21 Coffee, Tea, Cocoa

21.1 Coffee and Coffee Substitutes

21.1.1 Foreword

Coffee (coffee beans) includes the seeds of crimson fruits from which the outer pericarp is completely removed and the silverskin (spermoderm) is occasionally removed. The seeds may be raw or roasted, whole or ground, and should be from the botanical genus *Coffea*. The drink prepared from such seeds is also called coffee.

Coffee is native to Africa (Ethiopia). From there it reached Arabia, then Constantinople and Venice. Regardless of the prohibition of use and medical warnings, coffee had spread all over Europe by the middle of the 17th century. The coffee tree or shrub belongs to the family *Rubiaceae*. Depending on the species, it can grow from 3–12 m in height. The shrubs are pruned to keep them at 2–2.5 m height and thus facilitate harvesting. The evergreen shrubs have leathery short-stemmed leaves and white, jasmin-like fragrant flowers from which the stone fruit, cherry-like berries, develop with a diameter of about 1.5 cm. The fruit or berry (Fig. 21.1) has a green outer skin which, when ripe, turns red-violet or deep red and encloses the sweet mesocarp or the pulp and the stone-fruit bean. The latter consists of two elliptical hemispheres with flattened adjacent sides. A yellowish transparent spermoderm, or silverskin, covers each hemisphere. Covering both hemispheres and separating them from each other is the strong fibrous endocarp, called the "parchment". Occasionally, 10–15% of the fruit berries consist of only one spherical bean ("peaberry" or "caracol"), which often brings a premium price.

The coffee shrub thrives in high tropical altitudes (600–1200 m) with an annual average temperature of 15–25 °C and moderate moisture and cloudiness. The shrubs start to bloom 3–4 years after planting and after six years of growth they provide a full harvest. The shrubs can bear fruit for 40 years, but the maximum yield is attained after 10–15 years. Fruit ripening occurs within 8–12 months after flowering. Only 3 of the 70 species of coffee are cultivated: *Coffea arabica*, which provides 75% of the world's production; *C. canephora*, about 25%; and *C. liberica* and others, less than 1%. The quantity (in

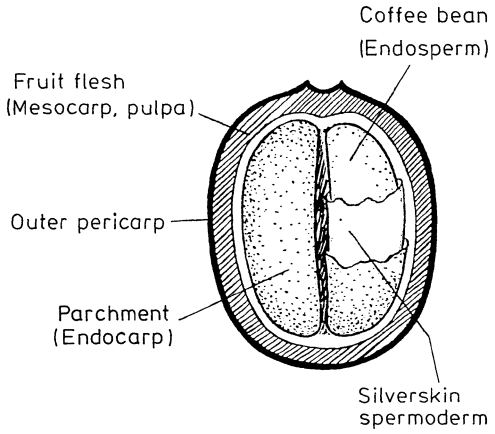


Fig. 21.1. Longitudinal section of a coffee fruit (according to *Vitzthum*, 1976)

Table 21.1. Production of coffee beans in 2006 (1000 t)

Continent	Raw coffee	Country	Raw coffee
World	7843	Brazil	2593
		Viet Nam	854
Africa	922	Colombia	696
America, Central	1020	Indonesia	653
America, North	3	Mexico	288
America, South		India	274
and Caribbean	4782	Ethiopia	260
Asia	2069	Guatemala	257
Europe	–	Honduras	191
Oceania	68	Peru	175
		∑ (%)[a]	75

[a] World production = 100%.

kg) of fresh coffee cherries which yields 1 kg of marketable coffee beans is for *C. arabica* 6.38, *C. canephora* 4.35, and *C. liberica* 11.5. The most important countries providing the world's coffee harvest in 1996 are listed in Table 21.1.

21.1.2 Green Coffee

21.1.2.1 Harvesting and Processing

The coffee harvest occurs from about December until February from the Equator north to the Tropic of Cancer, while south of the Equator to the Tropic of Capricorn harvest occurs from May until August. Harvesting is done by hand-picking of each ripe berry or by strip-picking all of the berries from three branches after most of the berries (often present as clusters) have matured. Harvesting may also be done by sweeping under the tree, i. e. collecting the ripe berries from the ground. Processing commences with removal of the fleshy pulp by using one of the two following processes:

The dry or natural process used in Brazil involves rapid transport of the harvested berries to a central processing plant, where the whole fruit is spread out on sun-drying terraces and dried until the beans separate by shrinking from the surrounding parchment layer.

Dehulling machines – conical screws with a helical pitch increasing toward the discharge end – remove the dried husks and parchment from the dried berries and, as much as possible, the silverskin. The dehulled and cleaned coffee beans are then classified according to size and packed in 60 kg bags. Often, the fresh cherries, instead of being spread on the drying terrace, are piled up, left for 3–4 days under their own heat to ferment the fruity pulp, and are then processed as outlined below. In both cases unwashed beans are obtained.

The wet (washing) process is more sophisticated than the dry process, and by general consent leads to better quality coffee. The method is generally used for Arabica coffee (except in Brazil) in Central America, Colombia and Africa. The freshly harvested berries are brought to a pulper in which the soft fruit is squeezed between a rotating cylinder or disc and a slotted plate, the gap of which is adjustable. The passage of the fruit produces a rubbing action which detaches the skin and the pulp from the beans without damaging the seed. The removed pulp is used as fertilizer.

The pulped beans still have the silver-skin, the parchment and a very adhesive mucilaginous layer (mucilage). Hence, such coffee is carried into water stream fermentation tanks made of concrete, the water is drained off and the beans are left to ferment for 12–48 h. During this time, the mucilaginous layer, which consists of 84.2% water, 8.9% protein, 4.1% sugar, 0.91% pectic subtances and 0.7% ash, is hydrolyzed by enzymes of the coffee and by similar enzymes produced by microorganisms found on the fruit skins. The mucilage is degraded to an extent which can be readily dispersed by washing with water. The beans are then collected, sun-dried on concrete floors or dried in mechanical dryers in a stream of hot air (65–85 °C). Beans dried in this way are still covered with the parchment shell ("pergament" coffee or "cafe pergmino") and are further processed by dehulling machines as in the dry process. This yields the green coffee beans. Premium-priced coffee beans are often polished to a smooth, glossy surface and the silverskin, except that retained in the centrecut of the beans, is removed.

21.1.2.2 Green Coffee Varieties

About 80 varieties of the three coffee bean species mentioned above are known. The most important of the species *Coffea arabica* are *typica, bourbon, maragogips* and *mocca*; and of *Coffea canephora* are *robusta* (the most common), *typica, uganda* and *quillon*. All varieties of *Coffea canephora* are marketed under the common name *"robusta"*.

The names of green coffees may be characteristic of the place of origin; i. e. the country and the port of export. Important washed Arabica coffees are, for example, Kenyan, Tanzanian, Colombian, Salvadorian, Guatemalon or Mexican.

Unwashed Arabica beans are the mild Santos and the hard Rio and Bahia beans. All three are from Brazil. Robusta coffees, mostly unwashed, are, for example, those from Angola, Uganda, the Ivory Coast and Madagascar.

Arabica coffees, particularly those from Kenya, Colombia and Central America, have a soft, rich,

clean flavor or "fine acid" and "good body". The Arabica Santos from Brazil is an important ingredient of roasted coffee blends because of its strong but mellow flavor. Robusta coffee, on the other hand, is stronger but harsh and rough in aroma.

The quality assessment of green coffee is based on odor and taste assays, as well as on the size, shape, color, hardness and cross-section of the bean. Major defects or imperfections are primarily due to objectionable off-flavored blemished beans, which are removed by careful hand sorting. Blemished beans consist of: unripe seeds (grassy beans) which stay light colored during roasting; overfermented beans with an off-flavor due to the presence of acetic acid, diacetyl, butanol and isobutanol; frost-bitten and cracked beans; insect and rainfall-damaged beans; and excessively withered beans. Even a single blemished bean can spoil the whole coffee infusion. Additional imperfections are the moldy, musty flavor of insufficiently dried and prematurely sacked coffee and earthy or haylike off-flavors. Coffee varieties grown at high altitudes are generally more valuable than those from the plains or lowlands.

21.1.2.3 Composition of Green Coffee

The composition of green coffee is dependent on variety, origin, processing and climate. A review of the differences between Arabica and Robusta coffee is provided in Table 21.2. The constituents will be covered in more detail in the section dealing with roasted coffee.

21.1.3 Roasted Coffee

21.1.3.1 Roasting

Green beans smell green-earthy, so they must be heat treated in a process called roasting to bring about their truly delightful aroma. Roasting in the temperature range between 100 and the final temperature of ca. 200 °C causes profound changes. The beans increase in volume (50–80%) and change their structure and color. The green is replaced by a brown color, a 11–20% loss in weight occurs, and there is a build-up of the typical roasted flavor of the beans. Simultaneously, the specific gravity falls from 1.126–1.272 to 0.570–0.694, hence the roasted coffee floats on water and the green beans sink. The horny, tough and difficult-to-crack beans become brittle and mellow after roasting.

Four major phases are distinguished during the roasting process: drying, development, decomposition and full roasting. The initial changes occur at or above 50 °C when the protein in the tissue cells denatures and water evaporates. Browning occurs above 100 °C due to pyrolysis of organic compounds, accompanied by swelling and an initial dry distillation; at about 150 °C there is a release of volatile products (water, CO_2, CO) which results in an increase in bean volume. The decomposition phase, which begins at 180–200 °C, is recognizable by the beans being forced to pop and burst (bursting by cracking along the groove or furrow); formation of bluish smoke; and the release of coffee aroma. Lastly, under optimum caramelization, the full roasting phase is achieved, during which the moisture content of the beans drops to its final level of 1.5–3.5%.

The roasting process is characterized by a decrease in old and formation of new compounds. This is covered in section 21.1.3.3, which deals with the composition of roasted coffee. The running of a roasting process requires skill and experience to achieve uniform color and optimum aroma development and to minimize the damage through over-roasting, scorching or burning.

During roasting, heat is transferred by contact of the beans with the walls of the roasting apparatus or by hot air or combusted gases (convection). Actual *contact roasting* is no longer of importance because heat transfer is uneven and the roasting times required are long (20–40 min). In the *contact-convection roasting* process (roasting time 6–15 min), efforts are made to increase the convection component as much as possible by suitable process management. Centrifugal roasters (rotating flat pans), revolving tube roasters, fluid-bed roasters (ca. 90% convection) etc. are used either batchwise or continuously. In the new *short-time roasting* process (roasting time 2 to 5 min), the heating-up phase is significantly shortened by improved heat transfer. Water evaporation proceeds by puffing, producing

Table 21.2. Composition of green Arabica and Robusta coffee[a,b]

Constituent	Arabica	Robusta	Components
Soluble carbohydrates	9–12.5	6–11.5	
Monosaccharides	0.2–0.5		Fructose, glucose, galactose, arabinose (traces)
Oligosaccharides	6–9	3–7	Sucrose (>90%), raffinose (0–0.9%), stachyose (0–0.13%)
Polysaccharides	3–4		Polymers of galactose (55–65%), mannose (10–20%), arabinose (20–35%), glucose (0–2%)
Insoluble polysaccharides	46–53	34–44	
Hemicelluloses	5–10	3–4	Polymers of galactose (65–75%), arabinose (25–30%), mannose (0–10%)
Cellulose, β(1–4)mannan	41–43	32–40	
Acids and phenols			
Volatile acids	0.1		
Nonvolatile aliphatic acids	2–2.9	1.3–2.2	Citric acid, malic acid, quinic acid
Chlorogenic acid[c]	6.7–9.2	7.1–12.1	Mono-, dicaffeoyl- and feruloylquinic acid
Lignin	1–3		
Lipids	15–18	8–12	
Wax	0.2–0.3		
Oil	7.7–17.7		Main fatty acids: 16:0 and 18:2 (9,12)
N Compounds	11–15		
Free amino acids	0.2–0.8		Main amino acids: Glu, Asp, Asp-NH_2
Proteins	8.5–12		
Caffeine	0.8–1.4	1.7–4.0	Traces of theobromine and theophylline
Trigonelline	0.6–1.2	0.3–0.9	
Minerals	3–5.4		

[a] Values in % of solids.
[b] Water content of raw coffee: 7–13%.
[c] Main components: 5-caffeoylquinic acid (chlorogenic acid: Arabica 3.0–5.6%; Robusta 4.4–6.6%).

a greater bean volume increase than conventional roasting processes. Therefore, the density in the ground state of coffee roasted by this process is 15–25% lower.

The roasting process is controlled electronically or by sampling roasted beans. The end-product is discharged rapidly to cooling sifters or is sprinkled with water in order to avoid over-roasting or burning and aroma loss. During roasting, vapors formed and cell fragments (silverskin particles) are removed by suction of an exhauster and, in larger plants, incinerated.

There are different roasting grades desired. In the USA and Central Europe, beans are roasted to a light color (200–220 °C, 3–10 min, weight loss 14–17%), and in France, Italy and the Balkan states, to a dark color (espresso, 230 °C, weight loss 20%).

21.1.3.2 Storing and Packaging

Roasted coffee is freed of faulty beans either by hand picking on a sorting board or, at large plants, automatically by using photo cells. Commercially available roasted coffee is a blend of 4–8 varieties which, because of their different characteristics, are normally roasted separately. Especially strong blends are usually designated as mocca blends.

While green coffee can be stored for 1–3 years, roasted coffee, commercially packaged (can, plastic bags, pouches, bottles), remains fresh for only 8–10 weeks. The roasting aroma decreases, while a stale, rancid taste or aroma appears. Ground coffee packaged in the absence of oxygen (vacuum packaging) keeps for 6–8 months but, as soon as the package is opened, this drops to 1–2 weeks. Little is known of the nature of the

changes involved in aroma and flavor damage. The changes are retarded by storing coffee at low temperatures, excluding oxygen and water vapor.

21.1.3.3 Composition of Roasted Coffee

Table 21.3 provides information about the composition of roasted coffee. This varies greatly, depending on variety and extent of roasting.

21.1.3.3.1 Proteins

Protein is subjected to extensive changes when heated in the presence of carbohydrates. There is a shift of the amino acid composition of coffee protein acid hydrolysates before and after bean roasting (Table 21.4). The total amino acid content of the hydrolysate drops by about 30% because of considerable degradation.
Arginine, aspartic acid, cystine, histidine, lysine, serine, threonine and methionine, being especially reactive amino acids, are somewhat decreased in roasted coffee, while the stable amino acids, particularly alanine, glutamic acid and leucine, are relatively increased. Free amino acids occur only in traces in roasted coffee.

Table 21.3. Composition of roasted coffee (medium degree of roasting)

Component	Content (%)[a]	
	Arabica	Robusta
Caffeine	1.3	2.4
Lipids	17.0	11.0
Protein[b]	10.0	10.0
Carbohydrates	38.0	41.5
Trigonelline, niacin	1.0	0.7
Aliphatic acids	2.4	2.5
Chlorogenic acids	2.7	3.1
Volatile compounds	0.1	0.1
Minerals	4.5	4.7
Melanoidins[c]	23.0	23.0

[a] Based on solids. Water content varies between 1 and 5%.
[b] Calculated as the sum of the amino acids after acid hydrolysis.
[c] Calculated as the difference.

Table 21.4. Amino acid composition of the acid hydrolysate of Colombia coffee beans prior to and after roasting

Amino acid	Green coffee (%)	Roasted coffee[a] (%)
Alanine	4.75	5.52
Arginine	3.61	0
Aspartic acid	10.63	7.13
Cystine	2.89	0.69
Glutamic acid	19.80	23.22
Glycine	6.40	6.78
Histidine	2.79	1.61
Isoleucine	4.64	4.60
Leucine	8.77	10.34
Lysine	6.81	2.76
Methionine	1.44	1.26
Phenylalanine	5.78	6.32
Proline	6.60	7.01
Serine	5.88	0.80
Threonine	3.82	1.38
Tyrosine	3.61	4.35
Valine	8.05	8.05

[a] A loss due to roasting amounts to 17.6%.

21.1.3.3.2 Carbohydrates

Most of the carbohydrates present, such as cellulose and polysaccharides consisting of mannose, galactose and arabinose, are insoluble. During roasting a proportion of the polysaccharides are degraded into fragments which are soluble. Sucrose (cf. Table 21.2) present in raw coffee is decomposed in roasted coffee up to concentrations of 0.4–2.8%. Monosaccharides also hardly occur.

21.1.3.3.3 Lipids

The lipid fraction appears to be very stable and survives the roasting process with only minor changes. Its composition is given in Table 21.5. Linoleic acid is the predominant fatty acid, followed by palmitic acid. The raw coffee waxes, together with hydroxytryptamide esters of various fatty acids (arachidic, behenic and lignoceric) originate from the fruit epicarp. These compounds are 0.06–0.1% of normally roasted coffee. The diterpenes present are cafestol (I, R = H), 16-O-methylcafestol (I, R = CH_3), and kah-

Table 21.5. Lipid composition of roasted coffee beans (coffee oil)

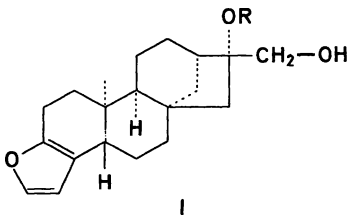
Constituent	Content (%)	Constituent	Content (%)
Triacylglycerols	78.8	Triterpenes	
Diterpene esters	15.0	(sterols)	0.34
Diterpenes	0.12	Unidentified	
Triterpene esters	1.8	compounds	4.0

Table 21.6. Chlorogenic acid content as a function of the degree of roasting

Raw/degree of roasting	Arabica	Robusta
Raw	6.9%	8.8%
Light	2.7%	3.5%
Medium	2.2%	2.1%
Dark	0.2%	0.2%

weol (II). Cafestol and kahweol are degraded by the roasting process.

Since 16-O-methylcafestol is found only in Robusta coffee (0.6–1.8 g/kg of dry weight, green coffee), it is a suitable indicator for the detection of the blending of Arabica with Robusta coffee, even in instant coffee.



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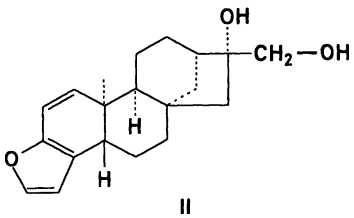
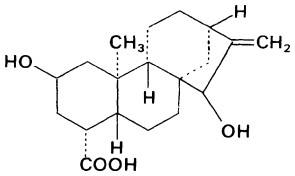


II (21.1)

A diterpene glycoside is atractyloside and its aglycon, atractyligenin:

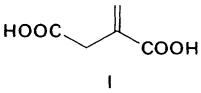


(21.2)

Sitosterol and stigmasterol are major compounds of the sterol fraction.

21.1.3.3.4 Acids

Formic and acetic acids predominate among the volatile acids, while nonvolatile acids are lactic, tartaric, pyruvic and citric. Higher fatty acids and malonic, succinic, glutaric and malic acids are only minor constituents. Itaconic (I), citraconic (II) and mesaconic acids (III) are degradation products of citric acid, while fumaric and maleic acids are degradation products of malic acid:



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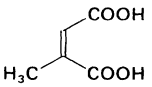

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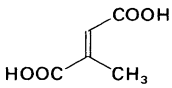


III (21.3)

Chlorogenic acids are the most abundant acids of coffee (Tables 21.2 and 21.3). The content of these acids drops on roasting as shown in Table 21.6.

21.1.3.3.5 Caffeine

The best known N-compound is caffeine (1,3,7-trimethylxanthine) because of its physiological effects (stimulation of the central nervous system, increased blood circulation and respiration). It is mildly bitter in taste (threshold value in water is 0.8–1.2 mmole/l), crystallizes with one molecule of water into silky, white needles, which melt at 236.5 °C and sublime without decomposition at 178 °C. The caffeine content of raw Arabica coffee is 0.9–1.4%, while in the Robusta variety, it is 1.5–2.6%. In contrast there are caffeine-free Coffea varieties. Santos, an Arabica coffee, is on the low side, while Robusta from Angola is at the top of the range given for caffeine content. Other purine alkaloids are theobromine (Arabica: 36–40 mg/kg, Robusta: 26–82 mg/kg)

and theophylline (Arabica: 7–23 μg/kg, Robusta: 86–344 μg/kg).
Caffeine forms, in part, a hydrophobic π-complex with chlorogenic acid in a molar ratio of 1:1. In a coffee drink, 10% of the caffeine and about 6% of the chlorogenic acid present occur in this form. The caffeine level in beans is only slightly decreased during roasting. Caffeine obtained by the decaffeination process and synthetic caffeine are used by the pharmaceutical and soft drink industries. Synthetic caffeine is obtained by methylation of xanthine which is synthesized from uric acid and formamide.

21.1.3.3.6 Trigonelline, Nicotinic Acid

Trigonelline (N-methylnicotinic acid) is present in green coffee up to 0.6% and is 50% decomposed during roasting. The degradation products include nicotinic acid, pyridine, 3-methyl pyridine, nicotinic acid methyl ester, and a number of other compounds.

21.1.3.3.7 Aroma Substances

The volatile fraction of roasted coffee has a very complex composition. Dilution analyses (cf. 5.2.2) have shown that of the 850 volatile compounds identified until now, only the 40 listed in Table 21.7 contribute to the aroma. Indeed, 28 aroma substances in the concentrations present in a medium roasted Arabica coffee drink (Table 21.8) can largely approximate its aroma. The correspondence becomes even better by the addition of 4-methoxy-2-methylbutan-2-thiol (cf.5.3.2.5), which has a concentration of 0.022 μg/kg in the drink.
The aroma profile of coffee is composed of the following notes: sweet/caramel-like, earthy, sulfurous/roasty and smoky/phenolic. Table 21.8 shows that most of the odorants can be assigned to these notes. The remaining odorants have a fruity or spicy odor. In the aroma profile, they are discretely detectable if their concentrations are considerably higher than shown in Table 21.8. Omission experiments (cf. 5.2.7) show that 2-furfurylthiol makes the most important contribution to the aroma of coffee.

Table 21.7. Odorants of roasted coffee – results of dilution analyses

Aroma substance
Acetaldehyde, methanethiol, propanal, methylpropanal, 2-/3-methylbutanal, 2,3-butandione, 2,3-pentandione, 3-methyl-2-buten-1-thiol, 2-methyl-3-furanthiol, 2-furfurylthiol, 2-/3-methylbutyric acid, methional, 2,3,5-trimethylthiazole, trimethylpyrazine, 3-mercapto-3-methyl-1-butanol, 3-mercapto-3-methylbutylformiate, 2-(1-mercaptoethyl)-furan, 2-methoxy-3-isopropylpyrazine, 5-ethyl-2, 4-dimethylthiazole, 2-ethyl-3, 5-dimethylpyrazine, phenylacetaldehyde, 2-ethenyl-3, 5-dimethylpyrazine, linalool, 2,3-diethyl-5-methylpyrazine, 3,4-dimethyl-2-cyclopentenol-1-one, guaiacol, 4-hydroxy-2, 5-dimethyl-3(2H)-furanone, 3-isobutyl-2-methoxypyrazine, 2-ethenyl-3-ethyl-5-methylpyrazine, 6,7-dihydro-5-methyl-5H-cyclopentapyrazine, (E)-2-nonenal, 5-ethyl-4-hydroxy-2-methyl-3(2H)-furanone, 3-hydroxy-4,5-dimethyl-2(5H)-furanone, 4-ethylguaiacol, p-anisaldehyde, 5-ethyl-3-hydroxy-4-methyl-2(5H)-furanone, 4-vinylguaiacol, (E)-β-damascenone, bis(2-methyl-3-furyl)disulfide, vanillin

Its precursors are polysaccharides containing arabinose, e. g., arabinogalactans, as well as cysteine in the free and bound form. A considerable part of furfurylthiol and the other thiols listed in Table 21.8 is present in roasted coffee as disulfide bound to cysteine, SH-peptides and proteins. On roasting, the formation of furfurylthiol is promoted by the water content and the slightly acidic pH value of the beans because under these conditions, the precursor arabinose in the polysaccharides is released by partial hydrolysis.
Robusta coffees contain alkylpyrazines and phenols in significantly higher concentrations than Arabica (Table 21.9). Correspondingly, the earthy and smoky/phenolic notes in the aroma profile are more intensive. Arabica coffees are usually richer in the odorants of the sweet/caramel-like group.
The pea-like, potato-like aroma note of raw coffee is produced by 3-alkyl-2-methoxypyrazines, 3-isobutyl-2-methoxypyrazine having the highest aroma value. Being very stable compounds, they easily survive the roasting process. However, this process yields very intensively smelling odor-

Table 21.8. Concentrations of potent odorants in Arabica coffee from Colombia[a] – Yields of odorants in the production of the beverage[b]

No.	Group/odorant	Concentration (mg/kg)	Yield (%)
	Sweet/caramel-like group		
1	Methylpropanal	28.2	59
2	2-Methylbutanal	23.4	62
3	3-Methylbutanal	17.8	62
4	2,3-Butandione	49.4	79
5	2,3-Pentandione	36.2	85
6	4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F)	120	95
7	5-Ethyl-4-hydroxy-2-methyl-3(2H)-furanone (EHM3F)	16.7	93
8	Vanillin	4.1	95
	Earthy group		
9	2-Ethyl-3,5-dimethylpyrazine	0.326	79
10	2-Ethenyl-3,5-dimethylpyrazine	0.053	35
11	2,3-Diethyl-5-methylpyrazine	0.090	67
12	2-Ethenyl-3-ethyl-5-methylpyrazine	0.017	25
13	3-Isobutyl-2-methoxy-pyrazine	0.087	23
	Sulfurous/roasty group		
14	2-Furfurylthiol	1.70	19
15	2-Methyl-3-furanthiol	0.064	34
16	Methional	0.239	74
17	3-Mercapto-3-methylbutyl-formiate	0.112	81
18	3-Methyl-2-butene-1-thiol	0.0099	85
19	Methanethiol	4.55	72
20	Dimethyltrisulfide	0.028	n.a.
	Smoky/phenolic group		
21	Guaiacol	3.2	65
22	4-Ethylguaiacol	1.6	49
23	4-Vinylguaiacol	55	30
	Fruity group		
24	Acetaldehyde	130	73
25	Propanal	17.4	n.a.
26	(E)-β-Damascenone	0.226	11
	Spicy group		
27	3-Hydroxy-4,5-dimethyl-3(5H)-furanone (HD2F)	1.58	78
28	5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone (EHM2F)	0.132	n.a.

[a] Degree of roasting: medium.
[b] Yield of the aroma substances in the production of the beverage (11) by percolation of coffee powder (54 g) with water (ca. 90 °C).
n.a.: not analyzed.

Table 21.9. Key odorants for the difference between Arabica and Robusta coffee

Aroma substance	Concentration (mg/kg)	
	Arabica	Robusta
2-Ethyl-3,5-dimethylpyrazine	0.326	0.940
2,3-Diethyl-5-methylpyrazine	0.090	0.310
Guaiacol	3.2	28.2
4-Ethylguaiacol	1.61	18.1
4-Vinylguaiacol	55	178

ants so that the odor of the methoxypyrazines is largely suppressed. An aroma defect, the potato taste, (Table 21.10) is produced in roasted coffee only if the concentrations of the alkyl-methoxypyrazines increase excessively. These compounds are synthesized by bacteria which penetrate into the coffee fruit after insects have done the groundwork. In particular, 2-furfurylthiol and guaiacol increase with increasing degree of roasting (Fig. 21.2).

The aroma of coffee is not stable, the fresh note is rapidly lost. Of the highly volatile odorants,

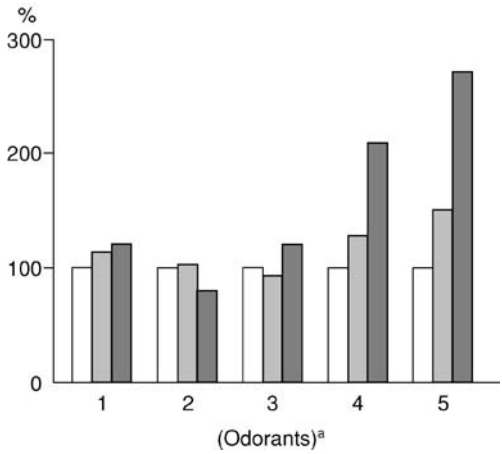


Fig. 21.2. Changes in the concentration of potent odorants in the roasting process (according to *Mayer* et al. 1999). Arabica coffee from Colombia was slightly (□), moderately (▨) and strongly (■) roasted. *1*, 2,3-Butandione; *2*, 4-Hydroxy-2,5-dimethyl-3(2H)-furanone; *3*, 2-ethyl-3,5-dimethylpyrazine; *4*, 2-furfurylthiol; *5*, guaiacol

Table 21.10. Aroma defects in coffee

Aroma defect	Key aroma substance	Cause
Phenolic, musty, medicinal	2,4,6-Trichloroanisole	Degradation of fungicides
Mouldy	2-Methylisoborneol	Microorganisms
Potato taste	Alkylmethoxypyrazines	Combination of insects and bacteria
Fruity, silage-like	Cyclohexanecarboxylic acid ethylester	Uncontrolled fermentation

Table 21.11. Losses of odorants in ground and open stored coffee

Odorants	Loss (%)[a]
Methanethiol	66
Acetaldehyde	45
2-Methylbutanal	32
3-Methylbutanal	27
2-Furfurylthiol	23
3-Isobutyl-2-methoxypyrazine	21
Guaiacol	18
2-Ethyl-3,5-dimethylpyrazine	12
4-Vinylguaiacol	5
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F)	1.4
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (HD2F)	1.1

[a] Loss in 30 minutes at room temperature.

methanethiol evaporates the fastest, followed by acetaldehyde (Table 21.11). The aroma profile changes because especially the slow-evaporating furanones remain (Table 21.11). As a result, the aroma balance can be destroyed by the spicy odor of HD2F (cf. 12.7.3.5) because it is individually detectable. In the case of open storage of intact beans, losses of the highly volatile aroma substances are significantly lower, e. g., evaporation of methanethiol is only 11% in 15 minutes at room temperature instead of 43%.

21.1.3.3.8 Minerals

As with all plant materials, potassium is predominant in coffee ash (1.1%), followed by calcium (0.2%) and magnesium (0.2%). The predominant anions are phosphate (0.2%) and sulfate (0.1%). Many other elements are present in trace amounts.

21.1.3.3.9 Other Constituents

Brown compounds (melanoidins) are present in the soluble fraction of roasted coffee. They have a molecular weight range of 5–10 kdal and are derived from *Maillard* reactions or from carbohydrate caramelization. The structures of these compounds have not yet been elucidated. Apparently, chlorogenic acid is also involved in such browning reactions since caffeic acid has been identified in alkali hydrolysates of melanoidins.

21.1.3.4 Coffee Beverages

In order to obtain an aromatic brewed coffee with a high content of flavoring and stimulant constituents, a number of prerequisites must be fulfilled. The brewing, leaching and filtration procedures used give rise to a variety of combinations. While in our society brewed coffee is enjoyed as a transparent, clear drink, in the Orient brewed coffee is prepared from pulverized beans (roasted beans ground to a fine powder) and water brought to a boil, and is drunk as a turbid beverage with the sediment (Turkish mocca). Coffee extract is made by boiling the coffee for 10 min in water and then filtering. In the boiling-up procedure the coffee is added to hot water, brought to a boil within a short time and then filtered. The steeping method involves pouring hot water on a bag filled with ground coffee and occasionally swirling the bag in a pot for 10 min. In the filtration-percolation method, ground coffee is placed on a support grid (filter paper, muslin, perforated plastic filter, sintered glass, etc.) and extracted by dripping or spraying with hot water, i. e. by slow gravity percolation. This procedure, in principle, is the method used in most coffee machines. In an expresso machine, which was

developed in Italy, coffee is extracted briefly by superheated water (100–110 °C), while filtration is accelerated by steam at a pressure of 4–5 bar. The exceptionally strong drink is usually turbid and is made of freshly ground, darkly roasted coffee. The water temperature should not exceed 85–95 °C in order to obtain an aromatic drink with most of the volatile substances retained. Water quality obviously plays a role, especially water with an unusual composition (some mineral spring waters, excessively hard water, and chlorinated water) might reduce the quality of the coffee brew. Brewed coffee allowed to stand for a longer time undergoes a change in flavor.

For regular brewed coffee, 50 g of roasted coffee/l (7.5 g/150 ml cup) is used; for mocca, 100 g/l; and for Italian espresso, 150 g/l. Depending on the particle size and brewing procedure, 18–35% of the roasted coffee is solubilized. The dry matter content of coffee beverages is 1–3%. The composition is presented in Table 21.12.

The taste of coffee depends greatly on the pH of the brew. The pH using 42.5 g/l of mild roasted coffee should be 4.9–5.2. At pH < 4.9 the coffee tastes sour; at pH > 5.2 it is flat and bitter. Coffees of different origins provide extracts with different pH's. Generally, the pH's of Robusta varieties are higher than those of Arabica varieties. Figure 21.3 shows the relationship between pH and extract taste for some coffees of known origin.

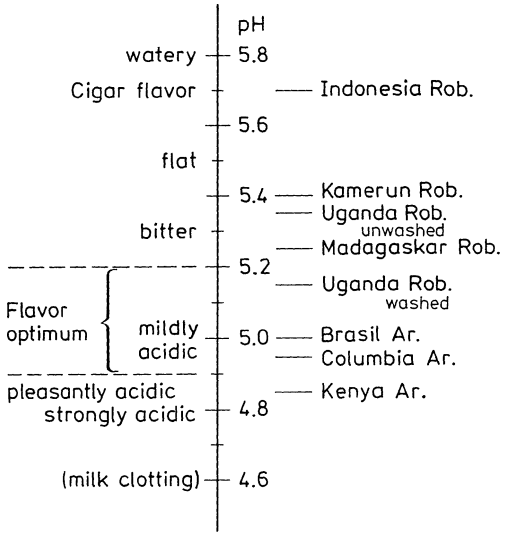


Fig. 21.3. The flavor of roasted coffee brew as related to pH value (according to *Vitzthum*, 1976)

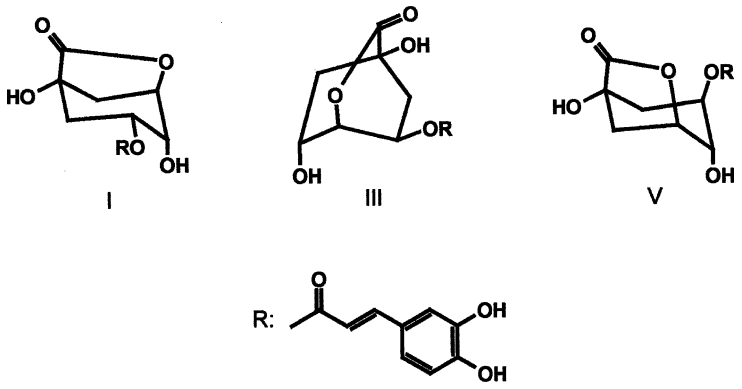
The difference between the aroma of the beverage and that of ground coffee is the more intensive phenolic, buttery, caramel-like note and a weaker roasty note. These changes are caused by shifts in the concentrations of the aroma substances during brewing (Table 21.8). Compounds like 2,3-butandione, the furanones 6, 7 and 27, 2-ethyl-3,5-pyrazine, the thiols 17 and 18 are extracted with yields of >75%, while only 25% or less of 2-ethenyl-3-ethyl-5-methylpyrazine, 3-isobutyl-2-methoxypyrazine, 2-furfurylthiol and β-damascenone pass into the beverage. The low yield of 2-furfurylthiol is partly due to reactions which occur during percolation of the coffee powder.

Caffeine and the quinic acid lactones listed in Table 21.13 are the bitter substances in the coffee drink. Accordingly, these lactones are almost exclusively responsible for the bitter note of a decaffeinated coffee drink (Table 21.13). Although the concentrations of the lactones III–VII, IX and X in the drink are lower than their threshold concentrations (cf. Table 21.13), they still additively contribute to the bitter taste (cf. 5.1.2: additive effect).

Table 21.12. Composition of coffee beverages[a]

Constituent	Content (% dry weight basis)
Protein[b]	6
Polysaccharides	24
Saccharose	0.8
Monosaccharides	0.4
Lipids	0.8
Volatile acids	1.4
Nonvolatile acids	1.6
Chlorogenic acids	14.8
Caffeine	4.8
Trigonelline	1.6
Nicotinic acid	0.08
Volatile aroma compounds	0.4
Minerals	14
Unidentified constituents (pigments, bitter compounds etc.)	29.4

[a] Arabica-coffee, medium roast, 50 g/l.
[b] Calculated as sum of the amino acids after acid hydrolysis.



(21.4)

Table 21.13. Bitter quinic acid lactones in a decaffeinated coffee drink[a]

No.	Quinic acid lactone (quinides)[b]	Threshold[c]	Concentration
		(mg/l)	
I	3-O-Caffeoyl-γ-	13.4	33.15
II	4-O-Caffeoyl-γ-	12.1	19.68
III	4-O-Caffeoyl-*muco*-γ-	11.2	8.27
IV	5-O-Caffeoyl-*muco*-γ-	9.7	6.12
V	5-O-Caffeoyl-*epi*-δ-	60.5	3.28
VI	3-O-Feruloyl-γ-	13.7	6.75
VII	4-O-Feruloyl-γ-	13.7	3.03
VIII	3,4-Dicaffeoyl-γ-	4.9	5.40
IX	4,5-Dicaffeoyl-*muco*-γ-	4.9	1.65
X	3,5-Dicaffeoyl-*epi*-δ-	24.9	0.80

[a] Made by the percolation of coffee powder (54 g) with water (80 °C, 1.1 l).
[b] The structures of the lactones I, III and V are presented in Formula 21.4.
[c] Threshold for the bitter taste.

21.1.4 Coffee Products

The coffee products which will be discussed are instant coffee, decaffeinated coffee and those containing additives.

21.1.4.1 Instant Coffee

Instant (soluble) coffee is obtained by the extraction of roasted coffee. The first technically sound process was developed by *Morgenthaler* in Switzerland in 1938. Ground coffee is batchwise extracted under pressure in percolator batteries or continuously in extractors. The water temperature may be as high as 200 °C while the temperature of the extract leaving the last extraction cell is 40–80 °C. The extracts exhibit a concentration of ca. 15% and are evaporated in vacuum film evaporators to a solids content of 35–70%. To minimize aroma losses, the extraction can be conducted in two stages. In a gentle stage, the first extract is obtained with a solids content of 25–27% and carries the main portion of the aroma. Without concentration, it is mixed with a second extract which was obtained under stronger conditions and concentrated. In addition, aroma concentrates can be isolated by stripping; they can be added back before or after drying. The technical extraction yields are 36–46%. Further processing involves spray or freeze drying. In the latter method, the liquid extract is foamed and frozen in a stream of cold air or an inert gas (−40 °C), then granulated (grain size of 2–3 mm), sifted and dried in vacuum in the frozen state. Spray-dried coffee extract can be agglomerated in vibration fluid beds by steam or spray.

The resultant extract powder is hygroscopic and unstable. It is packaged in glass jars, vacuum packed in cans, aluminum foil-lined bags, flexible polyethylene, laminated pouches or bags, or packaged in air-tight plastic beakers or mugs, often under vacuum or under an inert gas.

Like roasted coffee, instant coffee is marketed in different varieties, e. g., regular roasted or as a dark, strongly-roasted espresso, or caffeine free. Instant coffee contains 1.0–6.0% moisture. The dry matter consists of 7.6–14.6% minerals, 3.2–

13.1% reducing sugars (calculated as glucose), 2.4–10.5% galactomannan, 12% low molecular organic acids, 15–28% brown pigments, 2.5–5.4% caffeine and 1.56–2.65% trigonelline. The products are used not only for the preparation of coffee beverages but also as flavorings for desserts, cakes, sweet cookies and ice cream.

21.1.4.2 Decaffeinated Coffee

The physiological effects of caffeine are not beneficial nor are they tolerated by everyone. Hence, many processes have been developed to remove caffeine (<0.1%) from coffee. The following process steps are normally used:

- Swelling of the raw coffee with water or steam at 22–100 °C up to a water content of 30–40%,
- Extraction of the caffeine-potassium-chorogenate complex with a water-saturated solvent (methylene chloride, ethyl acetate) at 60–150 °C,
- Treatment with steam at 100–110 °C to remove the solvent (deodorization),
- Drying with warm air or under vacuum at 40–80 °C.

In another indirect process, used in the USA, initially all the water-soluble compounds including caffeine are extracted from the green beans. The aqueous extract is decaffeinated with an organic solvent (e. g., dichloroethane), then added back to the green beans and evaporated to dryness with the beans.

Swollen raw coffee can also be decaffeinated with supercritical CO_2 (crit. point: 31.06 °C; 73.8 bar) at 40–80 °C and a pressure of 200–300 bar. The high vapor pressure of carbon dioxide under normal conditions guarantees a product that is free from solvent residues. Apart from the extraction of caffeine, this process can also be applied in the extraction of odor- and taste-active substances from hops and other plant materials.

21.1.4.3 Treated Coffee

The "roast" compounds, the phenolic acids and the coffee waxes, are irritating substances in roasted coffee. Various processes have been developed to separate these constituents to make roasted coffee tolerable for sensitive people.

Lendrich (1927) investigated the effect of steaming green beans, without caffeine extraction, on the removal of some substances (e. g., waxes) and hydrolysis of chlorogenic acid. In a process developed by *Bach* (1957), roasted coffee beans are washed with liquid carbon dioxide. In another process, the surface waxes of the raw beans are first removed by a lowboiling organic solvent, followed by steaming, as used by *Lendrich*. The extent of wax removal can be monitored by the analysis of fatty acid tryptamides, which have already been mentioned (cf. 21.1.3.3.3).

21.1.5 Coffee Substitutes and Adjuncts

21.1.5.1 Introduction

Coffee substitutes, or surrogates, are the parts of roasted plants and other sources which are made into a product which, with hot water, provides a coffee-like brew and serves as a coffee substitute or as a coffee blend.

Coffee adjuncts (coffee spices) are roasted parts of plants or material derived from plants, mixed with sugar, or a blend of all three sources and, when other ingredients are added, are used as an additive to coffee or as coffee substitutes. The starting materials for manufacturing such products vary: barley, rye, milo (a sorghum-type grain) and similar starch-rich seeds, barley and rye malts and other malted cereals, chicory, sugar beets, carrots and other roots, figs, dates, locust fruit (St. John's bread) and similar sugar-rich fruits, peanuts, soybeans and other oilseeds, fully or partially defatted acorns and other tannin-free plant parts, and, lastly, various sugars.

Coffee substitutes have been known for a long time, as exemplified by the coffee brew made of chicory roots (*Cichoricum intybus* var. *sativum*) or by clear drinks prepared from roasted cereals.

21.1.5.2 Processing of Raw Materials

The raw materials are stored as such (all cereals, figs), or are stored until processing as dried slices (e. g., root crops such as chicory or sugar beet). After careful cleaning, steeping, malting and steaming in steaming vats, pots or pressure vats take place. Roasting follows, with a final

temperature of 180–200 °C, and then the grains may be polished or coated with sugar.
For the manufacture of substitutes and adjunct essences, liquid sugar juice (cane or beet molasses, syrup or starch-sugar plant extracts) is caramelized in a cooker by heating above 160 °C under atmospheric pressure. The dark, brown-black product solidifies to a glassy, strongly hygroscopic mass which is then ground.
Pulverized coffee substitutes are obtained from the corresponding starting materials, as with true coffee, by a spray, drum, conveyor or other drying process.
The starch present in the raw materials is diastatically degraded to readily-caramelized, water-soluble sugars in the manufacture of coffee substitutes during the steeping, steaming and, particularly, the malting steps. This is especially the case with malt coffee. Caramel substances ("bitter roast") formed in the roasting step, which provide the color and aroma of the brew, are derived from carbohydrate-rich raw materials (starch, inulin or sucrose). Since oilseeds readily develop rancidity, processing of carbohydrate-rich materials is preferred to oil- or protein-rich raw materials.
As aroma carriers, the oils from roasted products have been analyzed in detail, specially for malt and chicory coffees. From the volatiles identified in the coffee aroma, numerous constituents are also found in these oils. However, a basic difference appears to be that the numerous sulfur-containing substances, e. g., 2-furfurylthiol, that are present in roasted beans appear in considerably lower amounts.

21.1.5.3 Individual Products

21.1.5.3.1 Barley Coffee

Barley (or rye, corn or wheat) coffee is obtained by roasting the cleaned cereal grains after steeping or steaming. The products contain up to 12% moisture and have about 4% ash.

21.1.5.3.2 Malt Coffee

Malt coffee is made from barley malt by roasting, with or without an additional steaming step. It contains 4.5% moisture, 2.6% minerals, 74.7% carbohydrates (calculated), 1.8% fat, 10.8% crude protein, 5.6% crude fiber and provides an extract which is 42.4% soluble in water. Polycyclic aromatic hydrocarbons are also detected. Rye and wheat malt coffees are manufactured from their respective malts in the same way.

21.1.5.3.3 Chicory Coffee

Chicory coffee is manufactured by roasting the cleaned roots of the chicory plant possibly with addition of sugar beet, low amounts of edible fats or oils, salt and alkali carbonates. This is followed by grinding of the roasted product, with or without an additional steaming step or treatment with hot water. Chicory contains on the average 13.3% moisture, 4.4% minerals, 68.4% carbohydrates, 1.6% fat, 6.8% crude protein, 5.5% crude fiber andprovides an extract which is 64.6% soluble in water.

21.1.5.3.4 Fig Coffee

Fig coffee is made from figs by roasting and grinding, with or without an additional steaming step or treatment with hot water. It contains 11.4% moisture, 70.2% carbohydrates and 3.0% fat and provides an extract which is 67.9% soluble in water.

21.1.5.3.5 Acorn Coffee

This product is made from acorns, freed from fruit hull and the bulk of the seed coat, by the same process as used for coffee. It contains an average of 10.5% moisture, 73.0% carbohydrates and provides an extract which is 28.9% soluble in water.

21.1.5.3.6 Other Products

Coffee substitute blends and similarly designated products are blends of the above-outlined coffee substitutes, coffee adjuncts and coffee beans. Caffeine-containing coffee substitutes or adjuncts are made by incorporating plant caffeine extracts

into substitutes before, during or after the roasting step. The content of caffeine never exceeds 0.2% in such products.

21.2 Tea and Tea-Like Products

21.2.1 Foreword

Tea or tea blends are considered to be the young, tender shoots of tea shrubs, consisting of young leaves and the bud, processed in a way traditional to the country of origin. The tea shrub was cultivated in China and Japan well before the time of Christ. Plantations are now also found in India, Pakistan, Sri Lanka, Indonesia, Taiwan, East Africa, South America, etc. Table 21.14 shows some data on the production of tea.

The evergreen tea shrub (*Camellia sinensis*, synonym *Thea sinensis*) has three principal varieties, of which the Chinese (var, *sinensis* small leaves) and the Assam varieties (var. *assamica*, large leaves) are the more important and widely cultivated. Grown in the wild, the shrub reaches a height of 9 m but, in order to facilitate harvest on plantations and in tea gardens, it is kept pruned as a low spreading shrub of 1–1.5 m in height. The plant is propagated from seeds or by vegetative propagation using leaf cuttings. It thrives in tropical and subtropical climates with high humidity. The first harvest is obtained after 4–5 years. The shrub can be used for 60 to 70 years. The harvesting season depends upon the region and climate and lasts for 8–9 months per year, or leaves can be plucked at intervals of 6–9 days all year round. In China there are 3–4 harvests per year.

The younger the plucked leaves, the better the tea quality. The white-haired bud and the two adjacent youngest leaves (the famous "two leaves and the bud" formula) are plucked, but plucking of longer shoots containing three or even four to six leaves is not uncommon. Further processing of the leaves provides black or green tea.

Table 21.14. Production of tea in 2006 (1000 t)

Continent	Tea	Country	Tea
World	3649	China	1050
		India	893
Africa	486	Sri Lanka	311
America, Central	1	Kenya	311
America, North	–	Turkey	205
America, South		Indonesia	171
and Caribbean	95	Vietnam	142
Asia	3058	Japan	92
Europe	1	Argentina	68
Oceania	9	Iran	59
		∑ (%)[a]	90

[a] World production = 100 %.

21.2.2 Black Tea

The bulk of harvested tea leaves is processed into black tea. First, the leaves are withered in trays or drying racks in drying rooms, or are drum dried. This involves dehydration, reducing the moisture content of the fresh leaves from about 75% to about 55–65% so that the leaves become flaccid, a prerequisite for the next stage of processing: rolling without cracking of the leaves. Withering at 20–35 °C lasts about 4–18 h. During this time the thinly spread leaves lose about 50% of their weight in air or in a stream of warm air as in drum drying. In the next stage of processing, the leaves are fed into rollers and are lightly, without pressure, conditioned in order to attain a uniform distribution of polyphenol oxidase enzymes. These enzymes are present in epidermis tissue cells, spatially separated from their substrates. This is followed by a true rolling step in which the tea leaf tissue is completely macerated by conventional crank rollers under pressure. The cell sap is released and subjected to oxidation by oxygen from the air. The rolling process is regarded as fermentation and proceeds at 25 °C for tea leaves spread thinly in layers 3.5–7 cm thick. The traditional fermentation takes about 2–3 h. The fermented tea is dried in belt dryers counter-currently with hot air at ca. 90 °C to a water content of 3 to 4%. In this process the leaf material is heated to 80 °C, which is sufficient to inactivate the polyphenol oxidases. The sap released during rolling and fermentation solidifies during drying on the fine little hairs on the surface of the leaf. This tea extract has a gold or silver color. These are the "tips", which are a sign of good quality. They dissolve on brewing. During drying, aroma substances are formed and the coppery-red color is changed to black (hence "black tea").

India and Sri Lanka tea factories use both rollers and machines of continuous operation – the socalled CTC machines (crushing, tearing and curling). They provide a simultaneous crushing, grinding, and rolling of the tea leaf, thus reducing the rolling and fermentation time to 1 to 2 hours. Earl Grey tea is black tea perfumed with bergamot oil.

21.2.3 Green Tea

In the green tea manufacture, the development of oxidative processes is regarded as an adverse factor. The fresher the tea leaf used in manufacture, the better the tea produced. Since oxidative processes catalyzed by the leaf enzymes are undesirable, the enzymes are inactivated at an early stage and their reactions are replaced by thermochemical processes. In contrast to black tea manufacture, withering and fermentation stages are omitted in green tea processing.

There are two methods of manufacturing green tea: Japanese and Chinese. The Japanese method involves steaming of the freshly plucked leaf at 95 °C, followed by cooling and drying. Then the leaf undergoes high-temperature rolling at 75 to 80 °C. In the Chinese method the fresh leaves are placed into a roaster which is heated by smokeless charcoal, and roasted. After rolling and sifting, firing is the final step in the production of green tea. During the processing of green tea the content of tannin, chlorophyll, vitamin C and organic acids decreases only slightly as a consequence of enzyme inactivation.

Green tea provides a very light, clear, bitter tasting beverage. In China and Japan it is often aromatized by flowers of orange, rose or jasmin. Yellow tea and red tea (*Oolong*) occupy an intermediate position between the black and green teas, yellow tea being closer to green teas, and red tea to black teas.

Yellow tea production does not include fermentation. Nevertheless, in withering, roasting, and firing, a portion of tannins undergoes oxidation, and, therefore, dry yellow tea is darker than green tea.

Red tea is a partially fermented tea. Its special flavor which is free from the grassy note of green tea is formed during roasting and higher-temperature rolling.

21.2.4 Grades of Tea

The numerous grades of tea found in the trade are defined by origin, climate, age, processing method, and leaf grade. They can be classified somewhat arbitrarily:

- According to leaf grade (tea with full, intact leaves), such as Flowery Orange Pekoe and Orange Pekoe (made from leaf buds and the two youngest, hairy, silver leaves with yellowish tips); Pekoe (the third leaf); Pekoe Souchong (with the coarsest leaves, fourth to sixth, on the young twig).
- Broken-tea, with broken or cut leaves similar to the above grades, in which the fine broken or cut teas with the outermost golden leaf tips are distinguished from coarse, broken leaves. Broken/cut tea (loose tea) is the preferred product in world trade since it provides a finer aroma which, because of increased surface area, produces larger amounts of the beverage.
- Fannings and the fluff from broken/cut leaves, freed from stalks or stems, are used preferentially for manufacturing of tea bags.
- Tea dust, which is not used in Europe.
- Brick tea is also not available on the European market. It is made of tea dust by sifting, steaming and pressing the dust in the presence of a binder into a stiff, compact teabrick.

With regard to the origin, teas of especially high quality are those from the Himalayan region Darjeeling and from the highlands of Sri Lanka.

All over the world there is blending of teas (e. g., Chinese, Russian, East-Friesen blends, household blends) to adjust the quality and flavor of the brewed tea to suit consumer taste, acceptance or trends and to accommodate regional cultural practices for tea-water ratios. Like coffee, tea extracts are dried and marketed in the form of a soluble powder, often called instant tea.

21.2.5 Composition

The chemical composition of tea leaves varies greatly depending on their origin, age and the type of processing. Table 21.15 provides data on the constituents of fresh and fermented tea leaves. In fermented teas 38–41% of the dry matter is sol-

Table 21.15. Composition (%, dry weight basis) of fresh and fermented tea leaves and of tea brew

Constituent	Fresh flush	Black tea	Black tea brew[a]
Phenolic compounds[b]	30	5	4.5
Oxidized phenolic compounds[c]	0	25	15
Protein	15	15	+[d]
Amino acids	4	4	3.5
Caffeine	4	4	3.2
Crude fiber	26	26	0
Other carbohydrates	7	7	4
Lipids	7	7	+
Pigments[e]	2	2	+
Volatile compounds	0.1	0.1	0.1
Minerals	5	5	4.5

[a] Brewing time 3 min. [b] Mostly flavanols. [c] Mostly thearubigins. [d] Traces. [e] Chlorophyll and carotenoids.

Table 21.16. Phenolic compounds in fresh tea leaves (% dry matter)

Compound	Content
(−)-Epicatechin	1–3
(−)-Epicatechin gallate	3–6
(−)-Epicatechin digallate	+[a]
(−)-Epigallocatechin	3–6
(−)-Epigallocatechin gallate	9–13
(−)-Epigallocatechin digallate	+
(+)-Catechin	1–2
(+)-Gallocatechin	3–4
Flavonols and flavonolglycosides (quercetin, kaempherol, etc.)	+
Flavones (vitexin, etc.)	+
Leucoanthocyanins	2–3
Phenolic acids and esters (gallic acid, chlorogenic acids) p-Coumaroylquinic acid, theogallin	∼5
Phenols, grand total	25–35

[a] Quantitative data are not available.

uble in hot water; this is significantly more than for roasted coffee.

21.2.5.1 Phenolic Compounds (cf. 18.1.2.5)

Phenolic compounds make up 25–35% of the dry matter content of young, fresh tea leaves. Flavanol compounds (Table 21.16) are 80% of the phenols, while the remainder is proanthocyanidins, phenolic acids, flavonols and flavones. During fermentation the flavanols are oxidized enzymatically to compounds which are responsible for the color and flavor of black tea. The reddish-yellow color of black tea extract is largely due to theaflavins and thearubigins (cf. 21.2.6). The astringent taste is caused primarily by flavonol-3-glycosides. Quercetin-3-O-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranside] is especially active with a threshold value of 0.001 μmol/l. Also of importance are (threshold values): kaempferol-3-O-[α-L-rhamnopyranosyl-(1→6)-O-β-D-glucopyranoside] (0.25 μmol/l), quercetin-3-O-β-15-D-galactopyranoside (0.43 μmol/l), quercetin-3-O-β-D-glucoside (0.65 μmol/l) and kaempferol-3-O-β-D-glucopyranoside (0.67 μmol/l). The enzymes are inactivated in green tea, hence flavanol oxidation is prevented. The greenish or yellowish color of green tea is due to the presence of flavonols and flavones. Thus, tea which is processed into green or black tea is chemically readily distinguishable mainly by the composition of phenolic compounds. Green tea contains 17.5% and black tea 14.4% of polyphenols (expressed in gallic acid equivalents). The main components in green tea are the catechins (90% of the polyphenol fraction), which account for only 25% in black tea.

Changes in the content of the phenols occur during tea leaf growth on the shrub: the concentration decreases and the composition of this fraction is altered. Therefore, good quality tea is obtained only from young leaves. Among the remaining phenolic compounds theogallin (XI in Formula 18.14) plays a special role, since it is found only in tea and is correlated with tea quality.

21.2.5.2 Enzymes

A substantial part of the protein fraction in tea consists of enzymes.

The *polyphenol oxidases*, which are located mainly within the cells of leaf epidermis, are

of great importance for tea fermentation. Their activity rises during the leaf withering and rolling process and then drops during the fermentation stage, probably as a consequence of reactions of some products (e. g., o-quinones) with the enzyme proteins.

5-Dehydroshikimate reductase which reversibly interconverts dehydroshikimate and shikimate is a key enzyme in the biosynthesis of phenolic compounds via the phenylalanine pathway.

Phenylalanine ammonia-lyase which catalyzes the cleavage of phenylalanine into transcinnamate and NH_3, is equally important for the biosynthesis of phenols. Its activity in tea leaves parallels the content of catechins and epicatechins.

Proteinases cause protein hydrolysis during withering, resulting in a rise in peptides and free amino acids.

The observed oxidation of linolenic acid to (Z)-3-hexenal, which then partly isomerizes to (E)-2-hexenal, is catalyzed by a *lipoxygenase* and a *hydroperoxide lyase* (cf. 3.7.2.3) and also occurs by autoxidation. (Z)-3-Hexenal contributes to the aroma of green tea.

Chlorophyllases participate in the degradation of chlorophyll and *transaminases* in the production of precursors for aroma constituents.

Demethylation of pectins by *pectin methyl esterase* (cf. 4.4.5.2) results in the formation of a pectic acid gel, which affects cell membrane permeability, thus resulting in a drop in the rate of oxygen diffusion into leaves during fermentation.

21.2.5.3 Amino Acids

Free amino acids constitute about 1–3% of the dry matter of the tea leaf. Of this, 50% is theanine (5-N-ethylglutamine) and the rest consists of protein-forming amino acids; β-alanine is also present.

Green tea contains more theanine than black tea. Generally, there is a characteristic difference in amino acid content as well as difference in phenolic compounds between the two types of tea (Table 21.17).

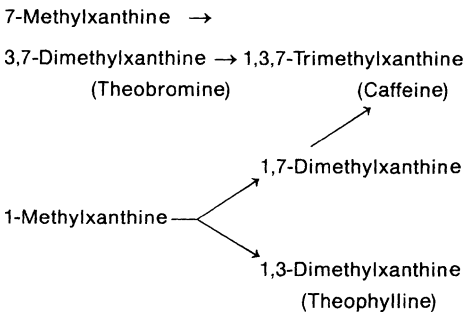
The contribution of theanine to the taste of green tea is discussed. Theanine biosynthesis occurs in the plant roots from glutamic acid and ethylamine, the latter being derived from alanine. The compound is then transported into the leaves. The analogous compounds, 4-N-ethylasparagine and 5-N-methylglutamine, are present at very low levels in tea leaves.

Table 21.17. Amino acids and phenolic compounds in green and black tea (% dry matter)

Tea	Phenolic compounds	Amino acids
Green tea		
Prime quality (Japan)	13.2	4.8
Consumer quality (Japan)	22.9	2.1
Consumer quality (China)	25.8	1.8
Black tea		
Highlands (Sri Lanka)	28.0	1.6
Plains (Sri Lanka)	30.2	1.7

21.2.5.4 Caffeine

Caffeine constitutes 2.5–5.5% of the dry matter of tea leaves. It is of importance for the taste of tea. Theobromine (0.07–0.17%) and theophylline (0.002–0.013%) are also preset but in very low amounts. The biosynthesis of these two compounds involves methylation of hypoxanthine or xanthine:



(21.5)

21.2.5.5 Carbohydrates

Glucose (0.72%), fructose, sucrose, arabinose and ribose are among sugars present in tea leaves. Rhamnose and galactose are bound to glycosides. Polysaccharides found include

cellulose, hemicelluloses and pectic substances. Inositol occurs also in tea leaves.

21.2.5.6 Lipids

Lipids are present only at low levels. The polar fraction (glycerophospholipids) in young tea leaves is predominant, while glycolipids predominate in older leaves.

Triterpene alcohols, such as β-amyrin, butyrospermol and lupeol are predominant in the unsaponifiable fraction. The sterol fraction contains only Δ^7-sterols, primarily α-spinasterol and Δ^7-stigmasterol.

21.2.5.7 Pigments (Chlorophyll and Carotenoids)

Chlorophyll is degraded during tea processing. Chlorophyllides and pheophorbides (brownish in color) are present in fermented leaves, both being converted to pheophytines (black) during the firing step.

Fourteen carotenoids have been identified in tea leaves. The main carotenoids are xanthophylls, neoxanthin, violaxanthin and β-carotene (cf. 3.8.4.1). The content decreases during the processing of black tea. Degradation of neoxanthin (cf. 3.8.4.4), as an example, yields β-damascenone, a significant contributor to tea aroma (Table 21.18).

21.2.5.8 Aroma Substances

The aroma substances of black tea are shown in Table 21.18. A number of aroma substances greatly increase when the drink is brewed. It has been proposed that a modified Strecker reaction (cf. 4.2.4.4.7) contributes to an increase in 2-methylpropanal, 2- and 3-methylbutanal. The o-diquinones, which are produced by the oxidation of the numerous phenolic compounds present in tea, then take on the role of the dicarbonyl compound. The increase in geraniol is probably due to the hydrolysis of the corresponding glycosides. Some aroma substances which are produced by

Table 21.18. Concentrations of potent odorants in black tea (Darjeeling Gold Selection) – yields in the making of the drink[a]

Aroma substance	Concentration (mg/kg)	Yield (%)
2-Methyllpropanal	0.25	2300
3-Methylbutanal	0.32	1105
2-Methylbutanal	0.54	1262
Hexanal	1.60	289
(E)-2-Hexenal	0.27	2406
(Z)-4-Heptenal	0.051	108
(Z)-3-Hexen-1-ol	1.60	500
(E)-2-Nonenal	0.032	103
R/S-Linalool	6.60	180
(E,Z)-2,6-Nonadienal	0.038	122
Phenylacetaldehyde	0.65	731
(E,E)-2,4-Nonadienal	0.087	45
3-Methylnonan-2,4-dione	0.062	65
(E,E)-2,4-Decadienal	0.073	330
(E)-β-Damascenone	0.0098	125
Geraniol	0.37	3227
(E,E,Z)-2,4,6-Nonatrienal	0.16	58
β-Ionone	0.17	75
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	0.10	2167

[a] Yield of the aroma substances obtained in the making of the drink from 12 g tea and 1 l water (95°).

Table 21.19. Concentrations of important aroma substances in the powder and brew of green tea

Compound	Amount[a]	
	Powder	Brew[b]
(Z)-1,5-Octadien-3-one	1.8	0.012
3-Hydroxy-4,5-dimethyl-2(5H)-furanone (HD2F)	49	0.6
3-Methyl-2,4-nonandione (MND)	83	0.56
(Z)-4-Heptenal	112	0.63
(Z)-3-Hexenal	101	0.28
(E,Z)-2,6-Nonadienal	61	0.48
l-Octen-3-one	6	0.03
(E,E)-2,4-Decadienal	127	0.9
(E)-β-Damascenone	9	0.01
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HD3F)	276	n.a.
2-/3-Methylbutyric acid	5280	63
2-Phenylethanol	1140	10.5
Linalool	206	1.0

[a] Values in μg/kg.

[b] Brew (1 kg) prepared from 10 g of the powder.

n.a., not analyzed.

the peroxidation of unsaturated fatty acids, play a role in black tea and are even more important in green tea (Table 21.19). Thus, (Z)-l,5-octadien-3-one, (Z)-3-hexenal and 3-methyl-2,4-nonandione (MND) are responsible for the green and hay-like notes in the aroma profile of this tea. Linolenic acid is the precursor of the first two carbonyl compounds. MND is a degradation product of furan fatty acids (cf. 3.7.2.1.5) and is present in tea in the concentrations shown in Table 21.19. A comparison of the values for tea and for the beverage made from it (Table 21.19) shows that the extraction yield for most of the aroma substances is >50%. β-Damascenone is an exception with a yield of 11%.

21.2.5.9 Minerals

Tea contains about 5% minerals. The major element is potassium, which is half the total mineral content. Some tea varieties contain fluorine in higher amounts (0.015–0.03%).

21.2.6 Reactions Involved in the Processing of Tea

Changes in tea constituents begin during the *withering* step of processing. Enzymatic protein hydrolysis yields amino acids of which a part is transaminated to the corresponding keto acids. Both types of acids provide a precursor pool for aroma substances. The induced chlorophyll degradation has significance for the appearance of the end-product. A more extensive conversion of chlorophyll into chlorophyllide, a reaction catalyzed by the enzyme chlorophyllase (cf. 17.1.2.9.1) is undesirable since it gives rise to pheophorbides (brown) and not to the desired oliveblack pheophytins. Increased cell permeability during withering favors the fermentation procedure. As already mentioned, a uniform distribution of polyphenol oxidases in tea leaves is achieved during the *conditioning* step of processing.

During *rolling*, the tea leaf is macerated and the substrate and enzymes are brought together; a prerequisite for fermentation. The subsequent enzymatic oxidative reactions are designated as "*fermentation*". This term is a misnomer and originates from the time when the participation of microorganisms was assumed. In this processing step, the pigments are formed primarily as a result of phenolic oxidation by the polyphenol oxidases. In addition, oxidation of amino acids, carotenoids and unsaturated fatty acids, preferentially by oxidized phenols, is of importance for the formation of odorants.

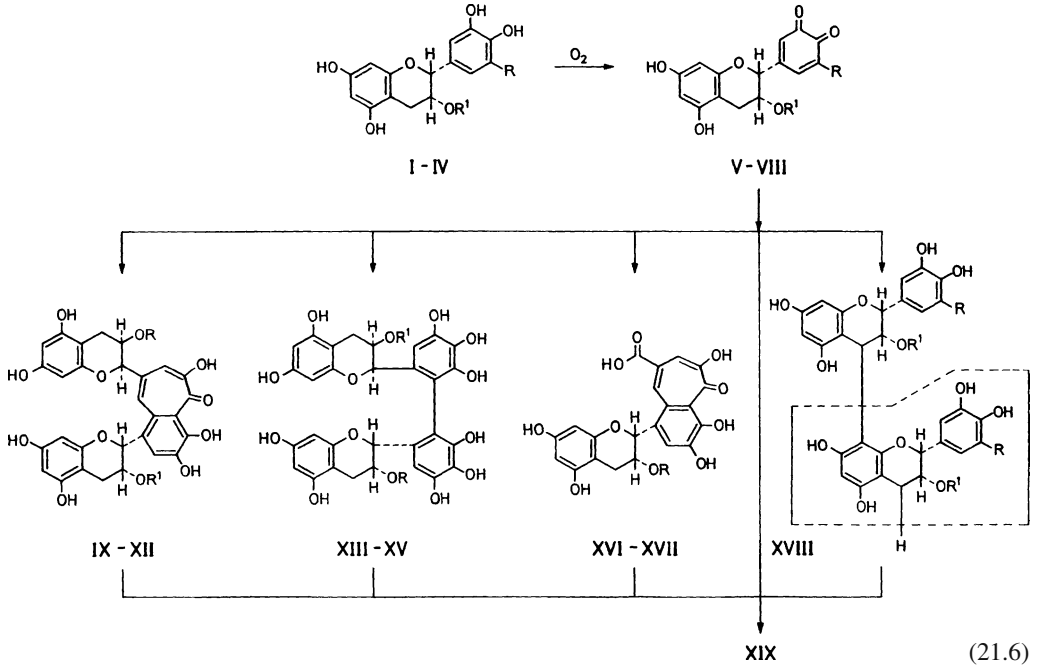
Harler (1963) described tea aroma development during processing: "The aroma of the leaf changes as fermentation proceeds. Withered leaf has the smell of apples. When rolling (or leaf maceration) begins, this changes to one of pears, which then fades and the acrid smell of the green leaf returns. Later, a nutty aroma develops and, finally, a sweet smell, together with a flowery smell if flavor is present."

The enzymatic oxidation of flavanols via the corresponding o-quinones gives theaflavins (Formula 21.6, IX–XII: bright red color, good solubility), bisflavanols (XIII–XV: colorless), and epitheaflavic acids (XVI, XVII: bright red color, excellent solubility). The theaflavins and epitheaflavic acids are important ben-zotropolone derivatives that impart color to black tea.

A second, obviously heterogenous group of compounds, found in tea after the enzymatic oxidation of flavanols, are the thearubigins (XVIII, XIX), a group of compounds responsible for the characteristic reddish-yellow color of black tea extracts (cf. 18.1.2.5.2, Formula 18.21). On the whole, the phenol fraction of black tea consists of the following main components (g/kg): thearubigens (59.5), epigallocatechingallates (16.5), epigallocatechin (10.5), epicatechingallate (8.0) and theaflavin gallate (6.6).

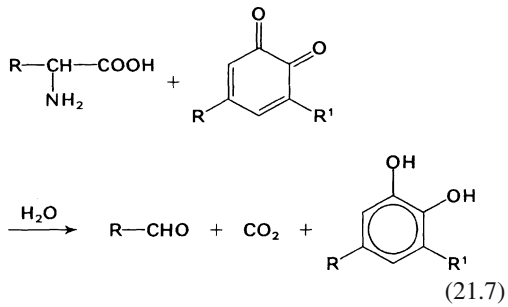
Aroma development during fermentation is accompanied by an increase in the volatile compounds typical of black tea. They are produced by *Strecker* degradation reactions of amino acids with oxidized flavanols (Formula 21.7) and by oxidation of unsaturated fatty acids and the carotinoid neoxanthin.

During the *firing* step of tea processing, there is an initial rise in enzyme activity (10–15% of the theaflavins are formed during the first 10 min), then all the enzymes are inactivated. Conversion of chlorophyll into pheophytin is involved in reactions leading to the black color of tea. A prerequisite for these reactions is high temperature



(21.6)

I: (−)-epicatechin, R^1, R^2 = H
II: (−)-epicatechin-3-gallate, R = H, R^1 = 3,4,5-trihydroxybenzoyl
III: (−)-epigallocatechin, R = OH, R^1 = H
IV: (−)-epigallocatechin-3-gallate, R = OH, R^1 = 3,4,5-trihydroxybenzoyl
V–VIII: o-quinones of compounds I–IV
IX: theaflavin, R, R^1 = H
X: theaflavin gallate A, R = H, R^1 = 3,4,5-trihydroxybenzoyl
XI: theaflavin gallate B, R = 3,4,5-trihydroxybenzoyl, R^1 = H
XII: theaflavin digallate, R, R^1 = 3,4,5-trihydroxybenzoyl
XIII: bisflavanol A, R = R^1 = 3,4,5-trihydroxybenzoyl
XIV: bisflavanol B, R = 3,4,5-trihydroxybenzoyl, R^1 = H
XV: bisflavanol C, R = R^1 = H
XVI: epitheaflavic acid, R = H
XVII: 3-galloyl epitheaflavic acid, R = 3,4,5-trihydroxybenzoyl
XVIII: thearubigins (proanthocyanidin-type), R = H, OH; R^1 = H, 3,4,5-trihydroxybenzoyl
XIX: thearubigins (polymeric catechins of unknown structure)



(21.7)

and an acidic environment. The undesired brown color is obtained at higher pH's. The astringent character of teas is decreased by the formation of complexes between phenolic compounds and proteins. The firing step also affects the balance of aroma substances. On the one hand there is a loss of volatile compounds, on the other hand, at high temperatures, an enhancement of the build-up of typical aroma constituents occurs, e. g., as a result of sugar-amino acid interactions.

21.2.7 Packaging, Storage, Brewing

In the country in which it is grown, the tea is cleaned of coarse impurities, graded according to leaf size, and then packed in standard plywood chests of 20–50 kg lined with aluminum, zinc or plastic foils. To preserve tea quality, the foils are sealed, soldered or welded. China, glass or metal containers are suitable for storing tea. Bags made of pergament or filter papers and filled with metered quantities of tea are also very common.

During storage, the tea is protected from light, heat ($T < 30\,^{\circ}C$) and moisture, otherwise its aroma becomes flat and light. Other sources of odor should be avoided during storage.

To prepare brewed tea, hot water is usually poured on the leaves and, with occasional swirling, left for 3–5 min. An initial tea concentrate or extract is often made, which is subsequently diluted with water. Usually 4–6 g of tea leaves per liter are required, but stronger extracts need about 8 g. The stimulating effect of tea is due primarily to the presence of caffeine.

21.2.8 Maté (Paraguayan Tea)

Maté, or Paraguayan tea, is made from leaves of a South American palm, *Ilex paraguariensis*. The palm grows in Argentina, Brazil, Paraguay and Uruguay, either wild or cultivated, and reaches a height of 8–12 m. To obtain maté, the palm leaves, petioles, flower stems and young shoot tips are collected and charred slightly on an open fire or in a woven wire drum. During such firing, oxidase enzymes are inactivated, the green color is fixed and a specific aroma is formed. The dried product is then pounded into burlap sacks or is ground to a fine powder (maté pulver, maté en pod). Maté may also be prepared by an alternative process: brief blanching of the leaf in boiling water, followed by drying on warm floors and disintegration of the leaves to rather coarse particles. In the countries in which it is grown, maté is drunk as a hot brew (yerva) from a gourd (maté = bulbshaped pumpkin fruit) using a special metal straw called a bombilla, or it is enjoyed simply in a powdered form. Maté stimulates the appetite and, because of its caffeine content (0.5–1.5%), it has long been the most important alkaloid-containing brewed plant product of South America. It contains on the average 12% crude protein, 4.5% ether-soluble material, 7.4% polyphenols and 6% minerals. About one third of the total dry matter of the leaves is solubilized in a maté brew, except for caffeine, which solubilizes to the extent of only 0.019–0.028%, and is 50% bound in leaves.

21.2.9 Products from Cola Nut

Cola (kola) nuts, called guru, goora and bissey nuts by Africans, are not nuts but actually seeds of an evergreen tree of the *Sterculiacea* family, genus *Cola*, species *verticillata, nitida* or *acuminata*, which grows wild in West Africa up to a height of 20 m. The tree is indigenous to Africa, but plantations of Cola are found on Madagascar, in Sri Lanka, Central and South America. Each fruit borne by the tree contains several red or yellow-white cola nuts, shaped like horse chestnuts. The nuts change color to brownish-red when dried, with the typical cola-red color resulting from the action of polyphenol oxidase enzymes. The nuts are on the average 5 cm long and 3 cm wide and have a bitter, astringent taste. The fresh nuts, wrapped in cola leaves and moistened with water, are the most enjoyed plant product of Western and Central Africa. They are consumed mostly in fresh form but are also chewed as dried nuts or ground to a powder and eaten with milk or honey. Cola nuts are used in the making of tinctures, extracts or medical stimulants in tablet or pastille form. They are also used in the liqueur, cocoa and chocolate industries and, especially, in the making of alcohol-free soft drinks, colawines, etc. The stimulating effect of cola nuts is due to the presence of caffeine (average content 2.16%), the main portion of which is in bound form. In addition, cola nuts contain on the average 12.2% moisture, 9.2% nitrogen compounds, 0.05% theobromine, 1.35% crude fat (ether extract), 3.4% polyphenols, 1.25% red pigments, 2.8% sugar, 43.8% starch, 15% other N-free extractable substances, 7.9% crude fiber and 3% ash.

21.3 Cocoa and Chocolate

21.3.1 Introduction

Cocoa, as a drink, is different from coffee or tea since it is consumed not in the form of an aqueous extract, i. e. a clear brew, but as a suspension. In addition to stimulating alkaloids, particularly theobromine, cacao products contain substantial amounts of nutrients: fats, carbohydrates and proteins. Unlike coffee and tea, cocoa has to be consumed in large amounts in order to experience a stimulating effect.

Cacao beans were known in Mexico and Central America for more than a thousand years before America was discovered by *Columbus*. They were enjoyed originally in the form of a slurry of roasted cocoa beans and corn which was seasoned with paprika, vanilla or cinnamon. In the first half of the 17th century, cacao beans were introduced into Germany. Cocoa became popular in the Old World only after sugar was added to the chocolate preparation. Initially, cocoa was treated as a luxury item, until the 19th century, when production of pulverized chocolate and defatted cocoa was established and they were distributed extensively as a food commodity.

The world production of cacao was 31,000 t in 1870/80, 103,000 t in 1900 and 1,585,000 t in 1979. The production in 2006 and the main cacaoproducing countries are listed in Table 21.20.

The processing of cacao beans into cocoa powder and chocolate is presented schematically in Fig. 21.4.

Table 21.20. Production cacao bean in 2006 (1000 t)

Continent	Cacao beans	Country	Cacao beans
World	4059	Côte d'Ivoire	1400
		Ghana	734
Africa	2922	Indonesia	580
America, Central	43	Nigeria	485
America, North	–	Brazil	199
America, South		Cameroon	165
and Caribbean	462	Ecuador	94
Asia	628	Togo	73
Europe	–	Mexico	38
Oceania	48	Colombia	37
		∑ (%)[a]	94

[a] World production = 100%.

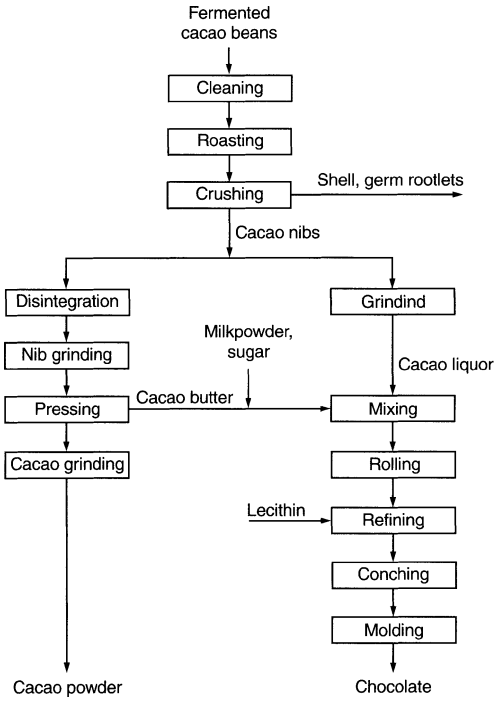


Fig. 21.4. Production of cocoa powder and chocolate

21.3.2 Cacao

21.3.2.1 General Information

Cacao beans are the seeds of the tropical cacao tree, *Theobroma cacao*, family *Sterculiaceae*. Originating in the northern part of South America and currently grown within 20 °C latitude of the Equator, the tree flourishes in warm, moist climates with an average annual temperature of 24–28 °C and at elevations up to 600 m. The tree, because of its sensitivity to sunshine and wind, is often planted and cultivated under shade trees ("cacao mothers"), such as forest trees, coconut palms and banana trees. The perennial tree grows in the wild to a height of 10–15 m, but on plantations it is kept at 2–4 m by pruning. The tree blooms all year round and the small red or white flowers bear 20–50 ripe fruits per tree. The ripe fruit or pod resembles a cantaloupe, 15–25 cm long and 7–10 cm wide. The pod is surrounded by a strong 10–15 mm thick shell. Embedded within the pod are pulpa, i. e. a sweet, mucilaginous pulp containing 10% glucose and fructose. The

pulp surrounds 20–50 almond-shaped seeds (cacao beans). The seed is oval and flattened, about 2 cm long and 1 cm wide, and weighs close to 1 g after drying. The embryo, with two thick cotyledons (nibs) and a germ rootlet, 5 mm long and 1 mm thick, is under a thin, brittle seed coat. The colors in the cross-section of a nib range from white to light brown, to greyish-brown or brown-violet, to deep violet.

The fruit is harvested year round but, preferentially, twice a year. The main harvest time in Mexico is from March through April; in Brazil, February and, in particular, July. The summer harvest is larger and of higher quality. After the tree is planted (progagation by seed or by vegetative methods), it begins to bear pods after five or six years, giving a maximum yield after 20–30 years, while it is nearly exhausted after 40 years of growth. After reaching full beaning capacity, a cacao tree provides only 0.5–2 kg of fermented and dried beans per year. Harvesting at the right time is of great importance for the aroma of cacao and its products. The fruit is harvested fully ripe but not overripe, avoiding damage to the seed during its removal from the fruit.

The tree species *Theobroma cacao* (the only one of commercial importance) is divided into two major groups. The "Criollo" tree (criollo = native) is sensitive to climatic changes and to attack by diseases and pests. It bears highly aromatic beans, hence their commercial name "flavor beans", but they are relatively low yielding. The second group of trees, "Forastero" (forastero = strange, inferior), is characterized by great vigor and the trees are more resistant to climatic changes and to diseases and are higher yielding. The purple-red Forastero beans are less flavorful than Criollo varieties. Nevertheless, the Forastero bean is by far the most important commercial type of cacao and accounts for the bulk of world cacao production (Bahia and Accra cacaos).

Other varieties worth mentioning are the resistant and productive Calabacillo and the Ecuadorian Amelonado varieties.

Cacao beans are differentiated by their geographical origin, grade of cleanliness and the number of preparation steps to which they are subjected prior to shipment. "Flavor beans" come from Ecuador, Venezuela, Trinidad, Sri Lanka and Indonesia, while "commercial beans" are exported by the leading cacao-growing countries of West Africa (Ghana, Nigeria, Ivory Coast and Cameroon), and by Brazil (the port of Bahia) and the Dominica Republic.

21.3.2.2 Harvesting and Processing

At harvest the fully ripe pods are carefully cut from trees, gathered into heaps, cut open and the seeds scooped out with the surrounding pulp. Only rarely are the seeds dried in the sun without a prior fermentation step (*Arriba* and *Machala* varieties from South America). The bulk of the harvest is fermented before being dried. In this fermentation step the seeds with the adhering pulp are transferred to heaps, ditches or fermentation floors, baskets, boxes or perforated barrels and, depending on the variety, are left to ferment for 2–8 days. From time to time the seeds are mixed to make the oxygen in the air accessible to the fermentation process. During this time the temperature of the material rises rapidly to 45–50 °C and the germination ability of the seeds is lost. First, alcoholic fermentation occurs, which later turns into the production of acetic acid. Flavor and color formation and partial conversion of astringent phenolic compounds also occur. The adhering pulp is decomposed enzymatically and becomes liquid. It drains away as a fermentation juice. In addition, there are reactions between constituents of the seeds and pulp. After fermentation is completed, the seeds may be washed (Java, Sri Lanka), and are dried to a moisture content of 6–8%.

Well-fermented seeds, called cocoa beans from this step, provide uniformly colored, dark-brown beans which are readily separated into their cotyledons. Inadequate or unripe fermented beans are smooth in appearance (violetas) and are of low quality.

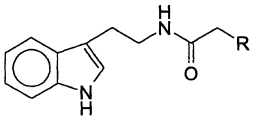
The cocoa imported by consuming countries is processed further. The cocoa beans are cleaned by a series of operations and separated according to size in order to facilitate uniform roasting in the next processing step. Roasting is being performed more and more as a two-step process. Roasting reduces the moisture content of the beans to 3%, contributes to further oxidation of phenolic compounds and the removal of acetic acid, volatile esters and other undesirable aroma components. In addition the eggs and lar-

vae of pests are destroyed. The aroma of the beans is enhanced, the color deepens, the seed hardens and becomes more brittle and the shell is loosened and made more readily removable because of enzymatic and thermal reactions. The ripeness, moisture content, variety and size of the beans and preliminary processing steps done in the country of origin determine the extent and other parameters of the bean roasting process. This process should be carried out in two stages. First, a drying phase and then a phase in which important aroma substances are formed. For instance, African cocoa is heated to between 120 and 130 °C and high-quality cocoa to less than 130 °C for 30 minutes. Losses induced by roasting are 5–8%. As with coffee, roasted beans are immediately cooled to avoid overroasting. The roasters are batch or continuous. Heat transfer occurs either directly through heated surfaces or by a stream of hot air, without burning the shell of the beans. Roasting lasts 10–35 min, depending on the extent desired.

Roasted beans are transferred, after cooling, to winnowing machines to remove the shells and germ rootlets (these have a particularly unpleasant flavor and impart other undesirable properties to cocoa drinks). During winnowing the beans are lightly crushed in order to preserve the nibs and the shells in larger pieces and to avoid dust formation.

The winnowing process provides on the average 78–80% nibs, 10–12% shells, with a small amount of germ and about 4% of fine cocoa particles as waste. All yields are calculated on the basis of the weight of the raw beans.

The whole nibs, dried or roasted, dehulled and degermed or cracked, are still contaminated with 1.5–2% shell, seed coats and germ. The debris fraction, collected by purifying the cocoa waste, consists of fine nib particles and contains up to 10% shell, seed coating and germ. Although the cocoa shell is considered as waste material of little value, it can be used for recovery of theobromine, production of activated charcoal, or as a feed, cork substitute or tea substitute (cocoa shell tea) and, after extraction of fat, as a fertilizer or a fuel. In the adulteration of cocoa, the detection of cocoa shells is promising if based on the indicators lignoceric acid tryptamide (LAT, Formula 21.8) and behenic acid tryptamide (BAT), which are present in the ratio of 2:1 in cocoa shells. These two tryptamides can be separated by HPLC with fluorescence detection and very exactly quantified. Cocoa shells contain 330–395 μg/g of LAT plus BAT, but the cotyledons only 7–10 μg/g.



R : $CH_3 - (CH_2)_{19}$ (BAT)
$CH_3 - (CH_2)_{21}$ (LAT) (21.8)

21.3.2.3 Composition

The compositions of fermented and air-dried cacao nib, cacao shell and germ are presented in Table 21.21.

21.3.2.3.1 Proteins and Amino Acids

About 60% of the total nitrogen content of fermented beans is protein. The nonprotein nitrogen is found as amino acids, about 0.3% in amide form, and 0.02% as ammonia, which is formed during fermentation of the beans.

Among the various enzymes, α-amylase, β-fructosidase, β-glucosidase, β-galactosidase, pec-

Table 21.21. Composition (%) of fermented and air dried cacao beans (1), cacao shells (2) and cacao germs (3)

Constituent	1	2	3
Moisture	5.0	4.5	8.5
Fat	54.0	1.5	3.5
Caffeine	0.2		
Theobromine	1.2	1.4	
Polyhydroxyphenols	6.0		
Crude protein	11.5	10.9	25.1
Mono- and oligosaccharides	1.0	0.1	2.3
Starch	6.0		
Pentosans	1.5	7.0	
Cellulose	9.0	26.5	4.3
Carboxylic acids	1.5		
Other compounds	0.5		
Ash	2.6	8.0	6.3

tinesterase, polygalacturonase, proteinase, alkaline and acid phosphatases, lipase, catalase, peroxidase and polyphenol oxidase activities have been detected in fresh cacao beans. These enzymes are inactivated to a great extent during processing.

21.3.2.3.2 Theobromine and Caffeine

Theobromine (3,7-dimethylxanthine), which is 1.2% in cocoa, provides a stimulating effect, which is less than that of caffeine in coffee. Therefore, it is of physiological importance. Caffeine is also present, but in much lower amounts (average 0.2%). A cup of cocoa contains 0.1 g of theobromine and 0.01 g of caffeine. Theobromine crystallizes in the form of small rhombic prisms which sublime at 290 °C without decomposition. In cocoa beans theobromine is often weakly bound to tannins and is released by the acetic acid formed during fermentation of the beans. Part of this theobromine then diffuses into the shell.

21.3.2.3.3 Lipids

Cocoa fat (cocoa butter), because of its abundance and value, is the most significant ingredient of cacao beans, and is dealt with in detail elsewhere (cf. 14.3.2.2.3).

21.3.2.3.4 Carbohydrates

Starch is the predominant carbohydrate. It is present in nibs but not in shells, a fact useful in the microscopic examination of cocoa powders in methods based on the occurrence of starch as a characteristic constituent. Components of the dietary fiber are amongst others pentosans, galactans, mucins containing galac–turonic acid, and cellulose. Soluble carbohydrates present include stachyose, raffinose and sucrose (0.08–1.5%), glucose and fructose. Sucrose hydrolysis, which occurs during fermentation of the beans, provides the reducing sugar pool important for aroma formation during the roasting process. Mesoinositol, phytin, verbascotetrose, and some other sugars are found in cocoa nib.

21.3.2.3.5 Phenolic Compounds

The nib cotyledons consist of two types of parenchyma cells (Fig. 21.5). More than 90% of the cells are small and contain protoplasm, starch granules, aleurone grains and fat globules. The larger cells are scattered among them and contain all the phenolic compounds and purines. These polyphenol storage cells (pigment cells) make up 11–13% of the tissue and contain anthocyanins and, depending on their composition, are white to dark purple. Data on the composition of these cells and that of the total tissue are given in Table 21.22.

The content of phenolic compounds is also of interest from the standpoint of chemoprevention. With 84 mg/g gallic acid equivalents (GAE) and

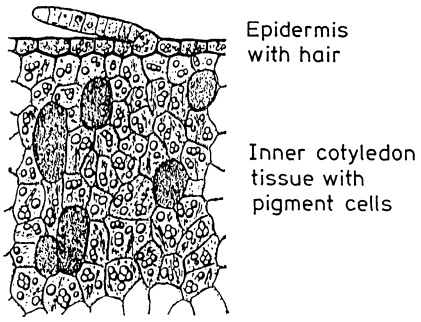


Fig. 21.5. A cross-section of cocoa cotyledon tissue

Table 21.22. Composition of polyphenol storage cells of cacao tissue

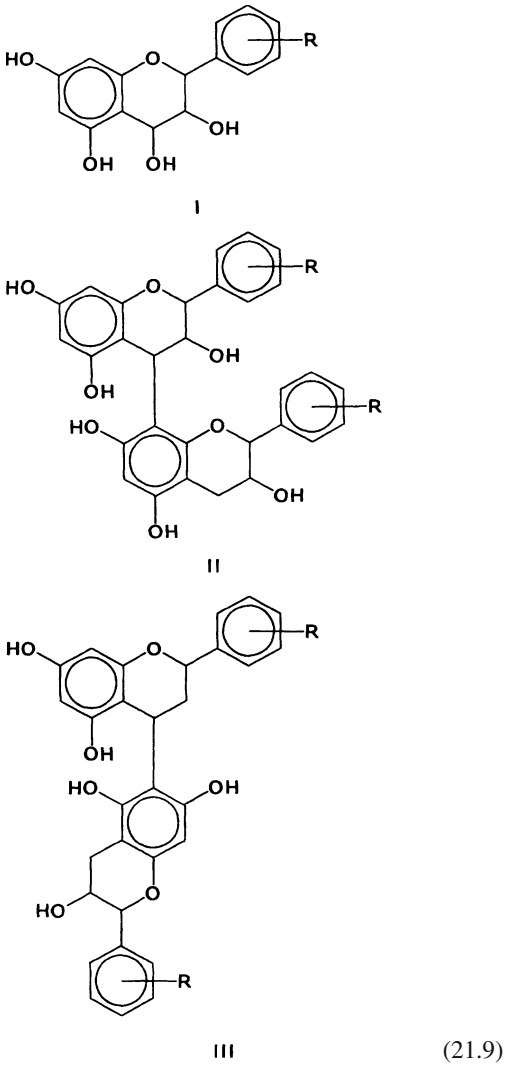
Constituent	Polyphenol storage cell (%)	Cotyledons (%)[a]
Catechins	25.0	3.0
Leucocyanidins	21.0	2.5
Polymeric leucocyanidins	17.5	2.1
Anthocyanins	3.0	0.4
Total phenols	66.5	8.0
Theobromine	14.0	1.7
Caffeine	0.5	0.1
Free sugars	1.6	
Polysaccharides	3.0	
Other compounds	14.4	

[a] As % of dry matter.

77 mg/g epicatechin equivalents (ECE), cocoa powder contains very high concentrations compared to, e. g., green (83 mg/g GAE, 24 mg/g ECE) and black tea (62 mg/g GAE, 17 mg/G ECE).

Three groups of phenols are present in cocoa: catechins (about 37%), anthocyanins (about 4%) and leucoanthocyanins (about 58%).

The main catechin is (−)-epicatechin, besides (+)-catechin, (+)-gallocatechin and (−)-epigal-locatechin. The anthocyanin fraction consists mostly of cyanidin-3-arabinoside and cyanidin-3-galactoside.



(21.9)

Pro- or leucoanthocyanins are compounds which, when heated in acidic media, yield anthocyanins and catechins or epicatechins, respectively. The form present in the greatest amount is flavan-3-4-diol (I in Formula 21.9) which, through 4 → 8 (II) or 4 → 6 (III) linkages, condenses to form dimers, trimers or higher oligomers (cf. 18.1.2.5.2, Formula 18.20).

Leucoanthocyanins occur in fruits of various plants in addition to cacao; e. g., apples, pears and cola (kola) nuts.

21.3.2.3.6 Organic Acids

Of the organic acids (1.2–1.6%), citric, acetic, succinic and malic acid contribute to the taste of cocoa (Table 21.23). They are formed during fermentation. The amount of acetic acid released by the pulp and partly retained by the bean cotyledons depends on the duration of fermentation and on the drying method used. Eight brands of cocoa were found to contain 1.22–1.64% total acids, 0.79–1.25% volatile acids and 0.19–0.71% acetic acid.

Table 21.23. Taste substances of roasted cocoa nibs

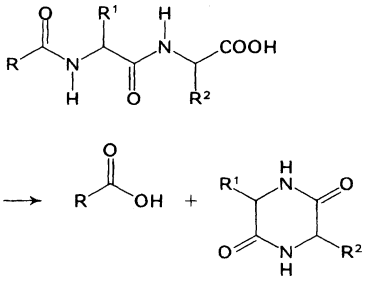
Compound	Concentration (mmol/kg)
Bitter Group	
cis-cyclo (L-Pro-L-Val)	8.9
Theobromine	63.6
cis-cyclo (L-Val-L-Leu)	0.82
cis-cyclo (L-Ala-L-Ile)	0.64
cis-cyclo (L-Ile-L-Pro)	0.54
Astringent Group	
N-[3′,4′-Dihydroxy-(E)-cinnamoyl]-3-hydroxy-L-tyrosine	0.9
(−)-Epicatechin	8.6
Quercetin-3-0-β-D-glucopyranoside	0.10
Quercetin-3-0-β-D-galactopyranoside	0.034
γ-Aminobutyric acid	5.0
Sour Group	
Citric acid	31
Acetic acid	17
Succinic acid	1.7
Malic acid	3.6

21.3.2.3.7 Volatile Compounds and Flavor Substances

Cocoa aroma is crucially dependent on harvesting, fermentation, drying and roasting. The fresh beans have the odor and taste of vinegar. The characteristic bitter and astringent taste and the residual sweet taste of fermented beans might be impaired by various faults, such as processing of unripe or overripe fruit, insufficient aeration, lack of mixing of the fruit, infection with foreign organisms and/or smoke damage as a result of improper drying.

The odorants of cocoa powder are listed in Table 21.24. A model (cf. 5.2.7) made by using the 24 aroma substances on the basis of deodorized cocoa powder reproduced the aroma of cocoa very closely.

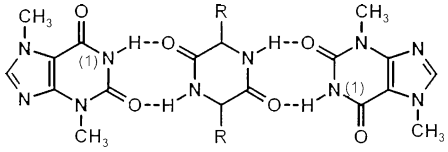
The taste of cocoa is described by the attributes bitter, astringent and sour. It can be reproduced by mixing 41 constituents dissolved in water (pH 5.5). The key compounds for the individual notes are the substances listed in Table 21.23. Apart from theobromine, a series of diketopiperazines are involved in the bitter taste (cf. Table 21.23), which are formed during the thermal degradation of proteins during roasting (Formula 21.10):



(21.10)

The intensity of the bitter taste of theobromine is increased by the interaction with certain diketopiperazines, a molar ratio of 2:1 giving the highest intensity. However, only those complexes are synergistically active in which the hydrogen bridges shown in Formula 21.11 can be formed. Thus, synergism does not occur when, e. g., in caffeine, the N(1)-atom in the purine ring is methylated.

Apart from the compounds mentioned in Table 21.23, epicatechin contributes to the astringent taste and also influences the bitter note.



(21.11)

Table 21.24. Concentrations of potent odorants in a cocoa powder[a]

Compound	Concentration (mg/kg)
Acetic acid	332
3-Methylbutanal	25.8
2-Methylbutanal	14.3
Phenylacetaldehyde	6.60
3-Methylbutyric acid	8.55
2-Phenylacetic acid	7.70
Methylpropionic acid	2.80
2-Methylbutyric acid	1.75
4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone	0.62
2-Phenylethanol	0.59
Butyric acid	0.32
2-Phenylethylacetate	0.32
2-Methoxyphenol	0.23
4-Methylphenol	0.12
Linalool	0.072
2-Ethyl-3,6-dimethylpyrazine	0.070
3-Methylindole	0.055
2-Ethyl-3,5-dimethylpyrazine	0.031
3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone	0.015
2,3-Diethyl-5-methylpyrazine	0.008
Dimethyltrisulfide	0.007
2-Acetyl-1-pyrroline	0.006
2-Methyl-3-(methylthio)-furan	0.0005
2-Isobutyl-3-methoxypyrazine	0.0009

[a] Partially defatted cocoa powder (fat content: 20%), treated with alkali.

21.3.2.4 Reactions During Fermentation and Drying

The reactions occurring within the pulp during fermentation of whole cacao fruit can be distinguished from those occurring in the nibs or cotyledons. The pulp sugar is fermented by yeast to alcohol and CO_2 on the first day. Lactic acid

fermentation may also occur to a small extent. Pectolytic enzymes and other glycosidases affect the degradation of polysaccharides. This is reflected in the fruit pulp becoming liquid and draining away. This improves aeration, resulting in oxidation of alcohol to acetic acid by acetic acid bacteria during the second to fourth days. The pH drops from about 6.5 to about 4.5 and the temperature increases to 45–50 °C. The seed cell walls become permeable, the living cacao seed is killed and an oxidative process takes over the entire mass. From the fifth to the seventh day, the oxidation and condensation reactions of phenolic compounds predominate. Amino acids and peptides react with the oxidation products of the phenolic compounds, giving rise to water-insoluble brown or brown-violet phlobaphenes (cacao-brown and red), which confer the characteristic color to fermented cacao beans. A decrease in the content of soluble phenols mellows the original harsh and astringent cacao flavor. Finally, the oxidation reactions are terminated by drying the seeds to a moisture content of less than 8%.

The hydrolysis of the proteins and peptides during fermentation yields with the free amino acids the precursors of aroma substances. Table 21.25 shows the increase in free amino acids during fermentation and the extent of their degradation to aldehydes and amines. The decisive step for the degradation is the roasting, not the fermentation. Hence, the *Strecker* reaction (cf. 4.2.4.4.7) has a considerably higher share in the formation of these aroma substances (exception 2-methylbutanal) than the corresponding enzymatic degradation reactions.

The proper running of the fermentation process prevents the growth of detrimental microorganisms, such as molds, butyric acid bacteria and putrefaction-inducing bacteria.

Table 21.25. Formation of free amino acids, accompanying *Strecker* aldehydes and amines in cocoa

Compound	Process		
	Without fermentation[a]	After fermentation[b]	After roasting[c]
Amino acid (mg/kg)			
L-Phenylalanine	190	1120	700
L-Leucine	170	1240	760
L-Isoleucine	140	390	280
Aldehydes (µg/kg)			
Phenylacetaldehyde	16	34	202
3-Methylbutanal	116	1636	8470
2-Methylbutanal	143	2075	3791
Amines (µg/kg)			
2-Phenylethylamine	227	1168	10,216
2-/-3-Methylbutylamine	129	1219	17,070

[a] After washing the pulp and drying in the sun.
[b] Fermentation (7 days) and drying in the sun.
[c] As in "b", then roasting of the nibs (15 min at 95°, increase in temperature in 20 min to 115 °C, cooling).

21.3.2.5 Production of Cocoa Liquor

After roasting and drying, the cocoa nib is disintegrated and milled in order to rupture the cell walls of aggregates and expose the cocoa butter. Knife-hammer mills or crushing rolls usually serve for disintegration, while rollerball, horizontal "stone", steel disc or disc attrition mills are used for fine disintegration of cocoa particles. The resultant product is a homogeneous mobile paste, a flowing cocoa mass or cocoa liquor.

21.3.2.6 Production of Cocoa Liquor with Improved Dispersability

The cocoa nib or the cocoa mass is subjected to an alkalization process in order to mellow the flavor by partial neutralization of free acids, improve the color and enhance the wettability of cocoa powder, improve dispersability and lengthen suspension-holding ability, thus preventing formation of a sediment in the cocoa drink. The process involves the use of solutions or suspensions of magnesium oxide or hydroxide, potassium or sodium carbonate or their hydroxides. It is occasionally performed at elevated temperature and pressure, usually using steam. In this process, introduced by *C.I. van Houten* in 1828 (hence the term "Dutch cocoa process"), the roasted nibs are treated with a dilute 2–2.5% alkali solution at 75–100 °C, then neutralized, if necessary, by tartaric acid, and dried to a moisture content of about 2% in a vacuum dryer or by further kneading of the mass at a temperature above 100 °C. This treatment, in addition to acid neutralization, causes swelling of starch and an overall spongy

and porous cell structure of the cocoa mass. Cocoa so treated is often incorrectly designated as "soluble cocoa" – the process does not increase solubility. Finally, the cocoa is disintegrated with fine roller mills. The "alkalized" cocoa generally contains 52–58% cocoa butter, up to 5% ash and up to 7% alkalized mass or liquor.

21.3.2.7 Production of Cocoa Powder by Cocoa Mass Pressing

To convert the cocoa mass/liquor into cocoa powder, the cocoa fat (54% of nib weight on the average) has to be reduced by pressing, usually by means of a hydraulic, mechanical or, preferentially, horizontally-run expeller press at a pressure of 400–500 bar and a temperature of 90–100 °C. To remove the contaminating cell debris, the hot cocoa butter is passed through a filter press, then molded and cooled. The bulk of the cocoa butter produced is used in chocolate manufacturing. The "stone hard" cocoa press cake, with a residual fat content of 10–24%, is disintegrated by a cook breaker, i. e. rollers with intermashing teeth. It is then ground in a peg mill and separated into a fine and a coarse fraction by an air sifter, the coarse fraction being recycled and milled repeatedly. Cocoa powders are divided according to the extent of defatting into lightly defatted powder, with 20–22% residual cocoa butter, and extensively-defatted powder, which contains less than 20% but more than 10% butter. Lightly defatted powder is darker in color and milder in flavor. Cocoa powder is widely used in the manufacture of other products, e. g., cake fillings, icings, pudding powders, ice creams and cocoa (chocolate) beverages.

21.3.3 Chocolate

21.3.3.1 Introduction

Switzerland has the highest per capita consumption of chocolate at 10.2 kg (2004), followed by Norway (9.2), Belgium (9.1), Germany (9.0), Ireland (8.8), Great Britain (8.8). The consumption of chocolate is low in Italy (3.5), Greece (2.5), Japan (1.8), Spain (1.6) and Brazil (1.0).

Chocolates were originally made directly from cocoa nibs by grinding them in the presence of sugar. Chocolate is now made from nonalkalized cocoa liquor by incorporating sucrose, cocoa butter, aroma or flavoring substances and, occasionally, other constituents (milk ingredients, nuts, coffee paste, etc.). The ingredients are mixed, refined, thoroughly conched and, finally, the chocolate mass is molded. To obtain a highly aromatic, structurally homogeneous and stable form and a product which "melts in the mouth", a set of chocolate processing steps is required, as described below.

21.3.3.2 Chocolate Production

21.3.3.2.1 Mixing

Mixing is a processing step by which ingredients such as cocoa liquor, high grade crystalline sucrose, cocoa butter and, for milk chocolate, milk powder are brought together in a mixer ("melangeur") or paster. A homogeneous, coarse chocolate paste is formed after intense mixing.

21.3.3.2.2 Refining

The refining step is performed by single or multiple refining rollers which disintegrate the chocolate paste into a smooth-textured mass made up of much finer particles. The rollers are hollow and can be adjusted to the desired temperature by water cooling. The refined end-product has a particle size of less than 30 to 40 µm. Its fat content should be 23–28%.

21.3.3.2.3 Conching

The refined chocolate mass is dry and powdery at room temperature and has a harsh, sour flavor. It is ripened before further processing by keeping it in warm chambers at 45–50 °C for about 24 h. Ripening imparts a doughy consistency to the chocolate and it may be used for the production of baking or other commercial chocolates. An additional conching

step is required to obtain fine chocolates of extra smoothness. It is performed in oblong or round conche pots with roller or rotary conches. The chocolate mass is mixed, ground and kneaded.

This process is usually run in three stages. The temperature is maximum 65 °C with milk-containing chocolate and 75 °C with milk-free chocolate. In the first, the mass is treated, depending on the recipe and process, for more than 6–12 h. Loss of moisture occurs (dry conching) during heating, a protion of the volatiles is removed (ethanal, acetone, diacetyl, methanol, ethanol, isopropanol, isobutanol, isopentanol and acetic acid ethyl ester) and the fat becomes uniformly distributed, so that each cocoa particle is covered with a film of fat. The temperature at this stage is not allowed to rise since important aroma substances, e. g., pyrazines (cf. 21.3.2.3.7), may be lost. In the second stage, the mass is liquefied by the addition of residual cocoa butter and at a higher stirring speed homogenized further. Here, too, the time required greatly depends on the desired product quality: about 6 to 40 h. In the third phase, which starts 2 to 3 h before the end of the conching process, lecithin and other ingredients are added. Up to a limit of about 1.5%, lecithin lowers the flow rate and the viscosity of the mass; 1 part of lecithin can replace about 8 to 10 parts of cocoa butter. Chemical processes involved in conching are only partially understood.

Efforts have been made to shorten this time-, energy- and space-consuming final refinement in conche pots. Processes have been developed that are based on the separate pre-refinement of cocoa nibs or cocoa mass. The spray-film technique uses a cocoa mass with its natural water content or, in the case of highly acidic cocoa varieties, with the continuous addition of 0.5–2% of water. In a turbulent film with direct heat transfer, the cocoa mass is continuously dehumidified, deacidified, degassed, and roasted in counterflow with hot air (up to 130 °C). For the final refinement, apart from the time-tested conche pots, newly developed intensive refiners can be used. They reduce the conching time to 8 hours. The development of continuously operated conche pots is also being expedited.

21.3.3.2.4 Tempering and Molding

Before molding, the mass must be tempered to initiate crystallization. For both the structure (hard nibs, filling the mold) and appearance (glossy surface that is not dull), this is an important operation in which crystal nuclei are produced under controlled conditions (pre-crystallization). Molten chocolate is initially cooled from 50 °C to 18 °C within 10 min with constant stirring. It is kept at this lower temperature for 10 min to form the stable β-modification of cocoa butter (cf. 3.3.1.2). The temperature of the chocolate is then raised within 5 min to 29–31 °C. The process conditions vary according to composition. Regardless of processing variables, tempering serves to provide a great abundance of small fat crystals with high melting points. During the cooling step, the bulk of the molten chocolate develops a solid, homogeneous, finely crystalline, heat-stable fat structure characterized by good melting properties and a nice glossy surface.

Before molding, the chocolate is kept at 30–32 °C and delivered to warmed plastic or metal molds with a metering pump. The filled molds pass over a vibrating shaker to let the trapped air escape. They then pass through a cooling channel where, by slow cooling, the mass hardens and, finally, at 10 °C, the final chocolate product falls out of the mold. Tempering, metering, filling, cooling, wrapping and packaging machines now provide nearly fully mechanized and automated production of chocolate.

21.3.3.3 Kinds of Chocolate

In a strict sense, chocolate represents a food commodity which may be molded and which consists of cocoa nibs, nib particles, or cocoa liquor and sucrose, with or without added cocoa butter, natural herbs or spices, vanillin or ethyl vanillin. Chocolate contains at least 40% cocoa liquor or a blend of liquor and cocoa butter, and up to 60% sugar. The content of cocoa butter is at least 21% and, when cocoa liquor is blended with cocoa butter, at least 33%.

The composition of the more important kinds of chocolates and confectionery coatings are shown in Table 21.26.

Table 21.26. Composition of some chocolate products

Product	Cocoa mass %	Skim milk powder %	Cocoa butter %	Total fat %	Butter fat (milk) %	Sugar %
Baking chocolate	33–50	–	5–7	22–30	–	50–60
Chocolate for coating	35–60	–	to 15	28–35	–	38–50
Milk cream chocolate	10–20	8–16	10–22	33–36	5.5–10	35–60
Whole milk chocolate	10–30	9.3–23	12–20	28–32	3.2–7.5	32–60
Skim milk chocolate	10–35	12.5–25	15–25	22–30	0–2	30–60
Icings	33–65		5–25	35–46		25–50

Baking chocolate is made by a special process. Other kinds of chocolates include: cream; full or skim milk; filled; fruit, nut, almond; and those containing coffee or candied orange peels. Cola-chocolate is a caffeine-containing product (maximum of 0.25% caffeine) prepared by mixing with extracts obtained from coffee, cola or other caffeine-containing plants. Diabetic- or diet-chocolates are made by replacing sucrose with fructose, mannitol, sorbitol or xylitol. Information about chocolate coatings is presented in Table 21.26. Chocolates can also contain nuts and almonds whose oil contents are occasionally reduced by pressing to reach $\frac{2}{3}$ of the original amount. This is because the oil has a melting point lower than that of cocoa butter. In filled chocolates, the filler is first placed into a chocolate cup and then closed with a chocolate lid or cover. Fine crumbs of chocolate are made by pressing low-fat chocolate through a plate with orifices. Hollow figures are made in two-part molds, by a hollow press or by gluing together the individually molded parts.

The term "praline" originates from the name of the French Marshal *Duplessis-Praslin*, whose cook covered sweets with chocolate. Only a few of the many processing options will be mentioned. For pralines with a hard core, the hot, supersaturated sugar syrup (fondant) is poured into molds dusted with wheat powder and left to cool. The congealed core (korpus) is dipped into molgen kuverture and, in this way, covered with a chocolate coat (creme-praline). The fondant can be fully or partly replaced by fruit pastes like marzipan, jams, nuts, almonds, etc. (dessert-pralines). Such pralines are prepared with or without a sugar crust. Products with a sugar crust are made from a mixture of thick sugar solution and liqueur by pouring the mixture into mold cavities. The solid crust crystallizes on the outer walls, while the inner portion of the mixture remains liquid. The core so obtained is then dipped into melted chocolate, as described above. For pralines without a sugar crust (brandy or liqueur), the processing involves hollow-body machines in which the chocolate shell is formed, then filled with, e. g., brandy, and covered with a lid in a second machine. The fondant may also contain invertase and, thereby, the praline filling liquefies after several days. Plastic pastes are made by preliminary pulverization of the ingredients in a mill and then refiner by rollers. The oil content of the ingredients (nuts, almonds, peanuts) provides the consistency for a workable paste after grinding. Chocolate for beverages or drinks (chocolate powder or flour) is made from cocoa liquor or cocoa powder and sucrose. It is customary to incorporate seasonings, especially vanillin. The sugar content in chocolate drink powders is at most 65%.

Chocolate syrups are made in the USA by adding bacterial amylase. The enzyme prevents the syrup from thickening or setting by solubilizing and dextrinizing cocoa starch. A fat coating is a glazing like chocolate coatings made from a fat other than cocoa butter (fat from peanuts, coconuts, etc.). It is often used on baked or confectionery products. Tropical chocolates contain high melting fats or are specially prepared to make the chocolate resistant to heat. The melting point of cocoa butter can be raised by a controlled precrystallization procedure. Another option is based on the formation of a coherent sugar skeleton in which the fat is deposited in hollow or void spaces. In this case, in contrast to regular choco-

late, there is no continuous fat phase to collapse during heating.

21.3.4 Storage of Cocoa Products

All products, from the raw cacao to chocolate, demand careful storage – dry, cool, well aerated space, protected from light and sources of other odors. A temperature of 10–12 °C and a relative humidity of 55–65% are suitable. Chocolate products are readily attacked by pests, particularly cacao moths (*Ephestia elutella* and *Cadra cauteila*), the flour moth (*Ephestia kuhniella*) and also beetles (*Coleoptera*), cockroaches (*Dictyoptera*) and ants (order *Hymenoptera*).
Chocolates not properly stored are recognized by a greyish matte surface. Sugar bloom is caused by storage of chocolate in moist conditions (relative humidity above 75–80%) or by deposition of dew, causing the tiny sugar particles on the surface of the chocolate to solubilize and then, after evaporation, to form larger crystals. A fat bloom arises from chocolate fat at temperatures above 30 °C. At these temperatures the liquid fat is separated and, after repeated congealing, forms a white and larger spot. This may also occur as a result of improper precrystallization or tempering during chocolate production. The defect may be prevented or rectified by posttempering at 30 °C for 6 h.

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