Herbs and Spices

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Herbs and spices are important food ingredients. The human consumption of herbs and spices can date back to 5000 BC. The world production of spices is estimated to be 8,730,271 tons in 2013 (FAOSTAT). The major producer countries are India, China, Thailand and USA. Table 12.1 summarizes some of the more common spices, the portion of the plant and their region of cultivation. Herbs and spices are consumed as is or formulated into various food, beverage and dietary supplement products. Due to their characteristic chemical compounds, herbs and spices are used to flavor foods and beverages, to inhibit microbial growth and preserve food quality. Increasing evidence also suggest consumption of certain herbs and spices bring in potential health benefits. Although the definitions sometimes overlap, generally herbs are plant leaves or flowering parts either fresh or dried and spices are small pieces from roots, bark or seeds of plants. Most spices also contain essential oils which are normally recovered by steam distillation.

The flavor contribution of spices and herbs comes primarily from the aroma of the volatile compounds in the product. Most spices are fairly complex mixtures of compounds that define the distinctive character of the product. In some cases one compound may dominate the aroma profile for example cloves, cinnamon, anise and thyme.

The aroma compounds in herbs and spices are either phenolics or terpene based compounds. Table 12.2 summarizes the terpene and phenolic compounds which are basic to the aromas. Terpenes represent a very large family of molecules which are frequently utilized for defense by the plants. Terpenes are the sources of typical aromas from bark and needles of conifers, citrus products and flowers. The aromas have been described as pine-like, citrus, fresh, and floral. These compounds contribute to the overall flavor of a broad range of herbs and spices. They are frequently associated with fresh flavors. They tend to be volatile so they can be lost during cooking. The phenolic compounds tend to be more dominant in the flavor of the herb or spice. Examples of phenolics contributing dominant flavors are vanillin in vanilla, cinnamaldehyde in cinnamon and Eugenol in cloves.

Figure 12.1 illustrates some typical structures of phenolics and terpenes found in spices and herbs. It can be seen that the phenolic compounds contain a benzene ring appended with at least one hydroxyl group. Terpenes all contain a block or at least five carbons in a zigzag formation. Both phenolic compounds and terpenes include a wide range of compounds with many aroma characteristics.

Spices contain volatile oils, usually referred to as essential oils, which are isolated by steam distillation. The primary constituents in essential oils are mono- and sesquiterpenes, phenolics or phenol ethers (Fig. 12.2).

The volatile components in spices are frequently complex mixtures, however in some

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Table 12.1 Common spices and region of origin

Common name	Latin name	Region of cultivation
Fruits		
Black Pepper	*Piper nigrum*	Tropical and sub-tropical regions
Vanilla	*Vanilla plantifolia, Vanilla fragans, Vanillathaitensis, Vanilla pompon*	Madigascar, Comore Island, Mexico, Uganda, Indonesia
Allspice	*Pimenta diocia*	Central America, Caribbean Islands
Paprika (Bell Pepper) Chili (Tobasco)	*Capsicum annuum* *Capsicum frutescens*	Widely distributed throughout the world
Bay tree fruits and leaves	*Crocus spinosa Laurus nobilis*	Mediterranean region
Juniper berries	*Juniperus communis*	Temperate climate
Aniseed	*Pimpinella anisum*	Mediterranean and southwest/Asia
Caraway	*Carum carvi*	Temperate climate
Coriander	*Coriandrum sativum*	Southern Europe and northern Africa to southwestern Asia
Dill	*Anethum graveolens*	Tolerates temperatures slightly below freezing
Seeds		
Fenugreek	*Trigonfoenum greacum*	Temperate and Mediterranean
Mustard White Black	*Sinapsis alba* *Brassica nigra*	Temperate regions
Nutmeg	*Myristica fragrans*	India, Indonesia, Siri Lanka
Cardamom	*Elettaria cardamomum*	India, Siri Lanks
Flowers		
Cloves	*Syzygium aromatiicum*	
Saffron	*Crocus sativus*	Mediterranean, India, Australia
Caper	*Capparis spinosa*	Mediterranean
Rhizomes		
Ginger	*Zingeiber Officianale*	South China, India, Japan. Caribbean, Africa
Turmeric	*Curcuma longa*	India, China, Indonesia
Bark		
Cinnamon	*Cinnamomum zeylanicum, C. aromaticum, C. burmanti*	China, Siri Lanka, Indonesia, Caribbean
Roots		
Horseradish	*Armoracia rusticana*	Temperate regions
Leaves		
Basil	*Ocimum basilcum*	Mediterranean, India
Parsley	*Petroselinum crispum*	Temperate regions
Savory	*Satureia hortensis*	Temperate regions
Tarragon	*Artemisia dracunculus*	Temperate regions
Marjorum	*Origanum majorana*	Mediterranean, temperate regions
Oregano	*Origanum heracleoticum, O. onites*	Temperate regions
Rosemary	*Rosmarinus officialis*	Mediterranean
Sage	*Salvia officialis*	Mediterranean
Chives	*Allium schoenoprasum*	Temperate regions
Thyme	*Thymus vulgaris*	Temperate regions

Table 12.2 Aromas contributed by phenolic and terpenes

Chemical compounds	Aroma descriptor
Phenolics	
Eugenol	Clove
Cinnamaldehyde	Cinnamon
Anethole	Anise
Vanillin	Vanilla
Thymol	Thyme
Cavacrol	Oregano
Estragole	Caraway
Terpenes	
Pinenes	Pine needles and bark
Limonene, terpinene, citral	Citrus fruits
Geraniol	Roses
Linalool	Lily of the valley
Cineole	Eucalyptus
Menthol and Menthone	Peppermint
L-Carvone	Spearmint
D-Carvone	Caraway

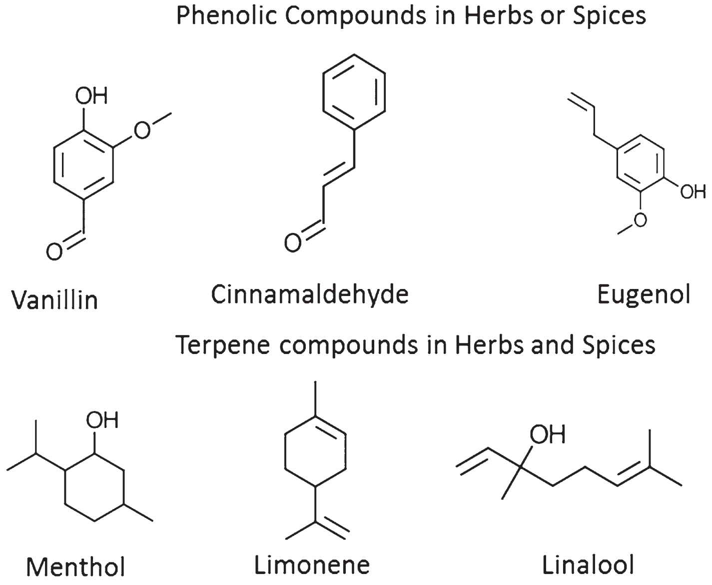


Fig. 12.1 Structures of phenolics and terpenes found in herbs and spices

cases the dominant volatiles define the aroma. For example eugenol in cloves, cinnamaldehyde in cinnamon and carvone in caraway. Table 12.3 summarizes the principal aroma compounds found in some of the major spices.

The aroma of many spices is the result of the major aroma producing compounds such as cinnamaldehyde in cinnamon, eugenol in cloves and (E)-anethole in caraway. Other spice aromas are much more complex.

The antimicrobial effects of herbs and spices are well recognized. Foodborne bacteria are sensitive to extracts from herbs and spices such as oregano, clove, cinnamon, citral, garlic, coriander, rosemary, parsley, lemongrass, sage, vanillin and mustard (Tajkarimi et al. 2010; Ceylan and Fung 2004). The essential oil fraction of herbs and spices are rich in antimicrobial compounds (Ceylan and Fung 2004). Phenols, alcohols, aldehydes, ketones, terpenes, ethers,

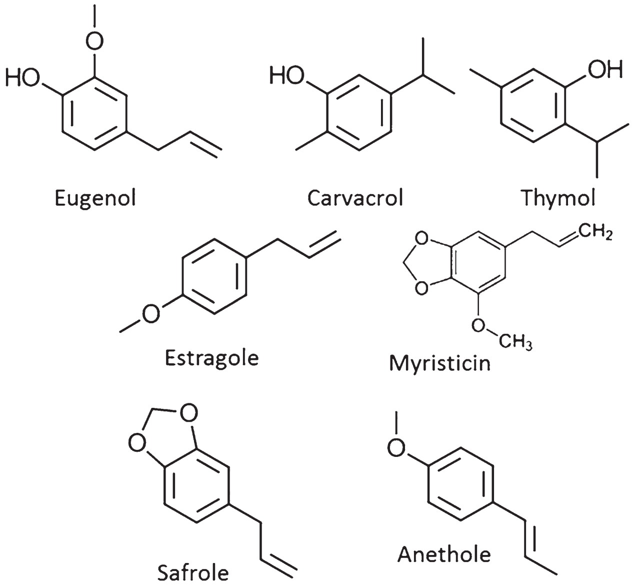


Fig. 12.2 Aromatic compounds found in essential oils

Table 12.3 Major aroma compounds found in spices and herbs

Spice/herb	Major aroma components
Black pepper	Germacrene d (11.01%), limonene (10.26%), β-pinene (10.02%), α-phellandrene (8.56%), β-caryophyllene, (7.29%), α-pinene (6.40%) and *cis*-β-ocimene (3.19%); *P. guineense* (black)—β-caryophyllene (57.59%), β-elemene (5.10%), bicyclogermacrene (5.05%) and α-humulene (4.86%)
White pepper	β-Caryophyllene (51.75%), *cis*-β-ocimene (6.61%), limonene (5.88%), β-pinene (4.56%), linalool (3.97%) and α-humulene (3.29%)
Vanilla	Vanillin, (r) (+)-*trans*—α-ionone, *p*-hydroxybenzylmethylether
Allspice	Eugenol, β-caryophyllene, methyleugenol, 1,8-cineole,α-phellandrene
Bay leaf	Cineole, α-pinene, β-pinene, α-phellandrene, linalool
Juniper berries	α-Pinene, myrcene, β-pinene, δ^3-carene, (e)-anethole
Aniseed	(e)-Anethole
Caraway	(s)(+)-Carvone, limonene
Coriander	(s)(+)-Linalool, (r)(−)-linalool, linalyl acetate, citral, 2-alkeales c_{10}–c_{14}
Dill (herb)	(s)-Carvone, (s)(+)-phellandrene, (3r,4s,8s)(+)-epoxy-p-menth-1-ene, myristican, limonene
Fenugreek	Linalool, 3-isobutyl-2-methoxypyrazine, 2-methoxy-3-isopropylpyrazine, 3-hydroxy-4,5-dimethyl-2(5H)-furanone
Nutmeg	α-Pinene, β-pinene, sabinene, limonene, safrole, myristicin, 1,8-cineole
Cardamom	1,8-Cineole, α-terpinyl acetate, limonene, sabinene
Clove	Eugenol, β-caryophyllene, eugenol acetate
Saffron	Safranal, 2,6,6-trimethyl-4-hydroxy-1-cyclohexene-1-formaldehyde
Ginger	(−)Zingiberene, β-bisabolene, (−)-sesquiphellandrone, (+)-ar-cucumene, citral, citronellyl acetate
Turmeric	Turmerone, ar-turmerone, zngiberene
Cinnamon	Cinnamaldehyde, eugenol, safrole, linaloor, camphor
Parsley	p-Mentha-1,3,8-triene, 2-sec-butyl-3-methoxypyrazine, 2-isopropyl-3-methoxypyrazine, (z)-6-decanal, (e,e)-2,4-decadienal, myrcene
Marjoram	*cis*-Sabinehydrate, *trans*-sabaninehydrate, 1-terpinen-4-ol
Rosemary	1,8-Cineol, camphor, α-pinene, camphene
Oregano	Carvacrol, thymol
Sage	1,8-Cineol, camphor, α-pinene, thujone
Thyme	Thymol, p-cymene, carvacol, linalool

Adapted from Belitz et al. (2009)

Table 12.4 Major antimicrobial compounds found in spices and herbs

Spice/herb	Major antimicrobial compounds
Rosemary	Anethole, apigenin, ascorbic acid, borneol, bornyl acetate, caffeic acid, camphor, delta-3-carene, carveol, caryophyllene, chlorogenic acid, 1,8-cineole, p-cymene, genkwanin, geraniol, glycolic acid, limonene, linalool, methyl eugenol, niacin, pinene, rosmarinic acid, safrole, terpinene, thujone, ursolic acid
Cinnamon	Benzaldehyde, camphene, camphor, caryophyllene, 1,8-cineole, cinnamaldehyde, cuminaldehyde, p-cymene, eugenol, farnesol, furfural, guaiacol, limonene, linalool, methyl eugenol, methyl salicylate, myrcene, niacin, pinene, piperitone, safrole, terpineol
Thyme	Borneol, bornyl acetate, caffeic acid, camphene, delta-3-carene, beta-carotene, carvacrol, chlorogenic acid, 1,8-cineole, p-cymene, geraniaol, limonene, linalool, methionine, myrcene, niacin, pinene, rosmarinic acid, terpinen-4-ol, terpineol, thymol, tryptophan, ursolic acid
Oregano	Anethole, apigenin, borneol, cadinene, caffeic acid, camphor, delta-3-carene, beta-carotene, carvacrol, carvone, caryophyllene, 1,8-cineole, p-cymene, geraniol, kaempferol, limonene, linalool, luteoline, niacin, pinene, rosmarinic acid, terpinene, thymol, ursolic acid
Bay	Acetic acid, benzaldehyde, borneol, bornyl acetate, cadinene, delta-3-carene, camphene, caryophyllene, 1,8-cineole, costulonide, cubebin, p-cymene, eugenol, geraniol, limonene, linalool, methyl eugenol, myrcene, pinene, terpinen-4-ol, terpineol
Garlic	Ajoene, allicin, alliin, allistatin-I, allistatin-II, arginine, ascorbic acid, choline, citral, diallyl disulfide, diallyl disulfide, geraniaol, glutamic acid, linalool, niacin, trypthophan
Cloves	Anethole, benzaldehyde, carvone, caryophyllene, chavicol, cinnamaldehyde, ellagic acid, eugenol, eugenyl acetate, furfural, gallic acid, kaempferol, linalool, methyl eugenol
Allspice	Anethole, ascorbic acid, cadinene, delta-3-carene, beta-carotene, caryophyllene, copaene, p-cymene, eugenol, linalool, methyl eugenol, myrcene, pinene, selinene, terpinen-4-ol, terpinene
Sage	Apigenin, ascorbic acid, borneol, bornyl acetate, camphor, beta-carotene, caryophyllene, chlorogenic acid, 1,8-cineole, limonene, linalool, myrcene, niacin, pinene, rosmarinic acid, terpinen-4-ol, terpinene, thujone, ursolic acid
Vanilla	Acetaldehyde, acetic acid, anisaldehyde, benzaldehyde, benzoic acid, cresol, eugenol, furfural, guaiacol, vanillic acid, vanillin, vanillyl alcohol

Adapted from Duke (1994)

hydrocarbons, alkaloids and peptides in herbs and spices are the effective antimicrobial components (Ciocan and Bara 2007; Ceylan and Fung 2004). The antimicrobial compounds in common herbs and spices are summarized in Table 12.4.

Oxidation is one of the reasons for deterioration of food quality. Free radicals form chain reactions in the food matrix, causing rancidity and unfavorably change in color and flavor. The chained reaction can be stopped by radical scavenging agents, also known as antioxidants. Strong antioxidants, including certain vitamins, phenols (flavonoids), terpenoids, carotenoids, phytoestrogens, minerals, etc. are found in many herbs and spices (Suhaj 2006). For example, rosemary extract containing diterpenes and carnosic acid can be used as a stabilizer of fatty oil and antioxidant in sausages. The antioxidant compounds in common herbs and spices are listed in Table 12.5. It is noteworthy that the category of aroma compounds and antimicrobial compounds sometimes overlap, meaning that the same compound may have both properties.

Recent scientific data support that chemical compounds in herbs and spices may provide health benefits including antioxidant and anti-inflammatory effects, reducing risks of cardiovascular diseases and diabetes, improving the overall health, cognition, GI health etc. (Butt et al. 2013; Suhaj 2006; Gruenwald et al. 2010; Jamal et al. 2006; Singletary 2010). The health benefits will be elaborated in the following individual herb and spice section.

Table 12.5 Major antioxidant compounds found in spices and herbs

Spice/herb	Major antioxidant compounds
Black pepper	Ascorbic acid, beta-carotene, camphene, carvacrol, eugenol, gamma-terpinene, lauric acid, linalyl acetate, methyl eugenol, myrcene, myristic acid, myristicin, palmitic acid, piperine, terpinen-4-ol, ubiquinone
Caraway	Beta-carotene, camphene, camphene, carvacrol, gamma-terpinene, gamma-terpinene, lauric acid, myrcene, myrcene, myristic acid, myristicin, myristicin, palmitic acid, quercetin, tannin, terpinen-4-ol
Chili pepper	Alanine, ascorbic acid, beta carotene, caffeic acid, campesterol, capsaicin, capsanthin, chlorogenic acid, hesperidin, histidine, kaempferol, lauric acid, lutein, methionine, myrcene, myristic acid, myristic acid, p-coumaric acid, palmitic acid, pentadecanoic acid, quercetin, scopoletin, stigmasterol, terpinen-4-ol, tocopherol, tryptophan
Coriander	Apigenin, ascorbic acid, beta-carotene, beta-carotene, beta-sitosterol, caffeic acid, camphene, chlorogenic acid, gamma-terpinene, isoquercitrin, myrcene, myristic acid, myristicin, p-hydroxybenzoic acid, p-hydroxybenzoic acid, palmitic acid, protocatechuic acid, protocatechuic acid, quercetin, rhamnetin, rutin, scopoletin, tannin, terpinen-4-ol, *trans*-anethole, vanillic acid, vanillic acid
Dill	Alpha-tocopherol, anethole, ascorbic acid, beta-sitosterol, caffeic acid, camphene, carvacrol, chlorogenic acid, eugenol, ferulic acid, gamma-terpinene, histidine, isoeugenol, isorhamnetin, kaempferol, lauric acid, methionine, myrcene, myristic acid, myristicin, palmitic acid, quercetin, scopoletin, selenium, stigmasterol, terpinen-4-ol, *trans*-anethole, vicenin
Ginger	6-Gingerol, 6-shogaol, alanine, ascorbic acid, beta-carotene, beta-sitosterol, caffeic acid, camphene, capsaicin, chlorogenic acid, curcumin, delphinidin, ferulic acid, gamma-terpinene, kaempferol, lauric acid, methionine, myrcene, myricetin, myristic acid, p-coumaric acid p-hydroxybenzoic acid, palmitic acid, quercetin, selenium, shikimic acid, sucrose, terpinen-4-ol, tryptophan, vanillic acid, vanillin
Nutmeg	Camphene, cyanidin, eugenol, gamma-terpinene, isoeugenol, kaempferol, lauric acid, methyl eugenol, myrcene, myristic acid, myristicin, myristicin, oleanolic acid, palmitic acid, quercetin, terpinen-4-ol
Oregano	camphene, carvacrol, gamma-terpinene, linalyl acetate, myrcene, terpinen-4-ol, thymol
Red (sweet) pepper	Alanine, alpha-tocopherol, ascorbic acid, beta-carotene, beta-sitosterol, caffeic acid, campesterol, camphene, capsaicin, capsanthin, chlorogenic acid, eugenol, gamma-terpinene, hesperidin, histidine, lupeol, lutein, methionine, myrcene, myristic acid, p-coumaric acid, palmitic acid, pentadecanoic acid, scopoletin, selenium, stigmasterol, terpinen-4-ol, tocopherol, tryptophan
Rosemary	apigenin, ascorbic acid, beta-carotene, beta-sitosterol, caffeic acid, camphene, camphene, camphene, carnosic acid, carnosol, carvacrol, chlorogenic acid, gamma-terpinene, hesperidin, hispidulin, isorosmanol, labiatic acid, luteolin, luteolin-3′-o-(3″-o-acetyl)-beta-D-glucuronide, luteolin-3′-o-(4″-o-acetyl)-beta-D-glucuronide, methyl eugenol, myrcene, oleanolic acid, rosmadial, rosmanol, rosmaridiphenol, rosmarinic acid, rosmariquinone, squalene, tannin, terpinen-4-ol, thymol, *trans*-anethole, ursolic acid
Sage	Alanine, apigenin, ascorbic acid, beta-carotene, beta-sitosterol, caffeic acid, campesterol, camphene, carnosic acid, carnosol, carnosol, carnosolic acid, catechin, chlorogenic acid, cholesterol, chrysoeriol, ferulic acid, fumaric acid, gallic acid, gamma-terpinene, hispidulin, labiatic acid, linalyl acetate, luteolin, myrcene, oleanolic acid, p-coumaric acid, palmitic acid, rosmanol, rosmarinic acid, salicylic acid, selenium, stigmasterol, terpinen-4-ol, thymol essential oil, ursolic acid, uvaol, vanillic acid
Thyme	4-Terpineol, alanine, anethole essential oil, apigenin, ascorbic acid, beta-carotene, caffeic acid, camphene, carvacrol, chlorogenic acid, chrysoeriol, eriodictyol, eugenol, ferulic acid, gallic acid, gamma-terpinene, isochlorogenic acid, isoeugenol, isothymonin, kaempferol, labiatic acid, lauric acid, linalyl acetate, luteolin, methionine, myrcene, myristic acid, naringenin, oleanolic acid, p-coumaric acid, p-hydroxybenzoic acid, palmitic acid, rosmarinic acid, selenium, tannin, thymol, tryptophan, ursolic acid, vanillic acid
Turmeric	Ascorbic acid, beta-carotene, caffeic acid, curcumin, eugenol essential oil, p-coumaric acid, protocatechuic acid, syringic acid, vanillic acid

Adapted from Suhaj (2006)

Black Pepper

Both black and white pepper are widely consumed. Black pepper is harvested before it is fully ripe the flesh is removed and the seed is dried. White pepper, which has a milder flavor, is from the seed or ripe fruit. The major aromatic compound in black pepper is (−)-rotundone. The main differences between black and white pepper is the concentrations in the product. The losses of aroma compounds account for the instability of pepper after it is ground. Therefore, fresh ground pepper provides better flavor in most food applications.

Blackening of fresh pepper is an oxidation of (3,4-dihydroxy phenyl) ethanol glycoside by an o-diphenol oxidase (PPO) which is present in the fruit. Bandyopadhyay et al. (1990) reported during the conversion of green pepper to black pepper 75% of the total pheolic content is lost. Included is a complete loss of o-diphenol oxidase oxidizable phenolic compounds. The major substrate for o-diphenol oxidase is 3,4-dihydroxy-6-(*N*-ethylamino) benzamide. Early work established the presence of α-pinene, β-pinene, 1-β-phellandrene, dllimonene, piperonal, and dihydrocarveol.

The volatile oils in black pepper constitute 2–5% of the dry berries. Pepper oil is traditionally prepared by steam distillation of the black peppercorns. Liquid carbon dioxide is now emerging as a useful technology to prepare essential oils including pepper oil. Liquid carbon dioxide was described by Ferreira et al. (1999). In studies on black pepper berries from India and Malaysia, the presence of optically active monoterpenes, indicated (±)-linalool, (+)-α-phellandrene, (−)-limonene, myrcene, (−)-α-pinene, 3-methylbutanal and methylpropanal were the most important aroma compounds in black pepper. Additionally, 2-isopropyl-3-methoxypyrazine and 2,3-diethyl-5-methylpyrazine identified as causing a moldy or musty off aroma in a black pepper sample from Malaysia (Jagella and Grosch 1999a).

Piperine is the most abundant constituent of pepper oleoresin (Borges and Pino 1993). The pungency of black pepper *(P. nigrum* L.) was attributed to the presence of piperine, the structure is shown in Fig. 12.4. After removal of piperine form the pepper resin the oleoresin was named chavicine (Govindarajan 1977). Chavicine was thought to possess greater bite the tongue than crystalline piperine, however it was later shown that piperine in solution was very pungent. Later research demonstrated that piperine was the major pungent principle and chavicine is a mixture of piperine and several minor alkaloids. Five additional pungent alkaloids have been identified in pepper extracts. They are piperettine, piperylin, piperolein, A and B and piperanine (Zachariah et al. 2008).

Structures of some of the major components in black pepper oil are found in Figs. 12.3 and 12.4.

The primary and most important in pepper oleoresin is piperine. Black pepper oil contributes the aroma, oleoresin constitutes the components that complete the overall taste with the alkaloidpiperine imparts pungency. β-Carophyllene, is the most abundant sesquiterpene hydrocarbon present in pepper oil. Other sesquiterpene hydrocarbons are β-bisabolene, α- and β-cadinenes, calamenene, α-copaene, α and β-cubebenes, *ar*-curcumene, β- and δ-elemenes, β-farnesene, α-guaiene, α- and γ-humulenes, isocaryophyllene, γ-muurolene, α-santalene, α- and β-selinenes, ledene, sesquisabinene and zingiberene (Zachariah and Parthasarathy 2008).

Beyond contribution to flavor, piperine is also the major ingredient related to black pepper's potential health benefits. Piperine in black pepper may be responsible for antioxidant, antimicrobial, anti-inflammatory, gastro-protective, antidepressant and anti-cancer activities of the spice (Li 2006; Butt et al. 2013). Most of these, however, are results from in vitro and animal studies; thus, further clinical research is warranted to explore the efficacy and safety on the health promoting use of black pepper.

Fig. 12.3 Major aroma compounds in black pepper

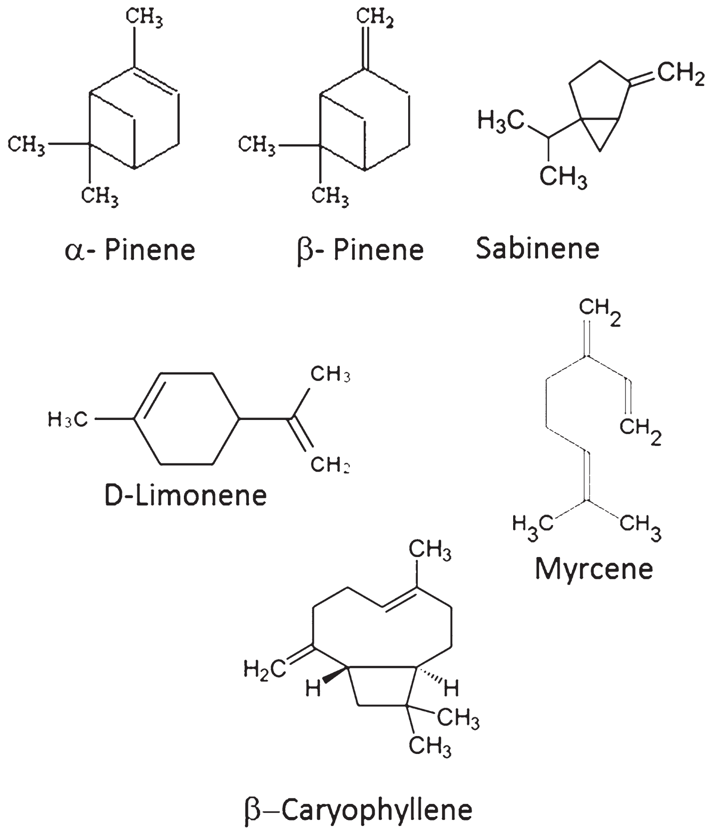
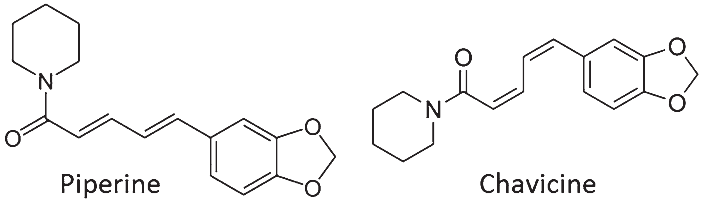


Fig. 12.4 Piperine and chavicine are the primary pungent compounds in black and white pepper



Vanilla

Like Cocoa, vanilla originated in Central America, where the Aztecs used it to flavor cocoa well before the discovery of the New World. The vanilla plant is a member of the orchidaceae family. The cultivated species of vanilla include *Vanilla fragans, Vanilla pompona* and *Vanilla tahitensis*. The vanilla bush is a tropical plant that requires a warm and humid climate. The temperature must be as even as possible. The major vanilla-producing countries are Madagascar, Indonesia, China, and Turkey. Madagascar which cultivates 64,000 ha, is the largest producer and some argue has the highest quality vanilla (Table 12.6). Vanilla is especially popular in ice creams, beverages, desserts, dairy products, chocolate, confectionery products and pastry.

Table 12.6 World country vanilla production

Country	Production (tons)	%
Madagascar	3719	48
Indonesia	2000	26
Papua New Guinea	510	6.6
Mexico	420	5.4
China	286	3.7
Turkey	280	3.6
Uganda	218	2.8
Tonga	186	2.4

2014 Top vanilla producers (Source: FAOSTAT 2017)

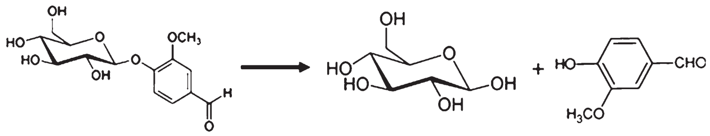


Fig. 12.5 Enzymatic hydrolysis of vanillin glucoside to produce vanillin

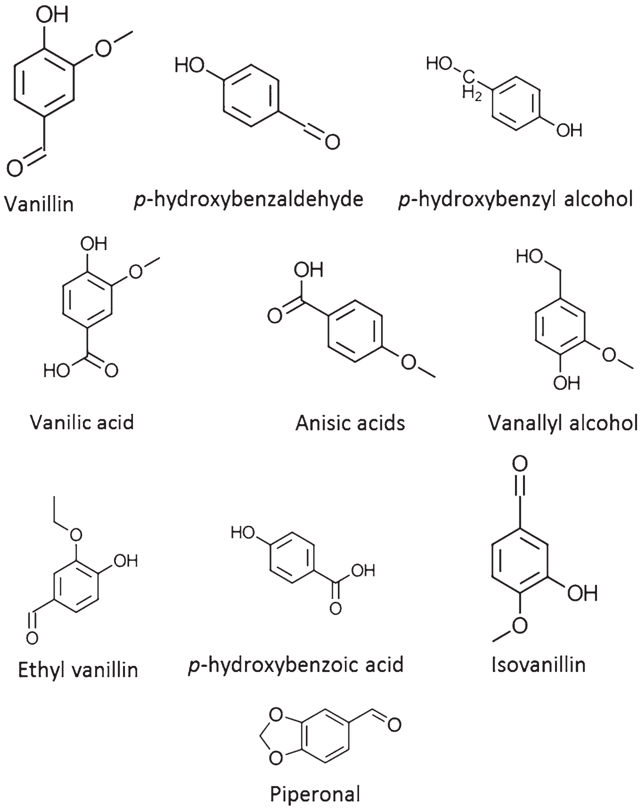

Vanillin
p-hydroxybenzaldehyde
p-hydroxybenzyl alcohol
Vanilic acid
Anisic acids
Vanallyl alcohol
Ethyl vanillin
p-hydroxybenzoic acid
Isovanillin
Piperonal

Fig. 12.6 Some major aroma compounds in vanilla

Vanilla is unique among spices because the processing is considerably more involved to produce the culinary form. Fresh vanilla pods have little or no taste. Vanillin which is the primary aroma/flavor constituent is bound as a glycoside which is enzymatically hydrolyzed to release the vanillin. The enzymatic reaction is induced by a sequence of blanching or steaming. During the curing process, the vanillin glycoside is hydrolyzed to yield vanillin and glucose and some other minor aromatic substances as shown in Fig. 12.5

Vanilla fruit grows quickly on the vine and matures for harvest in about 6 months. Vanilla fruits ripen at widely differing rates, thus daily harvest is required to ensure the optimum flavor from every fruit. Individual pods are hand-picked as it begins to split on the end. Overripe fruits are likely to split, causing a reduction in market value. The commercial value of vanilla beans is fixed based on the length and appearance of the pod.

Fruit is more than 15 cm (5.9 in) in length, it belongs to first-quality product. The largest fruits (greater than 16–21 cm) are reserved for the gourmet vanilla market. Fruits between 10 and 15 cm long, pods are under the second-quality category, and fruits less than 10 cm in length are under the third-quality category.

There are four basic steps in curing vanilla beans killing, sweating, slow-drying, and conditioning of the beans (Havkin-Frenkel et al. 2004, 2005).

In order to initiate the enzymatic hydrolysis of the vanillin glycosides the vegetative cells of the vanilla bean must be disrupted. This process called killing disrupts the cells and tissue of the fruits, imitating the enzymatic reactions responsible for releasing the aromatic compounds. Killing can be accomplished by heating in hot water, freezing, or scratching, heating in an oven or exposing the beans to direct sunlight. The different methods give different profiles of enzymatic activity allowing the glycosidase enzymes to act on the glucovanillin to release the free vanillin (Frenkel et al. 2010; Arana 1944).

Hot-water killing is accomplished by dipping the beans in hot water 63–65 °C (145–149 °F) for 3 min, or at 80 °C (176 °F) for 10 s. Fruits can be scratched lengthwise to disrupt the cells structure of the fruits (Arana 1944). Fruits can be frozen and thawed to initiate the release of enzyme and substrate however they must be thawed for the sweating stage. Frozen or quick-frozen fruits must be thawed again for the subsequent sweating stage. Fruits can also be tied bundles and rolled in blankets and heated in and oven at 60 °C for 36–48 h. The Aztecs exposed the fruits to sunlight until they turned dark brown to imitate the enzymatic reaction (Frenkel et al. 2010).

Sweating is a combination of hydrolytic and oxidative processes. Sweating is the process of holding the fruits, for 7–10 days at temperature of 45–65 °C with high humidity. At the end of the sweating process the fruits are brown and have developed the characteristic vanilla flavor and aroma. At the end of sweating they contain 60–70% moisture content by weight (Frenkel et al. 2010).

The drying process reduces the beans to 25–30% moisture which is sufficient to prevent rotting and stabilizes the aroma compounds in the pods. Traditionally the drying is accomplished by exposing the beans to intermittent shade and sunlight. Drying is the most difficult stage to control because it can result in uneven drying which can lead to loss is in vanillin (Frenkel et al. 2010).

Conditioning is accomplished by storing the pods for 5–6 months in closed boxes. During this stage the fragrance develops. The cured vanilla fruits contain an average of 2.5% vanillin.

Vanilla is one of the more complex aromas containing over 170 compounds. Vanillin is the primary aroma material thus “imitation” vanilla produced enzymatically is used in many food applications. Natural vanillin is produced from the enzymatic hydrolysis of a glycoside during fermentation of the fruit. Two other important contributors to the aroma of fresh vanilla are (R) (+)-*trans*-α-ionone and *p*-hydroxybenzylmethylether.

Other aroma compounds in vanilla have been reported including aromatic carbonyls, aromatic alcohols, aromatic acids, aromatic esters, phenols and phenol ethers, aliphatic alcohols, carbonyls, acids, esters and lactones. The levels of vanillin, *p*-hydroxybenzaldehyde and their respective acids (vanillic acid and *p*-hydroxybenzoic acid), are used as indicators of vanilla bean quality in commercial operations (Klimes and Lamparsky 1976; Adedeji et al. 1993; Ranadive 1994; Azeez 2008). The major aroma compounds in vanilla are shown in Fig. 12.6.

Chemical composition of processed vanilla Composition of processed vanilla beans variable and complex due to a number of variables such as species, growth conditions, soil composition, fruit maturity and mainly, the type of processing. All these variables define the relative content of the chemical constituents in the processed beans, which makes it difficult to define their typical composition. Perez-Silva et al. (2006) studied the volatile compounds in vanilla beans combining GC/MS analysis with GC-olifactory analysis to characterize the aroma contributors in vanilla beans. Table 12.7 summarizes the results of the study.

Vanillin can be synthesized by a number of methods and is frequently used as a replacement for the much more expensive natural vanilla. The ‘classical’ synthesis of vanillin from eugenol or isoeugenol was developed in 1896 and it remained the preferred method for about 50 years. Vanillin is now prepared industrially in large amounts by the Reimer–Tiemann reaction, starting with guaiacol, from which it is formed along with o-vanillin. A newer and more common means to produce vanillin is from the reaction of guracol and glyoxylic acid as shown in Fig. 12.7.

Table 12.7 Aroma compounds from vanilla beans and odor quality (from Perez-Silva et al. 2006)

Compounds	ppm	Odor quality	Intensity[a]
Phenols			
Guaiacol	9.3	Chemical, sweet spicy	+++
4-Methylguaiacol	3.8	Sweet, woody	+++
p-Cresol	2.6	Balsamic, woody, spicy	++
4-Vinylguaiacol	1.2	Chemical, phenolic	+
4-Vinylphenol	1.8	Sweet, woody	++
Vanillin	19,118	Vanilla, sweet	+++
Acetovanillone	13.7	Vanilla, sweet, honey	+++
Vanillyl alcohol	83.8	Vanilla like	+++
p-Hydroxybenzaldehyde	873	Vanilla like, biscuit	++
p-Hydroxybenzyl alcohol	65.1	Vanilla like, sweet	++
Aliphatic acids			
Acetic acid	124	Sour, vinegar	++
Isobutyric acid	1.7	Buttery	++
Butyric acid	<1	Buttery, oily	+
Isovaleric acid	3.8	Buttery, oily	++
Valeric acid	1.5	Cheese	+++
Alcohols			
2,3-Buranediol (Isomer 2)	8.0	Floral, oily	+
Anisyl alcohol	2.4	Herbal	++
Aldehydes			
2-Heptenal	2.1	Green, oily	+
E-2-decenal	1.8	Herblike, floral	++
(E,Z)-2,4-decadienol	1.4	Herb-like, fresh	++
(E,E)-2,4-decadienol	1.2	Fatty, wood	++
Esters			
Methyl salicylate	<1	Chalk	+++
Methyl cinnamate	1.1	Sweet	++
Ethyl linoleate	13.5	Sweet	++
Ketone			
3-Hydroxy-2-butanone	14.6	Buttery	+
Unknown[b]	6.2	Vanilla-like, chemical	+++

Aroma-active compounds detected by GC-O analysis of representative aroma extract from vanilla beans
[a](+) Weak, (++) medium, (+++) strong
[b]Mass fragmentation 91(90), 74(37), 69(34),89(25), 57(24), and RI 2528

Vanillin is also recovered as a by-product of paper pulp manufacture. Synthetic vanillin is used in both food and non-food applications, in fragrances and as a flavoring in pharmaceutical preparations.

In culinary applications vanilla flavoring in food can be achieved by adding vanilla extract or by adding vanilla beans to a liquid preparation. Natural vanilla gives a brown or yellow color to preparations, depending on the concentration. Good-quality vanilla has a strong aromatic flavor, but food with small amounts of low-quality vanilla or artificial vanilla-like flavorings are far more common.

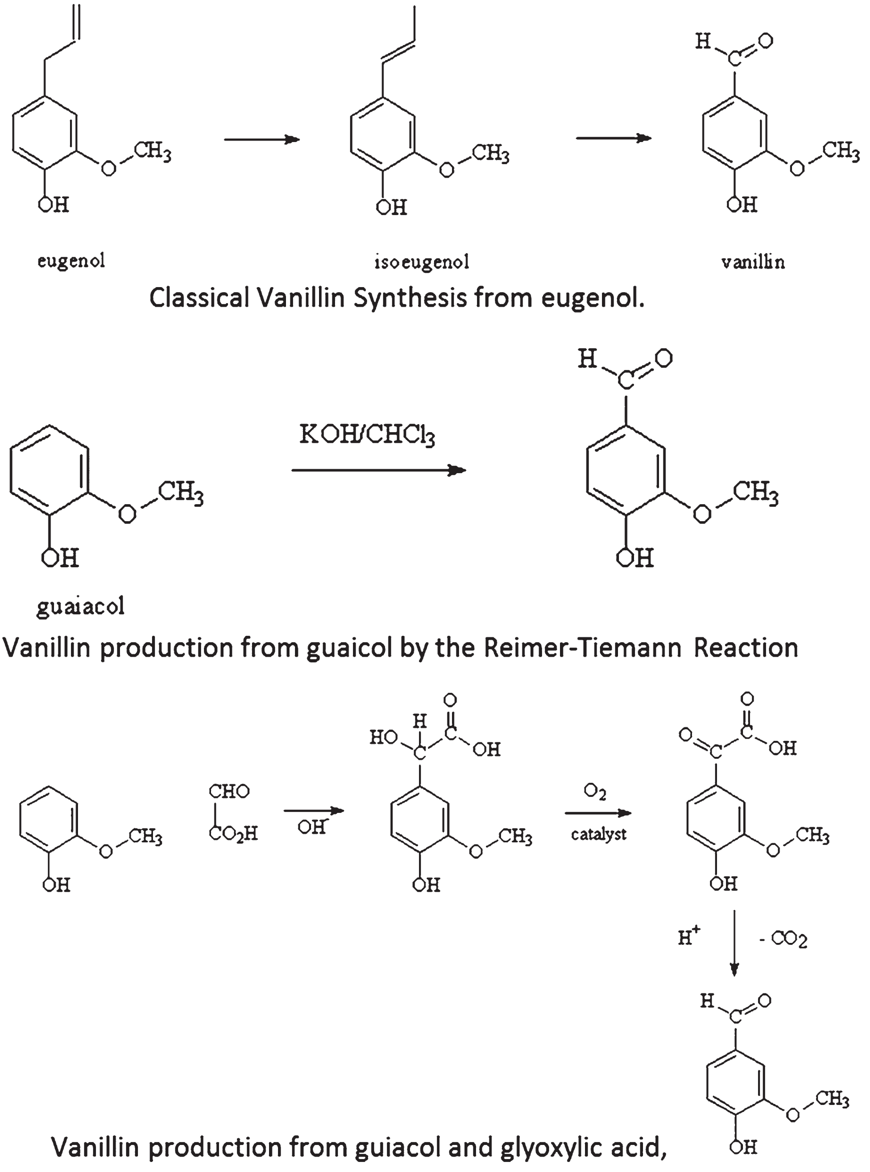


Fig. 12.7 Chemical approaches for the production of vanillin

Cardamom

Cardamom is a spice used in South and Southeast Asia, Middle East and Nordic countries. It is made from seeds of two plants (*Elettaria cardamomum* and *Amomum subulatum*). The major production countries are Guatemala, India and Sri Lanka. Cardamom is considered one of the most expensive spices after saffron and vanilla. The volatile oil components of cardamom first reported in detail by Nigam et al. (1965) and further summarized by Guenther (1975). The oil predominantly composed of oxygenated compounds, all which contribute to the aroma. Many of the alcohols, esters and aldehydes are found in many spice oils. The predominant volatiles in cardamom are 1,8-cineole and the esters,

Table 12.8 Main volatile components in cardamom oil

Component	Total oil (%)
α-Pinene	1.5
β-Pinene	0.2
Sabinene	2.8
Myrcene	1.6
α-Phellandrene	0.2
Limonene	11.6
1,8-Cineole	36.3
γ-Terpinene	0.7
p-Cymene	0.1
Terpinolene	0.5
Linalool	3.0
Linalyl acetate	2.5
Terpinen-4-ol	0.9
α-Terpineol	2.6
α-Terninyl acetate	31.3
Citronellol	0.3
Nerol	0.5
Geraniol	0.5
Methyl eugenol	0.2
Trans-Nerolidol	2.7

Source: Lawrence (1978); Govindarajan et al. (1982)

α-terpinyl and linalyl acetates (Lewis et al. 1966; Salzer 1975; Korikanthimath et al. 2002). The major components in cardamom oil are listed in Table 12.8. Structures of the main components are found in Fig. 12.8. Preliminary studies have found consumption of cardamom may have antioxidant (Kikuzaki et al. 2001), gut stimulatory and inhibitory, gastroprotective (Jamal et al. 2006), diuretic and sedative effects (Gilani et al. 2008), as well as alleviation of diarrhea, constipation, and high blood pressure (Gilani et al. 2008).

Ginger

Ginger is the rhizome of *Zingiber officinale* Roscoe and is one of the most widely used spices in a wide range of condiment for various foods and beverages. *Z. officinale* Roscoe, which is used for commercial ginger, and is grown extensively in many tropical countries. Like pepper (Piper nigrum) and the fruits of the Capsicum species, ginger is characterized by two classes of constituents: the odor (steam volatile) and non-volatile components responsible for the pungency.

Ginger oleoresin can be prepared from dried ginger by extraction using a variety of organic solvents. The oleoresin contains the major organoleptically important volatile oil and pungent principles. In addition the oleoresin includes triglycerides and a small amount of free fatty acids. Preparation and storage of the dried spice and oleoresin influences the organoleptic properties of these products. During storage of dried spice and particularly ground spice significant amounts of the volatile components in the oil are lost to evaporation. The oleoresin is prone to loss of pungency during as a result of degradation of the pungent gingerols. Heating ginger or the oleoresin from ginger results in the loss of both volatile and pungent factors.

The fatty oil of ginger ranges from 2 to 12% in dried gingers. Ginger fatty oil contain saturated and unsaturated fatty acids in a ratio of 46:53. The major fatty acids in ginger lipids are palmitic, oleic and linoleic (Zachariah 2008). The total lipid content varies widely (5.8–15%) among ginger varieties (Govindarajan 1982). The typical fatty acid profile of ginger lipid is shown in Table 12.9.

The composition of ginger oleoresin has a wide range depending on the variety and extraction conditions. Most commercial dried gingers contain 3.5–10% oleoresins and 15–30% volatile oils (Govindarajan 1982).

The non-volatile portion referred to as gingerols contain a 1-(4′-hydroxy-3′-methoxyphenyl)-5-hydroxyzlkan-3-one structure. The non-volatile pungent constituents in ginger include gingerols, shogaols, zingerone and paradols. All of these groups of compounds except zingerone contain hydrocarbon chains of 4–8 -CH_2- groups. The pungent non-volatile components in ginger are illustrated in Fig. 12.9.

The volatile composition of ginger oil is very complex. Miyazawa and Kameoka (1988) identified 72 components in the volatile oil extracted from the air-dried rhizomes.

The main components were zingiberene (21.8%), geranial (9.9%), geraniol (9.4%), β-bisabolene (7.9%), nerol (7.1%), 1,8-cineol

Fig. 12.8 Major components of cardamon oil (Chempakam and Sindhu 2008)

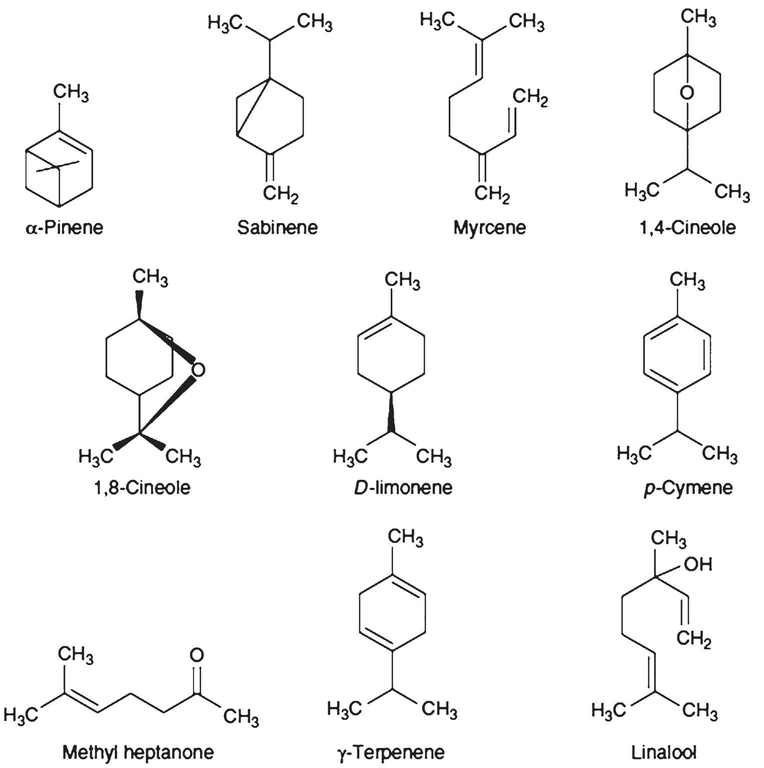


Table 12.9 Fatty acid composition of ginger lipids

Fatty acid	Fatty acid (%)
Caprylic acid	1.4
Capric acid	4.1
Lauric acid	7.6
Myristic acid	3.5
Pentadecanoic acid	0.4
Palmitic acid	23.2
Heptadecanoic acid	1.3
Stearic acid	3.3
Oleic acid	22.9
Linoleic acid	23.2
Linolenic acid	6.6
Arachidic acid	1.1

(6.2%), terpineol (5.6%), borneol (5.4%), phellandrene (3.1%), linalool (1.7%), methyl nonyl ketone (1.6%) and camphene (1.4%); the other components accounted for ~1% each of the volatile oil. The structures of the primary volatile compounds in ginger are shown in Fig. 12.10.

The impact of composition of ginger on ginger oil quality was summarized by Govindarajan (1982). It was proposed that Citral and citronellyl acetate were the most important attributes of aroma. Freshly prepared oil is rich in Zingiberene and β-sesquiphellandrene, and *ar*-Curcumene, increases during storage, and can be used as an indicator of aoil age and processing conditions. The ratio of zingiberene and β-sesquiphellandrene to *ar*-curcumene = 2:3 as a stable marker for identifying pure ginger oil. The lemony note from the citrals combined with the α-terpineol, β-sesquiphellandrene and *ar*-curcumene combine to form the basis of the characteristic ginger flavor.

Nerolidol contributes to the woody note; and *cis*- and *trans*-β-sesquiphellandrol were also contributors to the ginger flavor (Govindarajan 1982). Sesquiterpenes, particularly zingiberene, was identified as a major characteristic of ginger.

Ginger has been used as folk medicine since ancient time. With help from recent advances in analytical chemistry and nutrition, the bioactive compounds in ginger including gingerols,

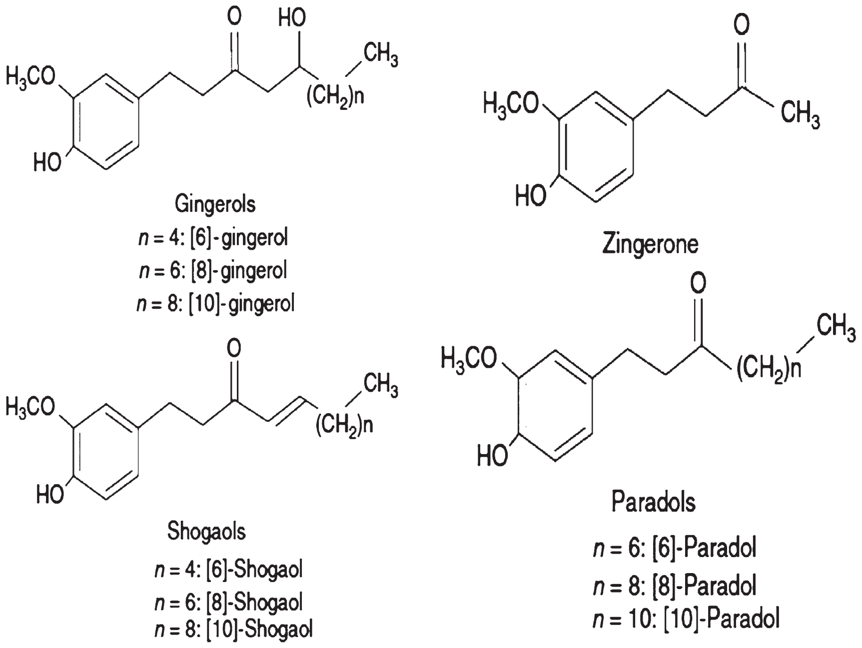


Fig. 12.9 Non volatile components of ginger oil

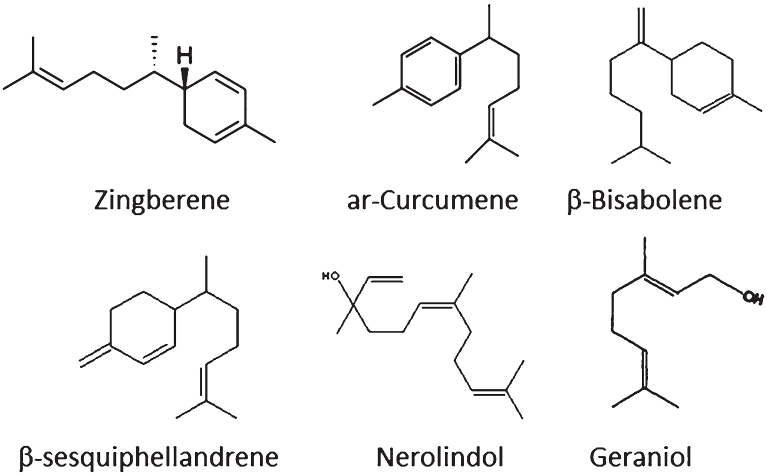


Fig. 12.10 Primary volatile compounds in ginger

β-carotene, capsaicin, caffeic acid, curcumin and salicylate have been identified (Tapsell et al. 2006). In vitro and animal studies suggest ginger has antioxidant, anti-inflammatory, and anti-platelet properties, as well as lipid and blood pressure lowering activities (Singletary 2010). In addition, a systematic review summarized 12 random clinical trials and concluded that ginger consumption is able to reduce pregnancy-associated nausea symptoms (Viljoen et al. 2014).

Turmeric

Turmeric, *Curcuma longa* L. (Zingiberaceae) is a spice cultivated in warm, rainy regions like India, China, Indonesia, Jamaica and Peru (Govindarajan 1980). The spice belongs to the genus *Curcuma*, which includes several plant species with underground rhizomes and roots. About 40 species of the genus are indigenous to India

(Velayudhan et al. 1999). The use of turmeric dates back nearly 4000 years to the Vedic culture in India, where it was used as a culinary spice but also had some religious significance.

Turmeric is used as a food additive to improve the palatability, storage and preservation of food. For example, turmeric is used in a wide range of curry powders and mustards. In Asian cuisines, dry or fresh turmeric, or ground turmeric, are used for vegetable and meat dishes and soup-like dishes (Govindarajan 1980). Turmeric oleoresin extract is used in brine pickle (Eiserlie 1966; Cripps 1967) and mayonnaise and relish formulations. It can be included in non-alcoholic beverages, or for garnishing and in some ice creams (Perotti 1975). Turmeric has in intense red orange color and it is commonly used as a natural food color (Govindarajan 1980).

The processing and storage condition can affect the quality of turmeric. Both dried rhizomes and leaves are used as raw materials to extract the volatile oil. Dried rhizomes contain 5–6% and leaves contain about 1.0–1.5% oil which is extracted by steam distillation. A large portion of volatile oil can be lost during processing (Chempakam et al. 2008a). The curcuminoids (a general terms for curcumin, demethoxycurcumin and bisdemethoxycurcumin) deteriorate on exposure to light and are also prone to oxidation which caused discoloration (Buescher and Yang 2000).

The primary component contributing to the unique aroma of turmeric is *ar*-turmerone. The primary compounds responsible for the color in the rhizomes are curcumin (1,7-*bis* (4-hydroxy-3-methoxy prenyl)-1, 6-heptadiene-3, 5-dione) and two related demethoxy compounds, demethoxy curcumin and *bis*-demethoxycurcumin (Fig. 12.11). Curcumin is insoluble in water but highly soluble in ethanol and acetone.

The oleoresin from turmeric is primarily used as a food color, and secondarily, to contribute a characteristic mild spicy aroma compatible with mustard, pickles, relish formulae, etc. Commercial oleoresin from turmeric has a curcuminoid content of 4.5–5.0%. It is highly viscous with a dark brownish-orange color. The product contains 30–40% curcumin, 15–20% volatile oil and delivers a fresh, clean, mildly pungent, woody-pungent, woody-spicy aroma of turmeric (Chempakam et al. 2008b).

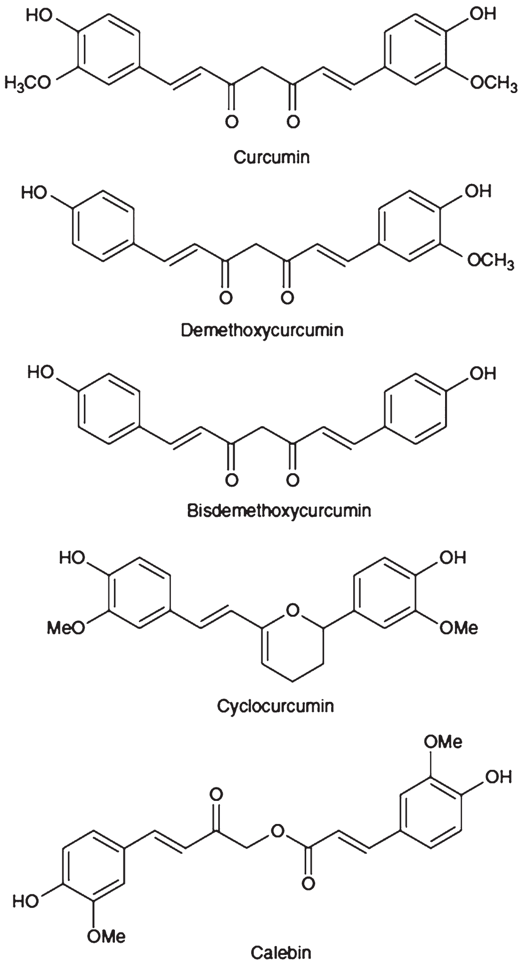


Fig. 12.11 Curcuminoids found in turmeric

Turmeric has gained lots of popularity recently due to increasing evidence on health benefits as well as promotion from celebrities and top chefs. In most studies, the active component of turmeric is considered to be curcumin. Consumption of curcumin showed lipid lowering effects in patients with type-2 diabetes and metabolic syndrome (Neerati et al. 2014; Yang et al. 2014). Curcuminoids may reduce inflammation in patients with cardiovascular diseases indicated by lowering C-reactive protein in blood (Sahebkar 2014). Curcumin was found to have anticancer activities in numerous studies (Hallman et al.

2017; Yue et al. 2016). A review also summarized that turmeric/curcumin products both oral and topical may improve skin health (Vaughn et al. 2016). Conclusive evidence on these health benefits are warranted.

Cinnamon

Cinnamon and its close relative, cassia, are among the earliest, most popular spices used by mankind. The genus *Cinnamomum* (family: Lauraceae) consists of 250 species of trees and shrubs distributed in Southeast Asia, China and Australia. True cinnamon, *Cinnamomum verum* syn. *C. zeylanicum*, is a native of Sri Lanka and South India. Cassia cinnamon is derived from different sources, including Chinese cassia (*C. cassia* syn. *C. aromatica*) from China and Vietnam, Indonesian cassia (*C. burmannii*) from Sumatra and the Java region and Indian cassia (*C. tamala*) from the north-eastern region of India and Myanmar (Baruah and Nath 2004; Leela 2008). Sri Lanka is the major cinnamon producing country with 60% of the world cinnamon trade. The dried inner bark of the cinnamon tree is used as a spice. Cinnamon oleoresin is obtained by solvent extraction of the bark, is used mainly for flavoring food products such as cakes and confectionary products. The volatile oil and oleoresin from cassia are also used for flavoring soft drinks and other beverages (Leela 2008). The genus Cinnamomum comprises several hundred species which occur naturally in Asia and Australia. They are evergreen trees and shrubs and most species are aromatic. *C. verum*, the source of cinnamon bark and leaf oils, is a tree indigenous to Sri Lanka, although most oil now comes from cultivated areas (Leela 2008). The major varieties and growing regions are listed in Table 12.10.

Table 12.10 Botanical sources of cinnamon and cassia

Cinnamon variety	Region of origin/production
Cinnamomum verum Presl (syn. *C. zeylanicum* Nees)	True or Ceylon cinnamon
C. cassia Presl	Cassia, Chinese cinnamon, "Cassia lignea"
C. burmannii Blume	Indonesian cassia
C. loureirii Nees	Vietnamese cassia
C. tamala (Buch.-Ham.) Nees & Eberm	Indian cassia

From Leela (2008)

Cinnamon bark oil delivers a delicate aroma of the spice and a sweet and pungent taste. Its major constituent in cinnamon bark is cinnamaldehyde, however it is the minor components impart the characteristic odor and flavor that makes *C. zeylanicum* unique. The cinnamon bark oil is used in food flavoring such as meat and fast food seasonings, sauces and pickles, baked goods, confectionery, cola-type drinks, tobacco flavors and in dental and pharmaceutical preparations. Perfumery applications are limited because the oil has some skin-sensitizing properties. Cinnamon leaf oil has a warm, spicy aroma, but the aroma can be harsh and it lacks the body of bark oil. Leaf oils major constituent is eugenol rather than cinnamaldehyde. Leaf oil is used in seasonings and savory snacks, as a low cost fragrance in soaps and insecticides. Table 12.11 lists the profiles of the volatile compounds found in *C. zeylanicum* leaves and bark.

Cinnamomum verum (C. zeylanicum) is used to produce both leaf and bark oils for flavoring and perfumes. The major component of bark oil is cinnamaldehyde and of leaf oil is eugenol. In cinnamon the volatile components are found in other parts of the plant including root bark, fruits, flowers, twigs and branches. The most important source is the bark which varies from 0.4 to 2.8% (Angmor et al. 1972; Wijesekera 1978; Krishnamoorthy et al. 1996). The oil from the stem bark of a commercial cinnamon sample contained 75% cinnamaldehyde, 5% cinnamyl acetate (Gruenwald et al. 2010), 3.3% caryophyllene, 2.4% linalool and 2.2% eugenol (Senanayake et al. 1978).

Cassia oil is distilled from a mixture of leaves, twigs and fragments of bark. Cinnamaldehyde is the major constituent and it is used mainly for flavoring cola-type drinks, with smaller amounts used in bakery products, sauces, confectionery and liqueurs. Like cinnamon bark oil, its use as a fragrance is limited by its skin sensitizing properties.

Table 12.11 The primary volatile components in *C. zeylanicum* leaf and bark extracts

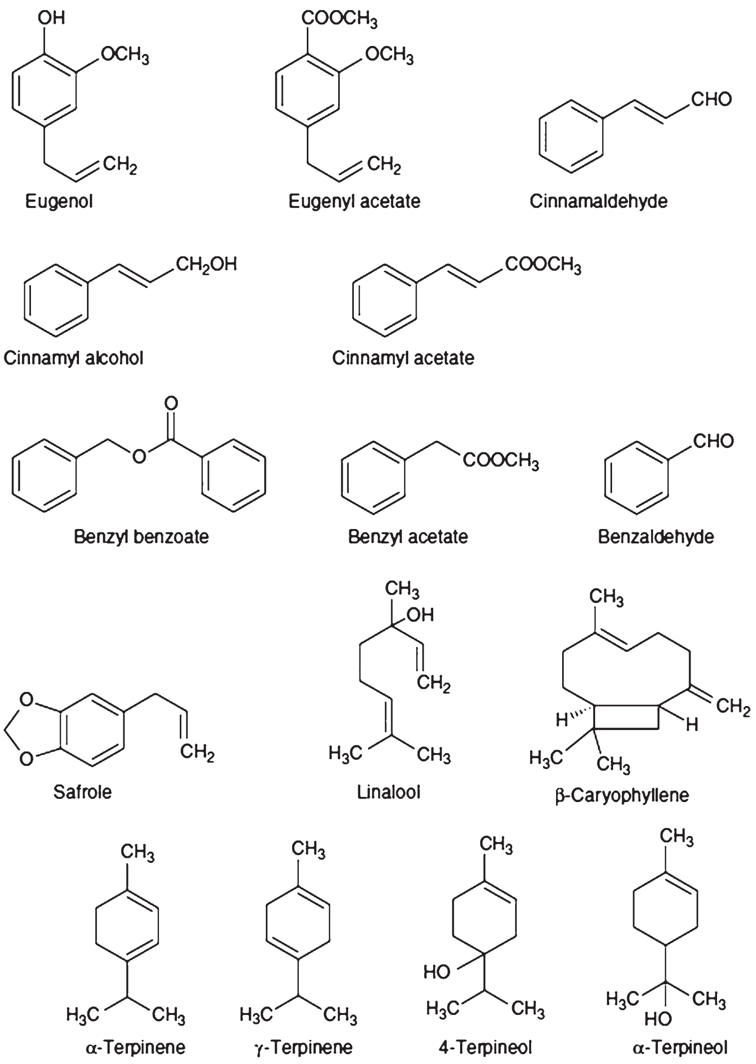
Leaf			Bark		
	Volatile oil	Oleoresin		Volatile oil	Oleoresin
	%	%		%	%
α-Thujene	0.1		α-Pinene	tr	
α-Pinene	0.5		Camphene	tr	
β-Pinene	tr		Sabinene	tr	
Myrcene	tr		β-Pinene	tr	
α-Phellandrene	1.9		Limonene	tr	
p-Mentha-1(7),8-diene	tr		1,8-Cineole	tr	
p-Cymene	0.7		Camphor	tr	
1,8-Cineole	0.7		Z-cinnamaldehyde	tr	1.5
Terpinolene	tr		E-cinnamaldehyde	97.7	50.0
α-Terpineol	tr		α-Copaene	0.8	4.6
α-Cubebene	tr		α-Amorphene	0.5	
Eugenol	87.3	87.2	δ-Cadinene	0.9	7.8
β-Caryophyllene	1.9	1.4	Terpinen-4-ol		0.1
Aromadendrene	1.1	0.8	β-Caryophyllene		1.0
α-Amorphene	tr	0.4	Coumarin		16.6
Germacrene-D	0.6	0.2	α-Muurolene		4.4
Bicyclogermacrene	3.6	1.7	β-Bisabolene		1.4
δ-Cadinene	0.4	0.6	Cadina-1(2), 4-diene		1.8
Spathulenol	0.5	1.7	Ortho-methoxy cinnamaldehyde		1.5
Sabinene		tr	Cubenol		0.5
γ-Terpinene		tr	1-Heptadecene		0.2
Terpinen-4-ol		tr	1-Nonadecene		0.4
δ-Elemene		1.0	Tetracosane		0.1
Viridiflorol		0.3	Octacosane		0.1
Methoxy-eugenol		0.1	Nonacosane		0.2
Isospathulenol		0.3			
Neophytadiene		0.3			
Docosane		0.1			
Nonacosane		0.1			
Vitamin-E		0.2			
Total	99.4	97.1	Total	100	92.3

Adapted from Singh et al. (2007)

The volatile distribution of *C. Cassia* differs significantly form *C. zeylanicum.* Table 12.11 compares the bark and leaf volatiles from *C. zeylanicum*. The dried inner bark of cinnamon and cassia contains volatile oil, fixed oil, tannin, resin proteins, cellulose, pentosans, mucilage, starch, calcium oxalate and mineral elements. Cinnamon delivers a spicy aroma from its volatile oil which is composed of a mixture of monoterpenes, sesquiterpenes and phenylpropenes. The major volatile components in cinnamon are illustrated in Fig. 12.12.

The primary components influencing cinnamon quality are associated with the volatile components, cinnamon also contains several diterpenes. The diterpenes include cinncassiols A, B, C1 and their glucosides, cinncassiols C2 and C3, cinncassiols D1, D2 and D3 and their glucosides, cinncassiol E, cinnzeylanol, cinnzeylanin, anhydrocinnzeylanol and anhydrocinnzeylanin. Cinnamon also contains several benzyl isoquinoline alkaloids, flavanol glucosides, coumarin, *b*-sitosterol, cinnamic acid, protocatechuic acid, vanillic acid and syringic acid.

Fig. 12.12 The major volatile components in cinnamon (Leela 2008)



Some important non-volatile components reported in *Cinnamomum* and *Cassia* are listed in Table 12.12 and the structures are shown in Fig. 12.13.

Cinnamon is one of the oldest herbal medicines, which has been recorded in Chinese publications 4000 years before (Qin et al. 2003). Cinnamon has been used to treat dyspepsia, gastritis, blood circulation disturbance and inflammatory diseases in many countries since ancient times (Yu et al. 2007). The significant anti-allergic, anti-ulcerogenic, antipyretic, anaesthetic and analgesic activities have been confirmed previously (Kurokawa et al. 1998; Lee and Ahn 1998). The in vitro investigation of cinnamon has revealed that its extract mimics the function of insulin, which potentiates insulin action in isolated adipocytes (Broadhurst et al. 2000). Cinnamon extract has been shown to improve the insulin receptor function (Jarvill-Taylor et al. 2001; Leela 2008). Current in vitro and in vivo evidence suggests that cinnamon has anti-inflammatory, antimicrobial, antioxidant, antitumor, cardiovascular, cholesterol lowering, and immunomodulatory effects (Scaglione et al. 1989). In vitro studies have demonstrated that cinnamon acts as an insulin mimetic, to potentiate insulin activity or to stimulate cellular glucose

Table 12.12 Non-volatile components in cinnamon and cassia

Compound	Plant part	References
Lyoniresinol 3 α-O-β-glucopyranoside	*C. cassia* stem bark	Miyamura et al. (1983)
2,4,5-Trimethoxy phenol β-D apiofuranosyl-(1-6)-β-glucopyranoside	*C. cassia* stem bark	Miyamura et al. (1983)
Syringaresinol	*C. cassia* stem bark	Miyamura et al. (1983)
5,7,3′-Trimetyl (−) epicatechin	*C. cassia* stem bark	Miyamura et al. (1983)
5,7-Dimethyl-3′-,4′-di-O-methylene (±) epicatechin	*C. cassia* stem bark	Miyamura et al. (1983)
Cinnamic aldehyde cyclic glycerol-1,3-acetol (9,2′ *trans*)	*C. cassia* stem bark	Miyamura et al. (1983)
Cinnamic aldehyde cyclic glycerol-1,3-acetol (9,2′ *cis*)	*C. cassia* stem bark	Miyamura et al. (1983)
Cimmacassiol D_4	*C. cassia* stem bark	Nohara et al. (1982)
Cimmacassiol D_4 -glucoside	*C. cassia* stem bark	Nohara et al. (1982)
2′-Hydroxy cinnamaldehyde	*C. cassia* stem bark	Kwon et al. (1996)
3-(2-Hydroxy phenyl)-propanoic acid	*C. cassia* stem bark	Tanaka et al. (1989)
Cinncassiol E	*C. cassia*	Nohara et al. (1985)

From Leela (2008)

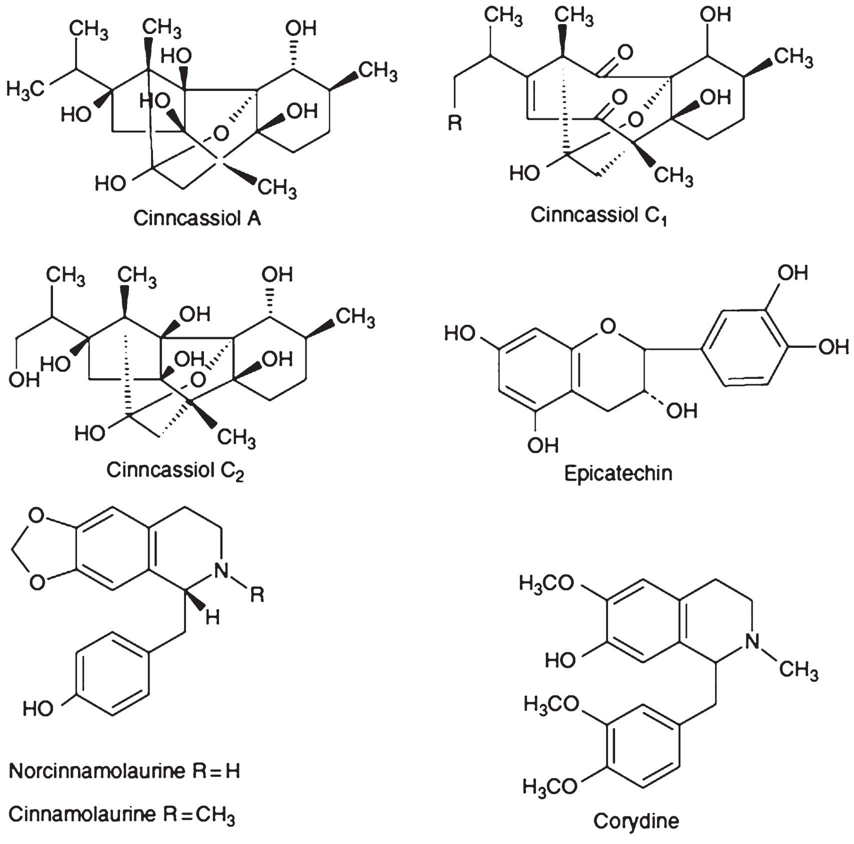


Fig. 12.13 Major non-volatile components in cinnamon

metabolism. Animal studies have demonstrated strong hypoglycemic properties. The use of cinnamon as an adjunct to the treatment of type 2 diabetes mellitus is the most promising area, but further research is needed before definitive recommendations can be made.

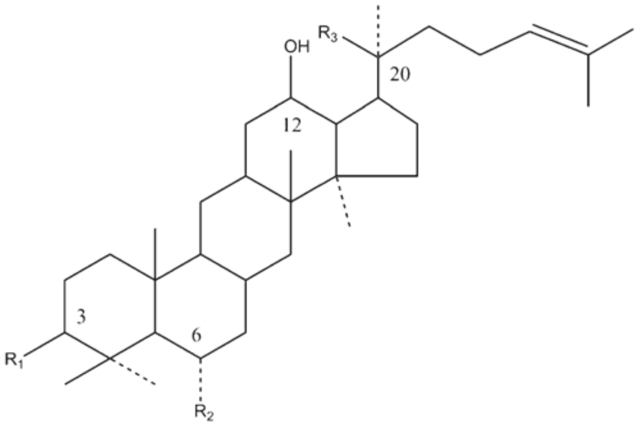
Ginseng

Ginseng is a traditional herb that has been used for a 1000 years by ancient East Asian. It was considered to be a panacea thus having the genus name *Panax*. There are 11 species in the genus *Panax* considered as ginseng. The edible part is the fleshy root of ginseng plant. Ginseng is grown in Asia and North America with China, South Korea, Canada, and the US being the four major producing countries, accounting for 99% of the annual 80,080 tons' production (Baeg and So 2013). As a functional food ingredient, ginseng has been found in over 11,000 retail products (Innova Market Insights 2017). Ginseng has been added into tea, energy drink, soup, candies, as well as dietary supplements in food and beverage.

The major bioactives in ginseng are ginsenosides, belonging to triterpene saponins. Most ginsenosides consist of a dammarane aglycone with different sugar moieties. The common ginsenosides are shown in Fig. 12.14. The composition of ginsenosides are affected by species, age, growing condition, harvesting method, as well as storage condition (Leung and Wong 2010).

The therapeutic potentials of ginseng and ginsenosides have been studied extensively. Consumption of ginseng has positive effects on cardiovascular diseases (Lee and Kim 2014), immune modulation (Scaglione et al. 1990), enhancement on Cognitive function (Vogler et al. 1999). The mechanism on efficacy of ginseng on cardiovascular diseases may include: inhibition of free radical production, stimulation of NO production, improvement in blood circulation, adjustment of vasomotor function, and improvement in the lipid profile (Lee and Kim 2014).

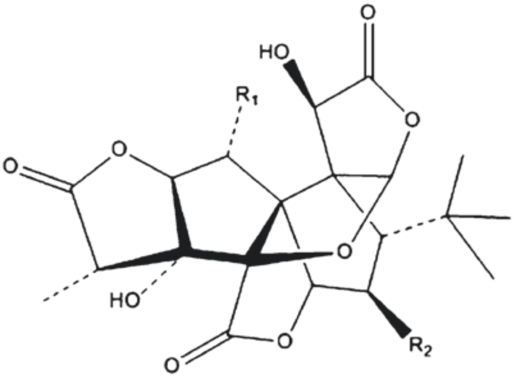
Fig. 12.14 Structures of common ginsenosides. Abbreviation: *Glc* glucopyranoside, *Ara(pyr)* arabinopyranoside, *Rha* rhamnopyranoside. Adapted from Choi et al. (2002)



Ginsenoside	R$_1$	R$_2$	R$_3$
Rb$_1$	-O-Glc-Glc	-H	-O-Glc-Glc
Rc	-O-Glc-Glc	-H	-O-Glc-Ara (pyr)
Re	-OH	-O-Glc-Rha	-O-Glc
Rf	-OH	-O-Glc-Glc	-OH
Rg$_1$	-OH	-O-Glc	-O-Glc

Ginkgo

Ginkgo (*Ginkgo biloba*) is a woody plant that has been grown widely in the world. Similar to ginseng, ginkgo leaf is considered a medicinal herb that has a rich history of consumption in China. Ginkgo has a variety of bioactives categorized into flavonoids (glycosides of kaempferol, quercetin, and isorhamnetin) and terpenoids (ginkgolide A, B, C, and J) (Kleijnen and Knipschild 1992). Figure 12.15 showed the structure of common ginkgolides. Ginkgo is usually made into extracts and is mainly added into dietary supplements or as prescribed herbal drugs. Standardized extracts from the leaves of ginkgo have a set ratio of bioactives. For example, EGb761 contains 24% of flavonoids and 6% of terpenoids. The extract EGb761 are commonly prescribed for dementia and cognitive impairment (O'Hara et al. 1998). A review of nine clinical trial found a 240 mg dose of EGb761 was able to improve cognition for the whole group of patients with Alzheimer's disease, vascular or mixed dementia, as well as for the Alzheimer's disease subgroup (Weinmann et al. 2010).



Ginkgolide	R_1	R_2
A	-H	-H
B	-OH	-H
C	-OH	-OH
J	-H	-OH

Fig. 12.15 Structures of terpenoids (ginkgolides) in Ginkgo

Food Fraud Risks

Herbs and spices are usually high value crops that require delicate care and intensive labor. They are mostly sold in powder, minced, oleoresin and essential oil forms. The combining factors above have made herbs and spices products susceptible to Economically Motivated Adulteration (EMA). Fraudulent adulteration of spices and herbs with added colors have been seen in international trade and retail markets (USP 2017). Market surveillance has showed 25% of the oreganos in the markets are adulterated with other plants (BBC 2015). Tested by Taiwan FDA, lead chromate has been found in one turmeric product at lead level as high as 1600 ppm (Liao 2016). Sudan dyes have been identified in paprika powders and oleoresins (USP 2017). With the enforcement of FSMA act, preventive controls have to be taken to ensure product quality and safety against EMA. The mitigation of risks would require a comprehensive supply chain control, a good QA testing system, as well as information tools such as database capturing fraudulent activities to be in place.

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