3.25 Chemistry of Coffee

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3.25.1 Overview

3.25.1.1 Coffee's Origin

The coffee plant most probably originated in Africa and Madagascar. Early cultivation is reported in the Ethiopian Highlands and also on the other side of the Red Sea, in Yemen – no surprise, since climate and geography are similar. According to legends, coffee stepped out of Africa most likely in the first millennium. Other narratives deal with the discovery of roasting, leading to the consumption of coffee as a beverage.

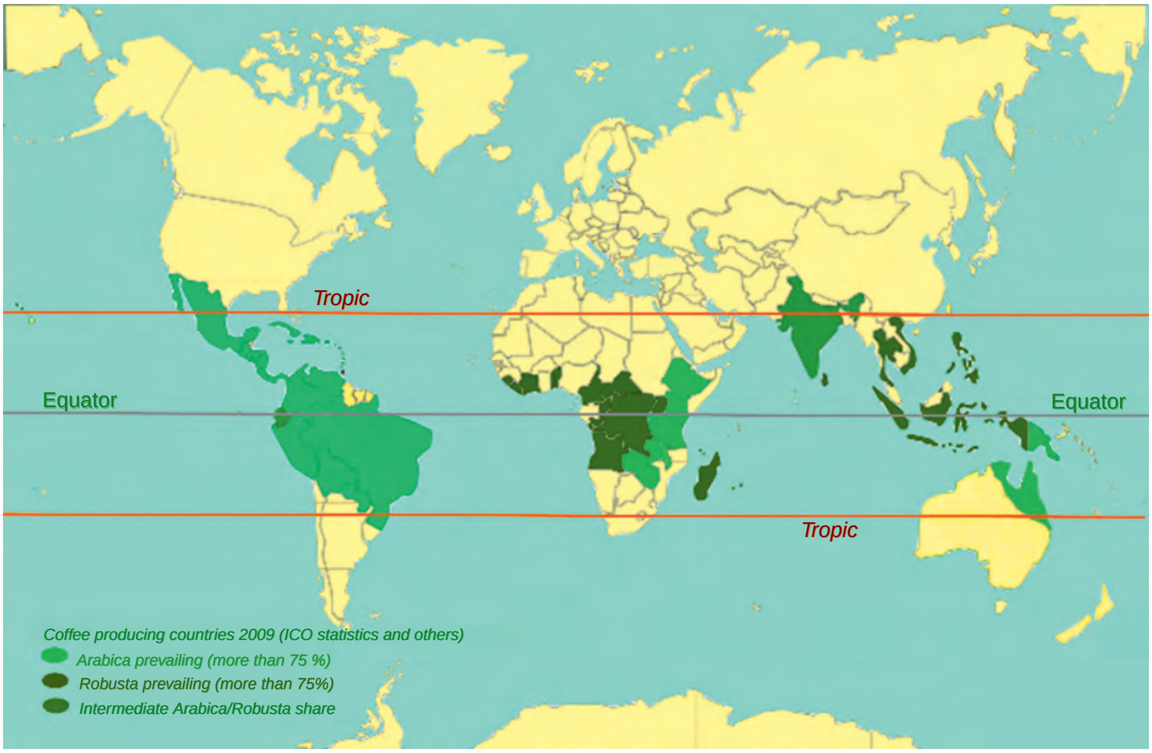


Figure 1 Coffee producing countries around the globe.

Coffee grows best in areas lying between the tropics. Today, it is found in all continents belonging to this geographic belt, **Figure 1**, even in Australia and very recently, not yet shown here, at the Northern tropic in the Yunnan highland of China. There are two main species of coffee, Arabica and Robusta, each with its own ecology.

3.25.1.2 Early Cultivation and Consumption

The first reference to coffee in the literature seems to be from Arab scientists in the ninth and tenth centuries (Rhazes, Persian physician (853–935); Avicenna, Arab physician (980–1037), polymath in the world of letters and sciences). Referenced to as 'bun', it was a stimulant food of Ethiopia and Yemen. It might have been chewed and eaten.

The oldest material source is dated about AD 1200. Carbonized paleobotanic Arabica coffee beans were found in 1997 in an archaeological excavation[1] on the eastern side of the Arabian Peninsula, near Oman, together with the early thirteenth-century pottery from Yemen. Since these beans were evidently not at their growing place, they indicate that coffee was traded at that time. The findings also reveal that the beans came from Yemen and people knew about roasting them.[2]

Until 1600, the cultivation of coffee was restricted to Arabia, and mainly centered in the highlands of Yemen, where a sophisticated system of irrigation was practiced.[3] To retain this monopoly, the export of coffee plants was strictly forbidden, and even the beans for trade were said to have been made infertile.

Coffee was economically important for both producers and traders. The Arab Islamic world was familiar with the beverage, even though there were times of restriction, based on whether or not religion permitted consumption of the beverage.[4] Mecca pilgrims took word of the beverage to their distant homelands.

The use of coffee spread with the Ottoman Empire, over its part of the Mediterranean. Coffee brewers progressed into a specialized guild, as reported by Austrian legation members about a procession of guilds at a celebration in Istanbul in 1582.[5]

Detailed information on coffee reached the Christian part of Europe about the same time, through travel reports of scientists[6,7] and books' prints with drawings of the plant and descriptions of its consumption. The naked beans had circulated among European scientists some time before, mentioned in the updated 1574 edition of an earlier standard work on tropical plants.[8]

Coffee as a commodity for trade did not enter the non-Islamic world until 1615, when a few bags arrived in Venice,[9] followed by demand and supply. The coffee trade's mainstream ran from Mocha, the port in Yemen involved in export, through ship and caravan to Cairo and Alexandria.[4] From there the coffee was distributed to the Ottoman customers and to the consumers in Europe, where coffee houses started flourishing. As early as 1668, coffee had crossed the Atlantic and arrived in Dutch New York.[10]

3.25.1.3 Ways Out of Arabia

Despite all of the protective restrictions adopted in the Arab world, the expanding interest in the beverage encouraged a search for a similar tropical climate for growing coffee plants and efforts to find ways of transferring plants. Possibly, the first expansion was to the west coast of India, where coffee was brought in by Muslim pilgrims from Mecca. The mystical origins of Indian coffee are traced to the seven beans brought to Karnataka by the legendary Baba Budan in 1600.[11,12]

From India, coffee is reported to have moved to Ceylon (now Sri Lanka) in 1658, to the plantations of the Netherlands East India Company, and to Java after 1696.[13] Java became the world's mass supplier for coffee outside Arabia and remained so for half a century; even today, in the United States, a cup of coffee is commonly called a 'cup of Java'.

From the Dutch colonies, single plants were sent to the botanical garden of Amsterdam in 1706; from there, living plants were transported to the Dutch colony in Surinam for cultivation and a grown-up tree was gifted to King Louis XIV in Paris in 1714.[14] Some plants of the next Parisian generation were transferred to French colonies in the Caribbean, for cultivation in an appropriate climate. There is a well-known textbook story of a single plant surviving on a ship to Martinique, nourished by the drinking water of its officer, in about 1720. This was reported by the officer himself 50 years later[15]. The coffee variety originating from Amsterdam, called Typica, made its way step by step into Latin America.

At the same time, there was another route of Arabica plants out of Yemen: 60 seedlings, an official present by the Yemenite sultan[16] to Louis XIV, were sent to the French Bourbon Island (La Réunion, today) in 1715; again, these were a limited number of plants. From there, the Bourbon variety of coffee entered the French colonies in the Americas and in other places.

Coffee cultivation was also promoted by other colonial powers such as Portugal, Spain, and England (and, for a few decades, by Germany also). These powers also expanded cultivation to their respective spheres of influence.

Bourbon and Typica are the prolific ancestors of most of today's Arabica crops – a genetically narrow route that expanded from a few single plants to millions of tons of Arabica per year, all within 300 years.

Other coffee types, which grew without international demand in the humid tropical areas of their origin, became objects of scientific surveys and explorations from the eighteenth century.

Today, independent coffee producing countries cooperate with the consuming ones in a worldwide research for the conservation of the coffee plant's genetic heritage and diversity. Numerous so-called wild or spontaneous varieties deserve genetic resource management. Since they are imminently threatened by advanced deforestation, an effective preservation strategy is needed.

3.25.1.4 Discovery of the Robusta Variety

The tropical areas of Africa, from Guinea to Angola and to Uganda in the east, host different species of coffee. The first to gain economic importance was the Ethiopian Arabica, with its early cultivation in Arabia.

Reports of other species in Africa and their indigenous cultivation and trade date from the nineteenth century. For the East African countries, expeditions of 1857[17] and 1862[18] informed that coffee was familiar to the people there, grown in homegardens,[19,20] and chewed and eaten as green bean for its stimulating effect.[21,22] Discussions on the identity of these species of coffee, whether they were wild Arabicas (prospector's hope) or sui generis, remained ongoing[23] till 1897. Several non-Arabica species were determined by Froehner,[24] including *Coffea canephora* Pierre,[25] with the later extension ex A. Froehner.

Cultivation of this species for use as roast coffee was initiated in 1898,[26,27] and promoted by a Belgian horticultural company.[28,29] This coffee was called Robusta by the Belgians as it proved more robust against diseases and had less ecological requirements in terms of humidity, temperature, and altitude of plantations. Although different in taste, it soon turned out to be a useful alternative for the vulnerable Arabicas, which were disease prone due to their narrow genetic origin.[30] There was an actual demand for resistant plants as a disastrous epidemic of leaf rust, caused by the devastating *Hemileia vastatrix* fungus, started in 1869.[31] The first to suffer from it were the Ceylon coffee plantations. There, at the abandoned plantations, coffee was replaced by tea. The next coffee countries soon to be attacked were India and, then, Indonesia. Eventually, the search for rust-resistant coffee types led to the substitution of Arabica by Robusta, after an intermezzo with the species *Coffea liberica*. During the last century, Robusta made its way to other coffee growing regions and witnessed an enormous expansion in its cultivation.

Besides pests and diseases, coffee crops can also be reduced by drought and frost,[32] thus influencing the available volume of coffee. This happened regularly after a frost in Brazil, causing declines in world supplies in the 1970s. Soon the cultivation of Robusta increased in West Africa, its original homeland.

Since 1990 there has been a steady increase in Robusta production in Vietnam, which is now the world's of coffee in general.[33]

3.25.1.5 Coffee as a Trade Commodity – World Production

The data of total coffee production since 1620 show the overall increase and the rise of new production areas. Compiled from several sources, these data are represented as a graph (**Figure 2**), with the volume of today's big players marked individually.

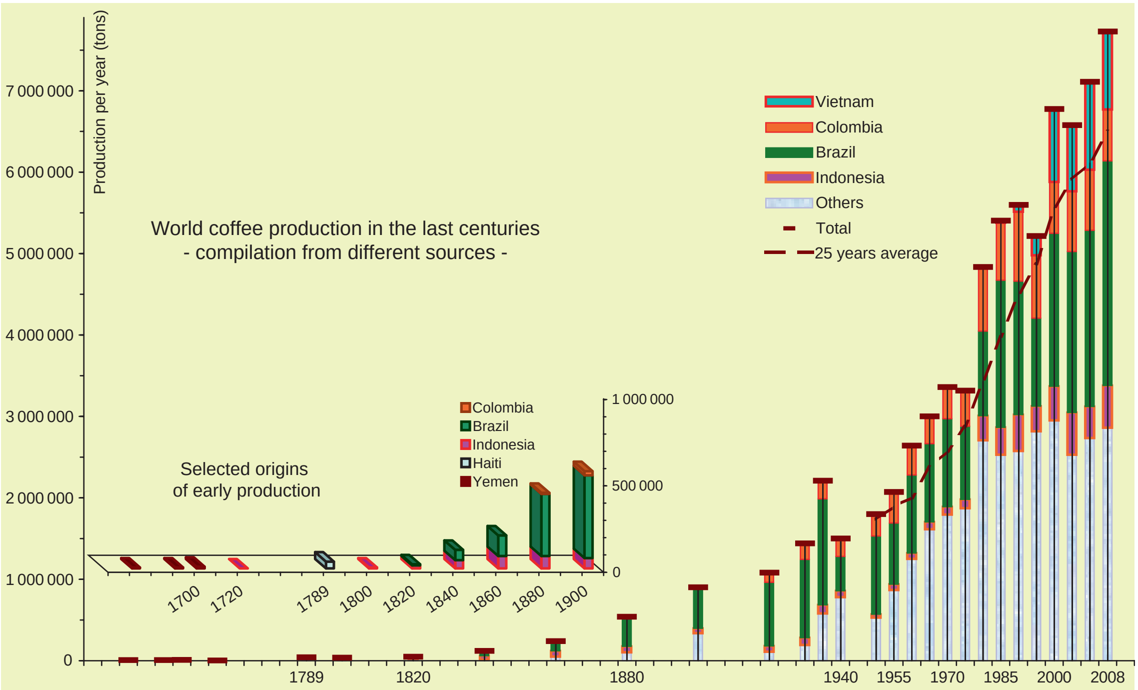


Figure 2 World Coffee production compiled from several sources.

A. 1620, 1700: Becker,[34] p 11.
B. 1670, 1955: Söhn,[35] pp 11, 98.
C. 1720: Eccardi; Sandalj,[9] p 48.
D. 1789, 1936: Dahlgren,[10] pp 22, 41.
E. 1800–1920, 1940, 1950, 1960, 1975: Sivetz,[36] pp 13.
F. 1980–1995: ICO,[33] historical data, total production of member plus non member countries (2009).
G. 2000–2008: ICO,[33] world supply, total production (accessed July 2009).

The known data for world coffee trade started with about 10 000 tons per year in 1700,[34] all from Yemen, followed by supply from Indonesia and from the Caribbean.[35,37] In 2008, a total of about 8 000 000 tons was traded (roughly, Brazil 35%, Vietnam 15%, Colombia 10%, and Indonesia 5%, followed by Ethiopia, Mexico, and India; Arabica constituted 60%). The world production figures are likely higher because there is domestic consumption as well. The volumes of world coffee production and trade before the seventeenth century is not clearly reported; compared with the volumes of today, it was negligible.

3.25.1.6 From Field to Physiology

Coffee passes through several steps to reach its final destination: human consumption. All of these steps – the seed maturation, postharvest processing, storage and transportation on land and ship, roasting, home brewing or industrial extraction, and eventual intermediate treatments – have an impact on its chemical composition.

The economic importance of coffee is evident in agriculture, occupation, and welfare both in producing and consuming countries. Production, international trade, and world wide consumption create normative rules in legislation, administration and standardization in the countries concerned, regarding registration, food surveillance, customs, subsidaries, analytical methods, and many other aspects. Coffee's agriculture has an impact even on the global ecology.

Originally, coffee's stimulating property, its oldest-known physiological effect, was the basis of its use; later on the focus shifted to enjoying aromatic roast coffee beverage as a psychoactive stimulant. Today, due to sophisticated research on the effects and mechanisms of action of coffee, a more balanced view has emerged on the effects of coffee on our well-being and health.

3.25.2 Botany

3.25.2.1 Plant Characteristics, Habit, and Growth

In nonrestricted growth, the coffee plant is a perennial tree or treelet with a single main trunk and horizontal branches, primary, secondary, and tertiary horizontal branches (plagiotropic); pruning can lead to multiple-stem plants.

Coffee's original place is the forest understorey. Coffee plants bear clusters of flowers and cherry-like fruits. A short central taproot fades into axillary and lateral roots and a manifold of feeder bearers and root hairs. The dark green elliptical leaves grow in opposite pairs on the main stem and branches. The wood is dense; the fruits, nectar, and leaves are food resources.

Under tropical conditions, flowering and fruiting happen in parallel; the nearer coffee plants are to the equator, the more pronounced is a bimodal cycle.

Multistem growth is trained by either capping the main stem, giving rise to suckers that develop into new vertical stems with horizontal branching, or bending the principal stem to the horizontal (agobiado technique), with several suckers in a row.

Periodic pruning is done to optimize the plant shape for good fruiting, easy harvesting, and effective disease and pest control, as well as to rejuvenate the plant.

Pests may attack the plants in the field and the beans in store by boring, biting, mining, and sucking, or living as parasites on the root system; fungi, viruses, and bacteria may cause severe coffee diseases.

Further characteristics and figures are given in **Table 1**. For each characteristic, the properties common to all species are written in the first line, followed by the differing ones beneath in separate columns for the species.

The development of flowers from the buds takes several weeks, that of the fruits several months after flowering, with periods of growth and of dormancy. The sequence of steps is enzymatically controlled in-plant and is triggered externally by photoperiodism, relief of water stress, and temperature drop.

In a days-after-flowering (DAF) scale,[43] depicted in **Figure 3**, the tissues of the growing fruit show marked changes in volume ranking of all pericarp, perisperm, and endosperm. Embedded in the start-up pericarp, the perisperm expands to equal the pericarp mass; then, it gets absorbed by the developing endosperm, the final organ for all storage compounds in the fruit.

Propagation to the next generation starts with either seeds from the farmer's own plants, sown directly in the fields, or seedlings from seeds or cuttings delivered by a nursery in plastic bags for planting. Development time in soil from the naked seed to the first leaves is 1–2 months at best. A third method for propagation *in vitro* is

Table 1 Coffee characteristics and requirements for cultivation

Species Character	*Coffea*	*Coffea arabica*	*Coffea canephora*	*Others*
Chromosome status		Amphidiploid ($2n = 4 = 44$ chromosomes)	Diploid ($2n = 22$ chromosomes)	
Ecology	Humid, evergreen tropical forest (cultivation with and without shade trees; intercropping)			
		tropical highlands, (950–) 1200–1950 m	tropical lowlands. (50–)250–1500 m	
		Temperature: moderate, 15–24 °C	Warm, 18–36 °C	
		Rainfall 1200–2200 mm year^{-1}	Rainfall 2200–3000 mm year^{-1}	
		Exceptional cultivations at sea level (Hawaii)	Sometimes in seasonally dry humid forest, or in gallery forest	
Plant height		4–6 m (pruned 2–3 m)	8–12 m (pruned 2–3 m)	*C.liberica* up to 18 m; also 2 m dwarf species
Canopy diameter		1.2–2 m	1.2–2 m	
Root system	Tap root 0.5–1 m; several axillary roots, vertical depth 1.5–3 m; many lateral roots parallel to the soil, distance 1.5–1.8 m from the trunk; hair roots overall; 90% of the root system in the upper 30 cm of the lateral parts			
		Deeper roots	Shallower roots	
Leaves	Elliptical; margin entire; tip accuminate; dark green to bronze green			
		Length 10–15, width 4–6 cm	Length 22, width 17 cm	
		Development time 7–8 weeks to full expansion and optimum photosynthesis (Arabica); life span 7–10 months (Robusta)		
Inflorescences	Paired, axillary; best flowering at 1-year-old wood; development time 4 months with periods of dormancy			
		4–12 with 16–48 flowers per node	30–100 flowers per node	
Flowers	Hermaphrodite; corollas white or rarely light pink; corolla lobes overlapping; anthers exerted; style long, exerted			
		Autogamous (self-pollinating)	Allogamous (cross-pollinating)	
		Time for pollination 1 day	Receptive to 6 days after flowering	
Fruit	Berry containing two seeds (rarely one or three); each seed with a deep groove, an invagination, on the flat ventral side ('coffee bean').			
		Length 12–18 mm	Length 8–16 mm	
		Fruit maturation 7–9 months after flowering	Fruit maturation 9–11 months after flowering	*C.racemosa*: 2 months

The table is compiled from several sources.[24,38–42]

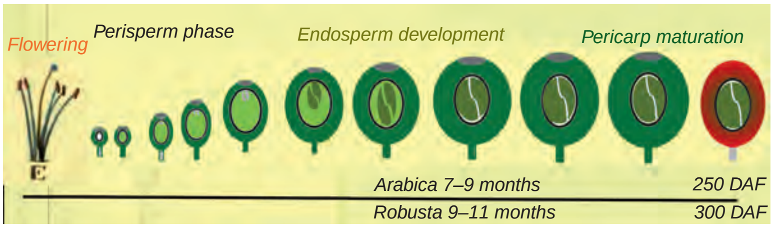


Figure 3 Fruit development in coffee, days-after-flowering scale, compiled from several sources. A. Flower: Linnaeus,[46] p 1. B. Bean development: De Castro; Marraccini,[43] p 177.

used in research: the cultivation of a fragment of tissue from a plant in a suitable substrate, producing a new plant that is genetically identical to the plant from which it originated.[44]

3.25.2.2 Species and Classification

The first attempts at coffee classification were as early as 1623, when Bauhin[45] in his *Pinax theatri botanici* (*Illustrated exposition of plants*) mentioned *Coffea* and set it in relation to Evonymus.

A century later, a comprehensive descriptive systematization was proposed by Linné; he set up plant classes with easily identifiable characters of the floral structure, including the genus *Coffea,* at the very beginning,[46,47] with publications in 1735 and 1737. The final naming of the species as *Coffea arabica* was presented in his '*Species Plantarum*' in 1753.[48] This work was based on direct observations in botanical gardens and herbaria,[49,50] and in discussions and exchanges with colleagues. He explicitly cited Jussieu's description of coffee for the Royal Academy in Paris in 1713/1715.[14]

In **Figure 4** shows the coffee of Linné's original private herbarium, pressed, dried, and fixed on a sheet (N° 2490 of the Linnaean Herbarium at the Linnean society London, Salvage No. 232.1; the mark "india" presumably indicating the origin of the specimen; collection purchased from Linné's widow in 1784).

The official reference for *C. arabica* L. is the type specimen from Clifford's herbarium,[51] which Linné had described in 1737.[49,50] It is designated as a lectotype[52] on the basis of the procedures of the International Botanical Code (the Vienna Code of 2005[53]). 'Lectotype' means that the first publisher had described the specimen prior to the reference to it – the requirement to explicitly design a reference specimen came up later.

Linné's typification became a benchmark for the botany of that time, as underlined by the title 'Order out of Chaos' for an anniversary book of 2007.[54] Although his classification was soon overtaken,[55] the binomial principle of naming remained – the first part indicates the botanic genus; the second is an epithet given by the first author, who is indexed. The overall genus for the coffee species is *Coffea* L., indexed as named by Linnaeus. The principal commercial species used for beverage preparation are *C. arabica* L., and *C. canephora* Pierre ex A.Froehner,[25] commonly called var. Robusta. *Coffea liberica* Bull ex Hiern and some other species are much less important today; there are numerous varieties, including cultivated ones (cultivars).

The botanical classification of coffee has reached a high degree of consensus, presented in international conferences[56,57] and with ongoing publication in the World Checklist of Rubiaceae[58] – coffee is positioned in this family since Jussieu 1789.[55]

Chevalier's system,[59] with four subgenera of *Coffea*, was popular for some decades of the last century. However, it became obsolete the more taxa of the different pools of coffee origin were described and classified.[60–62]

In terms of the Botanical Code, the classification lineage of coffee, starting at the family rank with Rubiaceae, goes down via subfamily Ixoriadeae, tribe Coffeae DC.,[63,64] to the genus *Coffea* L. Some 100 accepted species of the genus, belong to the subgenus *Coffea,* including all beverage coffees; subgenus *Baracoffea* holds about 10 species.[42] That is the actual status.

Nevertheless, there are follow-up refinements.[65]

Figure 4 'Caffe' in Linnés herbar, marked 'arabica' by his own hand, courtesy of the Linnean Society, London.

3.25.2.3 Modern Classifications

The changes in classification since Linné's time came along with a change of characterizing properties and of observables, morphological characters against molecular phylogenetics. Involved is a change in the philosophy of systematic biology, "from being considered a plan in the mind of the creator, . . . finally to a phylogenetic mapping of the tree of life".[66] Recently, a 'phylocode' had been proposed, to substitute the Botanical Code's system with its taxa and their hierarchy, at least partially.[67] Discussions are under way.

Modern analytical chemical measurements can now be used in combination with chemometric comparison of secondary plant metabolite levels such as caffeine or chlorogenic acids to classify varieties in phylogenetic trees. Studies of the molecular genetic variation help to identify the relationships of species help to identify their relationships, presented in dendrograms and resulting in genetic clusters of coffees, which can be compared to the biogeographical grouping of coffee clades. Several lineages with geographical or ecological coherence are now recognized,[68] as shown in **Figure 5**.

The phylogenetic approach widens the principles of classification from the morphological similarity of existing plants toward an evolutionary dimension, with genetic clades, where the taxa are traced back to ancestry.

With these instruments, the genetic origin of *C. arabica* could be investigated, with a strongly supported hypothesis: Arabica seems to have been formed by interspecific crossing of diploid progenitors, one species close to *C. eugenioides* as the maternal and another species close to the canephoroid group as the paternal

Figure 5 The tropical African origin of coffee, distribution map showing the location of groups of Coffea.

progenitor. This might have taken place in East–Central Africa, very likely in the late Quaternary period.[69] Several mechanisms were discussed – how the new species moved from a tetraploid via progressive diploidization toward the amphidiploid, which it is considered to be now. With the adaptation to the tropical mountain climate of Ethiopia, a low but continued natural selection may have occurred.[70]

In contrast, the high genetic diversity found in the canephora branch of coffee encourages an earlier dating of the origins, as some 500 000 years ago.[71] The clustering of natural *C. canephora* diversity groups, with some 40 species in continental Africa, supports the link to climatic variations in that tropical zone. In the last glacial maximum, an arid period 18 000 years ago, the environment became hostile and few forest refugia[72] remained. There, the differentiation of disseminated subgroups could have occurred,[73] with rare migration of species along the rivers[74] and with unpopulated gaps in-between due to adverse conditions. From the East African group, a dispersal to Madagascar and the neighboring islands might have taken place. They show more than 50 species of the genus *Coffea*, distinct from the continentals: no naturally occurring species is shared between Africa, Madagascar, and the Mascarenes.[42]

Not so far away in history emerged the question about the origin of Bourbon Pointu from Réunion, *C. arabica* 'Laurina' – whether it is a mutation of the Arabica introduced from Yemen or a result of crossing between this Arabica and the indigenous Café marron of the island. A combination of historical and modern analytical research revealed that it is a very young mutant of the Yemenite Arabica that was introduced in Réunion.[75]

The genomic era facilitates the understanding of coffee seed development. Using current knowledge, the metabolic pathways of the major seed storage compounds of coffee were elucidated.[76]

3.25.3 Chemistry Components and Processes

Coffee, as internationally agreed by coffee people, means in the vocabulary ISO, the "fruits and seeds of plants of the genus *Coffea*, usually of the cultivated species, and the products from these fruits and seeds, in different stages of processing and use intended for human consumption" (subclause 1.1. of the ISO 3509 coffee vocabulary),[77] and in the wording of the International Coffee Agreement, the "beans and cherries of the coffee tree, whether parchment, green or roasted, and includes ground, decaffeinated, liquid and soluble coffee" (Article 2 of the said Agreement).[78] Both definitions describe 'coffee' in terms of a series of stages from maturation to consumption.

The composition of coffee varies with the species and with the step in the line. **Table 2** gives an overview of analytical data.

The data are averages from literature reviews,[80] and from investigations executed in other analytical contexts,[82] where the components of constituent groups had been individually determined and summarized.[79]

The in-bean localization of distinct components during the development stages of growing and ripening of the coffee fruit had been observed with electron microscopy supported by tissue coloring. Consecutive papers presented at conferences of association for the science and information on coffee (ASIC) since 1977 featured impressive findings:[83] constituents had been distinguished in their cellular environment and their migrations observed.

An integral view – arrived at through the use of modern instruments – of key biosynthetic pathways of the main coffee seed storage compounds was published recently.[76] Readers may refer to this paper for the plant biochemistry as that will not be further elaborated here.

The following sections deal with the main components, caffeine, carbohydrates, chlorogenic acids, lipids, other nitrogenous compounds, volatiles, and melanoidins, and include the transformation processes.

The first compound covered here is caffeine, associated even by name to our subject, coffee. Caffeine is a nitrogenous compound that is not affected by the central process in coffee chemistry, roasting.

3.25.3.1 Nitrogenous Compounds I: Caffeine

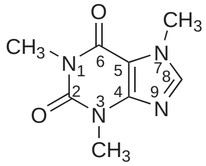
Caffeine, 1,3,7-trimethyl-xanthine, a purine alkaloid, is a secondary metabolite of the coffee plant: the biosynthesis starts from xanthosinemonophosphate.[84] In the metabolic pathway, subsequent methylation steps occur with different N-methyl transferases, methionine being the methyl donor. The purine catabolism of caffeine comprises its degradation via successive demethylation down to carbon dioxide and ammonia.[85]

Table 2 Chemical composition of coffee, mass percent in dry matter, different sources

	Arabica green[a]	*Robusta green*[a]	*Arabica roasted*[b]	*Robusta roasted*[b]	*Arabica instant*[a]	*Robusta instant*[a]
Constituent	*% DW*	*% DW*	*% DW*	*% DW*	*% DW*	*% DW*
Caffeine	1.3	2.3	1.2	2.4	2.5	3.8
Trigonelline	0.8	0.7	0.3[c]	0.3[c]	0.7	0.4
Carbohydrates	53.7	50.7	38	42	46.6	44.7
Chlorogenic acids	8.1	9.9	2.5	3.8	2.6	1.6
Lipids	15.2	9.4	17.0	11.0	0.11	0.26
Amino acids	11.1	11.8	7.5	7.5	6.2	6.0
Organic acids	2.3	1.7	2.4	2.6	8.1	7.9
Melanoidins	–	–	25.4	25.9	25.1	28.6
Volatile aroma	Traces	Traces	0.1	0.1		
Ash (minerals)	3.9	4.4	4.5	4.7	8.0	7.4
Others partly unknown			In melan oidines	Added to melan		

[a] Leloup[79].
[b] Illy and Viani[80].
[c] Macrae[81]

In the coffee plant, caffeine is present in all parts over the ground. The ecological effects of caffeine as an intrinsic chemical defense against herbivory, molluscs, insects, fungi, or bacteria[86] have often been discussed, but experimental results for clear support are difficult to obtain.[87]



Caffeine

Caffeine biosynthesis takes place in the leaves and in the pericarp, the outer part of the fruit. In aged leaves the caffeine content is lower.[88] In the pericarp tissues, light strongly stimulates the methylation step of caffeine synthesis. When the seed inside the fruit starts growing, caffeine is translocated through the membranes and accumulates in the endosperm. There, the final value is reached 8 months after flowering.[89]

The caffeine content of the coffee beans depends on species and variety, from 0.6% in Laurina up to 4% in some extreme Robustas; averages are given in **Table 3**.[90]

Not included here are coffees from the Mascaracoffea group of Madagascar, which do not belong to the 'beverage' coffees.[91] They have very low caffeine contents at the limit of analytical detection (caffeine free)[92] and may serve as genetic resources for further work. These low caffeine species also show low caffeine in their leaves.[93]

The caffeine content in dry matter base is not affected by postharvest processing, neither by the roasting. Although the roasting process occurs well above sublimation temperature, during it only a small percentage of caffeine vanishes, which is overbalanced by the organic weight loss.[91]

Caffeine is a physiologically active compound, and the human exposure to it after a cup of coffee is of interest. Some general calculations can be made: an aqueous extraction at regular brewing conditions transfers the caffeine almost completely into the beverage. A cup of 100 ml with a brew of 55 $g\,l^{-1}$ of roast and ground coffee, with the world trade ratio of 60% Arabica and an average caffeine content of **Table 2**, supplies about 100 mg caffeine.

Looking beyond the averages, **Table 4** roughly gives the variability (brewing strength 40 g/l)[94,95] of the value, omitting extremes and exotics – a range of plus/minus 100%.

But even the term 'cup' or 'serving' is in motion: the mug has become widespread, with a volume of about 250 ml, and 'jumbos' are on the market, of about 500 ml.

A cup of tea for comparison, has a slightly lower caffeine content: Prepared from a 1.75 g teabag with an average caffeine content for tea of 3%, a cup of 100 ml contains 50 mg, with a natural variability similar to the case of coffee.

The limit for mandatory caffeine labeling in non-coffee and non-tea drinks is set at 150 $mg\,l^{-1}$(sets the obligation for caffeine labelling at amounts exceeding 150 mg/l and a sentence intended as warning, "contains high amounts of caffeine," unless (Art.2 2) the beverage is based on coffee or tea);[96] this labeling should help consumers avoid unexpected caffeine intake.

The data given here reflect a standard beverage preparation – others exist. In an espresso-style percolation, for a cup of 30 ml, 6.5 g roast and ground are taken; with the same coffee, about 87 mg caffeine can be expected. The very short time available to extract caffeine from the cellular structure leads to 75–85% extraction yield only.[97]

Table 3 Caffeine content in green beans of different species and varieties

		Leaf	*bean*
Species	*Variety*	*% DW*	*% DW*
C. arabica	Mundo Novo	0.98	1.11
	Typica	0.88	1.05
	Catuai	0.93	1.34
	Laurina	0.72	0.62
C. canephora	Robusta	0.46	>4
	Kouilou/Conillon	0.95	2.36
	Laurentii	1.17	2.45

Table 4 Estimated ranges of caffeine content per cup, standard brewing of different strengths

Species (caffeine range)	*Arabica (0.9–1.6%)*	*Mix 60 Ar/40 Rob (1.7 %)*	*Robusta (1.4–2.9%)*
Brewing strength	*Caffeine per cup mg/100 ml*	*Caffeine per cup mg/100 ml*	*Caffeine per cup mg/100 ml*
$40\,g\,l^{-1a}$	36–64	67	56–116
$55\,g\,l^{-1b}$	50–88	92	77–160
$70\,g\,l^{-1c}$	63–112	118	98–203

Brewing strength according to
[a] NEVO, 1991, Dutch nutritional tables[94]: $40\,g\,l^{-1}$.
[b] Mean between a and c: $55\,g\,l^{-1}$ (German common use).
[c] ISO 6668:2008,[95]: $70\,g\,l^{-1}$.

While enjoying his coffee, the consumer may benefit from the stimulating effect of caffeine.

The alerting effects are well known and the mechanisms investigated.[98,99]

After its consumption, caffeine is readily and completely absorbed from the gastrointestinal tract. Within 1 h it is evenly distributed within the body, readily passing the blood–brain barrier. Peak plasma levels occur 30–60 min after ingestion.

Provoked by a cup of regular coffee of the previously-calculated concentration, a caffeine level of $2\,mg\,l^{-1}$ body fluid is reached (total body fluid taken as 60% of a 70-kg man), just in the range of the stimulatory level of about $1–4\,mg\,l^{-1}$ body fluid.[100] At blood concentrations such as these, the main mechanism of action in the central nervous system is the antagonism of adenosine receptors, which increases central nervous system activity, with effects on alertness and cognitive control.

During circulation, caffeine is metabolized in the liver via successive demethylation and oxidative degradation to uric acid. The breakdown products are excreted through the kidneys. About 5% of caffeine is excreted unchanged. The half-life ranges from 2.5 to 4.5 h in healthy male adults. For children, women, pregnant women, and people under stress, longer times were reported.

The caffeine content of coffee can be reduced by decaffeination. The process starts with a steam treatment of the green coffee to soften the tissues, followed by solvent extraction. The first patent dates back to 1905.[101] Today, processes run with dichloromethane, ethyl acetate, supercritical or fluid carbon dioxide, or water – each process with its own special technology.[102] In the United States, nondecaffeinated coffee is called ‘regular’ coffee.

Legal requirements on the caffeine content apply to decaffeinated coffee for the final product for consumption, that is, roast and soluble coffees. In the United States, decaffeination is measured through the degree of decaffeination; common are 97%.[103] The European legislation sets a maximum residual caffeine content of 0.3% for soluble coffee;[104] roast coffee is covered by national legislations, in general 0.1% on dry matter.

The standard analytical methods for caffeine determination employ chromatographic separation and spectrometric detection.[105]

Although caffeine as pure chemical has a clearly bitter taste (it can be used as a “bitter” standard in basic sensory tests), it plays only a minor role in giving a bitter tinge to the coffee beverage.

3.25.3.2 Processes and Reactions

3.25.3.2.1 Postharvest processing: dry and wet methods

The ripe coffee beans, cherry-like, embedded in the pulp of the fruit, need to be dissected soon after harvesting to avoid an uncontrolled fermentation in the wet mucilage, which would cause undesired ‘off-flavors’ in the cup. The cherries can be processed by either the dry method – sun drying on patios for 3–9 days followed by mechanical removal of the dried outer parts, resulting in ‘natural coffee’ – or the wet method – pulping, controlled fermentation of the mucilage in an 18–36 h process, then rinsing the residuals and drying to produce