lower content of norharman and harman (91 and 26.9 ng/mL, respectively) than Espresso (165.6 and 39.9 ng/mL, respectively).

4.4.3. Cafestol and Kahweol

Cafestol and kahweol (Figures 8a and 8b, respectively) are two pentacyclic diterpene alcohols based on the kaurane skeleton [25]. Methylated forms of cafestol and kahweol have been identified in Robusta.

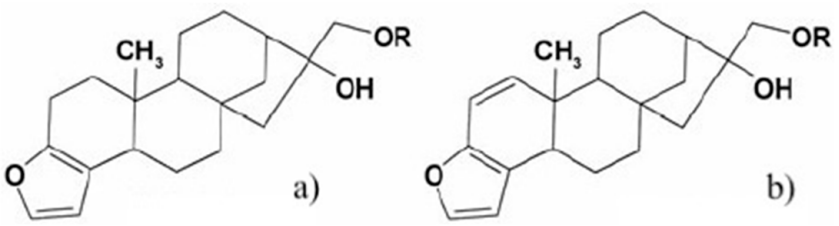


Figure 8. (**a**) Cafestol and (**b**) kahweol.

For a long time, they have been considered anti-nutritional factors of coffee beans and brews. Early studies effectively demonstrated their ability (especially of cafestol) to increase human plasma triacylglycerol and low-density lipoprotein (LDL), thus increasing the potential risk of inducing some cardiovascular diseases [104]. But, in addition to the deleterious effects on serum lipid levels, further studies highlighted a broad range of biochemical positive effects. In animal models and cell culture systems, cafestol and kahweol have been shown to reduce the genotoxicity of carcinogens such as 7,12-dimethylbenz[a]anthracene, aflatoxin B1, and benzo[a]pyrene- and 2-amino-1-methyl-6-phenylimidazo [4,5-b]pyridine. Further experimental studies revealed that the two diterpenes demonstrate multiple potential pharmacological actions, such as anti-inflammatory, hepatoprotective, antidiabetic, and anti-osteoclastogenesis activities [105].

Cafestol, kahweol, and their derivatives represent approximately 20% of the lipid fraction of coffee. Coffee bean cafestol contents, expressed as dry matter, are in the range 0.15–0.37 and 0.27–0.67% for Robusta and Arabica, respectively. Similarly, kahweol amounts to 0.1% in Robusta beans and 0.11–0.35% in Arabica beans [106]. According to [107], cafestol and kahweol are sensitive to roasting, being degraded to dehydrocafestol and dehydrokahweol after 8 min of treatment. Kahweol is more sensitive than cafestol to heat, oxygen, light, and acids and is, therefore, less abundant.

From an analytical point of view, these compounds can be easily determined by gas chromatography flame ionization detection (GC–FID) after Soxhlet extraction or saponification and silylation. As a valuable alternative, HPLC–UV at 230 nm for cafestol and 290 nm for kahweol can be used after solid phase extraction (SPE) and saponification or after Soxhlet extraction or after supercritical carbon dioxide extraction and saponification [108–110]. According to Oiggman et al. [111], LC-MS after microwave methanolysis was proved to increase selectivity.

Concerning the effects of the brewing methods, Gross et al. [108] found that concentrations of cafestol and kahweol in Espresso, Turkish-style, and French press preparations were significantly higher than in filtered or instant coffee. Urgert et al. [112] observed that Scandinavian-type boiled coffee, Turkish, and cafetière coffee contained the highest amounts of cafestol + kahweol, while Espresso contained intermediate amounts, and instant and filtered coffee only negligible amounts. Recently, Sridevi et al. [109] prepared coffee brews by 7 methods, including espresso, electrical drip, moka, Indian filter method, Turkish style, French press, and filter paper, and analyzed cafestol and kahweol profiles by HPLC-UV, at 230 nm for cafestol and 290 nm for kahweol, after Soxhlet extraction. The highest levels per cup of cafestol and kahweol were detected in French press coffee, followed by Turkish style, moka, and espresso (Figure 9). The cafestol and kahweol levels were very low in electrical drip, filter paper, and Indian filter (Figure 9).

Many are the reasons for the variation of cafestol and kahweol profiles in different coffee brews. They include the prepared coffee brew volume; the ground coffee-to-water ratio, the amount of coffee ground taken for preparing the brew, the method by which coffee brew is prepared and decanted/filtered, the influence of steam pressure and the time of contact of steam with coffee powder in the espresso preparation, and the presence of

"crema", rich in lipid fraction, in moka brews. The lowest diterpene concentrations detected in filtered and instant brews were easily explained by Moreira Novaes et al. [113] in their review article. During the preparation of any type of hot coffee, oil droplets of free-floating lipids are extracted from the powder by the hot water and form a second lipid layer soluble in the medium. Nevertheless, diterpenes are very little, soluble in hot water, and most of their content is confined to the interstices of spent coffee suspended in the beverage, which is then retained on the paper filter. Concerning instant coffees, most of them are produced from Robusta, which has lower diterpene contents than Arabica beans. Furthermore, a loss of diterpenes already occurs during industrial aqueous extraction, followed by filtration.

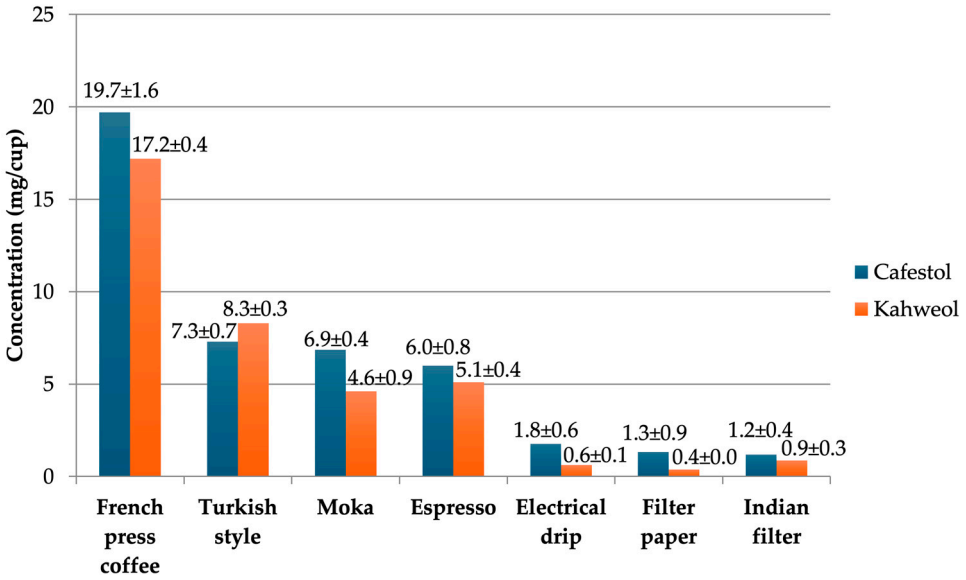


Figure 9. Concentrations of cafestol and kahweol in coffee brews produced according to several methods (elaboration of data of Sridevi et al. [109]).

De Souza Gois Barbosa et al. [114] tried to correlate the composition of green Arabica coffee beans with the sensory quality of the corresponding brews and found a positive association between a high cafestol/kahweol ratio in the green coffee beans and the sensory quality of the brew.

5. Effects of the Brewing Methods on the Extraction of Undesirable Compounds from Coffee Powder and Coffee Brews

Coffee can contain minor compounds considered undesirable for flavor or for their effects on human health. Most of these compounds are microbial by-products that can occur as a consequence of improper harvesting and storage or weather conditions during primary processing. They include ochratoxin A and some biogenic amines. Other undesirable compounds, formed during roasting, are represented by polycyclic aromatic hydrocarbons and acrylamide [25].

5.1. Ochratoxin A (OTA)

It is a mycotoxin produced by several *Aspergillus* and *Penicillium* species. From a chemical point of view, it has a di-hydro-iso-coumarin moiety linked through its 7-carboxy group to l-phenylalanine by a peptide bond. It exerts adverse effects on human health, being a potent nephrotoxin and hepatotoxin, with teratogenic, mutagenic, carcinogenic, and immunosuppressive effects even at trace levels [25]. It is estimated that coffee accounts for approximately 12% of the total intake of OTA and is the third source of OTA exposure [115]. A systematic review and meta-analysis performed by Khaneghah et al. [116] highlighted

that the global pooled concentration and prevalence of OTA in coffee and coffee-based products were 3.21 μg/kg and 53.0%, respectively. However, historical data do not highlight evidence suggesting that OTA is acutely toxic in humans from coffee consumption [117]. For years, the European Union has established the maximum levels for OTA in foods. However, in 2022, the Reg. EU 2022/1370 has partially reformed those limits, reducing them from 5 to 3 μg/kg for roasted coffee beans and ground roasted coffee and from 10 to 5 μg/kg for soluble coffee.

Although roasting led to a significant drop in OTA levels (65–100%), it may be useful to investigate how coffee preparation affects OTA levels [118] since its tolerable daily intake is 300 ng (for a 60 kg body weight, adult). Pakshir et al. [119] analyzed 50 coffee samples, including 18 black coffee beans, 8 green coffee beans, 12 coffee espresso powder samples, and 12 coffee torch powder samples from different brands. They observed that all samples were contaminated by ochratoxin A, but the percentage of samples having toxin concentrations higher than the acceptable level was 47% of black beans, 33.3% of green beans and torch, and 25% of Espresso. Moreover, black coffee had higher OTA mean concentrations than green coffee.

La Pera et al. [118] investigated the effects on OTA content of the most diffused brewing procedures, namely, Turkish, moka, and Americano. The highest reductions with respect to the OTA contained in the coffee powder were obtained with the Americano brewing (54–73%) and moka (51–75%) brewing procedures, while the Turkish preparation allowed for a limited decrease in OTA (17–25%). The explanation of this behavior is that OTA requires time to solubilize in the brew, and the long contact time between powder and water occurring in the Turkish preparation allowed a higher toxin solubilization. Gopinandhan and Kannan [120] evaluated the effects of filter brewing on the stability of OTA. Robusta coffee powder samples, naturally or artificially contaminated, were left in contact with hot water for 7, 15, and 20 min and then filtered. The analysis was performed by HPLC after cleaning on an immunoaffinity column. and the percentage of the reduction in OTA was calculated. Naturally contaminated coffee samples showed OTA reduction from 4 to 36.8% while artificially infected coffee samples showed OTA reduction from 7 to 28.3%. The percentage of OTA reduction increased as the contact time between the coffee powder and water increased. The study of Santini et al. [48] investigated the ability of 5 brewing methods, namely, Americano, moka, Italian espresso, Neapolitan, and Turkish, to extract OTA from artificially contaminated 100% Arabica coffee powder. HPLC coupled with a fluorimetric detector was used to quantify OTA. The highest extraction values (70–81%) were obtained for the Americano coffee preparation, which could be explained by the longer contact time between the coffee powder and the hot water, followed by Italian Espresso and moka. Turkish and Neapolitan methods extracted the lowest amount of OTA.

5.2. Biogenic Amines

From a chemical point of view, these low molecular weight compounds are aliphatic, alicyclic, or heterocyclic organic bases produced by decarboxylation of specific amino acids. In coffee, their production is generally due to the action of microbial decarboxylases, but their formation can occur during roasting due to amino acid decarboxylation or hydrolysis of conjugated amines [25].

In coffee, the main biogenic amine is putrescine, followed by spermidine and spermine. Cadaverine and tyramine contents are very low.

Biogenic amines are present in green coffee mainly as free forms, with low amounts of acid-solubleand acid-insoluble conjugated forms. Within the free forms, putrescine content is higher in Arabica than in Robusta samples. After roasting, biogenic amines are detected in very low amounts, since they are heat sensitive, and mainly as free forms [121].

Macheiner et al. [122] studied amino acid reduction and biogenic amine formation during the roasting process of Coffea arabica beans. Most of the investigated amino acids were already degraded within the first half of the roasting process. Histidine and arginine are significantly degraded by thermal decarboxylation, resulting in high intermediate contents of histamine and agmatine. Then, histamine degraded till the first crack and stabilized afterwards, while agmatine contents decreased. No significant formation of putrescine, ethylamine, ethanolamine, tyramine, tryptamine, cadaverine, phenylethylamine, octopamine, and ornithine was determined.

Restuccia et al. [123] investigated the effects of brewing methods on the concentrations of spermine, spermidine, putrescine, histamine, tyramine, phenylethylamine, cadaverine, and serotonin. The biogenic amines were detected by LC-UV at 254 nm after derivatization with dansyl chloride. The coffee brews were prepared according to the following methods: espresso machine, moka; capsule espresso machines, pod espresso machines, direct solubilization in water, and instant coffee through automatic vending machines. The amounts of total biogenic amines in the starting coffee powders ranged from 13.30 ± 0.22 to 85.85 ± 2.48 μg/g, with lower concentrations found in the coffee toasted at higher temperatures. The coffee brews contained very low levels of biogenic amines with respect to the corresponding roasted ground coffee. More specifically, the total biogenic amine contents ranged from 9.88 ± 0.04 to 3.04 ± 0.03 μg/mL, and they were in the following decreasing order: brews made by moka, capsule, pod, instant coffee, and espresso machine. Figure 10 shows the concentrations of various biogenic amines as a function of coffee brew methods. The results obtained with moka were explained by the lower pressure and longer brewing time that facilitated extraction. In a previous work of Özdestan [124], higher contents of total biogenic amines were found both in the ground coffee (126.0–352.2 mg/kg) and in the derived Turkish brewed coffee (5.7–48.9 mg/L).

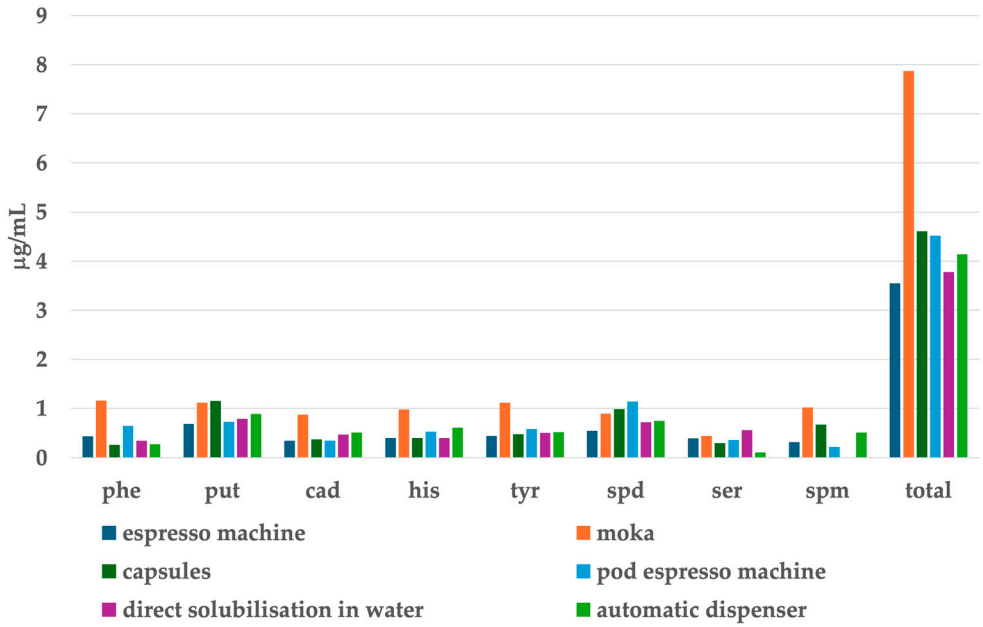


Figure 10. Concentrations of biogenic amines in coffee brews produced according to several methods (elaboration of data of Restuccia et al. [123]). phe, β-phenylethylamine; put, putrescine; cad, cadaverine; his, histamine; tyr, tyramine; spd, spermidine; ser, serotonine; spm, spermine.

5.3. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a large class of organic compounds containing two or more fused aromatic rings made up of carbon and hydrogen atoms [125]. They are formed by the incomplete combustion of organic matter, and their presence in coffee

samples may be attributed to either contamination of the initial green beans or formation of these compounds during the roasting step. In fact, a partial carbonization could take place as a result of intense thermal processes. According to previous studies, PAHs such as phenanthrene and anthracene form in coffee at temperatures above 220 °C, whereas the formation of pyrene, chrysene, and benzo[a]anthracene requires higher temperatures, from 250 to 260 °C [25,126]. High temperatures and long roasting times determine the formation of numerous cracks on the coffee surface so that the fat structure inside them becomes visible [127]. This favors the formation of lipophilic PAHs, especially of heavy PAHs. The pyrolysis of coffee lipids, carbohydrates, and amino acids during roasting is thought to lead to PAH formation. However, it is difficult to precisely describe the chemical reactions involved due to the complexity of coffee matrices [128].

Many PHAs are carcinogenic, and those that have not been found to be carcinogenic may synergistically increase the carcinogenicity of the other PAHs [129]. According to Orecchio et al. [129], the total concentrations of PAHs in coffee brew varied from 0.52 to 1.8 μg/L, while those of carcinogenic PAHs ranged from 0.008 to 0.060 μg/L. These results would indicate that the coffee contribution to the daily human intake of carcinogenic PAHs is negligible. The most abundant PAHs in roasted coffees are phenanthrene, fluoranthene, and pyrene, but these compounds present a lower risk with respect to the PAHs considered by the European Food Safety Agency as possible indicators of the carcinogenic potency of PAHs [130]. However, it should be interesting to investigate the effects of different brewing procedures on coffee brew PAH contents and clarify the role of caffeine in the PAH transfer to the coffee brew due to the known formation of a caffeine–PAH complex [131]. Nevertheless, the topic has been little investigated. Aresta and Zambonin [132] developed a solid-phase microextraction coupled with gas chromatography for the analysis of PAHs in dark-roasted and decaffeinated commercial coffees. Chrysene, ranging from undetectable to 95.6 ± 11 ng/g, and pyrene, varying from undetectable to 404.7 ± 42.0 ng/g, were the most representative congeners. Benzo[a]pyrene was detected only in two samples of dark-roasted coffee. Only 30% of the total PAHs were transferred from the coffee grounds to the infusion. According to the meta-analysis study of Hamrah et al. [133], the highest concentrations of PAHs in coffee products in America (57.21 μg/kg), Asia (10.89 μg/kg), Europe (19.17 μg/kg), and Africa (56.9 μg/kg) were related to the following specific compounds: pyrene, naphthalene, acenaphthylene, and phenanthrene, respectively. To the best of our knowledge, the maximum quantity of PAHs has not been legally regulated.

The analysis of PAHs can also be carried out through a previous extraction with hexane, cleaning of SPE cartridges, and the separation by HPLC coupled with a fluorescence detector [125] or by GC-MS [129]). Tfouni et al. [125] evaluated the effects of three roasting degrees of coffee from *Coffea arabica* cv. Catuaí Amarelo IAC-62 and *Coffea canephora* cv. Apoatã IAC-2258 and two brewing procedures (filtered and boiled) on the PAH contents of the resulting coffees. They found that the difference among the concentrations detected at the different roasting degrees was not statistically significant, as well as the influence of caffeine. Furthermore, coffee brews prepared with *Coffea arabica* showed mean PAH levels higher than those prepared with *Coffea canephora*, independently of the brewing procedure. Rattenarat et al. [134] proposed superheated steam roasting as an alternative to the traditional hot air roasting of Robusta coffee beans to reduce PHA formation. They found that the concentrations of fluorene, phenanthrene, and anthracene in dark-roasted beans were significantly lower when superheated steam roasting was applied.

5.4. Acrylamide

Coffee is an important dietary source of acrylamide (2-propenamide), a compound labeled as probably carcinogenic to humans by the International Agency for Research on Cancer [135].

Acrylamide formation occurs during roasting at high temperature as a consequence of the early Maillard reaction due to the condensation of asparagine and reducing sugars or reactive carbonyls [136]. Other reactions include decarboxylation of asparagine to 3-aminopropionamide upon heating in the absence of reducing carbohydrates and the Strecker reaction of asparagine [137,138]. *Coffea canephora* shows higher acrylamide content than *Coffea arabica* [136].

Concerning the effects of roasting, acrylamide formation starts at the beginning of the process and successively decreases due to physical and chemical losses. As a consequence of the above-described mechanisms of formation and loss, light-roasted coffee has significantly higher amounts than dark-roasted coffee. Furthermore, acrylamide is a highly water-soluble compound and is easily transferred from the coffee powder to the beverage, especially when the powder–water contact is prolonged. Considering both this finding and the adverse effects of acrylamide on human health, it is useful to evaluate its intake per serving cup and the way it is affected by brewing procedures. The already cited study of Rattenarat et al. [134] investigated the fate of acrylamide in hot air and superheated steam roasting, and the latter allowed for the production of dark-roasted beans with lower acrylamide contents.

Acrylamide is not stable during the storage of packed roasted coffee and significantly decreases from 771 to 256 μg/kg in soluble coffee stored at room temperature and in its original tightly closed container for 12 months. It also decreases in roasted coffee from 203 to 147 μg/kg stored at room temperature for 7 months [139].

In a survey on the acrylamide concentrations of coffee prepared through filter coffee machines and French press coffee makers, Granby and Fagt [140] did not find a significant difference between the two types of brewing, with the acrylamide concentrations being 8 ± 3 and 9 ± 3 μg/L, respectively.

Alves et al. [141] evaluated the effects of water volumes in the range of 20–70 mL for 6.5 g of coffee powder on the acrylamide contents of espresso coffees. Two coffee samples, one Arabica and one Robusta, were tested. Analyses were performed by GC/MS after a sample preparation that included a matrix solid-phase dispersion and a bromination step. The starting 6.5 g of Arabica and Robusta powder contained 1.82 ± 0.03 and 3.67 ± 0.03 μg of acrylamide, respectively. The extraction percentage varied from 59 to 98% for Robusta and from 62 to 99% for Arabica, in the water volume range of 20–70 mL. This means that for both coffee species, the acrylamide extraction increased with water volume. However, the brew concentration simultaneously decreased from 108.2 ± 1.5 to 50.1 ± 3.9 l μg/L for Robusta coffee and from 56.3 ± 1.3 to 24.2 ± 0.3 μg/L for Arabica. Concerning espresso coffee, Mesías and Morales [142] analyzed 41 samples acquired from coffee vending machines located in the Autonomous Community of Madrid (Spain) and found acrylamide concentrations ranging from 7.7 to 40.0 μg/L. These great differences were due to the differences in the type of coffee bean, roasting degree, coffee/water ratio, and water volume. Volumes ranged from 40 to 100 mL/cup, and the acrylamide content per serving ranged from 0.8 to 2.4 μg/cup, with an average value of 1.6 μg/cup. Santanatoglia et al. [143] quantified the acrylamide contents in coffee brews prepared from coffee beans subjected to three different roasting levels (light, medium, and dark) through eight different extraction methods, namely, Aeropress, Clever, Chemex, French press, moka, Pure Brew, Turkish, and V60. Such data, reported in Figure 11, highlight that moka coffee had the highest acrylamide levels when obtained from light-roasted (174.68 ng/mL) and dark-roasted

beans (170.06 ng/mL), together with French press coffee prepared from medium roasted beans (170.26 ng/mL). Clever coffee had the lowest acrylamide contents for each roasting level: 45.81 ng/mL for light, 47.68 ng/mL for medium, and 24.73 ng/mL for dark roast. According to the Reg. (EU) 2017/2158, the benchmark levels for the presence of acrylamide in roasted coffee and soluble coffee are 400 and 850 µg/kg, respectively.

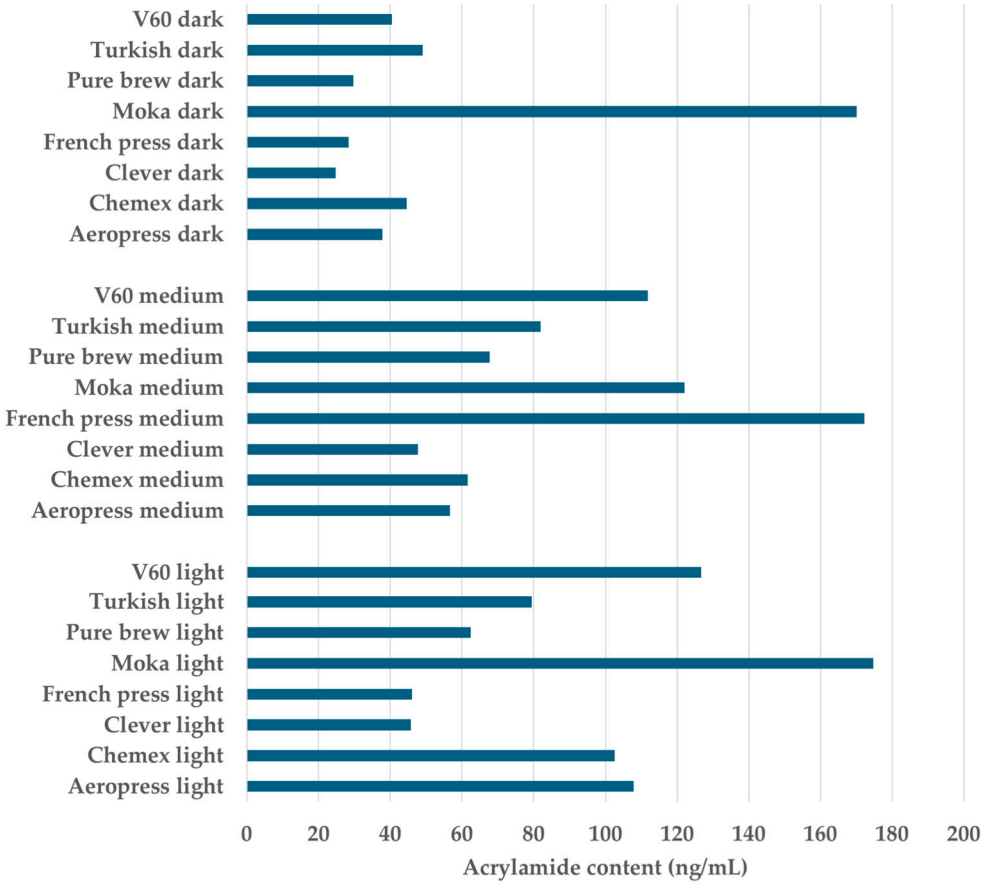


Figure 11. Concentrations of acrylamide in coffee brews produced according to several methods (elaboration of data of Santanatoglia et al. [143]).

According to Schouten et al. [144], the selection of high-quality Arabica green coffee beans and the application of high roasting thermal and short brewing techniques can be considered strategies to reduce the final acrylamide levels. Among the strategies considered useful to remove acrylamide from roasted coffee beans and brews, the following techniques can be included: the application of supercritical CO_2 (100 °C, 200 bar, 9.5% w/w ethanol) to roasted coffee [145] and the use of bacterial enzymes, even immobilized, or the application of yeast fermentation to remove acrylamide from coffee brew [146–149]. However, these techniques have not been tested for their impact on the coffee brew sensory quality or for their industrial feasibility.

6. Coffee Brew Volatile Compounds: Generation and Impact on Coffee Aroma

Coffee volatile composition is affected by a large number of variables during coffee production, such as growing environment, harvesting, and post-harvest practices, including roasting, grinding, and extraction method [150,151]. For example, coffee from high altitudes generally has more positive flavor attributes, such as chocolate and caramel notes [152]. Post-harvest processing methods, such as dry and wet processing, influence aroma profiles. Wet processing generally results in a higher concentration of aroma com-

pounds. Furthermore, using specific starter cultures during fermentation can significantly enhance flavor and aroma by impacting volatile compounds levels [150,153].

During roasting, hundreds of new volatile compounds are produced by chemical reactions from numerous precursors present in the bean [154].

The main chemical reactions that occur during roasting are non-enzymatic browning reactions, better known as Maillard reactions, between nitrogen-containing substances, amino acids, and proteins, as well as trigonelline, serotonine, carbohydrates, hydroxy-acids, and phenols. Other important reactions include the Strecker degradation, the degradation of individual amino acids (particularly sulfur amino acids, hydroxy amino acids, and proline), the degradation of trigonelline, the degradation of sugar, the degradation of phenolic acids (particularly quinic acid), and the degradation of lipids, as well as the intermediate decomposition products [7,154].

Roasted coffee has been reported to contain 841 volatile compounds, including 80 hydrocarbons, 24 alcohols, 37 aldehydes, 85 ketones, 28 carboxylic acids, 33 esters, 86 pyrazines, 66 pyrroles, 20 pyridines, 52 other bases (e.g., quinoxalines, indoles), 100 sulfur compounds, 126 furanones, 49 phenols, 35 oxazoles, and 20 others [154].

Quantitatively, the top classes in coffee are furans, ketones, and pyrazines, while qualitatively, sulfur-containing compounds together with pyrazines are considered the most significant for coffee flavor, both for their coffee-like/toasty odors as well as for their lower odor thresholds [154,155].

Furans are produced through the thermal degradation of carbohydrates, ascorbic acid, and unsaturated fatty acids during roasting. Furans not containing sulfur are generally associated with sweet, nutty, and caramel odors, while those containing sulfur are responsible for sulfur, garlic, or toasty odor notes. They exhibit a malty and sweet roasted odor [154], but their contribution to coffee aroma is less important compared to other groups of coffee volatiles because they have higher odor thresholds. In recent years, furan and other furanic compounds have received special attention due to their negative health impacts. In fact, furan has been classified by the International Agency for Research on Cancer as Group 2B as "possibly carcinogenic to humans" (https://monographs.iarc.fr/list-of-classifications-volumes/, accessed on 5 August 2025). 2-Methylfuran has been reported to produce, in a similar manner to furan, highly reactive intermediates, leading to a similar toxicity on the liver of rats [156]. The level of furan in roasted coffee ranged from 1 to 5 mg/kg, while 2-methylfuran ranged from 4 to 20 mg/kg [157,158]. Higher concentrations of furan were found in Coffea canephora species, and darker roasted ground coffee has a tendency to form higher levels of furans [159,160]. In coffee brewing, their level is greatly reduced and is influenced by the brewing procedures. It ranges from 8 to 352 µg/L and from 135 to 1360 µg/L for furan and 2-methylfuran, respectively, and the highest levels were found for espresso coffee [158,161–163]. However, a balanced blend of 60% Arabica and 40% Robusta, with specific particle size, has been shown to have lower furan and 2-methylfuran levels in espresso coffee by up to 11.4% and 18.8%, respectively [164].

Pyrazines are formed by complex interactions between α-amino acids and carbohydrates. Among them, the alkyl-pyrazines have a key role in the aroma of coffee brew, exhibiting a walnut-like, earthy, cracker, toast-like, and coffee-like odors in coffee. For example, they have been reported to be responsible for the characteristic earthy odor of Robusta coffee [153]. Even if the presence of 3-isobutyl-2-methoxypyrazine is found at low concentrations in roasted Arabica coffee beans, it has a significant impact on roasted Arabica coffee [164] because it has a very low perception threshold of 0.002 ppb [154].

Along with pyrazines, thiazoles and thiols have the lowest odor thresholds. Among them, 2,4-dimethyl-5-ethylthiazolethere is suspected to be formed via sugar degradation

and is responsible for the nutty, roasty, meaty, earthy odors. 2-Furfurylthiol exhibits a roasted aroma and has been reported widely in roasted and brewed coffee as an impact aroma compound. Methanethiol is a thiol biosynthesized from methionine pyrolysis and is responsible for cabbage-like cheese, garlic, and sulfur odor.

Furanones are generated in coffee mainly via the Maillard reaction and subsequent aldol condensation. The most important in terms of abundance and odor intensity are 4-hydroxy-2,5-dimethyl-3(2H)-furanone (furaneol) and 2(5)-ethyl-4-hydroxy-5(2)-methyl-3(2H)-furanone, 3-hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon), and 4-ethyl-3-hydroxy-5-methyl-2(5H)-furanone responsible for the sweet/caramel aroma of coffee [154].

Pyrroles are described as furan degradation products and amino acid derivatives, but they also originate from the thermal degradation of Amadori intermediates. The most abundant compound of this class is pyrrole, 1-methyl-(1H-pyrrol-2-yl)-1-ethanone.

Phenolic compounds were described as essential contributors to the aroma of coffee brew, exerting a smoky-like odor [154]. These phenolic compounds are formed by the thermal degradation of chlorogenic acids (mainly ferulic, caffeic, and quinic acids), and among them, there are guaiacol, 4-ethylguaiacol, and 4-vinylguaiacol [165]. Their concentration in a roasted bean is useful for differentiating the Robusta from Arabica varieties. In fact, chlorogenic acids are present in higher amounts in green beans of Robusta compared to Arabica coffee; thus, Robusta shows a higher level of phenolic compounds [166,167].

Aldehydes such as 2-methylbutanal and 3-methylbutanal are formed by the oxidative degradation of amino acids when they interact with sugars at high temperatures and exhibit a malty odor in coffee brew [167]. On the contrary, others like hexanal are formed through an autoxidation or thermal oxidation of unsaturated fatty acids. Hexanal has been reported to contribute a green note to the aroma of coffee [168].

Other volatile compounds, such as 2,3-pentanedione and β-damascenone, are formed by thermal degradation of furaneol and carotenoids, respectively, and are responsible for the buttery and fruity odors.

Gonzalez-Rios et al. [169] analyzed the chemical composition of ground Arabica coffee by using solid phase microextraction–gas chromatography/mass spectrometry (SPME-GC/MS) found that furans were the most abundant, followed by ketones, pyrazines, pyridines, and pyrroles. Upon comparing green and roasted coffee, they found 27 common volatile compounds. Compounds with thermal origins, furfural, furfurylic acid, guiacol, pyridine, 1-methylpyrrole, and maltol increased after roasting, while non-thermal compounds, including certain esters and alcohols, decreased or disappeared. Most of these compounds confer positive notes to coffee, which usually can increase in odor intensity with the degree of roast [165,170,171]. Petisca et al. [172] also found that slow roasting speed promoted pyridine formation, while medium and fast roasting speed promoted ketone formation.

The degree of roast (light, medium, and dark) affects the aroma compounds in coffee brew [173]. The effect of roasting on the volatile compounds was reviewed by Toledo et al. [174]. They reported, for example, that volatile acids and some furans became less important as the roasting degree increased (from light to medium roast), but at the same time, there were increases in the contributions of the less volatile compounds, such as other furans, pyrazines, and pyridines.

Grinding roasted coffee beans also plays a crucial role in releasing volatile organic compounds and maximizing extraction efficiency during brewing. By increasing the surface area, this process enhances solubilization and promotes the release of gases like carbon dioxide, which, in turn, facilitates the liberation of volatile compounds [23]. Furthermore, the aroma profile of an espresso can be influenced by the specific bimodal particle size distribution of ground coffee [175].

Coffee volatile compounds can be present at parts per million (ppm) to parts per trillion (ppt) levels. However, not all the volatile compounds contribute with the same intensity to coffee brew aroma. Among the hundreds of volatile compounds in the coffee brew, few of them are considered key odorants in defining coffee aroma since they are present at higher levels with respect to their odor thresholds (Table 2). In fact, the concentration–odor threshold ratio is known as "odor activity value" that allows establishing an estimation of the contribution of each compound to the global aroma of roasted coffee or coffee beverage. Some authors used the odor activity value (OAV) and found that different volatile compounds may have an odor impact on the aroma of each type or style of coffee [154].

Research on the sensory impact of potent odorants (odor-active compounds) for coffee brews showed that alkylpyrazines, furanones and phenols, 2-furfurylthiol, methional, and 3-mercapto-3-methylbutyl formate were the main cause of the typical odor of the coffee brew. This result was obtained by using a mixture of odorants simulating a medium-roasted Arabica coffee, in solutions where some specific compounds were missing (omission test) [176].

Another important method to detect the powerful odor compounds is gas chromatography–olfactometry (GC-O). This technique combines separation by gas chromatography and the human nose of the operator as a detector, and is a practicable investigation, useful for converting the results of instrumental analysis of the volatile compounds into sensory data. With this technique, the human nose is used to detect compounds at the end of the GC column that are responsible for a smell (sniffing). Usually, a trained panel of sniffers are employed who also provide a sensory description of the perceived odor [177]. Among the different GC-O methods known, combined hedonic aroma response measurement (CHARM) and aroma extract dilution analysis have been mostly employed for coffee [178].

Table 2. Aroma compounds of roasted coffee grouped in chemical classes.

Chemical Class	Compound	Odour Description	Odor Threshold (ppb)
Acid	2-methylbutanoic acid	Pungent, acidic-like, sour, fermented pineapple, sweaty	10
	3-methylbutanoic acid	Pungent, acidic-like, sour, sweaty	540
	4-methylbutanoic acid	Sweet, acid	
	acetic acid	Sour, acid, vinegar	
	butanoic acid	Butter rancid	240
Aldehydes	2-methylpropanal	Malty, fruity, buttery, oily, roasted cocoa	0.7
	2-methylbutanal	Buttery	1.3
	3-methylbutanal	Buttery, malty	0.35
	4-methylbutanal	Buttery	
	hexanal	Fatty, green, grassy, butter rancid	4.5
	(E)-2-nonenal	Fatty, waxy, cucumber, buttery	0.08
	acetaldehyde	Fruity	10
	propanal	Roasted, fruity	10
	(E)-2-methyl-2-butenal	Sweet, fruity, floral, honey	
	E,E-2,4-decadienal	Citrus, fatty, green	0.07
Ethers	3-methyl-1-butanol formate	Sweet, plum, fruity, black currant, apple	2.5

Table 2. *Cont.*

Chemical Class	Compound	Odour Description	Odor Threshold (ppb)
Esters	ethyl-2-methylbutyrate	Fruity	0.5
	ethyl-3-methylbutyrate	Fruity, apple-like	0.6
Furans	2-furanemethanol acetate		
	2-methylfuran		
	5-methyl-2-furancarboxyaldehyde		6000
	furfurylmethyl ether		
	furfurylformate		
	furfuryldisulfide		
	2-(methylthio-methyl)furan	Smoky, roasted	
	2-furancarboxaldehyde (furfural)	Sweet, burnt, bready, nutty, caramel	280
	2-furfurylthiol	Coffee, roasted	0.01
	2-methyl-3-furanthiol	Meaty, fishy, roasted, chicken-like	0.007
	1-(2-furanyl)-2-butanone		
Furanones	dihydro-2-methyl-3(2H)-furanone		0.005
	4-hydroxy-2,5-dimethyl-3(2H)-furanone (furaneol)	Caramel, sweet	10
	2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone (homofuraneol)	Caramel, sweet	1.15
	3-hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon)	Spicy, sweet, caramel-like	20
	5-ethyl-3-hydroxy-4-methyl-2(5H)-furanone (abhexon)	Spicy, seasoning-like, caramel-like	7.5
Indole	3-methylindole	Coconut, phenolic	
Ketones	1-octen-3-one	Mushroom	0.0036
	2,3-hexadione		
	3,4-dimethyl-2-cyclopentenol-1-one	Caramel-like, sweet	
	4-(4′-hydroxyphenyl)-2-butanone (raspberry ketone)	Sweet fruity	1–10
	2,3-butanedione	Buttery, oily	15
	2,3-pentanedione	Buttery, fermented dairy, creamy, sweet, oily	30
	2-hydroxy-3-methyl-2-ciclopenten-1-one (Cycloten)	Sweet, caramel	300
Norisoprenoids	(E)-β-damascenone)	Cooked apple, sweet, fruity, honey-like	0.00075
Phenols	phenylethanal	Floral, sweet, fruity	4
	vanillin	Vanilla	25
	2-methoxyphenol (Guaiacol)	Phenolic, roasted, burnt	2.5
	4-methoxyphenol	Phenolic	68
	4-ethylguaiacol	Phenolic, spicy	25
	4-ethenyl-guaiacol	Phenolic	
	4-vinylguaiacol	Phenolic, clove, spicy	0.75
	p-anisaldehyde	Minty	27

Table 2. *Cont.*

Chemical Class	Compound	Odour Description	Odor Threshold (ppb)
Pyrazines	2-methoxy-3,5-dimethylpyrazine	Earthy	0.006
	2-ethyl-3,5-dimethylpyrazine	Earth, nutty-roast, hazelnut, roasted	0.04
	3-ethyl-2,5-dimethylpyrazine	Earthy	43,000
	3-isopropyl-2-methoxypyrazine	Earthy, roasty	0.002
	2-(sec-butyl)-3-methoxypyrazine	Green-earthy	0.001
	2-ethenyl-3-ethyl-5-methylpyrazine	Earthy	0.000014
	2-isobutyl-3-methoxypyrazine	Earthy, peasy	0.002
	2-ethenyl-3,5-dimethylpyrazine	Earthy, nutty	0.000012
	2,3-dimethylpyrazine	Hazelnut, roasted	800
	2,5-dimethylpyrazine	Hazelnut, roasted	80
	2-ethylpyrazine	Peanuts, roasted	62
	2,3,5-trimethylpyrazine	Roasted, nutty	9
	2-ethyl-3,6-dimethylpyrazine	Burnt, coffee, nutty-roast	8.6
	2-ethyl-6-methylpyrazine	Peanuts, roasted	
	6,7-dihydro-5H-cyclopentapyrazine	Hazelnut, roasted	4000
	6,7-dihydro-5-methyl-5H-ciclopentapyrazine	Hazelnut, nutty-roast	6000
	2,3-diethyl-5-methylpyrazine	Hazelnut, roasted, nutty-roast	0.09
Pyranones	3-hydroxy-2-methyl-4-pyran-4-one (maltol)	Candy, caramel	20,000
Pyridine	pyridine		77
Pyrroles	1-methyl pyrrole	Negative notes–defective beans	
	(2-acetyl-1-pyrrolidine)	Nutty-roast	
Sulphur compounds	dimethyl trisulfide	Cabbage-like	0.001
	bis(2-methyl-3-furyl)disulphide	Meaty	0.00076
	3-(methylthiol)propanal (methional)	Boiled potato, soy sauce	0.2
	2-(methylthiol)propanal	Soy sauce	
Thiols	3-mercapto-3-methylbutylformate	Green blackcurrant	0.0035
	3-mercapto-3-methylbutylacetate	Roasty	
	3-methyl-2-buten-1-thiol	Smoke, roasted, amine-like	0.0003
	3-mercapto-3-methylbutanol	Hazelnut, roasted	0.0035
	methanethiol	Cooked potato	0.2
	3-mercapto-3-methylbutyl formate	Cassis, cat, green	0.0035
Terpenes	linalool	Flowery	0.17
	limonene		4
	geraniol		1.1
Thiazoles	2,4-dimethyl-5-ethylthiazole	Earthy, roasty	
	2-acetyl-2-thiazoline	Roasted	
Thiophene	3-methylthiophene		
	3,5-dihydro-4(2H)-thiophenone	Smoke, roasted	

Source: Sunarharum et al. [154]; Toledo et al. [174]; Toci and Boldrin [179].

Laukaleja et al. [180] studied coffees roasted and brewed by different coffee brewing methods and identified 56 volatile compounds, 30 of which were odor-active compounds,

i.e., odorous compounds. In addition, they developed a sensory vocabulary featuring 23 distinct aromas, including sweet, musty, leather, skunky, burnt, and nutty. The study found that light-roasted coffee exhibited floral and nutty notes, while dark-roasted coffee had fewer sensory descriptors but contained higher concentrations of aroma compounds.

Mahmud et al. [181] investigated the odor-active compounds influencing consumer preferences in coffee-flavored dairy beverages. Their findings revealed that fat content and coffee concentration significantly influenced these compounds. The study also grouped the compounds into three groups based on consumer preferences. Twenty-five compounds, such as 2-(methylsulfanylmethyl)furan (coffee-like odor), were positively associated with being liked. Sixteen compounds, including 2-methoxyphenol (bacon, medicine-like odor), were negatively associated with being liked. Meanwhile, eleven compounds, such as butane-2,3-dione (butter, fruit-like odor), showed no correlation with consumer preferences. Therefore, given the extensive differences in the genetics, growing, geographical origins, and processing of coffee, the volatile composition varied significantly in concentration and odor intensity [182,183]. These can explain why different coffee types may exhibit such diverse and specific flavors that affect the final drink quality and consumer acceptability.

However, coffee's aroma changes quickly over time, resulting in a significant loss of freshness. This is due to the evaporation and oxidation of volatile compounds. Maintaining low water activity and using appropriate packaging can help preserve the aromatic quality of powder coffee [150]. Storing coffee at lower temperatures helps preserve its aroma and flavor. By contrast, storage at higher temperatures leads to more significant changes in the volatile profile and sensory quality. This results in stronger earthy, sharp, and smoky notes while reducing the perception of chocolatey and sweet notes [184].

7. Effects of the Brewing Methods on the Aroma Composition of Coffee Brew

The profile of volatile compounds was similar in ground and brewed Arabica coffee, but some compounds were quantitatively higher in the beverage [172]. Other authors reported that some polar compounds have higher yields than nonpolar compounds [168]. The yield in aroma extraction also depends on the preparation methods. In fact, all methods vary by extraction pressure, coffee/water ratio, water quality, contact time, particle size distribution, and temperature, all factors that affect the extraction of volatile compounds [16].

For instance, certain potent odorants in coffee, such as 2,3-butanedione, 2,3-pentanedione, some furanones, 2-ethyl-3,5-dimethylpyrazine, and thiols, are more effectively extracted using hot water, achieving extraction rates exceeding 75%. For other compounds, extraction rates below 25% have been observed, including 2-ethenyl-3-ethyl-5-methylpyrazine, 3-isobutyl-2-methoxypyrazine, 2-furfurylthiol, and β-damascenone [185].

Cordoba et al. [16] reviewed the effect of coffee extraction parameters on the physicochemical characteristics and flavor of coffee brews. The authors identified 117 volatile compounds across all coffee brew methods evaluated.

Turkish coffee seems to have the largest number of volatile compounds, followed by filtered, espresso, and French press. On the contrary, a lower number of volatile compounds has been reported in coffee prepared by the moka method. Pyrazines are the main chemical class of volatile compounds found in coffee brew, followed by furans, aldehydes, and ketones. Pyrazines have been reported mainly in Turkish coffee brew, followed by espresso and filtered coffees. Furanones, pyridines, and thiols have been reported less in coffees prepared using the moka method. Thiols are also less important in the Turkish and French press coffees (Figure 12). The volatile composition of the coffee beverage produced by each preparation method is described in detail below.

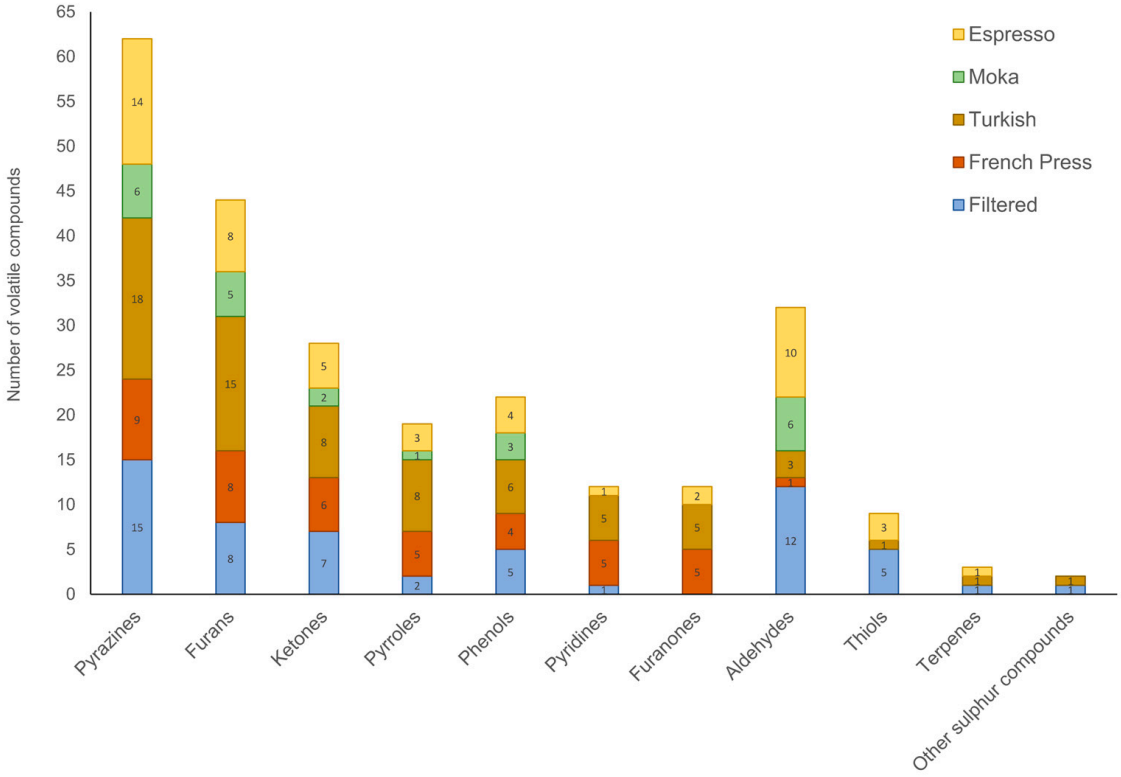


Figure 12. The number of volatile compounds grouped in chemical classes in filtered, French press, Turkish, moka, and espresso coffee beverages (adapted from Cordoba et al. [16]).

7.1. Filtered Coffee

Semmelroch and Grosch [167] identified thirty odors in the headspace of Arabica and Robusta coffee powders by gas chromatography–olfactometry. The most potent odorants of both Arabica and Robusta coffee were 2,3-butanedione, 2,3-pentanedione, 3-methyl-2-buten-1-thiol, methional, 2-furfurylthiol, and 3-mercapto-3-methylbutylformate, which are responsible for the buttery, animal, boiled potato, and roasty odors. The main difference between the two varieties of coffee was the greater odor impact of 2-methyl-3-furanthiol, 2,3-diethyl-5-methylpyrazine, and an unknown compound in Robusta coffee compared to Arabica. These volatile compounds were responsible for the boiled meat, earthy, and roasty odors. The authors also compared the coffee powder with the filtered beverage and found that the odorous impact of most volatile compounds decreases during the preparation of the filtered coffee, with the exception of acetaldehyde, propanal, methylpropanal, 3-methylbutanal, and dimethyltrisulphide, which increase. Therefore, drinking filtered coffee would increase the fruity, malty, and cabbage odors compared to the powder.

The same authors also quantified the volatile compounds of coffee brew from Arabica and Robusta varieties in order to calculate the OAV and, for seventeen of them, also the extraction yield [168]. They found that, except for one, all volatile compounds showed OAV values higher than 1 for both filtered coffees. Polar compounds such as guaiacol, furanones, 2,3-butanedione, and vanillin had higher yields (73–100%) than nonpolar compounds such as β-damascenone and 2-isobutyl-3-methoxypyrazine (12–26%).

The most important odorants with an OAV higher than 1000 were 2-furfurylthiol (roasty), β-damascenone (honey-like, fruity), 3-mercapto-3-methylbutylformate (roasty), methylpropanal (fruity, malty), 2-methylbutanal (malty), 3-methylbutanal (malty), and methanethiol (cabbage-like).

The study has revealed the potent odorants that are responsible for differences in the profile of beverages prepared from Arabica and Robusta coffees. The filtered bever-

age from Arabica was mainly characterized by 3-hydroxy-4,5-dimethyl-2(5H)-furanone, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, 3-mercapto-3-methylbutylformate, and 2-isobutyl-3-methoxypyrazine, while the Robusta coffee was mainly characterized by 2-furfurylthiol, 2-ethyl-3,5-dimethylpyrazine, β-damascenone guaiacol, 4-vinilguaiacol, methylpropanal, 2-methylbutanal, 3-methylbutanal, and methanethiol.

According to the different composition and odor of volatile compounds, Arabica coffee could be characterized by higher caramel/sweet and green odors than Robusta. On the contrary, Robusta coffee could be characterized by higher roasty, honey/fruity, burnt, and malty odors.

Another study that investigated the yield of volatile compounds in the filtered beverage from Arabica coffee found that some pyrazines (3-isobutyl-2-methoxypyrazine, 2-ethenyl-3-ethyl-5-methylpyrazine and 2-ethenyl-3,5-dimethylpyrazine), some thiols (furfurylthiol and 2-methyl-3-furanthiol), β-damascenone, and 4-vinylguaiacol had low yields ranging from 19 to 30% [176]. Additionally, this work reported that furanones, 2,3-butanedione, 2,3-pentanedione, and vanillin had yields higher than 79%. In the second part of this study, the aroma of the filtered coffee was reconstructed using the 25 compounds at the concentration found in the coffee sample, and the impact of volatile compounds on the coffee aroma was analyzed using the omission experiment. This experiment consists of omitting one or more compounds in the aroma model of coffee and comparing each reduced aroma model in a triangular test with two complete aroma models. This way, if the assessors performing a sensory evaluation on all the aroma models find modifications in the aroma of the reduced model, it can be established that the compounds omitted from the model solution are key odors.

The results obtained from the omission experiment indicated that the aroma of the brew was mainly due to the presence of some alkylpyrazines, furanones, phenols, 2-furfurylthiol, methional, and mercapto-3-methylbutyl formate. Thus, these volatile compounds can better explain the earthly, caramel/sweet, smoky/burnt, and roasty odors usually perceived when drinking a filtered coffee.

Miyazato et al. [186] investigated odor-active compounds in filtered beverages obtained from roasted Brazilian Arabica coffee by Aroma Dilution Extract Analysis (AEDA). The study revealed 34 odor-active compounds present in the coffee brew, 10 of which showed the highest AEDA values.

Guaiacol (phenolic, medical, smoked), unknown (sweaty), and 3-phenylpropionic acid (honey-like) were the most intense compounds, followed by 2-ethyl-3,5-dimethylpyrazine (natty, roasty), isovaleric acid and 2-methylbutanoic acid (cheese-like), β-ionone (green tea-like, violet), 4-hydroxy-2,5-dimethyl-3(2H)-furanone (caramel-like), cis-2,6-dimethyl-1,4-cyclohexanedione (pungent, spicy), and 5-vinylguaiacol (phenolic, banana-like, sweet). Some of them were also reported in previous studies, i.e., guaicol, 2-ethyl-3,5-dimethylpyrazine, and 4-hydroxy-2,5-dimethyl-3(2H)-furanone, while others were reported for the first time in coffee brew, such as 5-vinylguaiacol, 3-phenylpropionic acid, and cis-2,6-dimethyl-1,4-cyclohexanedione. 5-Vinylguaiacol was reported in raw coffee beans [187], but it has never been reported in roasted coffee. It has a more intense AEDA value than 4-vinylguaiacol, which has been generally found as an odor-active compound in roasted coffee. cis-2,6-Dimethyl-1,4-cyclohexanedione was characterized by a low odor threshold (0.002–0.007 ng/L in air; 0.025 mg/L in water), and model reactions revealed that it was formed from monosaccharides via thermal degradation under alkaline conditions.

Caporaso et al. [50] monitored 24 key aroma compounds of Arabica coffee in the headspace of moka, Neapolitan, Americano, and espresso coffee brews. Although the volatile compounds were not quantified, and only normalized values were reported, furfuryl methyl ether, 2,3-pentanedione, 2,5-dimethylfuran, β-damascenone, hexanal,

2-methylpropanal, 2-methylbutanal, and 3-methylbutanal were found to be higher in filtered coffee than in the other three coffee preparations. These volatile compounds were reported in the literature to be responsible for the nutty, buttery, ethereal, fruity, green, malty, and chocolate odors.

7.2. Espresso Coffee

Caprioli et al. [188] studied the effect of temperature and pressure of the espresso machine on coffee quality. They used two espresso machines to prepare the beverages from Arabica and Robusta coffee, one with a pressure of 9 bar and maintaining constant temperature (94 °C), and the other with pressure ranging from 2 to 8 bar and temperature ranging from 88 to 98 °C. The sensory results and the measure of 10 key odorants indicated that the usual espresso machine temperature and pressure settings (i.e., 92 °C and 9 bar) are very close to those needed to obtain the best quality espresso. In fact, at 9 bar and 92 °C, for both varieties, espresso coffees contained a greater number of positive notes than negative ones.

Mestdagh et al. [189] studied the extraction kinetics of 20 volatile compounds during the preparation of a coffee beverage by a commercial espresso machine. The results indicated that the kinetics were related to the volatile compounds' polarity rather than volatility. Particularly, higher polar components, such as 2,3-butanedione, were released much faster than compounds with an average polarity, such as β-damascenone. In contrast, the odorants' volatility did not seem to play a major role.

Other studies evaluated the volatile profile of espresso coffee in order to differentiate the beverages prepared from different botanical coffee varieties (Arabica and Robusta) and types of roast (Natural and Torrefacto) [190,191]. It has been found that the major chemical class present in espresso coffee is furans, followed by pyrazines, aldehydes, and pyridines. The results showed that furans were present in higher amounts in the Arabica blends than in the Robusta blends, while the pyrazine and aldehyde were present in lower amounts in the Arabica than Robusta blends. In addition, comparing the blend Robusta torrefacto with and without the sugar addition, the volatile composition was similar, demonstrating that sugar did not affect the volatile composition.

Rocha et al. [191] also revealed that the volatile composition of coffee brew was related more to the botanical origin (Arabica or Robusta) than to the espresso or plunger method. However, the espresso coffee showed a higher level (GC peak area) of the total volatile compounds than plunger coffee.

Michishita et al. [192] found that the volatile composition of espresso coffee is affected by both the roasting degree and the origin of the coffee beans. A total of 73 aroma compounds were identified in espresso, but only 36 were the most powerful odorants. They were grouped by smell similarity determined by GC/O analysis (CHARM) in eleven groups of the sensory descriptors. In particular, the highest CHARM values were found for the descriptor buttery-oily, followed by smoke-roast, phenolic, sweet-caramel, nutty-roast, sweet-fruity, and green-earthy. The aroma compounds mostly responsible for these sensory descriptors were 2-methylpropanal, 2 and 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione and trans-2-nonenal for buttery-oily; 3-methyl-2-butane-1-thiol, 2-furanemethanethiol, 2-((methylthio)methyl)furan, and 3-mercapto-3-methylbutanol for smoke-roast; guaiacol, 4-ethyl guaiacol, and 4-vinyl guaiacol for phenolic; furaneol and 4,5-dimethyl-3-hydroxy-2(5H)-furanone for sweet-caramel; 2-ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine for nutty-roast; β-damascenone for sweet-fruity; 2-methoxy-3-isopropylpyrazine and 2-methoxy-3-(1-methylpropyl) pyrazine for green-earthy.

Lopez-Galilea et al. [193] found 47 volatile compounds in commercial coffee brews from conventional and torrefacto roasted coffee (i.e., a coffee obtained through a roasting

process in which sugar is added to robusta coffee), prepared by a filter coffee maker or an espresso machine. Among them, 34 volatile compounds were odor-active compounds. Pyrazines, pyridines, and pyrroles were found in higher amounts in torrefacto coffee brews than in conventional ones, but some differences were also observed in using the two preparation methods. Specifically, ketones, which are responsible for buttery and fruity notes, were found in higher amounts in filtered coffee, whereas aldehydes, responsible for chocolate-like odors, were found at higher levels in espresso coffee.

Charles et al. [194], in a study on aroma release in espresso coffee evaluated by mass spectrometry-nose (MS-nose) analysis, showed that most of the aroma compounds are released in the mouth in larger quantities when a stronger roasting degree is used. The sensory descriptors associated with the increase in aromas were burnt, roasted, astringent, and bitter. Some of the volatiles could be powerful odorants of coffee, i.e., 2-methylpropanal and guaiacol, explaining burnt and roasted odors.

In a comparison with filtered, moka, and Neapolitan coffees, espresso was better characterized by acetaldehyde, butanal, 2-methylpropanal, 2-methylbutanal, methanethiol, and 2-furanmethanol acetate, mainly responsible for fruity/ethereal, chocolate, malty/toasty, malty/roasty, cabbage-like, and ethereal-floral odors [50].

Finally, in a study on the volatile composition of 65 capsule-brewed espresso coffees commercialized by 5 of the most representative brands in Italy, Lolli et al. [195] identified more than 70 volatile compounds, including 7 furans, 12 pyrazines, 9 aldehydes, 10 ketones, 5 pyrroles, 9 esters, 2 pyridines, 2 sulfur and 6 phenolic compounds, 3 terpenes, and others. The results showed that the qualitative aroma chemical profiles were similar for all 65 capsule-brewed espresso coffees, especially within the same brand. From a quantitative point of view, the inter-brand variability was within the range of 20–75%. The authors explained that this high variability in the level of volatile compounds within capsules of the same brand could be due to a wide selection of coffee products. Pyrazines and sulfur compounds (especially for two brands) showed the highest variation, while the lowest variation was found for pyrroles. The difference in the level of these chemical classes suggests that this could be due primarily to the different roasting grades of coffee beans.

Crema is a key factor in evaluating espresso coffee, dramatically impacting consumers' acceptance and appreciation due to its visual appearance, as well as its effect on mouthfeel and aroma [19]. Greater crema amounts are associated with stronger roasted flavors. The release of pleasant volatile compounds, especially those associated with roasted flavors, decreases dramatically when there is little crema in the coffee brew [196]. For single-service espresso coffees, Dold et al. [197] reported an experiment using the Nespresso system to investigate different foam structures by using water with varying levels of mineral content. It was shown that the structure of the foam can affect volatile compound release; however, the effect is absent or very limited at the beginning of the extraction, e.g., during the first 2.5 min. After this extraction time, the foam stability influences the release of aroma compounds through gas bubble stability, evaporation, and diffusion, thus providing a barrier for the aroma diffusion. This reflects a lower above-the-cup concentration of volatile compounds and, thus, a stronger retention of these compounds in the brew.

7.3. Turkish Coffee

Even if the aim of the work of Bicchi et al. [198] was to apply a method to discriminate between roasted coffees of different origins, it has been possible to establish some information on the volatile composition of Turkish coffee. It was found that carboxylic acids (acetic, propanoic, pentanoic, and hexadecanoic acids) and other polar compounds, such as furans, were extracted more efficiently from coffee powder, confirming that compounds with high polarity were the most representative of Turkish coffee. In fact, among

the thirty-six volatile compounds reported in commercial Arabica and Robusta coffee powder blend, only seven were found in the coffee beverage: pyridine, 2-furanomethanol, 5-methyl-furancarboxyaldehyde, 2-furanomethanol acetate, phenol, 2-hydroxy-3-methyl-2-cyclopentanone, and 3-hydroxy-3-methylpyran-4(4H)-one.

The volatile profile of light-, medium-, and dark-roasted Turkish-style coffee brews was studied by Kivancli and Elmaci [199]. The authors identified sixty-five volatile compounds from twelve chemical classes (furans, pyrazines, pyrroles, phenols, pyridines, ketones, oximes, alcohols, aldehydes, thiophenes, benzenes, and terpenes). Among them, Turkish coffee was abundant in furans, pyrazines, pyrroles, and phenols. They concluded that these chemical classes could explain the roasted/burnt, spicy, woody, and fermented odor perceived by sensory analysis.

Amanpour and Selli [200] identified and quantified in Turkish coffee a total of 60 volatile compounds, which included different chemical classes (furans, lactones, phenolic compounds, pyridines, pyrazines, acids, cyclopentenes, pyrroles, furanones, ketones, alcohols, aldehydes, and thiols). Also, in this case, furans were reported to be at the highest levels, followed by lactones. Particularly, furfuryl alcohol followed by β-butyrolactone, pyridine, hexadecenoic acid, maltol, 2-methyl pyrazine, and furfuryl acetate were found in large amounts. However, the most impacted aroma compounds for Turkish coffee, based on the odor activity value (OAV), were guaiacol, 2,3-butanedione and furfuryl acetate. These volatile compounds are reported in the literature to be responsible for the smoky, buttery, and ethereal-floral odor, respectively.

A study utilizing GC-MS–olfactometry on Coffea arabica beans identified 26 key odorants in medium-roasted Turkish coffee samples and 28 key odorants in dark-roasted samples [201]. The highest flavor dilution (FD) factor of 2048 was identified for 2-ethyl-3,5-dimethylpyrazine in the medium roast and for 2-ethyl-3-methylpyrazine in the dark roast. Notably, there was a significant difference in the phenolic and burnt odor of guaiacol, which was more pronounced in the dark roast. Sensory analysis revealed that the medium-roast coffee brew achieved higher scores in overall impression and favorable coffee descriptors compared to the dark-roast coffee brew.

In another study, the effects of brewing Turkish coffee in different pots (an automatic coffee machine, a stainless-steel pot, and a copper pot buried in hot sand) on the levels of pyrazines, total phenolic content, and antioxidant activity were investigated [202]. The samples brewed in a copper pot buried in hot sand exhibited the highest levels of pyrazines, followed by those prepared in a stainless-steel pot and an automatic coffee machine. Conversely, the coffee produced by the automatic machine demonstrated a higher total phenolic content and antioxidant activity, with the stainless-steel pot and the copper pot buried in hot sand following in sequence. The authors hypothesized that this could be attributed to the shorter boiling time of the coffee machine, approximately 90 s, which may have minimized the degradation of phenolic compounds and limited the formation of pyrazines.

7.4. French Press Coffee

The French press (cylinder with plunger) beverage contains a lower total amount of volatile compounds compared to espresso. The study identified pyrazine and pyridine as the characteristic components of plunger coffee, while furans are the characteristic components of espresso [191]. Also, Gloess et al. [32] found a higher concentration of volatile compounds in espresso-type coffee than in "Lunghi" like French press. The main factor ascribable to this result was hypothesized to be the dilution effect. In fact, the "Lungo" had a higher ratio of water to coffee, leading to lower overall concentrations in the coffee solution and, therefore, to lower concentrations of the aroma molecules in the

gas phase above the cup. Amanpour and Selli [200], comparing French press with Turkish coffee, observed a similar volatile composition, different only in two volatile compounds that were absent in French press, namely, 2-ethyl-3-methylpyrazine and 4-methyl thiazole.

7.5. Moka Coffee

Caporaso et al. [50] monitored 24 key aroma compounds of Arabica coffee in the headspace of moka, Neapolitan, Americano, and espresso coffee brews. They found that moka coffee was characterized by the presence of guaiacol, 2-ethyl-6-methylpyrazine, 2-methyl-3-trans-propenylpyrazine, and 2-ethyl-3,5-dimethylpyrazine, responsible for smoky, hazelnut, roasty, and nutty odors, respectively. The high concentrations of these volatile compounds (they increased as the degree of roasting increased) could be due to the higher extraction temperatures applied in the preparation of moka coffee.

Another study established that pressure-brewing procedures, such as espresso and moka, extract more volatiles (some furan, pyrrole, and thiophene compounds) with antioxidant properties, originating from the Maillard reaction, compared to plunger and filter procedures [203].

7.6. Neapolitan Coffee

Neapolitan coffee brew had higher amounts of hexanal, β-damascenone, and some pyrazines with respect to other procedures, such as espresso, moka, and filtered coffees, which can be considered a distinctive characteristic of Neapolitan coffee aroma [50] (Figure 12). β-Damascenone and hexanal are also well correlated with filtered coffee brew (Americano) and contribute to fruity and green notes in the beverage. The authors explained that the higher hexanal content in Neapolitan coffee brews, as well as in filtered coffee, could be due to the considerably higher brewing time, and a higher oxygen exposure of the ground coffee could promote carotenoid degradation and lipid oxidation, precursors from which these two aroma compounds originate. In fact, longer preparation times lead to the formation of a higher amount of these compounds, indicating a high susceptibility to oxidation and degradation during coffee brewing.

Neapolitan coffee brews contain lower levels of aldehydes than espresso and lower levels of guaiacol and 2-methyl-3-trans-propenylpyrazine than moka coffee. The latter two compounds are associated with the brewing temperature of moka coffee [204]. This gives Neapolitan coffee a lower nutty, roasty, or smoky odor.

Despite the similarities of the brewing techniques for Americano, the Neapolitan coffee was much more similar to moka [205] but with lower smoky notes and more fruity, sweet, and green notes (Figure 12). The difference between Neapolitan and Americano coffee brew could be mainly due to the different ground coffee-to-water ratio that differentiates the two coffee preparation techniques, while the difference compared to moka and mostly to espresso could be explained by different water temperature and pressure.

7.7. Cold Drip and Cold Brew Coffee

In the last few years, cold brew has become a growing market within the coffee industry, and the scientific interest in its chemical composition has increased. Cordoba et al. [206] reported the effects of grinding (medium-coarse particle size) and extraction time (14–22 h) on the physicochemical and sensorial properties of cold brew coffee produced using Arabica coffee from two Colombian areas (Huila and Nariño). The findings of this study confirmed that particle size, contact time, and coffee type are important factors affecting the flavor profile, also for cold brew coffee. In fact, it has been demonstrated that the shortest time (14 h) and coarse grinding for both coffee types (Huila and Nariño) determined a higher score in all sensory descriptors. Nariño and Huila cold brew coffees presented a high relative level of furans, pyrazines, ketones, and aldehydes. Among

the furans, furfural was the major volatile compound in the cold brew coffee, followed by 5-methylfurfural and 3-furanmethanol. These compounds are mainly associated in the literature with sweet and caramel notes. The most abundant pyrazines were ethyl pyrazine, 2,5, and 2,6-dimethyl pyrazines, described as having nutty, earthy, roasty, and green aromas. Among ketones and aldehydes, the most abundant volatile compounds were 2,3-pentanedione, 2- and 3-methylbutanal, responsible for buttery, chocolate, and malty odors, respectively. It is possible to speculate that the cold brew method provides a more aromatic coffee beverage because at low temperatures the volatility of the aroma compounds is lower than at high temperatures, thus the volatile compounds are better retained.

Another study examined the use of negative-pressure extraction to reduce the extraction time for cold brew coffee. Sensory evaluation revealed that the optimal extraction time was 5 h, significantly enhancing the extraction efficiency of cold brew coffee with two key aroma compounds predominant in the sample: 2,3-diethyl-5-methylpyrazine and 3-ethyl-2,5-dimethylpyrazine [207]. However, Cordoba et al. [206] also revealed that cold brew coffee has less intensity in the aroma, taste, aftertaste, acidity, and body than its hot counterparts. The differences between a cold brew and hot coffee were also confirmed in another study that found a higher value in all sensory and chemical attributes, except Brix, in hot than cold brew coffee [33].

A study using gas chromatography–mass spectrometry and odor activity value calculations confirmed the role of pyrazines in the aroma of cold brew coffee [208]. Sensory tests revealed that cold brew coffee is fruitier and less bitter and astringent than hot brew coffee. These differences were attributed to the presence of specific compounds: pyrazines, linalool, and furfural acetate for the aroma, and quercetin-3-O-(6′-O-*p*-coumaroyl)-galactoside for the taste. Cold immersion and French press coffee were sweeter and had more intensity of nutty, caramel, and malt notes, unlike cold drip coffee [209]. Cold brew preparation, compared to cold drip, showed some differences in terms of chemical composition, physical properties, and sensory attributes of the coffee. The cold brew method was characterized by a higher intensity of sugar caramelization attribute and sweet taste, whereas the cold drip method was characterized by a higher overall intensity of odor and bitterness. The latter is mainly related to higher contents of caffeine and chlorogenic compounds in cold drip [55]. Both cold brew and cold drip coffees were more astringent, sour, sweet, and with a global flavor intensity than French press coffee [55].

A study comparing cold and hot brewing methods revealed that the degree of roasting has a greater impact on the physicochemical and sensory properties than the extraction temperature. The authors concluded that using light-roasted coffee beans with cold brewing techniques results in coffee that has better physicochemical properties and sensory characteristics [53]. Maksimowski et al. [210] also found that light-roasted beans are the best option for producing cold brew coffee.

Another research on cold brew coffee and espresso examined how different roasting conditions, particle size distribution, brewing method, and water type affected the volatile compounds. Cold brew coffee contained higher levels of 2-methylpyrazine, 1-methylpyrrole, and 2-acetylfuran than espresso. Higher roasting temperatures and longer roasting times increased 2,2′-methylene-bis-furan, guaiacol, and 4-ethylguaiacol while reducing furfural. The grind size was inversely related to the intensity of volatile compounds. Coffee brewed with filtered water contained higher levels of 2-methylpyrazine, 2,5-dimethylpyrazine, and 2-methoxy-4-vinylphenol than coffee brewed with tap or bottled water [211].

Finally, Lapčíková et al. [212] compared four extraction techniques (cold brew, espresso, French press, and AeroPress) and found that espresso and cold brew were the most effective methods for antioxidant activity and sensory quality. Espresso coffee exhibited the highest

antioxidant activity and the highest levels of most coffee volatile compounds. Meanwhile, cold brew coffee was rated as the preferred option in terms of sensory characteristics and flavor.

8. Exploring the Impact of Tasting and Serving Modalities on Coffee Aroma Perception

The perception of coffee brew flavor occurs through two distinct modalities. The first takes place during inhalation, when coffee odorants are released from the coffee cup into the air (headspace of cup) and pass through the external nostrils to stimulate the olfactory receptors in the nasal cavity (orthonasal route). The second modality takes place when the coffee brew is introduced into the mouth. Various chemical stimuli are dissolved in the mouth and come into contact with taste and other receptors on the tongue. These chemical stimuli are responsible for the taste, tactile, and mouthfeel sensations of coffee, particularly the sensation of bitterness, but also sourness, sweetness, savory, astringency, etc.

Moreover, coffee odorants can interact with odor receptors by moving from the mouth to the nasal cavity via the nasopharynx (retronasal route). In this case, we refer to the aroma of the coffee brew.

Akiyama et al. [213], using a device developed to analyze retronasal aroma perception by simulating the mouth conditions [214], found that volatile compounds grouped with a similar odor note, such as buttery-oily, sweet-fruity, and green-earthy odor, exhibited significantly higher retronasal aroma intensities compared to orthonasal odor, with an increase of 97%, 87%, and 48%, respectively. The volatile compounds grouped in the buttery-oily odor descriptor were reported to be aldehydes (2-methylpropanal; 2-and 3-methylbutanals; (Z) and (E)-2-nonenal) and ketones (2,3-butanedione and 2,3-pentanedione). The sweet-fruity odor descriptor was represented by linalool, β-damascenonce, and benzene acetaldehyde. The volatile compounds grouped in the green-earthy odor descriptor were reported to be methoxy pyrazines, mainly 2-methoxy-3-(1-methylethyl) pyrazine and 2-methoxy-3-(1-methylpropyl) pyrazine. On the contrary, furanone compounds (furaneol, homofuraneol, and sotolone), responsible for the relative charm value of sweet-caramel odor, were larger in the orthonasal than retronasal cavity, with an increase of 60%.

The coffee brew aroma, similar to that of other foods and drinks, is significantly affected by the oral process, and this is the reason why the sensations of odor (orthonasal odor) and aroma (retronasal odor) could be perceived differently, even though the same olfactory sense is involved.

Such differences are due to factors that are able to affect the volatility of coffee odorants and, consequently, the concentration of aroma compounds of coffee in the mouth headspace when drinking coffee, such as salivary constituents, salivation flow, mouth size, breathing, and temperature.

An alternative approach to studying the retronasal aroma is the in vivo MS-nose space analysis. This method enables the observation of aroma compounds within the taster's nose during the tasting process. A study conducted by Charles et al. [194] successfully integrated MS-nose analysis with a sensory evaluation using the temporal dominance of sensations (TDS) method. The study underscored the significant role of taste–smell interactions in flavor perception, particularly between sweetness and distinct coffee flavors. MS-nose analysis revealed that adding sugar did not markedly affect the release of volatile compounds but altered the sensory perception of coffee in the mouth, as indicated by TDS analysis. As anticipated, sweetness became the dominant note over bitterness and sourness, enhancing overall flavor complexity by accentuating caramel and nutty notes while diminishing roasted or burnt tones.

A study confirmed the role of saliva in aroma release, emphasizing the differences between the orthonasal and retronasal odor perception across four coffee brewing methods [215]. The research specifically examined filtered coffee (Americano), moka, Neapolitan, and espresso preparations.

The method of brewing significantly influences the release of aroma compounds, which is further affected by the coffee's fat content and its interaction with saliva. Notably, the polarity of saliva can modify the volatility of certain odor compounds through the emulsion formed with coffee fat. Filtered coffee, characterized by its lower fat content, tends to release more hydrophilic compounds, which are associated with chocolate and roasted notes. Conversely, espresso, with its higher fat content, accentuates hydrophobic compounds, resulting in honey and smoky aromas.

A complicating factor in coffee aroma perception via the retronasal route is significant variations in oral parameters among individuals, including saliva flow and composition. These variations can be influenced by factors such as sex, age, ethnic group, health status, hunger, or satiety [216,217]. In addition, the visual, auditory, olfactory, and tactile aspects of the environment have all been shown to impact the experience of tasting and drinking coffee [218]. All these factors lead to differences in coffee aroma perception from person to person. This observation may also account for why various tasters frequently perceive a different aroma in the same coffee brew.

Additionally, different methods of serving coffee, such as container shape, serving volume, and temperature, as well as a sipping technique, affect the tasting experience.

Chapko and Seo [219] analyzed three Arabica varieties from Ethiopia, Kenya, and Colombia at temperatures of 70, 55, 40, and 25 °C. Stronger aromas, such as "coffee impression", "roasted aroma", and "chocolate/cocoa aroma", were revealed at higher temperatures (70 and 55 °C), while lower temperatures (40 and 25 °C) showed more sour and stale flavors. The variation in sensory attributes was primarily attributed to serving temperature rather than coffee variety.

Adhikari et al. [220] demonstrated similar findings, revealing that the intensity of sensory attributes was significantly higher in filtered coffee brewed at 70 °C compared to 50 °C and 60 °C. However, the consumption temperature affected Arabica, Robusta, and a blend of Arabica and Robusta coffee differently. Arabica maintained consistent sensory characteristics across all temperatures, whereas Robusta exhibited reduced intensity in key attributes like "roasted" and "burnt" at 50 °C compared to 70 °C. The study concluded by recommending a consumption temperature of 70 °C to optimize sensory intensity without posing a scalding risk.

The effects of different serving temperatures were consistent for both freshly brewed coffee, served 15 min after brewing, and aged coffee, served 90 min after brewing. However, the freshness of the coffee (i.e., the time elapsed between brewing and serving) also influenced the "green-ripe" and "astringency" sensory attributes, though its impact was less significant compared to the serving temperature [219].

Another study investigated six serving temperatures ranging from 31 °C to 62 °C [221]. As expected, the total volatile release increased with increased temperatures; however, it was shown that individual volatile compounds had different behaviors. Obviously, increasing the temperature leads to an increase in the amount of vapor that is formed and, thus, the vapor pressure of each volatile compound. It follows that those aliphatic ketones, alkylpyrazines, some furans, and pyridines increase most notably at temperatures $\geq$ 50 °C, and thus, the overall intensity, roasted and bitter sensory perceptions are strongly perceived in the coffees served at temperatures between 50 °C and 62 °C. This is possible because the volatile compounds with higher vapor pressure (higher volatility) make a larger contribu-

tion than the compounds with lower vapor pressure. On the contrary, the sensory notes of tobacco and 'sweet' were mostly associated with the coffees served at 31–44 °C.

When coffee is kept hot at around 40 °C for 30 min, its flavor can degrade due to the reduction of some key compounds. This degradation is influenced not only by temperature, which can drive off the most volatile compounds but also by interactions with non-volatile compounds such as melanoidins and hydroxyhydroquinone.

Sun et al. [222] conducted a study examining the behavior of thiols in brewed coffee incubated at 40 °C for 30 min. Significant losses of over 60% were observed for 2-furfuryl thiol, methanethiol, and 2-methyl-3-furanthiol. 2-furfuryl thiol, which is linked to coffee and roasting aromas, decreased to just 3.3% of its original concentration. Methanethiol and 2-methyl-3-furanthiol, which are responsible for the aromas of boiled potatoes and roasting, declined to 25.5% and 34.4%, respectively. This reduction in thiols was found to correlate with the concentration of low-molecular-weight melanoidins (less than 3 kD). High-molecular-weight melanoidins had a minimal impact. Additionally, hydroxyhydroquinone was shown to bind strongly to thiols in the coffee model, further accelerating their loss. Another critical factor contributing to thiol reduction was the lipid content. The same study demonstrated that increasing the lipid content in a mimic coffee model from 0% to 3.6% resulted in a decrease in headspace concentrations of lipophilic thiols. This reduction in the coffee headspace is attributed to the tendency of these compounds to dissolve in the lipid phase rather than the air phase. Consequently, this leads us to think that all volatile compounds with higher oil–water partition coefficients are likely to exhibit reduced concentrations in the coffee brew after 30 min.

Other studies have highlighted how the shape of a container generates multisensory associations that significantly impact our sensory experience of the taste and aroma of food and beverages [223]. For instance, research conducted by Carvalho and Spence [224] revealed that rounded coffee cups not only enhance the hedonic judgments but also positively impact the perceived sweetness of the coffee in both amateur and expert specialty coffee consumers. They stated that a rounded shape likely triggers associations with softer, sweeter flavor profiles, positively influencing taste perception even before the first sip.

In another sensory study, the "descriptive analysis method" was used to evaluate whether the sensory quality of coffee was affected by mug shapes (short/wide vs. tall/narrow) and beverage volumes (100, 150, 200, and 250 mL) for two types of coffee (Arabica vs. Robusta) at two different powder concentrations, 0.8 g/100 mL and 1.6 g/100 mL [225]. The results showed that the sensory quality of instant coffee remained stable across different mug shapes and beverage volumes for three out of the four coffee types studied. The exception was found for Arabica coffee at lower concentrations (0.8 g/100 mL), which had its orthonasal aroma intensity and complexity, as well as roasty and malty notes, enhanced when served in larger volumes (e.g., 250 mL) in a short/wide mug.

In addition, the metallic finish of cups notably influenced sensory attributes such as aroma, flavor, and sweetness, as well as hedonic characteristics like likability and elegance [226]. This phenomenon arises due to the influence of cup color on sensory perception through cross-modal associations. For example, the reddish-bronze hue of the bronze cup enhanced the perception of sweetness in coffee, aligning with the common association of red tones with sweetness. On the other hand, cups with metallic coatings, particularly platinum, conveyed a more pronounced metallic taste in coffee compared to white cups. Additionally, coffee experts and consumers exhibited differing preferences regarding cup finishes. For instance, consumers favored coffee served in a gold cup, associating it with premiumness.

Other variables can impact consumer sensory evaluations, such as the "way of drinking" coffee, i.e., with large or small sips. The sip is a critical factor influencing coffee aroma nuances. The preference for whether a coffee brew smells better with a larger or smaller sip volume varies from person to person. However, what is certain is that the aromatic profile of the coffee will shift, with certain sensory notes becoming more pronounced, while others may diminish in intensity. It has been shown that larger sips result in a higher total aroma release [216]. This finding is partially obvious since the higher the amount of coffee brew is put into the mouth, the higher its aroma release will be to the nose receptors by the retronasal way, and the higher will be the perceived aroma. However, the release of aroma compounds resulted in different sensations. In particular, when coffee brew is consumed in one sip, it involves an increase in some aldehydes that, from a sensory point of view, are mainly related to chocolate, malty, and caramel-like odors. On the contrary, when coffee is tasted by smaller sips, there is a decrease in the perception of aldehydes, and an increase in the level of β-damascenone and 4-vinylguaiacol. The former are responsible for fruity and/or sweet odors, while the latter have smoky and/or spicy notes. The sip volume will probably also have an effect on the taste, by giving stronger taste perceptions due to the more extended interactions with the receptors.

In conclusion, by carefully considering factors such as container design, serving volume, temperature, and sipping techniques during coffee tasting, consumers can elevate their satisfaction and preferences, leading to a more sophisticated and enjoyable coffee-drinking experience.

9. Conclusions

The quality of a cup of coffee is intricately linked to both the inherent properties of the beans and the specific brewing methods employed. While factors such as origin, post-harvest processing, roasting, and grinding establish the potential quality of coffee, the brewing process determines the final sensory and physicochemical characteristics experienced by the consumer. Diverse brewing techniques lead to notable differences in parameters such as pH, total dissolved solids, lipid and fatty acid content, acidity, and the formation of crema, each influencing the aroma, taste, mouthfeel, and overall acceptability of the final beverage. Espresso, for instance, is distinguished by a stable and persistent crema, high viscosity due to lipid emulsification, and a higher extraction of solids, whereas methods like French press yield brews with increased fatty acid content and slightly elevated pH.

Moreover, extraction conditions, including contact time, temperature, and filtration medium, play a pivotal role in solubilizing bioactive compounds such as caffeine, chlorogenic acids, and other methylxanthines, directly impacting the brew's antioxidant capacity and perceived bitterness. Hot brewing processes generally result in lower pH and higher total solids compared to cold brewing, while filter methods tend to retain more lipophilic compounds, therefore lowering lipid content. Importantly, consumer perception remains at the heart of coffee quality assessment, as sensory characteristics such as aroma, flavor, and mouthfeel ultimately drive preference and market success.

In summary, brewing methods exert a profound influence on the coffee cup quality by modulating the chemical composition and sensory attributes of the beverage. Ongoing research into the effects of different extraction techniques and conditions will continue to enhance our understanding of how to optimize coffee preparation for both quality and consumer satisfaction.

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Abbreviations

The following abbreviations are used in this manuscript:

^{1}H NMR	Proton Nuclear Magnetic Resonance
AEDA	Aroma Dilution Extract Analysis
ATR	Attenuated Total Reflectance
Bia	Espresso—Bialetti
Bo	Lungo—French Press
CFQA	Caffeoylferuloylquinic Acid
CHARM	Combined Hedonic Aroma Response Measurement
CoA	Coenzyme A
CQA	Caffeoylquinic Acid
CQI	Coffee Quality Institute
DAD	Diode Array Detector
DART	Direct Analysis in Real-Time Ionization
DE	Espresso from semi-automatic machine
diCQA	diCaffeoylquinic Acid
DL	Lungo from semi-automatic machine
F	Lungo—Filter Coffee
FQA	Feruloylquinic Acid
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-O	Gas Chromatography-Olfactometry
GC–FID	Gas Chromatography Flame Ionization Detector
GC–MS	Gas Chromatography Mass Spectrometry
HPLC-DAD	High-Performance Liquid Chromatography with Diode Array Detection
HPLC-MS	High-Performance Liquid Chromatography Mass Spectrometry
HPLC-PDA	High Performance Liquid Chromatography with Photodiode Array Detection
HPLC-TOF	High Performance Liquid Chromatography Time of Flight
HPLC-UV	High-Performance Liquid Chromatography Ultra-Violet
ICO	International Coffee Organization
KK	Lungo—Karlsbader Kanne
LC–MS	Liquid Chromatography Mass Spectrometry
LDL	Low-Density Lipoprotein
MEKC	Micellar Electrokinetic Chromatography
MS-Nose	Mass Spectrometry-Nose
NE	Espresso—NEspresso
OAV	Odor Activity Value
OTA	Ochratoxin A
PAHs	Polycyclic Aromatic Hydrocarbons
*p*CoQA	*p*-Coumaroylquinic Acid

RP-HPLC	Reverse Phase High-Performance Liquid Chromatography
SCA	Specialty Coffee Association
SCAA	Specialty Coffee Association of America
SCI	Specialty Coffee Institute
SE	Espresso from fully automatic machine
SL	Lungo from fully automatic machine
SPE	Solid Phase Extraction
SPME-GC/MS	Solid Phase Microextraction–Gas Chromatography/Mass Spectrometry
TDS	Temporal Dominance of Sensations
TPC	Total Phenolic Content
UHPLC-DAD-ESI-MS	Ultra-High-Performance Liquid Chromatography coupled with Diode Array Detection and Electrospray Ionization Mass Spectrometry
UHPLC-MS/MS	Ultra-High-Performance Liquid Chromatography–Tandem Mass Spectrometry
UV	Ultra-Violet

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