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Our Everyday Cup of Coffee: The Chemistry behind Its Magic

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Coffee beverages are so popular all over the world that there is hardly the need to describe them. Their fragrance and flavor are the first stimuli that strike our senses early in the morning, they crown an excellent meal, and are recurring visions during never-ending work sessions. After all, our cup of coffee is a dear old friend, about which we only think we know everything. When examining it from a chemist's viewpoint, we must nevertheless acknowledge that its nature is so complex that vast gaps remain in scientific understanding.

The history of coffee starts with the legends about the discovery of coffee as a food. These legends tell the story of Abyssinian shepherds consuming the seeds of some *Coffea* plant, by chewing either raw or cooked, generally roasted, fruits *(1)*. For those of you who have tried to munch on a bean, it is hard to imagine that the success of coffee—today the most traded food commodity—could have ever occurred, had those primitive habits persisted.

On one hand, it seems logical that the appeal of coffee to those early "food-science pioneers" derived essentially from their experiencing stimulation that proved to be beneficial to their activities *(2)*. In other words, the primordial reason for coffee consumption must have been the physiological effects of caffeine in the human organism, by now well documented *(3)*. On the other hand, it is pretty obvious why coffee has become so popular, achieving the position of the second most largely consumed beverage after water. It is a question of flavor or, better still, of overall impact on our senses. Sensory evaluation, which used to be considered magic because "taste is a matter of taste", is now earning the status of a highly respected analytical tool (cup-testing is its technical name), able to produce key information with good reliability.

While people like the flavor of coffee, they do not like the disturbing sensory feeling of chewing and swallowing hard particles deriving from a bean. This fact makes beverage preparation a fundamental step for enjoying the benefits of this commodity and sometimes for transforming it into a specialty.

Production and Consumption Patterns

The coffee tree belongs to the Rubiaceae family, where two species of the genus *Coffea* are economically important, *C. arabica* and *C. canephora (4)*. The latter is better known as robusta coffee, a term derived from its ability to thrive in the harsh environment of the west African rain forest. Arabica coffee, which is indigenous to the Ethiopian highlands and prospers in cooler mountain regions of the tropical belt (up to 2500 m), accounts for more than two-thirds of the world production and is considered to give the best, mildest cup of coffee.

Figure 1. Laborers handpicking a harvest of coffee fruit.

Ripe cherries, the name for the fruit of the coffee plant, are usually picked by hand (Figure 1). The immediate post-harvest process, either direct sun drying or depulping, releases two seeds per fruit, the raw coffee beans. Beans are usually shipped in jute bags to the roasting facilities overseas.

As an international trade commodity, global coffee production ranks second in value only to petroleum and results in more than 6 billion kg of coffee per year. Cultivation occurs in some 50 tropical countries (Figure 2). As most of these coffee-producing countries have less-developed economies, coffee often represents the main source of hard-currency income.

Coffee consumption has spread worldwide, especially in Europe, the United States, and Japan (Figure 3). The type of related beverages and the pattern of consumption are strictly associated with social habits and culture of the country. Differences in the raw bean composition, in roasting conditions, and in the extraction procedures used to prepare coffee brews result in a great diversity of chemical composition in the final product, the cup of coffee. Also the size of a single serving is highly variable, ranging from 15 mL of concentrated Italian *espresso* to over 250 mL in many English-speaking countries. Moreover, a coffee serving can be derived from brewing a

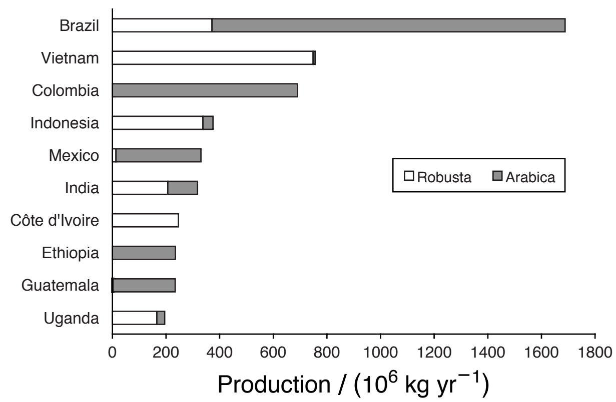

Figure 2. Major coffee-producing countries in year 2001 *(5)*.

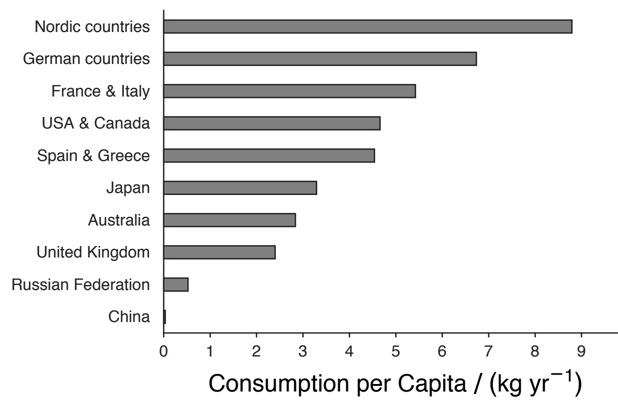

Figure 3. Major coffee-consuming countries in year 2000 *(5)*.

quantity of roasted ground coffee ranging from as little as 5 g to as much as 15 g or more.

A remarkable difference between coffee and all the other beverages is the extraordinary variety of brewing techniques that have been developed and are used traditionally in different countries; decoction methods (boiled coffee, Turkish coffee, percolator coffee, and vacuum coffee), infusion methods (drip filter coffee and Napoletana), and the original Italian pressure methods (Moka and *espresso*) *(6)*.

Espresso is a way to enjoy a cup of coffee that is gaining a great deal of popularity throughout the world, especially in the European countries with Latin origins and in recent years also in the United States and Japan. Its roots are found in the Italian culture of foods and beverages, which developed a typical lifestyle linked to coffee drinking *(7)*. Its success lies in the greater satisfaction it gives to the consumer, when compared with coffee brews prepared by other methods.

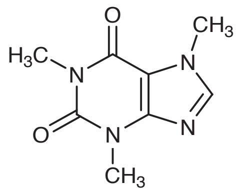

Figure 4. Structure of caffeine.

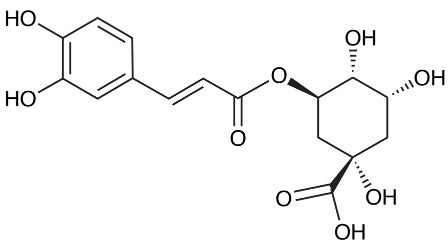

Figure 5. Structure of chlorogenic acid.

Raw Coffee Composition and Changes from Roasting

Proximate analysis of raw arabica coffee indicates: ~12% moisture, more than 50% carbohydrates, 16% lipids, and 10% proteinaceous material. With reference to compounds that are more coffee-specific, yet abundant, one should mention the 1.2% of caffeine (Figure 4), also known as trimethyl-xanthine, and the 6.5% of chlorogenic acid[1] (Figure 5), the esterification product of the polyphenol caffeic acid with quinic acid.

The main compositional differences of robusta coffee as compared to arabica coffee are higher caffeine content (2.2%), lower lipid content (10%), and higher chlorogenic acid content (10%). The presence of some of the less-expensive robusta coffee in a blend with arabica coffee can be determined precisely, by analyzing for presence of the diterpene 16-methoxycafestol, which is specific to the *canephora* species *(8)*. The typical compositions of raw coffee for the two main botanical species are shown in Table 1.

Raw coffee can hardly be defined as edible, and there are no claims of such material to produce a beverage, even if the active physiological component, caffeine, can be effectively extracted by hot water from crunched raw seeds. The grassy, astringent taste of such a brew is surely a deterrent against any commercial venture in that direction. The roasting

Table 1. Typical Composition of Raw Coffee for the Two Main Botanical Species

Components	*C. arabica* (Arabica) (%)	*C. canephora* (Robusta) (%)
Caffeine	0.9–1.2	1.6–2.4
Minerals	3.0–4.2	4.0–4.5
Lipids	12.0–18.0	9.0–13.0
Trigonelline	1.0–1.2	0.6–0.75
Proteins	11.0–13.0	11.0–13.0
Aliphatic Acids	1.5–2.0	1.5–2.0
Chlorogenic Acids	5.5–8.0	7.0–10.0
Oligosaccharides	6.8–8.0	5.0–7.0
Polysaccharides	50.0–55.0	37.0–47.0

NOTE: The data are expressed as percentage of dry matter *(9)*.

process is required to produce a coffee that, when ground to increase surface area exposed to water, allows people to enjoy a pleasurable beverage.

During roasting, pyrolytic reactions take place inside coffee cells (Figure 6) that could be compared to minuscule autoclaves with an internal pressure up to 25 bar. This is due to the unusual thickness of the cell walls as compared to other plants' seeds. The highest final roasting temperature, as applied to beans to be used for the preparation of *espresso* coffee, may reach 220 °C *(10).*

Roasting modifies chemical composition drastically: while the overall contents of caffeine and lipids remain almost unchanged, the quantities of sugars and of free or protein-bound amino acids decrease substantially. These are consumed as reactants in Maillard reactions *(11).* These reactions of condensation between a carbonyl group of a reducing sugar and an amino group are fundamental to the chemistry of cooking: their labile intermediates decompose into a number of low molecular weight compounds, the most reactive of which polymerize to ill-known structures. In coffee they produce, along with the release of large volumes of carbon dioxide, many hundreds of volatile substances imparting roast coffee's characteristic aroma *(12).*

Since the structures of the polymeric Maillard products, called melanoidins, are largely unknown, they must be generically defined as macromolecular materials (mass > 10,000 Da) that are brown and contain nitrogen. Melanoidins usually act as pigments, imparting the color of roasted coffee; because they are water soluble, they are one of the major components of coffee beverages *(13).* Their composition varies in different foods: for coffee, it has been reported that melanoidins contain approximately 30% carbohydrates, 9% proteins, and 33–42% of polyphenols *(14).* This suggests the possibility of the presence of a non-colored carbohydrate skeleton bearing a variety of chromophoric substructures, coming in part from the Maillard reaction and in part from degradation of chlorogenic acids. The latter is also the source of further coffee aroma compounds, pertaining to the classes of catechols and guaiacols.

While initial research on roasted coffee was largely devoted to understanding factors that could improve flavor, in the last decade melanoidins, too, have attracted much interest because of their influence on flavor binding *(15)* and on foam stabilization *(16).*

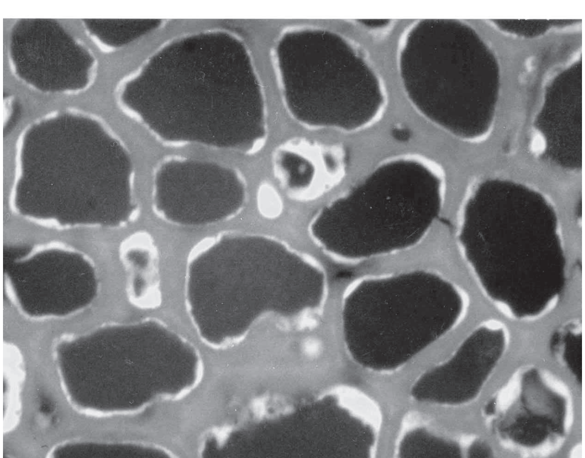

Figure 6. Fluorescence microscopy of roasted coffee cellular structure.

Coffee Is More Than Caffeine

Little is known with certainty about the physiological aspects of coffee, but a bewildering array of health and mood effects are attributed to it. For the reasons mentioned above, any figure quoted in quantitative assessments of effects of coffee consumption must be taken with caution. A plethora of epidemiological studies on the effect of coffee have been published in the last 20 years *(17)* although their conclusions have not always led to clear-cut answers. More than 90% of the research carried out on the physiological properties of coffee has been devoted to caffeine, an alkaloid that stimulates the central nervous system *(18, 19).* Caffeine, regarded as the most used pharmacologically active substance, is also present in other common beverages such as tea, colas, and chocolate. While producing a general habit, its daily consumption by the majority of human population has never been substantiated as addictive; this is probably because caffeine, unlike opioids, nicotine, and even alcohol does not act on the limbic system of our brain, where reward sensation originates *(20).*

For coffee lovers who wish to reduce the stimulant effects of caffeine intake without abating the number of cups per day, industry has developed a number of processes that virtually eliminate the alkaloid directly from the green beans *(21).* However, decaffeination technology is quite complex and beyond the scope of this article. It resorts to procedures based on extraction with various dissolving agents, followed by thorough removal of the solvent and recovery of the caffeine, which mainly ends up in pharmaceuticals as well as in other artificial beverage formulations. Unfortunately, some of the aroma precursors are extracted as well as caffeine.

In any case, coffee is much more than caffeine. Its complex composition and the presence of other substances as yet unidentified, but with evident physiological effects, indicate that further research is needed to demonstrate both the wholesomeness of coffee as well as the favorable effects this beverage can have on humans. For example, one of the constituents found in green coffee beans that may be beneficial to human health is trigonelline (Figure 7), which has received considerable attention as its thermal transformation products are important both from sensory and nutritional points of view. Found in quantities up to 1%, trigonelline is readily degraded by roasting into several aroma compounds (mainly pyrazines) and into nicotinic acid, or niacin, that is also known as vitamin PP (pellagra preventing) or vitamin B_3 *(22).* An average coffee consumer's niacin intake can represent up to 50% of the recommended daily dose. Traces of another vitamin precursor, the lipophilic tocopherol or provitamin E, have been identified in the oil fraction of coffee.

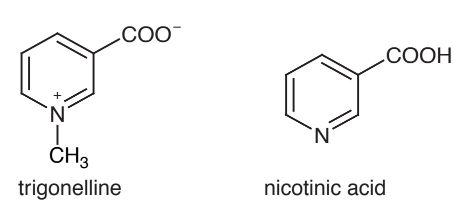

Figure 7. Thermal degradation of trigonelline results in nicotinic acid and other products (not shown).

Other constituents of coffee beans are phenolic compounds, among which chlorogenic, caffeic, *p*-coumaric, and ferulic acids were identified. Most of those substances display potent antioxidant activity in vitro and are supposed to play an important protective role in several human pathologies acting as antiinflammatory, antimutagenic, and anticarcinogenic agents. Their absorption, metabolic fate, and availability for antioxidant protection in humans are not, however, fully understood.

Recently, research has given evidence that coffee possesses an antioxidant activity attributable to the development of Maillard reaction products. Antioxidant activity increases up to the medium-dark roasted stage then decreases with further roasting. This experimental observation is explained by a partial decomposition of the freshly formed antioxidant compounds *(23)*. A particularly interesting finding is the fact that antioxidant activity is also present in human blood serum, as an acute result of the administration of 200 mL of coffee beverage prepared starting from 12 g of roast and ground coffee blend *(24)*. Latest research points to an ionic Maillard product, methylpyridinium, as an active antioxidant and detoxifying agent *(25)*.

Chromatography of Volatiles

When considering that coffee is the second most largely consumed beverage after water, one must acknowledge that its popularity has been achieved for its flavor. It is therefore no surprise that considerable money is spent on coffee aroma research, mainly by the major companies.

Aroma is the ensemble of volatile molecules given off by roasted coffee that can be perceived by the human sense of olfaction either as odor or as flavor. To make the difference clear, it is useful to explain that olfaction operates through thousands of receptors located in the inner mucosae of the nose. The receptors can be reached directly when inhaling the molecules arising from ground coffee or from the cup; odor is appraised this way. The perception of flavor comes when volatile substances evolve in the mouth after sipping and reach the nasal cavity by the pharyngeal (backward) pathway *(6)*.

Green coffee beans, straight from the tree via traditional agricultural practices, do not show either roasted beans' color or aroma. Both are formed during the roasting process, where the latter develops mainly as a consequence of Maillard reactions and concentrates mostly in the coffee oil, an effective aroma carrier. Albeit made up of almost one thousand volatile compounds, aroma constitutes just 0.1% of the weight of roasted ground coffee *(26)*.

The identification of some early aroma compounds, such as guaiacols and furfurylmercaptans, was done by food chemistry pioneers in the 1930s *(27)*. From then on, the number of compounds identified has grown greatly as a result of gas chromatography techniques. Because a key coffee aroma compound was never identified, it appeared to make little sense to increase the number of compounds by lowering detection thresholds. A newer concept, GC-olfactometry, made the search of sensory-active compounds possible, spotting them via sniffing ports at the end of a chromatographic column *(28)*.

Today, the aroma analysis of a coffee sample includes several steps:

- Isolation of volatile substances by steam distillation, followed by extraction with solvents such as diethylether or pentane. The relevant standard method is the simultaneous distillation extraction, also known as the Likens–Nickerson technique. An alternative, solvent-free technique based on adsorption has begun to gain popularity, and furthermore, it requires a small sample size. It is called solid phase microextraction.
- Fractionation by a variety of chromatographic configurations with packed or capillary columns operated under an oven and injection temperature program. Flame ionization detectors are still used for peak sensing. Pulsed flame photometric detectors are indispensable when looking for sulfur-containing compounds. For sensory correlation, gas chromatographs must be equipped with sniffing ports where trained or naive assessors can record their qualitative and quantitative impressions.
- Identification of peak compounds, facilitated by the universal use of affordable analyzers based on mass spectrometry (MS). For deeper investigation and better recognition of more complex compounds, multiple fragmentation instruments are also at hand, the so-called MS/MS system, in the triple quadrupole configuration or even in the MS^n configuration made possible by use of an ion trap.
- Final confirmation of structure would require NMR analysis or IR analysis, if the sample quantity could allow it. For this purpose, some attention is currently being paid to the exploitation of preparative GC.

Several hundred substances, such as hydrocarbons, aldehydes, and esters, along with sulfurated and nitrogenated compounds, have been identified as a result of these techniques. Some of them have been highlighted as key aroma compounds, applying the concept of flavor dilution factor. This refers to the process of consecutive halving of the quantity of concentrate injected into the column, to find the greatest dilution for which aroma is still perceivable from the sniffing port at the relevant elution time (Table 2).

Table 2. Main Aroma Compounds Identified in Roasted Coffee

Compound	Dilution Factor
3-Mercapto-3-methylbutylformate	2048
2-Ethyl-3,5-dimethylpyrazine	2048
(*E*)-β-Damascenone	2048
4-Vinylguaiacol	512
2-Isobutyl-3-methoxypyrazine	512
2,3-Diethyl-5-methylpyrazine	512
3-Hydroxy-4,5-dimethyl-2[5H]-furanone	512
5-Ethyl-3-hydroxy-4-methyl-2[5H]-furanone	512

NOTE: Data from ref *29*.

Along with the search for volatile compounds contributing to coffee aroma, the same degree (or even more) of attention has been paid to spotting the agents responsible for off-flavors, namely the obnoxious sensations caused by rotten or defective beans. Unfortunately, those “bad guys” can be easily noticed by our sense of olfaction even when present in very small quantities. Among them, there are some infamous coffee taints, such as the "old crop" note, the "stinker" defect, the "jute bag" flavor, and the "peasy" flavor: each of those flaws is responsible for substantial reduction in value of the affected lots.

The most remarkable achievement in this field is the discovery of the compounds responsible for two frequent negative traits: the so-called Rio-taste and the flavor typical of robusta. Both have been ascribed to metabolic pathways of infecting microorganisms producing tiny quantities, in the sub-ppb (parts per billion) range, of potent odorants identified as 2,4,6-trichloroanisole and 2-methylisoborneol, respectively (Figure 8). The former compound is possibly the most potent odorant discovered so far: its sensory detection concentration threshold has been reported *(30)* to be as low as 0.03 ng/kg, corresponding to a few thousandths of parts per trillion!

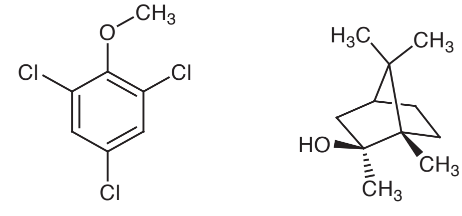

Figure 8. Structures of compounds responsible for off-flavor odor in coffee.

Cup-Testing as an Analytical Tool

In the coffee industry, some objective form of sensory evaluation is needed to ascertain overall product quality along with the constancy of that quality over time and in varying process conditions *(31).* The "tool" commonly put to use is a panel of assessors, who may be either coffee experts (professional cup-testers) or naive consumers after a very basic training. The reason for employing more than one person is obvious since, by averaging responses, the risk of incorrect judgment owing to a possible bad mood or minor illness of one person is minimized. Another panel potential is the synergy that can be gained by debating coffee characteristics among the assessors during open sessions. This procedure may yield more information, since individual sensitivities and perception thresholds may be different.

Sensory tests may be grouped in three basic types, listed by increasing difficulty for the panel members:

- Trio tests, used to determine whether any perceivable difference exists between two samples. In this configuration each sample is split in two cups, but one cup is discarded and only three cups are presented to the panel. The assessors are requested to tell which is the "foreign" single cup, as opposed to the pair of "sister" cups. A variation called duo–trio presents the panel with five cups, where two "sister foreigners" are shuffled with three "sister controls". This approach has the advantage of making hits by chance much less likely (1/10 vs 1/3).
- Duo tests, where two or more single cups are presented to the panel and panel members are asked to rank the cups of coffee in relationship to one sensory variable. When more than one variable is to be determined, a pre-filled card proves useful to summarize the evaluations.
- Absolute tests, in which some complex variable, such as aroma or overall merit, is to be determined by comparison with a mental paradigm present in each assessor's memory by previous experience. Coffee aroma profiling *(32)* as well can be included in this type, since it is based on assessors' recall of variegated flavor knowledge present in their experience.

Cup-testing sessions cannot be too long or frequent during the day, because some fatigue develops after the first dozen cups. This is particularly true for *espresso* tasting, owing to the presence of tiny coffee oil droplets in emulsion; they stick on the tongue and mouth membranes and impart a lingering aftertaste. Rinsing the mouth with water, albeit necessary between each sampling, is not effective in removing the taste completely. On the contrary, cool whole milk seems to be better for this purpose perhaps because, being itself an oil-in-water emulsion, it can displace coffee oil droplets from the tongue by dilution.

A collection of sensory data can be utilized for the calibration of instrumental screening methodologies such as near infrared reflectance (NIR). This analysis, using spectroscopy in the near-infrared wavelengths (1100–2500 nm), is a technique that measures scanned monochromatic light absorption by the material to be examined, whose energy is dissipated in rotational and vibrational movements of the molecular bonds and ultimately transformed into heat *(33).* The energy absorption pattern provides information about the molecular configuration of the tested material.

NIR analysis takes advantage of the fact that it is a rapid, nondestructive fingerprinting technique apt to supply simultaneous forecasts of many chemical characteristics of the sample examined, provided that a good calibration has been previously obtained by statistical correlation with conventional, time-consuming analytical methods. This secondary method is suitable also for modeling sensory data, bearing in mind that since several preprocessing steps are needed to obtain the actual coffee beverage tested, regression coefficients not better than 60% are to be expected *(34).*

Five Senses Are Involved in *Espresso* Enjoyment

Few everyday experiences can compete with a good cup of coffee, based on sheer sensory pleasure. It is clear that most of the quality of such a beverage is determined by its flavor or, better still, by its overall sensory impact. In this context, *espresso* is the brewing method that offers the consumer the most powerful experience, even if a high quality cup it is not easy to obtain. *Espresso*'s very strength, the ability to concentrate aromas, is also its weak point because, while enhancing qualities, at the same time it brings out all the latent defects that may exist in the raw material.

The main features of *espresso* coffee derive from the way it is prepared:

- Preparation on order. Unlike other brews that wait for a customer, it is the latter who must wait for his or her *espresso* cup.
- Brewing by a specific method—percolation—that uses high water pressure (around 9 bar).
- Rapid extraction (30 s), admitting into the cup just the best, most palatable material.

Figure 9. Cross-sectional detail of a typical *espresso* percolation device.

Percolation is a process in which a small quantity of hot water under pressure is squeezed through a tightly packed layer of ground roasted coffee, the so-called cake (Figure 9). This process efficiently produces a concentrated brew containing not only soluble solids, but also some lipophilic substances lacking in other brew types.

The resulting beverage is peculiar from a physical and chemical perspective, inasmuch as the foam on the top and the opaque brew are unique to *espresso*. The former, a velvety, thick, reddish-brown froth called *crema*, is composed of tiny gas bubbles arranged in a honeycomb structure that locks in the coffee's distinctive aroma. The latter is due to the presence of a dispersed phase formed by small oil droplets in emulsion that are perceived in the mouth as a special creamy sensation, the body. Furthermore, oil droplets preserve many aromatic components that would otherwise either escape into the atmosphere or be destroyed by contact with water as in the other brewing techniques. Because of oil droplets the rich coffee taste lingers in the mouth for several minutes *(35)*.

Often considered a "strong" cup of coffee, *espresso* fully deserves this attribute based on its sensory properties. When it comes to caffeine, on the contrary, *espresso* is surprisingly moderate with an average content of less than 80 mg (if prepared from pure arabica). This is due both to the small size of the serving, usually brewed from as little as 6.5 g of roasted ground coffee, and to the short contact time with water allowed during extraction. Since caffeine dissolution is slow, a good quarter of the caffeine remains with the spent grounds.

As already stressed, *espresso*'s main characteristics are of sensory nature. All human senses (with the moot exception of hearing: think about the distinctive whistling of coffee makers!) are involved in appreciation of a cup of *espresso:*

- Vision evaluates foam's aspect, examining its color and consistency and persistence.
- Touch assesses the beverage mouthfeel, or "body", a property linked with density and viscosity.
- Taste judges the bitter–acidic balance and the presence of a sweet caramel-like aftertaste.
- Olfaction evaluates both the fragrance of the vapors arising from the cup (the direct pathway) and the flavor of the volatile substances evolving in the mouth, by upstream diffusion.

Coffee connoisseurs consider perfectly brewed *espresso* to be the superlative form of coffee, because its special preparation amplifies and exhibits the inherent characteristics of the beans. To the young food chemist, *espresso* could be a challenge for deeper research, because its structure of a polyphasic colloidal system along with its complex composition may be seen as the quintessence of all the other techniques by which coffee can be brewed *(36)*. Knowing *espresso* is to know coffee in all its forms.

Conclusion

To develop a fruitful knowledge base, worthy of being called "coffee science", research strategy should prompt scientists with different backgrounds (food technology, food chemistry and biochemistry, nutrition, consumer science) to team up and work closely with coffee companies in investigating all aspects that are crucial to product acceptance. Superior coffee is the result of close control over a multitude of factors in the field, in industrial processing, and in the cup. Science, with chemistry in a prominent place, is a key ally to strengthen the quality chain from agriculture to industry, keeping in mind that each and every link of the chain deserves the best possible care to prevent any decline in the overall result. Only in this way can the highest satisfaction be assured to every customer enjoying a cup of coffee. Scientifically—sure!—but without forgetting the magic behind it.

Note

1. The classical Greek meaning of chlorogenic is "turning something green". Actually, a better name for chlorogenic acid would be caffeoylquinic acid.

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