BIOCHEMISTRY

THE COMPLEXITY OF COFFEE

One of life's simple pleasures is really quite complicated

By Ernesto Illy, with Andrea Illy

FOR SHEER SENSORY ENJOYMENT, FEW EVERYDAY EXPERIENCES CAN COMPETE WITH A GOOD cup of coffee. The alluring aroma of steaming hot coffee just brewed from freshly roasted beans can drag sleepers from bed and pedestrians into cafés. And many millions worldwide would find getting through the day difficult without the jolt of mental clarity imparted by the caffeine in coffee. But underlying this seemingly commonplace beverage is a profound chemical complexity. Without a deep understanding of how the vagaries of bean production, roasting and preparation minutely affect the hundreds of compounds that define coffee's flavor, aroma and body, a quality cup would be an infrequent and random occurrence.

IN BRIEF

Your morning cup of java is the produce of centuries of experimentation with the coffee bean and sophisticated technologies aimed at getting the richest, most satisfying flavor into each sip.

Every stage of preparation en route to your espresso—from the selection, drying and roasting of the beans to the grinding and the high-pressure extraction of the crema—is crucial to quality.

The best beans are individually selected by automated inspectors. The aromas so important to flavor are analyzed using gas chromatographs and mass spectrometers.

Drip and pod machines make good coffee easy. Pulling a truly great espresso shot takes skill—but it helps to have a working knowledge of the biochemistry that makes this beverage so delicious.

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Connoisseurs agree that the quintessential expression of coffee is espresso: that diminutive, heavy china cup half-filled with a dark, opaque brew topped by a velvety thick, reddish-brown froth called crema. Composed of tiny gas bubbles encased in thin films, the surprisingly persistent crema locks in the coffee's distinctive flavors and aromas and much of its heat as well. Espresso—the word refers to a serving made on request expressly for the occasion—is brewed by rapidly percolating a small quantity of pressurized, heated water through a compressed cake of finely ground roasted coffee. The resulting concentrated liquor contains not only soluble solids but also a diverse array of aromatic substances in a dispersed emulsion of tiny oil droplets, which together give espresso its uniquely rich taste, smell and "mouthfeel."

Aficionados consider perfectly brewed espresso to be the ultimate in coffee because its special preparation amplifies and exhibits the inherent characteristics of the beans. Espresso is useful for our purposes as it is in effect a distillation of all the numerous techniques by which coffee can be made, including the Turkish method and various infusion and filter drip processes [*see box on page 14 for descriptions of alternative methods for preparing coffee*]. To know espresso is to know coffee in all its forms.

High-quality coffee arises from maintaining close control over a multitude of factors in the field, in the plant and in the cup. Coffee cultivation entails myriad variables that must be monitored and regulated. Once a coffee bean is grown, nothing can be added or removed: the quality must already be present. For a single portion of espresso, 50 to 55 roasted coffee beans are required; a single imperfect bean will taint the whole sufficiently to be noticeable. This is because human olfaction and taste senses originated as defense mechanisms that protected our ancestors from rotten—hence, unhealthy—foods. Only through modern technology can one economically and consistently identify 50 nearly perfect beans.

GROWING COFFEE

RAW COFFEE BEANS are the seeds of plants belonging to the Rubiaceae family, which comprises at least 100 species of the genus *Coffea*. The two species that are commercially exploited are *Coffea arabica,* which accounts for two thirds of world production, and *Coffea canephora,* often called robusta coffee, with one third of global output. Robusta coffee plants and all wild coffee species have 22 chromosomes, whereas arabica has 44. Therefore, arabica cannot be crossed with other coffee species to produce a hybrid plant.

Robusta is a high-yielding and disease-resistant tree standing up to 12 meters tall that grows best in warm, humid climes. It produces a cup featuring substantial body, a relatively harsh, earthy aroma, and an elevated caffeine content that ranges from 2.4 to 2.8 percent by weight. Although robusta is sold by many purveyors, it does not give rise to the highest-quality coffee.

Arabica, which originated in the Ethiopian highlands, is a medium- to low-yielding, rather delicate tree from five to six meters tall that requires a temperate climate and considerable growing care. Commercially grown coffee bushes are pruned to a height of 1.5 to 2.0 meters.

TIMELINE

From Kefa to Cafe

People have enjoyed the flavors and stimulative kick of coffee for thousands of years. And in many parts of the world, the beverage is still growing in popularity.

1000 B.C. to A.D. 500 The nomadic Oromos tribe, living in the kingdom of Kefa (in modern-day Ethiopia), eat coffee, crushed, mixed with fat and shaped into golf ball–size portions, as a pick-me-up.

Circa 600 Coffee is brought by traders across the Red Sea into Arabia (modern-day Yemen).

Late 1400s to early 1500s Coffee beans, heretofore an Arabian monopoly, are brought to Turkey, Egypt and Syria by Muslim pilgrims returning from Mecca. Arabian-influenced coffeehouses open in Constantinople, Damascus and other Near Eastern cities, where European traders, particularly Venetians, are introduced to the beverage.

Circa 1600 Calling it "the bitter invention of Satan," advisers urge Pope Clement VIII to reject the favorite drink of the infidel Ottoman Turks. Instead he decides to give papal authority to coffee, making it acceptable for Roman Catholics.

1616 Dutch entrepreneurs start to cultivate coffee commercially, beginning with a coffee plant obtained from Yemen. By 1658 (according to some sources, the 1690s), the Dutch are growing coffee in Ceylon and their East Indian colony of Java.

1714 The mayor of Amsterdam presents the French king, Louis XIV, with a coffee plant from Java.

1723 Gabriel Mathieu de Clieu, a French naval officer, carries three coffee seedlings obtained under questionable circumstances from the Royal Botanical Gardens on a perilous voyage to the Caribbean island of Martinique, where one of the plants thrives.

1727 After having been called to arbitrate a border dispute between two coffee-growing colonies, Dutch Guiana and French Guiana, Francisco de Melo Palheta, a Portuguese Brazilian official, smuggles several coffee seedlings to his home estates.

1903 German coffee importer Ludwig Roselius perfects decaffeinated coffee.

1933 Francesco Illy patents the first automatic espresso machine.

1961 Ernesto Valente of Faema, an Italian coffee machine maker, designs the archetype of the modern espresso machine.

2014 With more than 700 billion cups consumed every year, coffee may be the world's most popular beverage (besides water, of course).

Coffee ranks second only to petroleum in terms of dollars traded worldwide. The International Coffee Organization estimates that exports of coffee in 2014 totaled 6.7 billion kilograms, worth at least $18 billion.

Controversy continues over whether shade-grown coffee should be promoted to enhance bird habitats.

According to a survey of 2,741 Americans conducted by the National Coffee Association in 2014:

Sixty-one percent of adults (older than 18 years) in the U.S. drink coffee every day, representing 148 million daily drinkers. Another 18 percent of adults (44 million) drink coffee at least once a year.

American coffee drinkers consume, on average, 3.4 (nine-ounce) cups of coffee a day.

Coffee and caffeine have been the subject of extensive scientific study during the past quarter of a century, with 1,500 to 2,000 papers published every year on the topic. Despite this close scrutiny, few negative health effects have been definitively linked to the moderate consumption (two cups a day) of caffeinated coffee. On the contrary, recent epidemiological studies have observed that coffee consumption is associated with a lower risk of several diseases.

Coffee made from arabica beans has an intense, intricate aroma that can be reminiscent of flowers, fruit, honey, chocolate, caramel or toasted bread. Its caffeine content never exceeds 1.5 percent by weight. Because of its superior quality and taste, arabica sells for a higher price than its hardy, rougher cousin.

A good rainfall induces arabica coffee plants to blossom, and some 210 days afterward red or yellow fruit called cherries appear. Each cherry contains two oblong seeds—the coffee beans. Because both fruit and flower can be present simultaneously on the same branch, the picker's forefinger and thumb are the best tools to gather just the ripe cherries. Stripping entire branches by hand or using automated harvesting machines does not discriminate between the ripe and the unripe cherries.

The ultimate quality of the resulting coffee beans depends on the genetics of the plant, the soil in which it grows and the microclimate, which encompasses factors such as altitude, the amount of rainfall and sunlight, and daily temperature fluctuations. Along with the roasting processes that are applied, these agricultural and geographical considerations are responsible for the taste differences among the many kinds of coffee beans that suppliers combine to produce the various distinctive blends one can purchase.

FROM CHERRY TO BEAN

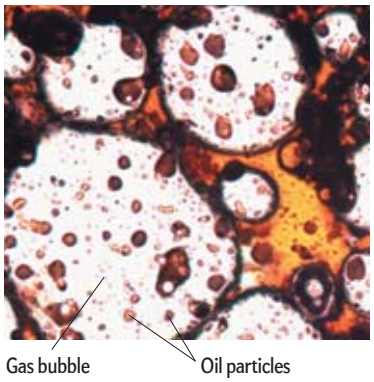
COFFEE CHERRIES must be processed immediately after harvest to prevent spoilage. Producers either sun-dry the cherries or wash them. Sun-drying involves spreading the cherries out on a patio and stirring the desiccating fruit frequently to evenly heat and aerate them. The dried cherries are run through a machine that crushes the hulls and then removes both the hulls and the surrounding parchment membrane layer, thus freeing the beans for sorting and bagging. In the alternative approach, the fruit is mechanically pulped, washed, and finally dried and liberated from the parchment covering. The goal of either route is the same: the 65 percent water content of the coffee cherry is reduced to the 10 to 12 percent moisture level of a prime raw, or green, coffee bean.

One of the greatest challenges in producing superior coffee is ensuring that one starts with exceptional green beans. Premium producers, such as illycaffè, our company based in Trieste, Italy, use many sophisticated process-control techniques to minimize the percentage of defective coffee beans, including ultraviolet fluorescence analysis to spot moldy beans and trichromatic mapping to generate a color fingerprint (yellow-green, red and infrared) of each lot of beans. At illycaffè, a dichromatic sorting system developed

BEHIND THE BUZZ

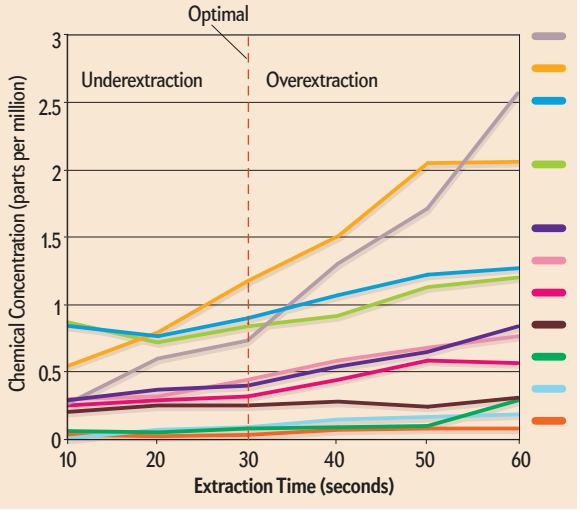
Coffee Chemistry

A perfect cup depends on what is in the beans (*bottom*) and how it is brewed (*right* and *below*). Crema, the dense, reddish-brown foam that tops an espresso, is seen in an enlarged cross section at the right. Composed mainly of tiny carbon dioxide and water-vapor bubbles (*large circles*) surrounded by surfactant films, it also includes emulsified oils containing key aroma compounds (*particles with red borders*) and dark fragments of the coffee bean cells.



How the Chemical Composition of Espresso Depends on the Extraction Time

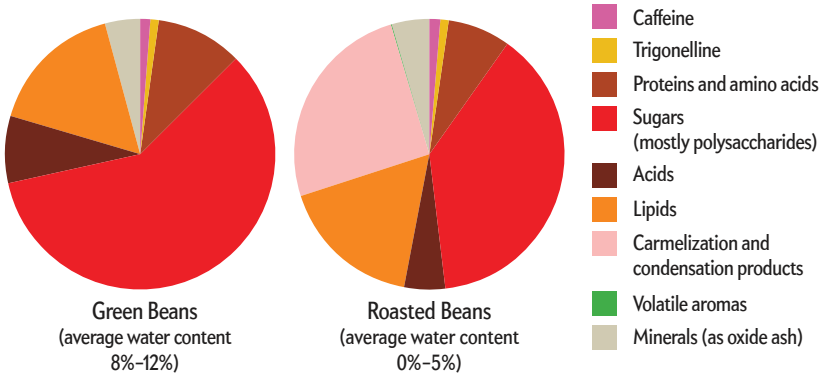
As hot water is forced through coffee grounds, the concentration of undesirable, less soluble aroma compounds (*red type*) rises. A 30-second extraction produces the optimal flavor.



Compound	Aroma
2,4-decadienal	Rancid
Ethylgujacol	Smoke
2-ethyl-3,5-dimethylpyrazine	Chocolate
2-ethyl-3,6-dimethylpyrazine	Chocolate
2,4-nonadienal	Rancid
Methylsalicilate	Cinnamon
B-damascenone	Tea
DMTS	Sulfur
Isovaleraldehyde	Sweet
A-ionone	Flowers
Linalool	Flowers

Composition of Raw and Roasted Arabica Coffee (percentage of dry matter)

Roasting improves the flavor of green beans by caramelizing sugars and reducing acids.



ILLYCAFFÈ (*micrograph*); NINA FINKEL (*illustrations*)

OTHER TECHNIQUES

Coffee by the Pot—or Pod

Filter drip (Chemex, Melitta, auto drip) coffee was invented by the French in the early 18th century and improved in 1908 by Melitta Benz, who introduced the paper filter. Automatic and manual drip coffee makers yield results that vary from light- to heavy-bodied, depending on the shape and material of filter used. One tablespoon of medium-fine coffee grounds is added to the filter for every 10 ounces of water. When prepared manually, hot water is slowly poured over the grounds until the desired volume is reached. Filter drip coffee has a well-balanced, clean taste.

Pods and capsules are designed to deliver a single portion of coffee with consistency and ease. Two kinds of capsules are common. One simply holds ground coffee through which water passes to extract the brew. The other is a two-phase system. First a coffee-filled capsule is infused with water under pressure. An emulsion phase then follows and creates an espresso having a pleasantly thick crema.

Turkish coffee is full-bodied, thick and sweet. It is prepared in an Ibrik, a copper/brass pot with a long handle. One tablespoon of coffee, ground to a fine powder, is added for every three ounces of water (and often generous helpings of sugar). Placed on medium heat, the Ibrik will begin frothing slightly. The coffee is then gently stirred. The process of slow heating and stirring is repeated twice. Turkish coffee is served in a demitasse.

French press coffee originated in France around 1852 and was later refined by Italians. One tablespoon of medium-coarse grounds is used for every four ounces of water. After the hot water (not boiling) is added, the coffee should steep for two to four minutes. The grounds are then forced to the bottom of the pot by pressing down on a metal mesh filter. The result is a full-bodied, bold coffee.

in collaboration with the English company Sortex is applied as a final control right before roasting. As beans fall into bins, photoelectric CCD cameras detect duds, signaling for them to be rejected individually with a puff from an air nozzle. The sorting operation is accomplished at a speed that no human hand can match (22,000 beans a second by a 64-chute machine) and with a precision that exceeds that of even the most highly trained eye.

A perfect mature green coffee bean is composed of cells having uncommonly thick walls: as much as seven microns, an exception in the vegetal kingdom. During roasting, these 30- to 40-micron-diameter cells serve as tiny reactors in which all of the crucial, heat-driven chemical reactions that generate coffee's seductive taste and fragrance occur. The cells of immature beans have thinner walls. Unripe beans also lack the important aromatic precursor proteins that develop in the last stages of the ripening process. Fermented beans are composed of cells that have been emptied of these crucial constituents by molds or bacteria.

THE SCIENCE OF ROASTING

ROASTING is a pyrolytic (heat-driven) process that greatly increases the chemical complexity of coffee. The aroma of green coffee contains some 250 different volatile molecular species, whereas roasted coffee gives rise to more than 1,000.

When subjected to the staged heating of a roasting machine (basically, a huge, hot, rotating cylinder), residual water inside each cell boils into steam, which promotes diverse, complicated chemical reactions among the cornucopia of sugars, proteins, lipids and minerals within [*see box on preceding page*]. At high heat, from 185 to 240 degrees Celsius, sugars combine with amino acids, peptides and proteins, following well-known processes such as caramelization and the Maillard reaction. The end products are brownish, bittersweet glycosylamine and melanoidins—which give rise to coffee's dominant taste—along with carbon dioxide.

Simultaneously, a wide variety of lighter aroma compounds emerge; these volatile molecules give coffee its familiar fragrance. Pressure inside each cell increases to 20 to 25 atmospheres as the steam and carbon dioxide try to escape but are sealed in by the thick, nearly impermeable cell walls and a thin film of oil. Some cells eventually burst, creating the characteristic popping sound of roasting coffee. Roasting boosts beans' volume by half or more and decreases their mass by a fifth.

Depending on the temperatures and procedures applied, the roasting process can last from 90 seconds to 40 minutes. Twelve minutes is the traditional duration. The thermodynamics of the intracellular reactions differ according to roasting time, and so does the final result. A short roasting time, which requires a great deal of thermal energy, minimizes weight loss but imparts to the cup a metallic bitterness resulting from the presence of polyphenols that do not have enough time to react properly. Long roasting periods, frequently used in poorer countries in which many consumers can afford only low-priced, defective beans, forces all the off-flavors and fragrances to leave the beans. Sadly, the desirable tastes and aromas flee as well, yielding a rather bitter cup.

CHRIS KOLBU *Getty Images*

The higher the final temperature of the roasting, the less desirable the aroma will be, and the stronger the bitterness. Conversely, low roasting temperatures fail to develop fully the welcome aromas, and acidity tends to come to the fore.

AN AROMA LIKE NO OTHER

AROMA SCIENCE is highly complex. Researchers typically analyze the fragrances evolved during coffee bean roasting by gas chromatography coupled with olfactometry, in which skilled testers sniff and define the smell of each recognizable element. Mass spectrometry is frequently then applied to identify the chemical composition of each odor. Sniffing roasted coffee aromas that have been fractionated by a gas chromatograph is an enlightening experience: one may recognize the aromas of roses, Darjeeling tea, chocolate, vanilla and violets, as well as truffles, soup, cheese, sweat and even what is called cat scent, which, if diluted, smells like sauvignon blanc wine but in a concentrated sample is disgusting.

At illycaffè, technicians focus on the strongest odorants. Imagine listening to a recording of a choir of 800 singers that includes the strong solo voices of Jessye Norman, Luciano Pavarotti and several other virtuosi who tend to dominate the ensemble. If the volume of the playback is reduced, the stronger voices will still be recognizable even as the choir's sound fades away. Diluting the aroma of coffee is analogous; beyond a certain point, only the strongest compounds are perceived. Unfortunately, the most powerful molecules in the smell of a coffee sample are those originating from defective beans.

Molecules such as ethylbutanoate and ethylglycolate, which are responsible for the unpleasant aroma of immature beans, ruin a cup of coffee by their very presence. Likewise, methylisoborneol and trichloroanisole (TCA) molecules produce the characteristic earthy, chemical smell of robusta coffees. TCA, which is also called Rio taste because it was first discovered in coffees grown around Rio de Janeiro, can be found in corked wines as well. Its perception threshold to the human olfactory system is shockingly low—six millionths of a billionth of a gram per milliliter.

EXTRACTING THE BREW

THE NEXT MAJOR STEP in the transformation of roasted beans into a cup of espresso is the extraction of the active components in the roasted and ground coffee by heated water. The interaction of hot water and coffee grounds is, however, subtly different when making common drip coffee than when making espresso.

When filter drip coffee is prepared, hot water passes through a loose aggregation of medium-size coffee grounds. During the four to six minutes of contact with the boiling water, most of the soluble substances present in the roasted coffee pass into solution. Thus, large quantities of highly soluble acids and caffeine dissolve into the cup. In contrast, the much shorter percolation time of espresso allows less acid and only 60 to 70 percent of the caffeine to dissolve into the brew.

Brewing espresso requires specialized equipment that can heat water to a temperature of 92 to 94 degrees C and pressurize it to nine atmospheres. Coffee, ground to a fine to medium consistency, is placed in a perforated basket and firmly tamped down to create a compacted bed of particles. The compressed grounds adhere to one another thanks to a thin coating of oil, which is as viscous as honey. The oil binds the particles together into a condensed maze of minuscule air passages. Experimentation has shown that the hydraulic resistance of this bed of coffee grounds must be slightly less than the pressure of the steaming-hot extraction water, allowing it to flow through at a rate of around a milliliter a second.

Using the recommended 30 seconds of percolation, a skilled barista (coffee bar technician) produces about 30 milliliters of dense coffee liquor covered by the all-important crema. If the color of the foam topping is light, it means that the espresso has been underextracted, probably because the grind was too coarse, the water temperature too low or the time too short. If the crema is very dark in hue and has a "hole" in the middle, it is likely that the consistency of the coffee grounds was too fine or the quantity of grounds was too large. An overextracted espresso exhibits either a white froth with large bubbles if the water was too hot or just a white spot in the center of the cup if the brewing time was too long.

The percolation process also washes out components present on the surface of the coffee grounds, including aroma-filled oil and bits of the cellular structure. The high pressure generated by the espresso machine emulsifies a small amount of the oils, about 0.1 gram a cup. Intact cells in the grounds create a fine effervescence, which is derived from gases (especially carbon dioxide) passing through tiny pores in the cell walls. Some very fine grounds can also find their way into the beverage, along with cell wall fragments, which endow the foamy crema with what is called the tiger-skin look.

The final result is a polyphasic colloidal system, in which water molecules are bound to the dispersed gas bubbles, oil droplets and solid fragments, all of which are less than five microns in size. The colloidal character of the dispersion gives the drink high body, high viscosity and low surface tension. Espresso thus visibly coats our tongues and continues to release the aromatic volatiles dissolved in the emulsified oils as long as it remains there. These oily flavor/fragrance carriers mean that the great taste and aroma of a good espresso can be savored for as long as 20 minutes after it has been drunk. Luckily, the drinker need not know anything about the complex chemistry of coffee to enjoy it. SA

Ernesto Illy was chairman of illycaffè, a family business based in Trieste, Italy, from 1963 to 2004. He died in 2008. This article, written by Ernesto Illy in 2002, was updated for this issue by his son Andrea, who is the current chairman of illycaffè. Over six million illy espressos are served every day in more than 140 countries around the world.

MORE TO EXPLORE

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