Flavors

D.W.S. Wong, *Mechanism and Theory in Food Chemistry, Second Edition,*
https://doi.org/10.1007/978-3-319-50766-8_6

Flavor is the sensation produced by a material perceived principally by the senses of taste and smell. In certain cases, flavor also denotes the sum of the characteristics of the materials which produce the sensation. The primary role of flavor in food processing is to make the food palatable. Many food products may become unattractive for consumption without the supplementation of flavors, either unintentionally or intentionally. The use of flavors also adds variety to the diet and the functional and economic values of food products. The application of flavor technology depends often on the identification of the sensory active compounds. Most synthetic flavor compounds are imitates of the key flavor constituents of natural origin.

The biochemical and chemical reactions that generate the many characteristic flavors in food are extremely complex. There are about 4000 flavor compounds identified in approximately 200 types of fruits, spices, and other foods. Few detailed pathways are known, and many of these mechanisms are postulated from model studies. The structure-activity relationship of flavor compounds is an area of great interest for food applications.

6.1 The Sensation of Taste

Taste is a combination of chemical sensations perceived by the papillae of the tongue. There are five basic taste sensations: sourness, saltiness, sweetness, bitterness, and umami. Many substances do not have a single taste, but a complex sensation comprising more than one of the five basic components.

Sour taste is caused by hydrogen ions: acids, acid salts, and other substances that generate hydrogen ions in contact with water to give the sour taste. The threshold is about 0.002 *N* acid. Sour taste can also be induced by passing electric current through the tongue, presumably due to the hydrolysis of acid or water with the generation of hydrogen ions. Strong currents, however, induce a bitter taste. Some acid substances, for example, potassium acid oxalate and protocatechuic acid, stimulate both sour and bitter tastes.

Saltiness is stimulated by soluble salts. Most salts of high molecular weight are bitter rather than salty. Low-molecular-weight salts, notably chlorides of sodium, potassium, and calcium, are salty. The threshold level is 0.007–0.016% salt solution.

Sweetness of a substance is related to the functional groups that make up the glycophore units in a tripartite model. The molecular theory of sweet taste is well developed and will be discussed in ▶ Chap. 7.

Bitter compounds require a polar (electrophilic or nucleophilic) group and a hydrophobic group. The structure-activity relationship of bitter-tasting compounds has not been firmly established [4]. There are large numbers of bitter substances in plants, which are classified into alkaloids and glycosides.

The fifth basic taste, umami, is a delicious savory taste sensation, relating to L-amino acids. The first umami amino acid, monosodium glutamate (MSG), was isolated from dashi (a fish) and seaweed in 1908. Several umami enhancers (potentiators) have been since discovered, including: IMP (inosine 5′-monophophate) isolated from dried bonito tuna in 1914; and GMP (guanosine 5′-monophosphate) from shitake broth in 1960. A synergistic effect often occurs between glutamate and inosinate or guanylate. (Refer to section "Taste Enhancers".)

6.2 The Mechanism of Taste Sensations

During ingestion and chewing of foods, chemicals from the food enter the taste pores of taste buds on the tongue, where they interact with specialized epithelial cells, known as taste receptor cells (TRC). Each taste bud has 50–150 taste receptor cells, each of which consists of chemoreceptors that detect one of the five taste sensations. Binding of a food chemical (tastant) to a specific receptor triggers a reaction sending signals to the medulla in the brain. Two types of mechanisms are utilized in generating the basic sensations [11, 26].

1. Salty and sour sensations rely on the control of ion channels. Sodium chloride triggers taste cells when Na^+ ions enter through the ion channel. Accumulation of sodium ions causes depolarization allowing calcium ions (Ca^{2+}) entering the cell. The calcium ions in turn trigger the cell to release neurotransmitters. Repolarization occurs with potassium ions exiting the cell. For sour taste, the acid generates hydrogen ions (H^+) entering into the cell, blocking potassium ions (K^+) channels, or facilitating other positive ions entering the cell. The accumulation of positive ions/charges inside the cell (intracellular acidification) causes depolarization and release of neurotransmitters.
2. Bitter, sweet, and umami rely on a G protein-coupled receptor (GPCR) casade systems (involving regulation by GTP, guanosine triphosphate) [2, 11]. Sequence comparison of all known GPCRs defines three families: (1) Family A GPCR is composed of rhodopsin and related receptors, including odorant receptors; (2) Family B is composed of receptors activated by large peptides, such as secretin and glucagon; and (3) Family C includes metabotropic glutamate receptors, some heromone receptors, as well as taste receptors. Relating to sweet and umami tastes, the GPCRs are membrane proteins of about 850 amino acids, carrying (1) a large N-terminal extracellular domain that resembles a venus flytrap (VFTD), which is the ligand (tastant) binding region, and (2) a transmembrane segment consisting of hydrophobic stretches, linked by (3) a cysteine-rich domain (Fig. 6.1). Two distinct families of taste receptors are known to exist. The taste receptor type 1 family comprises 3 members (T1R1, T1R2, and T1R3). These T1Rs assemble in combination to form heterodimers: (1) the T1R1 plus T1R3 heterodimer functions as the unami receptor; (2) the T1R2 plus TIR3 heteromer forms a sweet taste receptor (See ▶ Chap. 7). In contrast, the taste receptor type 2 family, which functions to recognize bitter substances, comprises about 35 highly divergent T2R members. These proteins contain 300–330 amino acids with a short N-terminal extracellular domain (without a Venus flytrap structure). Most T2Rs are expressed in the same TRCs, functioning as broadly tuned sensors for bitter chemicals.

Gustducin, the G-protein for the mechanism has been identified. The binding interaction between ligands (tastants, taste compounds) and receptors causes the dissociation of the subunits of gustducin and initiates a cascade of reactions in the release of neurotransmitters. Two hypotheses have been put forward to explain how taste information is processed. (1) The "labeled-line model" refers to a coding model in which the peripheral or central neurons that respond to a given taste stimulus carry the information to the brain in an individual pattern. Receptor cells are tuned to respond to single taste modalities, and are innervated by individually tuned nerve fibers. (2) The "across fiber pattern" refers to

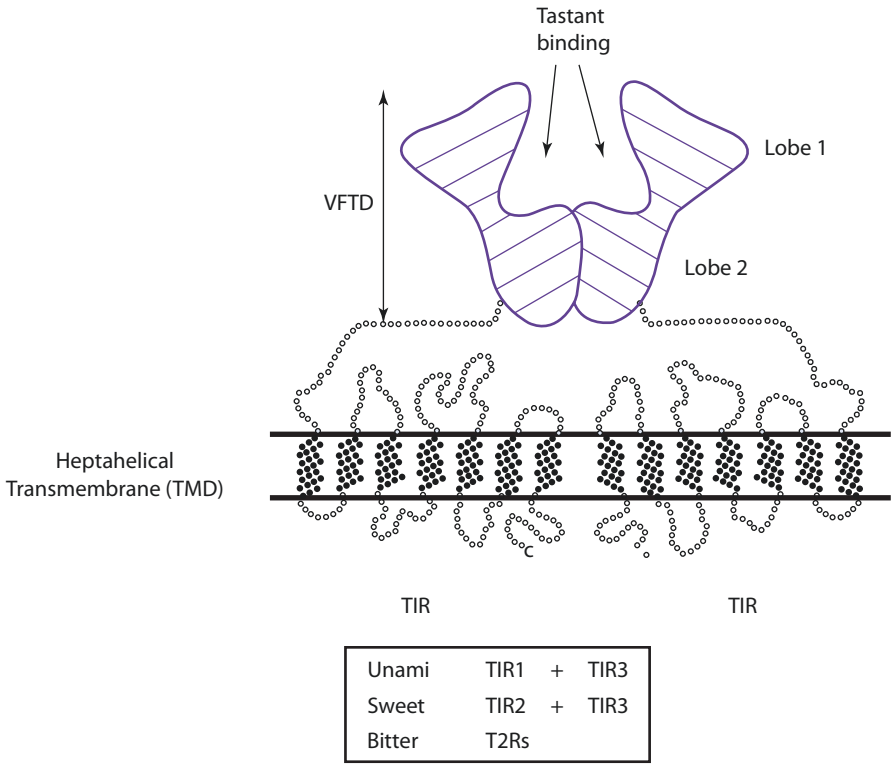


Fig. 6.1 Schematic representation of human taste receptors (From Assadi-Porter et al. [2] with permission. Copyright 2010 Elsevier)

ensemble coding in which the information about a taste stimulus is extracted by comparative activities across a neuron population or ensemble that responds with different intensity levels to multiple stimuli. Neurons activated in response to TRC activation are often broadly tuned. Each neuron cell type responds typically to more than one tastant with dissimilar taste qualities, but responds more strongly (higher intensity or activity) to one type of the basic taste stimuli. Taste discrimination will depend on the relative activity of different neuron types to multiple taste stimuli.

6.3 Glutamate and Umami Receptor

Only the L-form glutamate possesses umami activity, and dicarboxlates with four to seven carbons have been shown to have similar property. The pK_a of α-COOH, γ-COOH, and α−NH_2 in glutamic acid are 2.19, 4.25, and 9.67, respectively. At low pH, the free acid form is predominant and MSG becomes less soluble. MSG is prepared in monosodium form, and is most effective in food systems in the pH range of 5.5–8.0.

In the umami receptor, L-glutamate binds close to the hinge region formed by the two lobes in the VFTD of T1R1. In the active form, T1R1 is in the "closed" conformation and T1R3

is in the "open" conformation. In the T1R1 binding site, the glutamate α-carboxylate group maintains favorable interactions with the backbone NH group of Thr149 and Ser172, and the side chain OH of Ser148 and Thr149. The glutamate amino nitrogen maintains favorable interactions with the backbone oxygen of Ala170, the side chain oxygen of Ser172, and side chain carboxylate of Glu301. The γ-carboxylate of the glutamate molecule interacts with the backbone NH group of Arg277 and the side chain guanidium group of Arg151 and Arg277 [10].

6.4 Taste Enhancers

Purine ribonucleotides, such as inosine 5′monophosphte (IMP) and guanosine 5′monophosphate (GMP), are naturally occurring enhancers known to strongly potentiate the unami intensity by allosteric modulation.

Structurally, the binding site for the 5′-ribonucleotides (such as IMP, GMP) lies adjacent to the glutamate binding site close to the hinge opening of the VFTD of T1R1. The binding provides synergistic effect in activating the umami taste receptor via allosteric modulation [53]. It further stabilizes the closed conformation by coordinating the positively charged residues via their phosphate groups.

The enhancers MSG, IMP, and GMP are disodium salts at neutrality (Fig. 6.2). Only the 5′-nucleotides are active, although three possible isomers (2′, 3′, and 5′) can exist. GMP and IMP are produced by enzymatic degradation of yeast RNA, using 5′-phosphodiesterases. The products are usually an equal mixture of IMP and GMP. The threshold levels for the nucleotides are in the range of 0.01–0.03%. The threshold levels are greatly reduced when the nucleotides are combined synergistically with MSG (Table 6.1). Maximum flavor-enhancing activity is obtained when the nucleotide and MSG are in a 1:1 mix. Lower or higher ratio of mixing tends to reduce the effectiveness. GMP shows about four times the effectiveness in the synergistic action compared to IMP (Table 6.2) [24].

It has been postulated that the nucleotide interacts with its receptor at three sites. Sites A and B are electrophilic and interact with the two phosphoryl oxygens and the C6 oxygen, respectively. Site X interacts with the substituent at C2 [25]. The distance between sites A and B is about 8 Å. The flavor-enhancing activity depends on the electron density of the C6 oxygen. The site X interaction depends largely on the ability of delocalization of

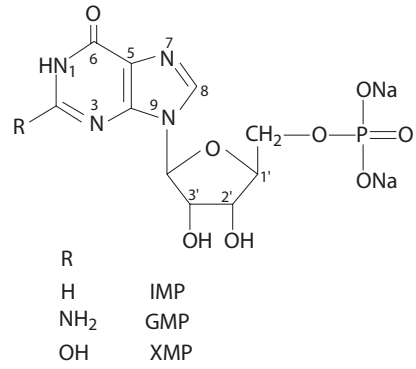


Fig. 6.2 Nucleotide flavor potentiators

Table 6.1 Synergistic interaction between MSG and 5′-nucleotide in the reduction of individual threshold levels

	Threshold level (%)		
	IMP	GMP	MSG
Water	0.012	0.0035	0.03
0.1% MSG	0.0001	0.00003	—
0.01% IMP	—	—	0.002

From Kuninaka [24, 25]

Table. 6.2 Flavor activity of mixtures of MSG and 5′-nucleotide

Mixture		Relative flavor activity per unit weight	
MSG	IMP OR GMP	IMP	GMP
1	0	1.0	1.0
1	1	7.5	30.0
10	1	5.0	19.0
20	1	3.4	12.4
50	1	2.5	6.4
100	1	2.0	5.5

From Kuninaka [24, 25]

the substituent at C2. Thus GMP, with the C2 substituent being NH_2, has a comparatively higher activity than IMP. Association of the molecule with a receptor initiates an umami sensation, and simultaneously activates other receptors whose sensitivity for their respective flavor compounds are enhanced.

6.5 Odor: The Stereochemical Theory for Olfaction

In order to be odorous, a compound must be sufficiently volatile, and there has to be physical interactions between the odorous compound and the receptor site. Based on the relationship between odor and chemical structure of the odor compound [1], there are seven primary odors: camphoraceous, ethereal, musky, floral, minty, pungent, and putrid. For each class of these odorous compounds, there are receptor sites that are complementary to the size, shape, and electronic status of the molecule. The ethereal, camphoraceous, and musky odors depend primarily on the size of the molecule, and the floral and the minty depend on the shape, whereas pungent and putrid are caused by electrophilic and nucleophilic molecules, respectively. The minty structure also has an additional requirement of possessing, near the point of the wedge-shaped molecules, a group capable of

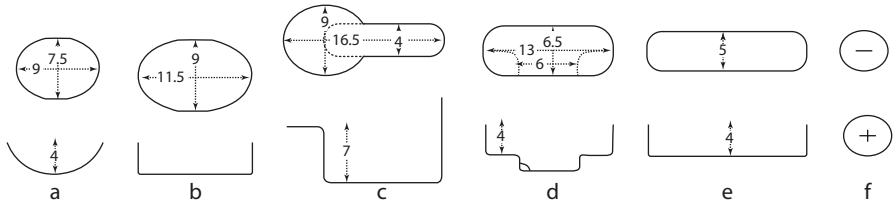


Fig. 6.3 Olfactory receptor sites: **a** Camphoraceous (δ-camphor, 2,3-dinitropentane, acetylenetetrabromide;) **b** musky (androstan-3α-ol, 3-methylcyclopentadecanone, undecyl-γ-butyrolactone); **c** floral (diphenylamine, geraniol, anisole); **d** minty (1-menthone, methyl 2,4-dimethylphenyl ketone, cyclopentanone); **e** ethereal (diethyl ether, ethylene, acetylenetetrabromide); and **f** pungent (electrophilic compounds, such as isocyanate, isothiocyanate, and chloraminel), and putrid (nucleophilic compounds such as mercaptan and amines) (From Amoore [1] with permission. Copyright 1964 John Wiley & Sons)

forming a hydrogen bond with the receptor site. The primary odors are perceived when there is a fit between a molecule and the corresponding receptor site, in a way similar to the lock-and-key mechanism (Fig. 6.3).

A compound can develop more than one primary odor if the molecule can fit more than one type of receptor site. For example, acetylene tetrabromide fits both sites for camphoraceous and ethereal. It is also possible for molecules to come together to fill a common site, giving complex odors. In short, a given complex odor is a mixture of the appropriate primary odors. The following are some examples of complex odors and their primary odor compounds.

Odor	Components (primary odor)
Almond	Camphoraceous, floral, minty
Lemon	Camphoraceous, floral, minty, pungent
Garlic	Ethereal, pungent, putrid
Rancid	Ethereal, minty, pungent

The molecular shape requirements are inadequate to explain the distinct odors exhibited by many small molecules. The use of electrophilic and nucleophilic properties to relate pungent and putrid recognizes, to a certain degree, the importance of a particular functional group in the molecule. The profile-functional group theory [3] postulates that while the shape and size of an odorous molecule is responsible for the quality of the odor, the functional group determines the orientation of the molecule at the receptor site. It has an important influence on the homogeneity of the orientation pattern and on the affinity of the interaction complex. Removal of the functional group changes the orientation pattern, resulting in randomness and decreased affinity in absorption to the receptor site. For example, the isochromene in Fig. 6.3 has a musk odor, but substitution with a methyl group at positions causing steric hindrance of the functional ether oxygen results in the loss of odor. Replacing the oxygen with nitrogen decreases the intensity.

6.6 Character-Impact Compounds

A characteristic taste of a food can usually be related to a particular compound or a class of compounds. However, an odor is usually attributed to a combination of numerous volatile compounds, each of which individually smells very differently. The difference in the characteristics of certain odors is partially due to varying proportions of many widely distributed volatiles, such as esters, acids, alcohols, aldehydes, and ketones that occur in the food. These volatiles are called "contributing flavor compounds." However, some substances contain trace amounts of a few unique volatile compounds which possess the characteristic essence of the odor. These are called "character-impact compounds." Unfortunately, there are not very many character-impact compounds that have been identified. Nonetheless, the focus in this chapter will focus on unique compounds which contribute the most significant characteristic flavor to a particular food.

6.7 Odorant Receptors: Molecular Mechanism of Odor Recognition

With the advent of molecular biology techniques, it is now known that humans have about 500 (G-protein coupled) odorant receptors. The olfactory epithelium in the nasal cavity contains millions of olfactory sensory neurons, and each olfactory neuron expresses one odorant receptor (OR) gene. The number of OR genes amounts to roughly 1–5% of the total genes in the genome devoted to the detection of odorants. OR proteins belong to the superfamily of seven transmembrane domain proteins that interact with G proteins to generate intracellular signal transduction (GPCR) Family A. (Refer to section on "Chapter 7: Sweet Taste Receptors"). The primary structure of OR proteins contains 300–330 amino acids, with seven hydrophobic stretches of 19–26 amino acids that transverse the cell plasma membrane, linked by six loops (four extra- and three intracellular), which serve as binding sites of odorous chemicals (Fig. 6.4) [8].

It has been estimated that humans can smell 10,000 and more chemicals as distinct odors. How can the binding interactions between ORs and odorous chemicals be transmitted and organized into a signal input? First, each OR can recognize multiple odorants. Second, each odorant is detected by multiple different ORs. Third, different odorants are recognized by different combinations of ORs. In summary, different odorants are encoded by different combinations of ORs, known as "receptor codes." Given the number of possible combinations of 500 different ORs in humans, this coding scheme would allow the detection and discrimination of an astronomical number of odorants [29]. Figure 6.5 illustrates the combination codes for a number of volatile compounds, clearly showing different odorants encoded by different combinations of receptors. The binding interactions of odors with OR proteins initiate a cascade of G-protein coupled signaling events propagated by olfactory neuron to the olfactory bulb of the brain. From there, the signals are relayed to the primary olfactory cortex, thereby allowing both perception of and physiological response to the odors.

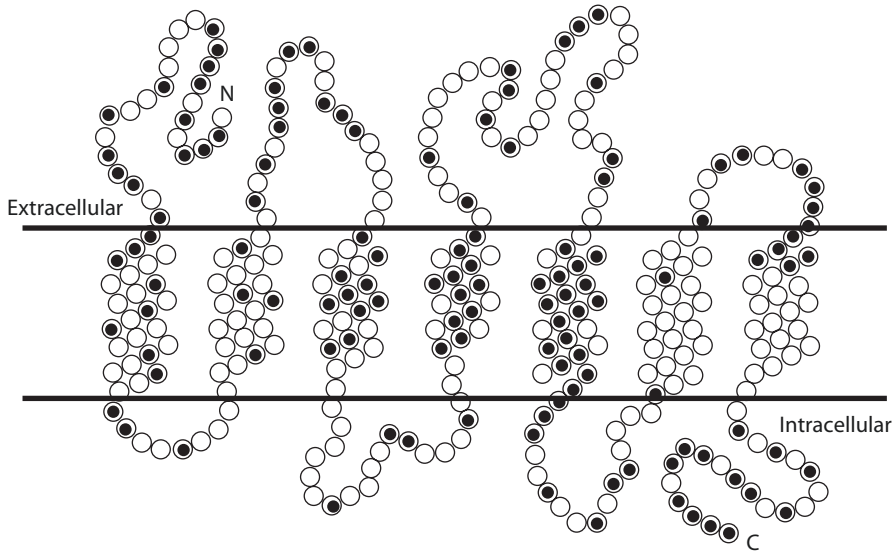


Fig. 6.4 Schematic illustration of an odorant receptor protein showing it traversing the plasma membrane seven times with loops extending intra- and extracellularly. More variable amino acid residues are drawn in dotted circles (From Buck and Axel [8] with permission. Copyright 1991 Elsevier)

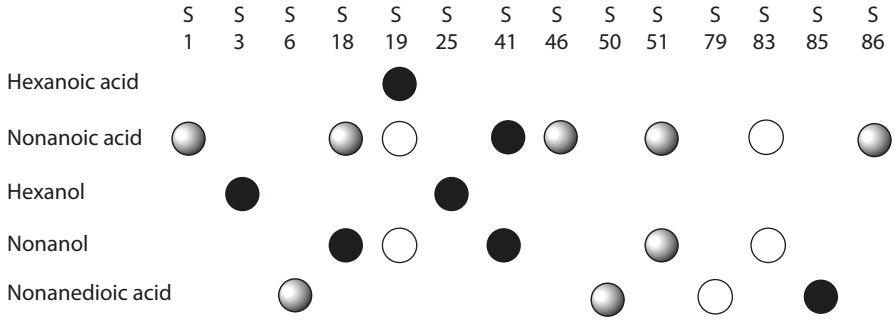


Fig. 6.5 The combinatorial profiles of individual odorant receptors in the recognition of odorants. Shade intensity reflect the level of response (Malnic et al. [29])

6.8 The Origin of Flavor

6.8.1 Biosynthesis

Many flavors, especially those in fruits and vegetables, are the products or byproducts of metabolic pathways. Schematically, the biosynthesis of these flavors is represented by Fig. 6.6.

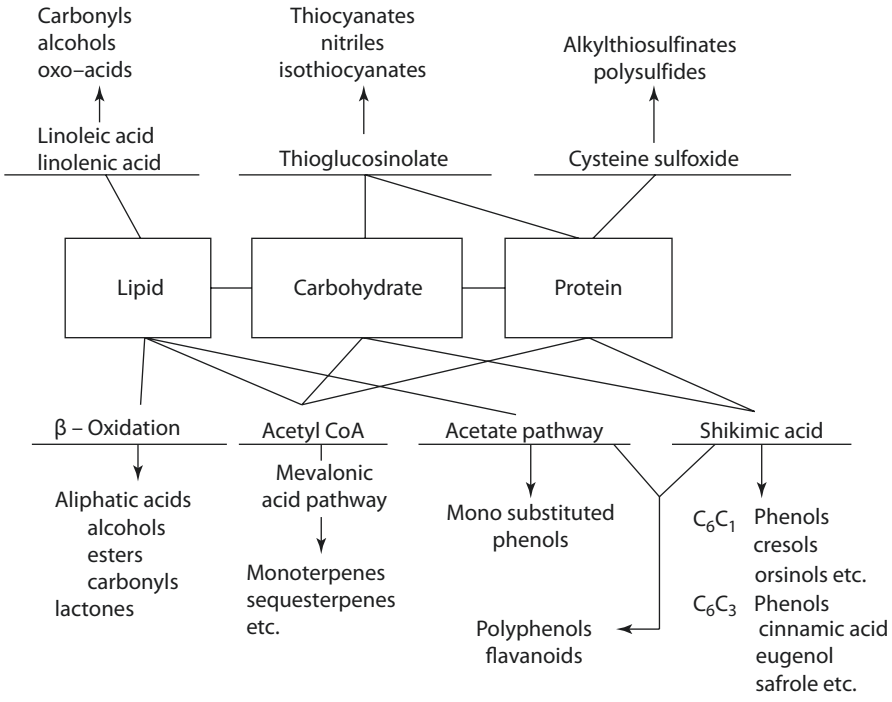
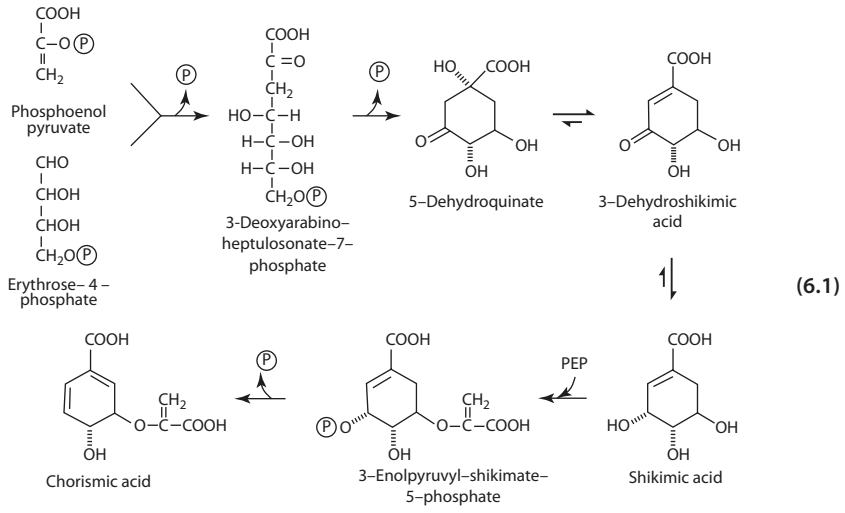


Fig. 6.6 Biosynthesis of flavor compounds

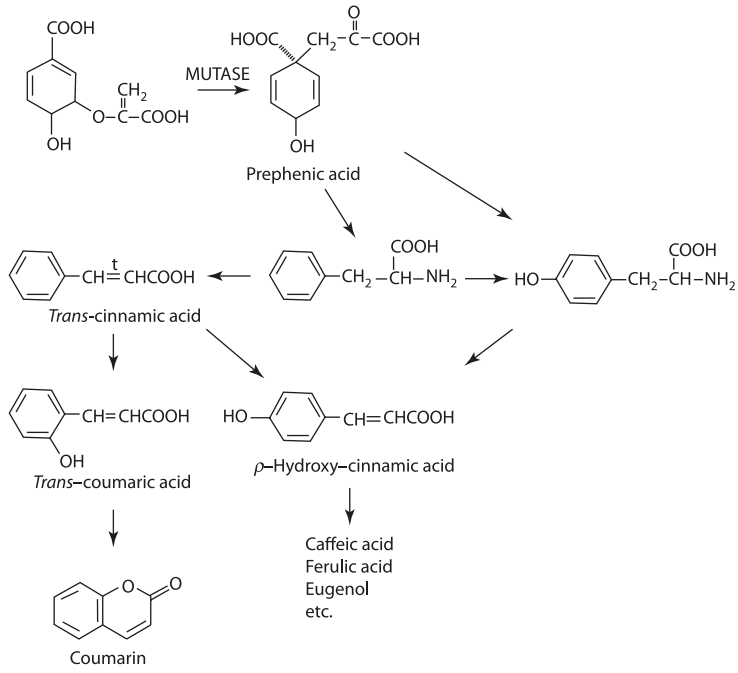
The Shikimic Pathway

The initial step is the condensation of phosphoenolpyruvate, an intermediate from glycolysis, and erythrose-4-phosphate (from the pentose phosphate pathway). The C7 product cyclizes and undergoes further dehydration and reduction to yield shikimic acid. Condensation with a second molecule of phosphoenolpyruvate yields chorismic acid (Eq. 6.1).



(6.1)

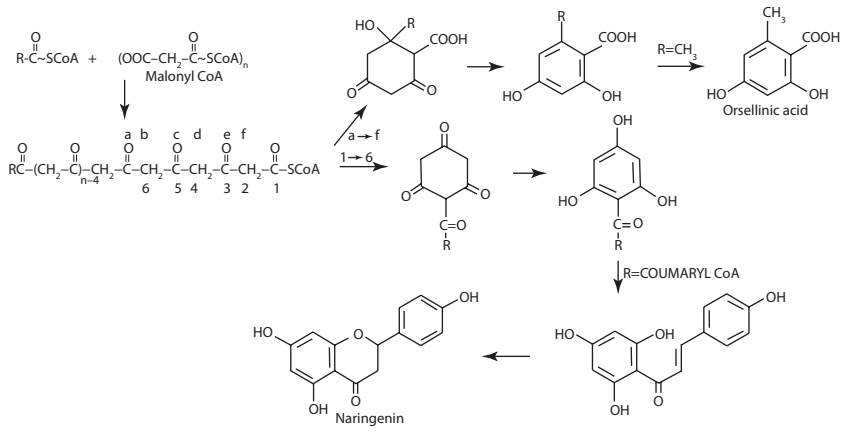
Chorismic acid is the precursor of the aromatic amino acids phenylalanine and tyrosine, which undergoes deamination to yield *trans*-cinnamic acid, the parent compound of many C6C3 phenolic compounds (Eq. 6.2)



(6.2)

The Polyketide Pathway

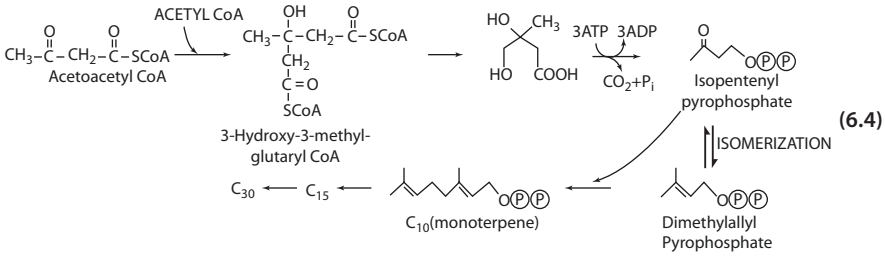
The main reaction involves the addition of malonyl CoA to acyl CoA. Successive additions of malonyl CoA extend the chain to give a ketide unit, which then cyclizes to form various phenolic compounds (Eq. 6.3). All phenols synthesized via the polyketide pathway are meta-substituted.



(6.3)

The Isoprene Pathway

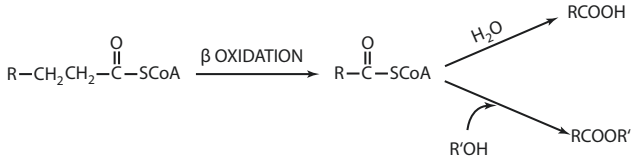
The isoprene pathway involves the condensation between acetyl CoA with the formation of mevalonic acid. Decarboxylation and phosphorylation of mevalonic acid gives isopentenyl pyrophosphate, which through self-condensation yields the terpenes (Eq. 6.4). Monoterpenes are usually volatile and odorous. Mevalonate is also the key intermediate in the synthesis of cholesterols.



(6.4)

β-Oxidation

Saturated fatty acids are degraded to short acyl chains by the β-oxidation pathway, which involves the reaction sequence of oxidation, hydration, oxidation, and hydrolysis (Eq. 6.5). This pathway gives rise to many of the naturally occurring acids, esters, and lactones.

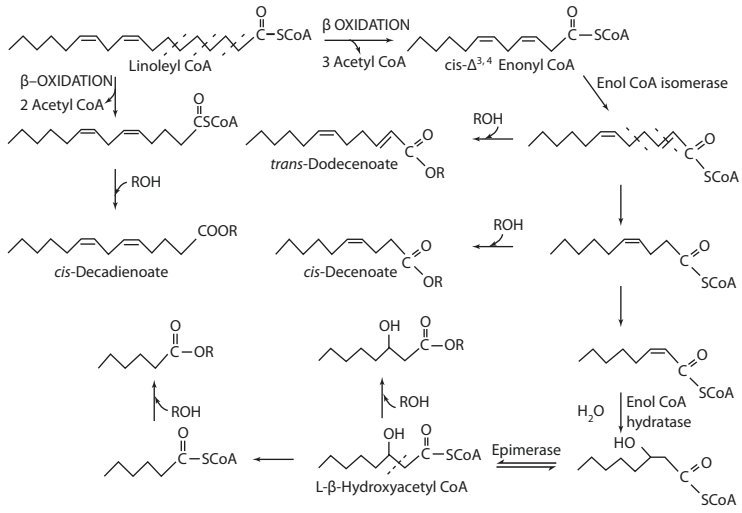


(6.5)

The oxidation of unsaturated fatty acids undergoes many reactions similar to those of saturated fatty acids. However, as is now well known, *cis*-Δ3,4 enonyl CoA is not a substrate for acyl CoA dehydrogenase. The position and configuration of the *cis*-Δ1,4 double bond must be isomerized in position and configuration. A similar rearrangement also occurs with the *cis*-Δ2,3 double bond (Eq. 6.6). Unsaturated fatty acids are the precursors of numerous unsaturated esters, which characterize various flavors in many food systems.

Lipoxygenase and Lipase

In plant tissues, lipid hydroperoxides are both enzymatically formed and decomposed (refer to ▶ Chap. 5), yielding specific aldehydes and corresponding alcohols. For example, the characteristic flavor of cucumber is due to 2-nonenal and 2,6-nonadienal and their alcohols. In tomatoes, *cis*-2-hexanal and *cis*-3-hexenal contribute to the fresh flavor. The flavor of green beans is partly due to 2-hexenal and 1-octen-3-ol. Hydrolysis of milk fat in milk by lipase is responsible for the development of rancid flavor.



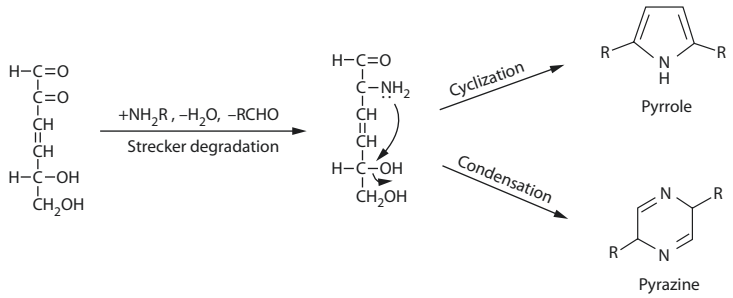
(6.6)

6.8.2 Chemical Reactions During Processing

The Maillard reaction occupies a unique position in the generation of flavor compounds in processed food products. The primary reactions have been described in ▶ Chap. 3 in connection with the chemistry of monosaccharides. Only the secondary reactions that are best understood and are significant in their contribution to flavors are presented here. Flavor products of the Maillard reaction include furans, pyrones, carbonyls, and acids from dehydration and/or fragmentation; and pyrroles, pyrazines, oxazoles, thiazoles, and sulfur compounds formed via the Strecker degradation, condensation, and further reactions. The reaction intermediates in the Maillard reaction that are responsible for generating flavor products are the dicarbonyl compounds. For simplicity, glucose is the aldohexose used in the following reaction schemes.

■■ Formation of Pyrrole and Pyrazine

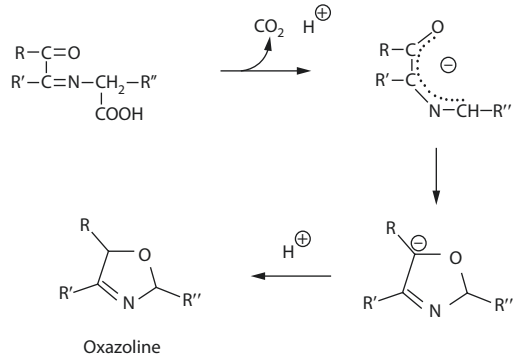
The 3-deoxyglycosulose and the unsaturated glycosulos-3-ene formed by 1,2-enolization of the amadori compound produce furfurals, pyrroles, and pyrazine derivatives. Formation of the latter two types of compounds is due to the Strecker degradation, where the heterocyclic nitrogen is derived from the α-amino acid. Pyrroles are formed by cyclization of the aminocarbonyl product of Streker degradation. Condensation of the aminocarbonyl compound followed by oxidation yields pyrazines (Eq. 6.7) [37].



(6.7)

Oxazoles and Derivatives

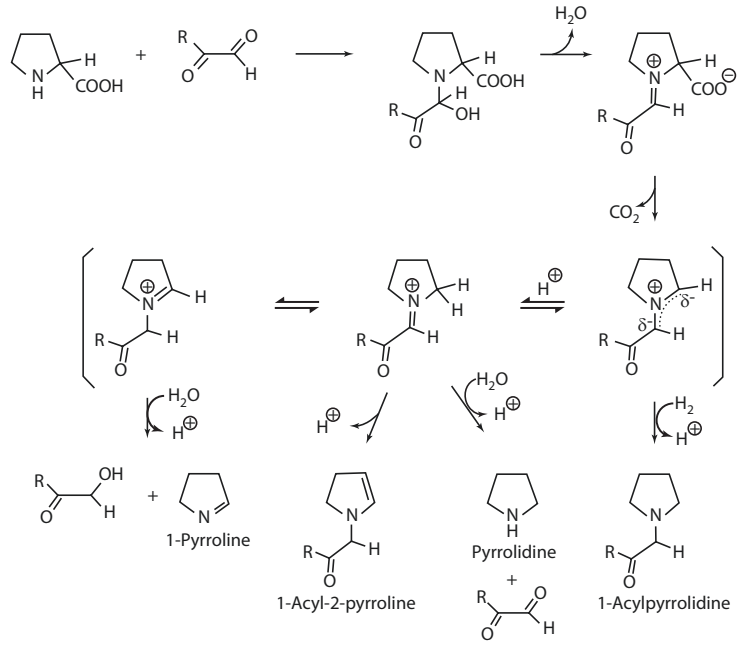
Oxazoline formation is favored when, in the reaction in Eq. 6.8, cyclization occurs before hydrolysis of the Schiff base, followed by protonation of the resulting oxazolidine ion (Eq. 6.8) [36].



(6.8)

Pyrrolines and Pyrrolidines

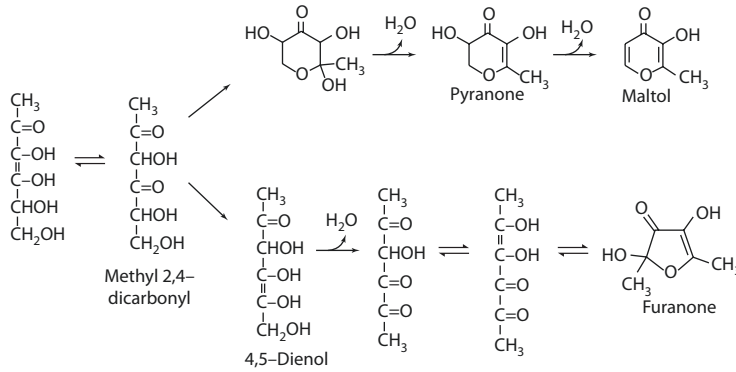
Both pyrrolines and pyrrolidines form via the Strecker degradation of proline with a dicarbonyl compound. Condensation of the aldehyde and the secondary amine forms an iminium carboxylate intermediate that is transformed by decarboxylation into a reactive ylide or iminiumion [48]. Further hydrolysis yields pyrroline and pyrrolidine, while reduction yields *N*-acylpyrrolidine (Eq. 6.9).



(6.9)

Formation of Pyrones

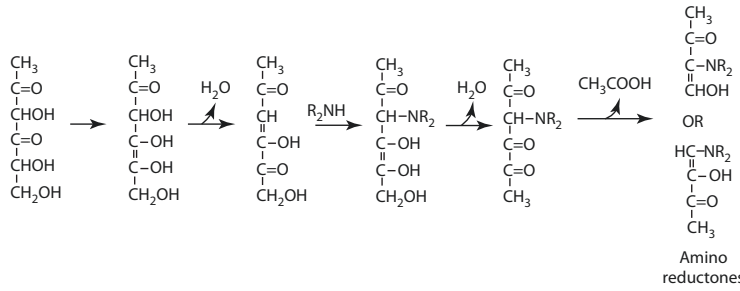
The methyl dicarbonyls formed via 2,3-enolization in the Maillard reaction may undergo cyclization, followed by degradation to yield pyrones [30]. They may also form the 4,5-dienol, which readily loses the C6–OH to produce a triketone. Ring closure of the 2,3-enolic form of triketone yields the furanone (Eq. 6.10).



(6.10)

Formation of Reductones

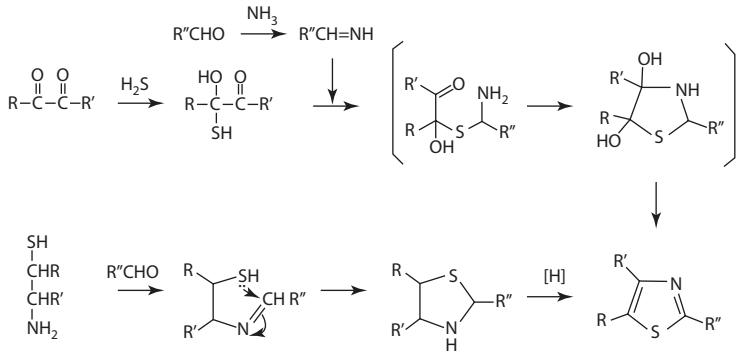
The 2,4-dicarbonyl may undergo allylic loss of a hydroxyl group at C3 to form the α,β-unsaturated intermediate, which reacts with amino derivatives to form amino triketone. Scission between C2–C3 or C4–C5 leads to the formation of amino reductones (Eq. 6.11).



(6.11)

Thiazole and Thiazoline

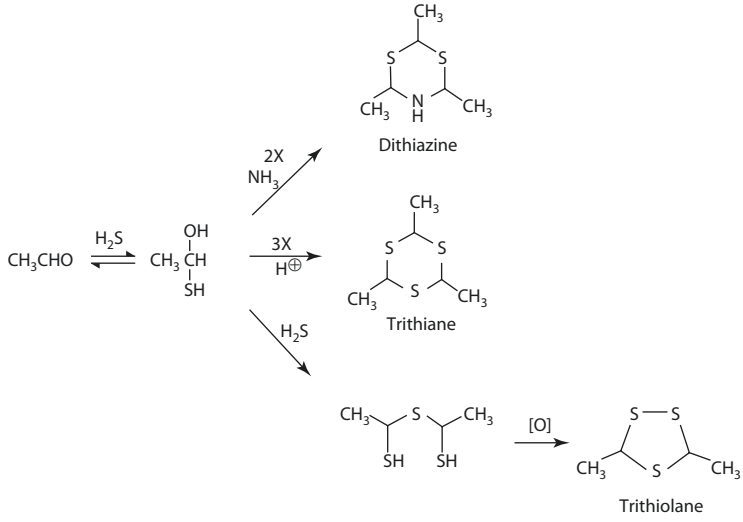
Dicarbonyls react with H_2S and NH_3 to form thiazole or thiazoline. Both H_2S and NH_3 are derived from the degradation of amino acids. Alternatively, the condensation of cysteine and a carbonyl compound, followed by cyclization, also yields a thiazole (Eq. 6.12) [43].



(6.12)

■■ Polysulfide Heterocyclic Compounds

Cyclic polysulfide compounds are found in cooked meat products. The formation of these products may result from the reaction of H_2S with aldehyde and ammonia via condensation reactions (Eq. 6.13).



(6.13)

■■ Lipid Degradation

Lipid degradation during food processing contributes a significant part in flavor formation, both desirable and undesirable. Numerous saturated and unsaturated acids, aldehydes, alcohols, ketones, esters, hydrocarbons, lactones, and aromatic compounds originate from the lipid constituents in food. These may be due to autoxidation, photosensitized oxidation, irradiation, thermal degradation, or enzymatic breakdown. All these processes have been covered ▶ Chaps. 2 and 5.

6.9 Beverage Flavor

6.9.1 Tea

The formation of flavor (and color as well) during the fermentation of tea leaves is related predominantly to the oxidation of phenolic compounds. The major reaction involves the oxidation of the flavanols catalyzed by catechol oxidase. The tea flavanols contribute 15–25% of the dry weight and are mostly tea catechins (which is a term commonly referring to both the catechins and their gallic acid esters)

In the catechin structure, there are two chiral centers in the molecule at C2 and C3, resulting in four stereoisomers: (1) the *trans* configuration: (+)-catechin (2*R*, 3*S*), and (−)-catechin (2*S*, 3*R*); and (2) the *cis* configuration: (+)-epicatechin (2*S*, 3*S*), and (−)-epicatechin (2*R*, 3*R*). The two isomers, (+)-catechin and (−)epicatechin, as well as their gallic acid conjugates (Fig. 6.7) are the main flavanols found in tea and cocoa. Catechins impart bitterness and astringency to green tea infusion. The content of these catechins are present in green tea, oolong tea, and black tea in the order of decreasing concentrations. In the production of oolong (semifermented) and black (fermented) tea, the catechins and gallate derivatives undergo controlled oxidation to form the typical characteristic color, strength, and body.

In tea leaf tissues, the flavanols (catechins) are enzymatically oxidized (by polyphenol oxidases) to the quinones, followed by condensation to form the dimer theaflavin and polymeric proanthocyanidin (thearubigins) (Eq. 6.14). The orange-red theaflavins are astringent and contribute to the distinct tea flavor known as "briskness" [39]. The oxidized flavanols (i.e., the quinones) interact further and cause oxidative degradation of other compounds in the tea leaf to generate numerous aroma compounds. Figure 6.8 shows

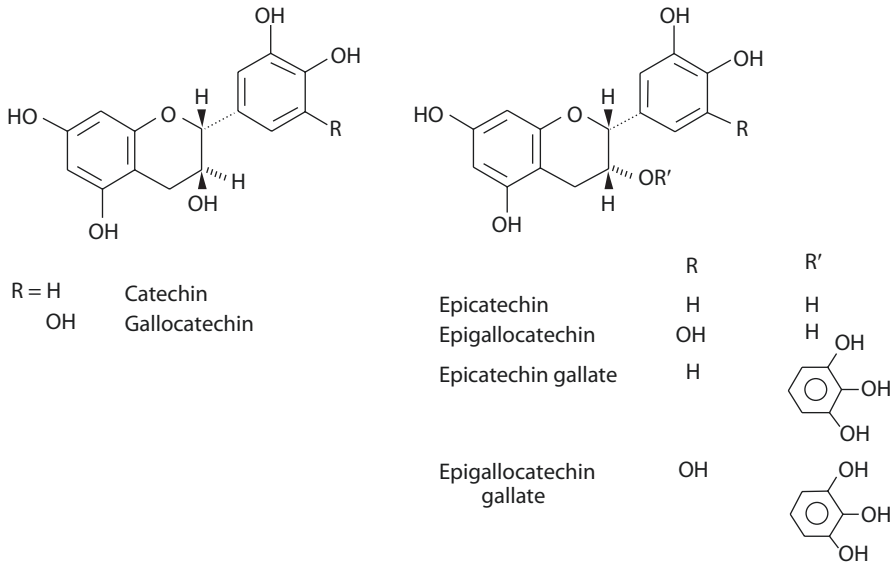
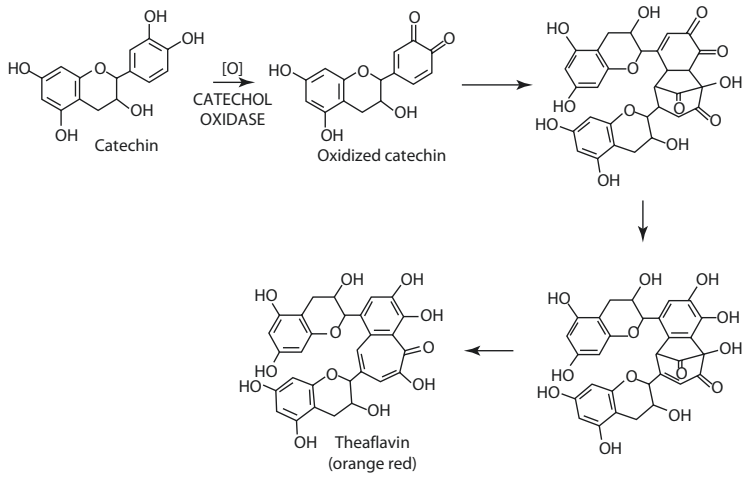


Fig. 6.7 Catechin and derivatives



(6.14)

the relationship between various oxidative changes of carotenoids, lipids, amino acids, and glycoside precursor induced by the oxidation of tea flavanols [38].

The major volatile aroma compounds in tea are β-damascenone (fruity) and ionones (woody) and their epoxy derivatives (Fig. 6.9a). β-Damascenone is an essential odor in black tea infusion, derived from the enzymatic oxidation of neoxanthin. β-Ionone derived from the oxidation of β-carotene contributes significantly to green and black tea.

Fatty acid-derived volatiles include saturated and unsatured C6 aldehydes and alcohols, such as *cis*-3-hexenol and *trans*-2-hexenal from α-linolenic acid, and n-hexanol from linoleic acid, which are known to contribute to the fresh green odor. Methyl jasmonate and its derivatives derived from α-linolenic impart the jasmine-like (floral, sweet) aroma in green and oolong tea (Fig. 6.9b).

During processing, the oxidized flavanols (the catechin quinones) react with amino acids to yield various aldehydes via the Strecker degradation. Isobutanal, 2-methylbutanal, isovaleraldehyde, and phenylacetaldehyde found to be present in fermented tea aroma are produced from the amino acids valine, isoleucine, leucine, and phenylalanine, respectively (Eq. 6.15).

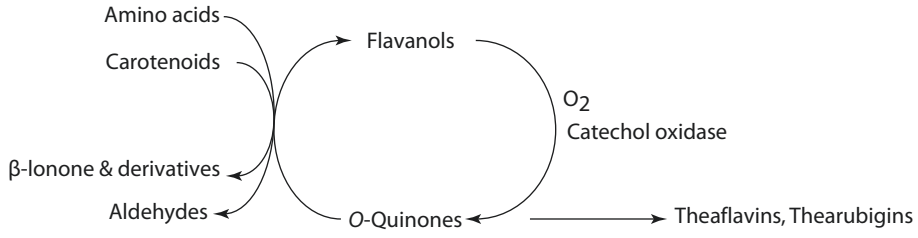


Fig. 6.8 Oxidative changes induced by the oxidation of tea flavanols

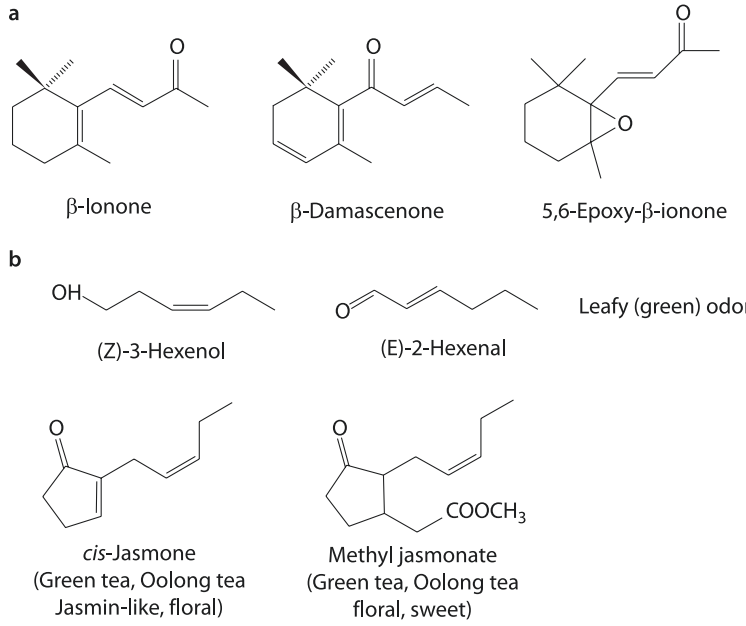
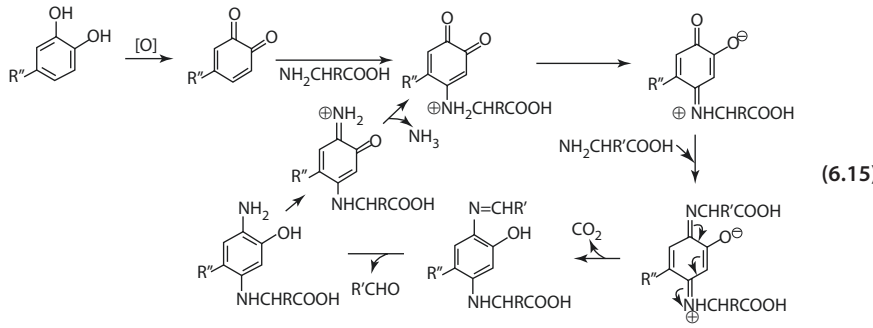


Fig. 6.9 Aroma compounds of tea derived from **a** carotenoids, and **b** lipids (Ho et al. [19])



(6.15)

Volatile compounds in tea occur not only in free forms, but some are derived from glycosidic precursors. The release of the free volatile compound from its glycosidic precursor requires the enzymatic action of glycosidases. The characteristic floral aroma of oolong and particularly black tea are due to the enzymatic release of geraniol (sweety green), linalool (floral, citrus like), and linalool oxides (sweet floral, fruity) from their glycoside precursors (Fig. 6.10).

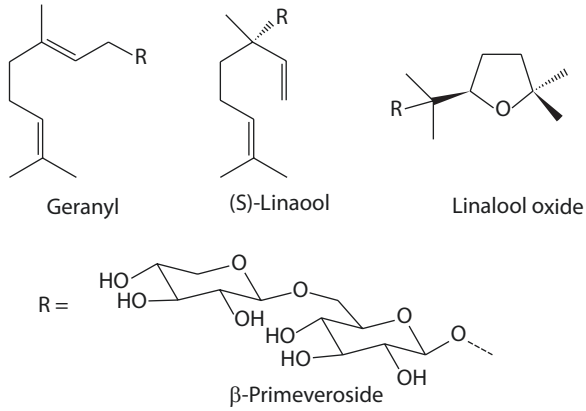


Fig. 6.10 Tea aroma compounds released from glycoside precursors

6.9.2 Beer

The characteristic bitter note in beer is ascribed to hop "resins." Hop resins are classified into soft (soluble in water) and hard (insoluble in hexane). Soft resins include α-acids (humulone, cohumulone, adhumulone) and β-acids (lupulone, colupulone, adlupulone (Fig. 6.11).

In the brewing process, the α-acids isomerize into iso-α-acids, which possess a bitter taste. Isomerization of an α-acid produces two pairs of stereoisomers as indicated for humulone in Fig. 6.11.

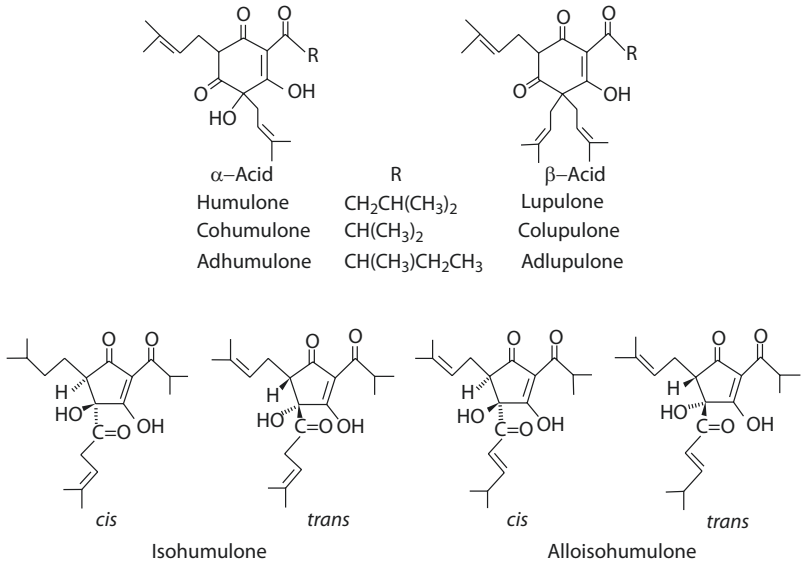
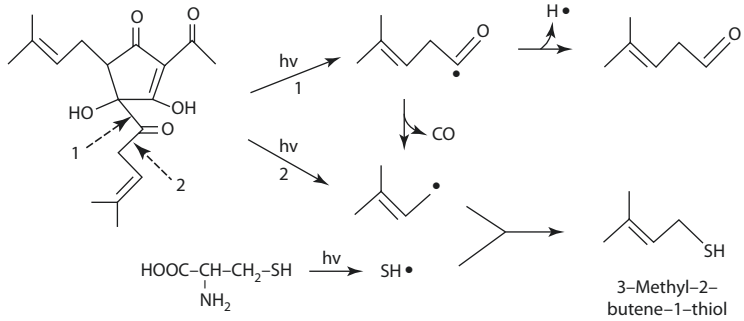


Fig. 6.11 α-Acids and β-acids in hop resins

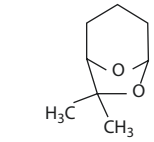
Beer, when exposed to sunlight, develops an unpleasant sulfur odor, termed "sunstruck" flavor. Its formation has been attributed to 2-methyl-2-butene-1-thiol, which is derived from the photolysis of hop-derived bitter iso-α-acids in the presence of sulfur-containing amino acids [17] (Eq. 6.16).



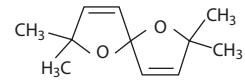
(6.16)

The characteristic hop flavor in beer is due to the transfer of some essential oil-derived compounds to beer. More than 100 aroma constituents have been identified, including esters, ketones, alcohols, ethers, terpenoids, and sesquiterpenoids. The cyclic esters and the oxygenated sesquiterpenoids are constituents with a strong hop aroma. The esters have predominantly bicyclic structures, and the sesquiterpenoids have either an epoxide or a hydroxyl constituent [47]. A few examples are given in Fig. 6.12.

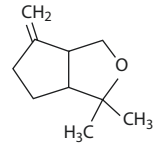
Fig. 6.12 Cyclic esters present in hop flavor



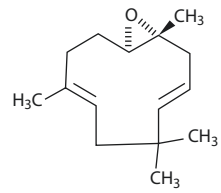
7,7 - Dimethyl - 6,8 - dioxabicyclo [3.2.1] octane



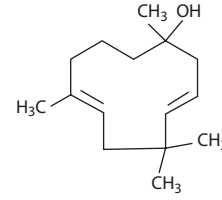
2,2,7,7 - Tetramethyl - 1,6 - dioxaspiro [4.4] nona - 3,8 - diene



Hop ether



Humulene epoxide



Humulol

6.9.3 Coffee

More than 1000 compounds have been identified in roasted coffee. The aroma in roasted ground coffee is derived from a complex collection of many volatile compounds. The potent ones include: (1) sulfur-containing compounds, (2) alkyl pyrazines, (3) furanones, (4) aldehydes and dicarbonyls, and (5) phenolics. The chemical structures of some examples are presented in Fig. 6.13. In coffee brews, the aroma change (from that of the roasted ground coffee) is caused by a shift in the concentrations of the odorants due to hot water extraction and not by the appearance of new potent odorants.

The significant contributions of sulfur-substituted furans have been characterized in green and roasted coffee. The compound 2-furylmethanethiol (2-furfurylthiol) has long been considered a character-impact compound of roasted coffee [45]. The threshold is 0.01 ppb in water, and at concentrations of 0.1–5 ppb, the compound has the aroma of roasted coffee. At increasing concentrations (as occurred during storage of roasted coffee beans), it develops a strong sulfur odor.

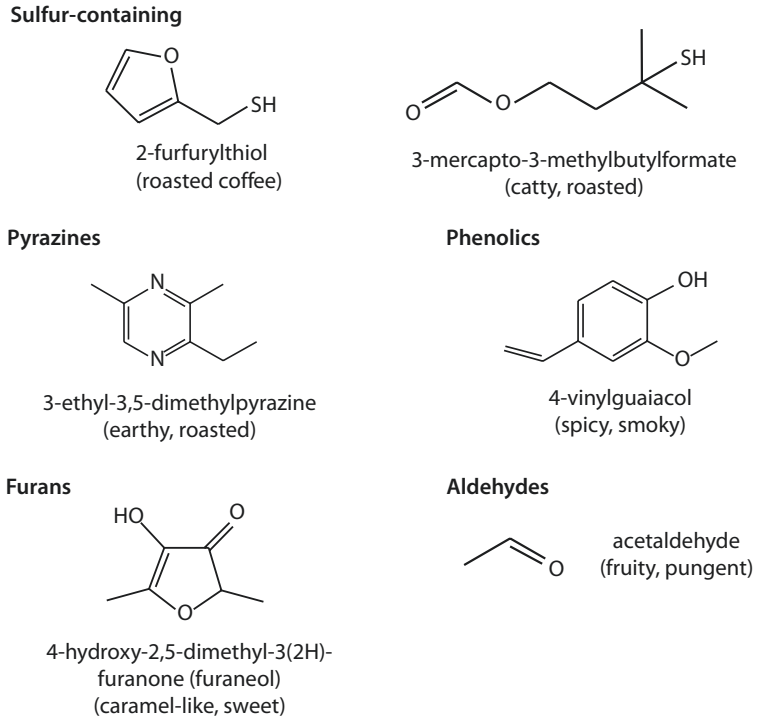
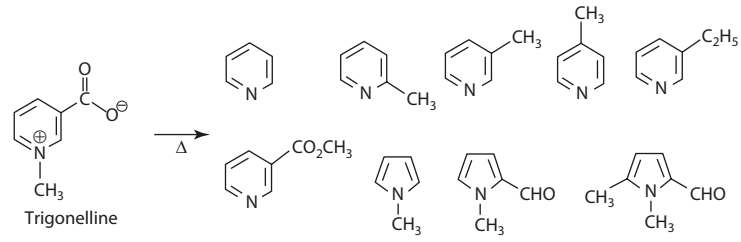


Fig. 6.13 Some volatile compounds in roasted coffee

Nonvolatiles may also be important contributors to the flavor of coffee beverages after roasting. The compound worth mentioning is trigonelline, which is present at a 1% level in coffee beans. Unlike caffeine, which is thermally stable, trigonelline decomposes readily at roasting temperatures to give a series of aroma compounds, pyridines and pyrroles [5] (Eq. 6.17).



(6.17)

The "acid" flavor in coffee is caused by the presence of organic acids. Phenolic acids, in particular, average about 7.5% total dry weight in coffee beans. The major phenolic acids belong to a family of chlorogenic acids (Fig. 6.14), which are esters formed between cinnamic acids (caffeic, ferulic, *p*-coumaric) with quinic acid. Esterification may occur at the hydroxyl groups at C3, C4, and C5. Diesters are also formed. The most abundant chlorogenic acid in coffee beans is 5-caffeoylquinic acid (commonly called chlorogenic acid). Chlorogenic acid confers astringent, bitter, and acid flavors to the coffee brew.

Aside from taste and smell, the most attractive ingredient is caffeine, a methylxanthine with bitter characteristics. Caffeine acts as a stimulant by binding to and blocking the

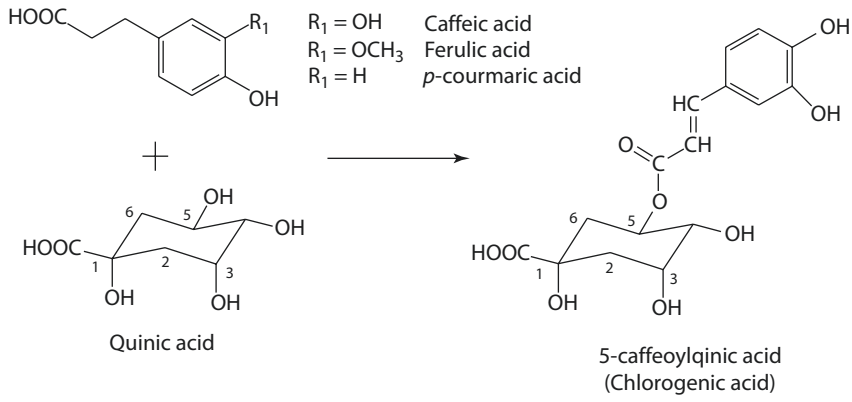
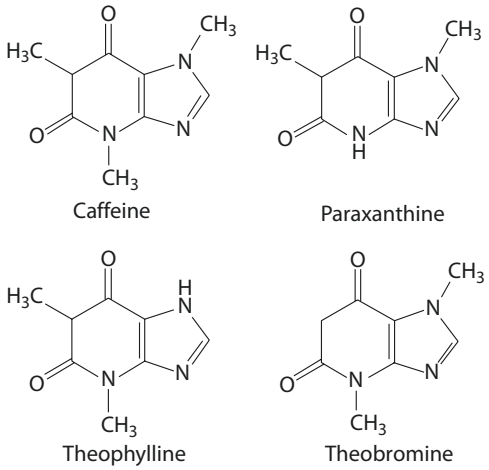


Fig. 6.14 Phenolic compounds contributing to the "acid" flavor of coffee

Fig. 6.15 Caffeine and its metabolites



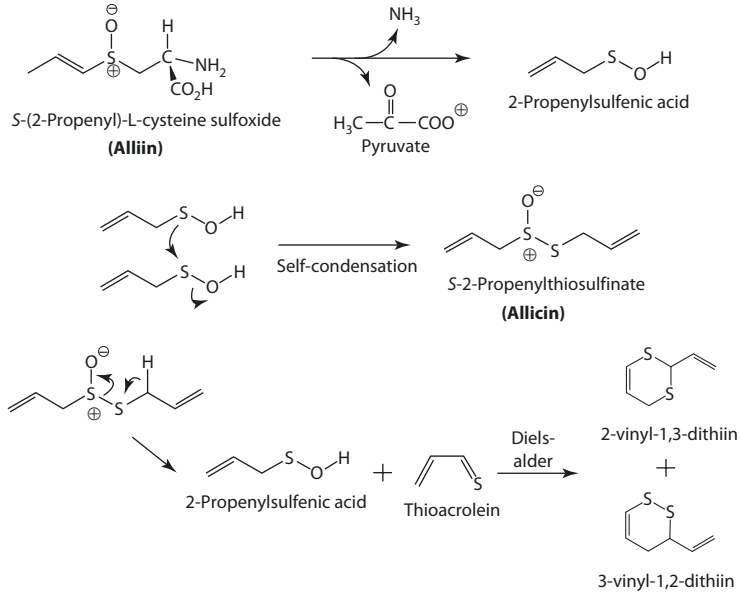
adenosine receptors from interactions involved in nerve cell activities in the brain and the heart. The primary metabolites of caffeine include paraxanthine, theophylline, and theobromine, each of which has its own physiological effects on the body (Fig. 6.15).

6.10 Spice Flavor

In food processing, spices are often applied in the form of essential oils or oleoresins. Essential oils are prepared by water and steam distillation of the dried ground spices. The oil contains the volatile flavor compounds. Oleoresins are extracts of freshly ground spices. The ground spice is repeatedly extracted with an organic solvent that is eventually removed to give a product that consists of volatile essential oil, nonvolatile resinous materials, and the active principle characteristics of the spice.

6.10.1 Garlic and Onion

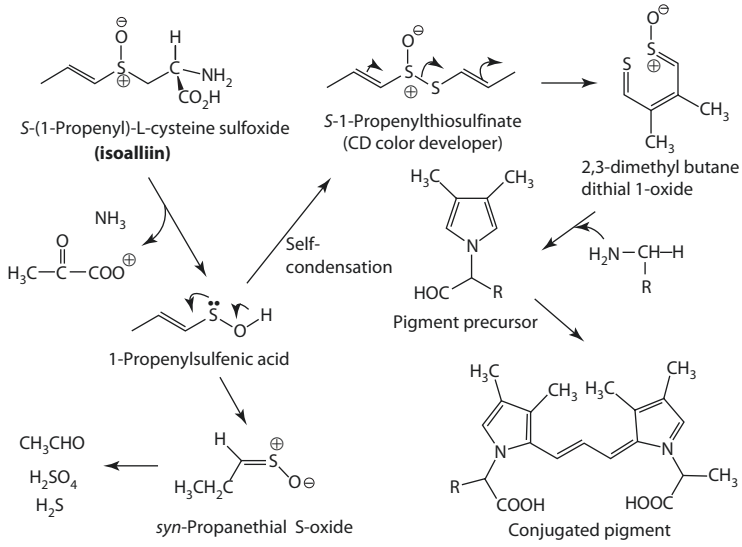
The odor of garlic is derived from *S*-2-propenylthiosulfinate (allicin). The odor develops only when the garlic is cut or crushed. The enzyme alliinase (EC 4.4.1.4, pyridoxal 5′-phosphate dependent α,β-eliminating lyase) present in the cell vacuole comes in contact with the odorless substrate, *S*-(2-propenyl)-L-cysteine sulfoxide (alliin) in the cytosol. The resulting product is 2-propenesulfenic acid (Eq. 6.18.1), which then dimerizes (self-condensation) to form allicin (Eq. 6.18.2). Allicin readily decomposes to 2-propenesulfenic acid and thioacrolein. The latter self-condenses via a Diels-Alder reaction to form cyclic sulfur compounds (Eq. 6.18.3) [5, 6].



(6.18)

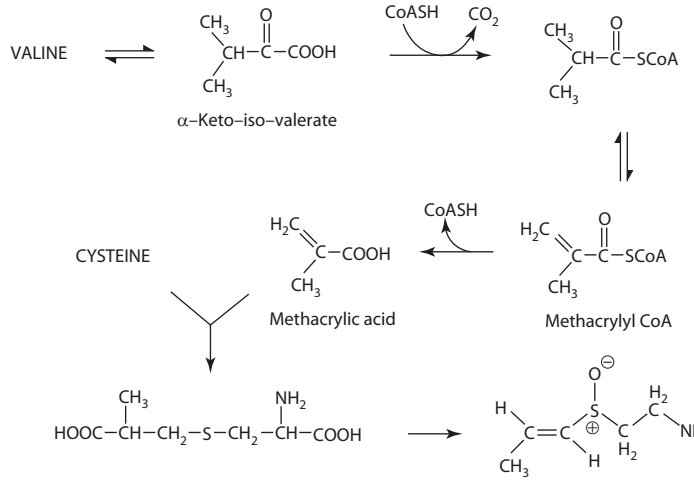
6

In onion, the precursor is *S*-(1-propenyl)-L-cysteine sulfoxide (isoalliin), a positional isomer of alliin. Garlic also contains isoalliin as a minor metabolite, but with increased concentration upon storage. The alliinase in onion converts isoalliin into 1-propenesulfenic acid, which rearranges to form *syn*-propanethial-*S*-oxide, the lacrimatory factor that causes the eye to tear. The oxide readily hydrolyzes to yield propionaldehyde and hydrogen sulfide (Eq. 6.19). The 1-propensulfenic acid can also dimerize to form *S*-1-propenylthiosulfinate, a key compound involved in allium discoloration (Eq. 6.19).



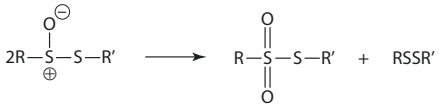
(6.19)

The flavor precursor, *S*-(1-propenyl)cysteine sulfoxide, is biosynthetically derived from valine and cysteine (Eq. 6.20). In nature, as much as half of the precursor is bound as a peptide, γ-L-glutamyl-*S*-allylcysteine sulfoxide. The peptide is not susceptible to the action of alliinase. The enzyme γ-glutamyl transpeptidase is required for the formation of the alk(en)yl cysteine sulfoxide.



(6.20)

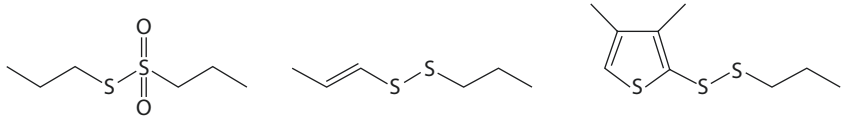
Many other compounds, including sulfides (mono-, di-, tri-, and tetra-), thiophenes, and thiosulfonates, found in the essential oils also contribute to the flavor [7]. Disulfides and thiosulfonates are formed by disproportionation of the unstable thiosulfinates (allicin is an alkenyl thiosulfinate) (Eq. 6.21). Thiosulfonates with four or more carbon atoms possess the distinct odor of freshly cut onions. Propyl and propenyl di- and tri-sulfides possess cooked-onion flavor.



(6.21)

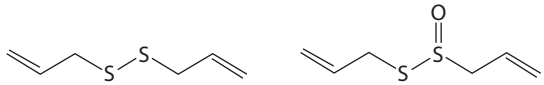
The character-impact compounds of onion and garlic are primarily sulfur-containing molecules (Fig. 6.16). In raw, fresh onion, the aroma contributors are propyl propanethiosulfinate, propenyl propanethiosulfinate, thiopropanal *S*-oxide, and propyl methanethiosulfinate. For cooked onion, dipropyl disulfide and 1-propenyl propyl disulfide are the potent aroma compounds. The distinct fried onion aroma is characterized by 2-(propyldithiol)-3,4-dimethylthiophene with a threshold of 10–50 ppm in water. For garlic, di-2-propenyl disulfide and the corresponding diallylthiosulfinate (allicin) are character-impact compounds. Thiophenes are formed, along with mono- and tri-sulfides, from the decomposition of alkyl and alkenyl disulfides (Eq. 6.22).

a Character-impact aroma compounds of onion



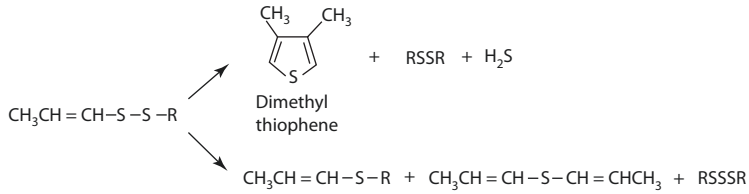
Propyl propanethiosulfonate (raw onion) | 1- Propenyl propyl disulfide (cooked onion) | 2-(propyldithiol)-3,4-dimethyl-thiophene(fried onion)

b Character-impact aroma compounds of garlic



Diallyl disulfide | Diallyl thiosulfonate

Fig. 6.16 Some character-impact compounds of onion and garlic



(6.22)

Discoloration in processed garlic and onion, such as maceration in the production of powder, puree, or paste, occurs slowly when in storage, and more quickly at low temperature and acidic pH. The development of pink-red color (pinking or reddening) in onion and green-blue color (greening) in garlic involves mainly 1-propenyl-containing thiosulfinates (such as *S*-1-propenylthiosulfinate) (Eq. 6.19). The thiosulfinate reacts with amino acids to form pyrrole compounds, as pigment precursors [21].

The pigment precursor molecules are crosslinked by reacting with carbonyl compounds (such as pyruvate, formaldehyde, acetaldehyde, propionaldehyde, acrolein, allicin, etc.). The colored pigment may be di, tri, tetra, and polypyrrole compounds. The color depends on (1) the structure of the 1-propenyl-containing thiosulfinate, (2) structure of the amino acid side groups, (3) the carbonyl compound, and (3) the degree of oligomeric crosslink.

6.10.2 Black Pepper

Pepper (*Piper nigrum* L.) oleoresin contains the pungent alkaloid piperine: 5-(3,4-methylenedioxyphenyl)-2,4-*trans*,*trans*-pentadienoic acid. Geomeric isomers of piperine are found to be present; however, only the *trans*, *trans*-piperine has a strong pungent taste. Other piperamides, such as piperyline and piperettine, with higher threshold concentrations for pungency have also been identified (Fig. 6.17). On average, the total piperamide content (40–50 mg/100 g) of peppers consists of 84% piperines and 16% other piperamides [13].

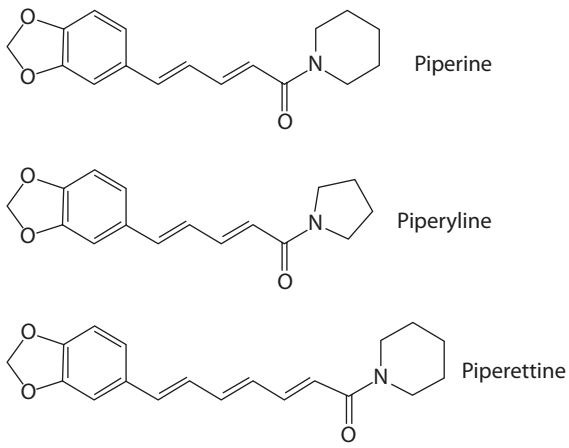
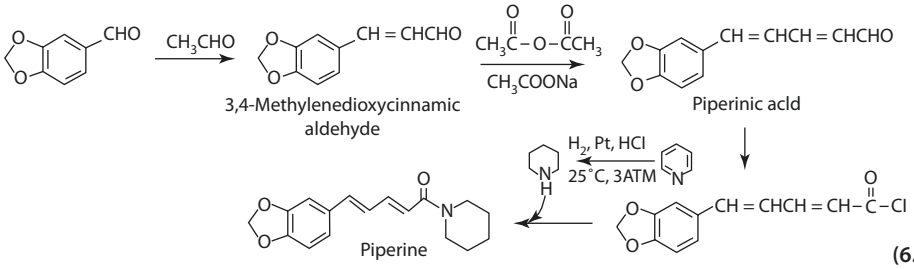


Fig. 6.17 Piperines and piperamides

Piperine can be synthesized by the aldol condensation of piperonal with acetaldehyde. Further reaction with acetic anhydride yields piperinic acid, which then reacts with an acid chloride to yield the piperine [16] (Eq. 6.23).



(6.23)

Rotundone, a sesquiterpene, has been identified as a character-impact compound with a strong, spicy peppery aroma (Fig. 6.18). Its concentration reaches 1.2 ppm and 2.0 ppm in black and white pepper, respectively [40].

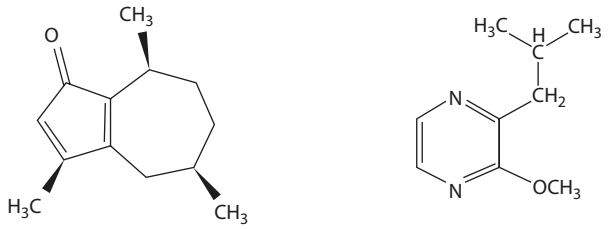


Fig. 6.18 Character-impact aroma compounds of pepper

6.10.3 Hot Pepper

Mild and hot peppers belong to the genus *Capsicum*. The common domesticated species include: *C. annuum* (cayenne or red chili pepper, jalapeno), *C. chinense* (habanero or yellow-lantern chili), and *C. frutescens* (variety tabasco). Bell peppers, also belong to *C. annuum*, but do not have the "hot" taste associated with hot peppers.

The "hot" taste is due to the presence of the nonvolatile compound capsicum, which is attributed mainly to a class of alkaloid compound collectively known as capsaicinoids [44] (Fig. 6.19). Synthetically, capsaicinoids can be made by reacting vanillyl amide with an acid chloride (Eq. 6.24).

The aroma profiles of both red chili pepper and green bell pepper suggest that 2-isobutyl-3-methoxypyrazine process a characteristic pepper-like note, with a very low detection threshold of 2 ppt in water (Fig. 6.18) [9]. 2-Heptanethiol has also been identified to produce bell pepper-like smell, with thresholds of 3 ppm [41].

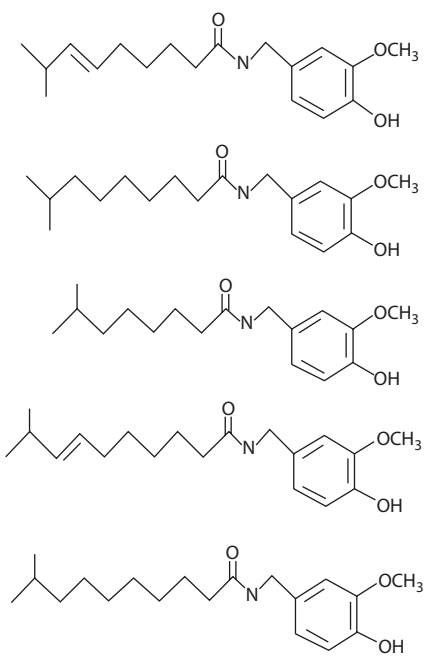
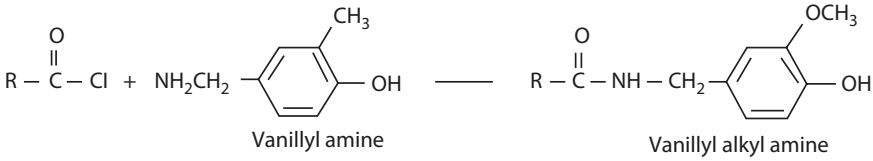
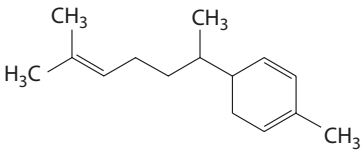


Fig. 6.19 Capsaicinoids and their pungency thresholds



(6.24)

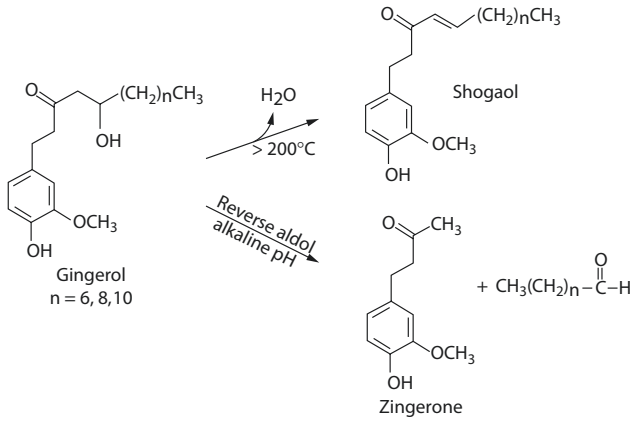
Fig. 6.20 Zingiberene



6.10.4 Ginger

Ginger (*Zingiber officinale* Roscoe) is a fibrous-rooted perennial plant. The oil and oleoresin are obtained from the rhizome. The essential oil is made up largely of terpenoids (4% monoterpenes, 63% sesquiterpenes, and 17% of terpene alcohols). Zingiberene is the most abundant sesquiterpene, making up to 30% of the root's essential oil (Fig. 6.20).

The pungent substance in the ginger oleoresin is gingerol, with the amount present in older ginger twice that in green ginger. The aliphatic chain in the structure may range from 6, 8, 10 carbons, but [6]-gingerol is the major form. Gingerols are thermally labile due to the presence of a β-hydroxy-keto function. Gingerol undergoes dehydration to shogaol or reverse aldol reaction to zingerone and aldehyde (Eq. 6.25). The former reaction is accelerated by alkaline pH, and the latter reaction occurs at a high temperature [12]. Both zingerone and shogaol are less pungent than gingerol. The aliphatic aldehyde causes the formation of off-flavors. These undesirable changes occur rarely in fresh ginger but more often in preparing and storing the oleoresin.



(6.25)

6.10.5 Peppermint

Peppermint oil is obtained from *Mentha piperita* plants. The important aroma constituents are the monocyclic monoterpenoids, menthol (50–60%), and to a lesser extent, menthone and menthofuran (Fig. 6.21).

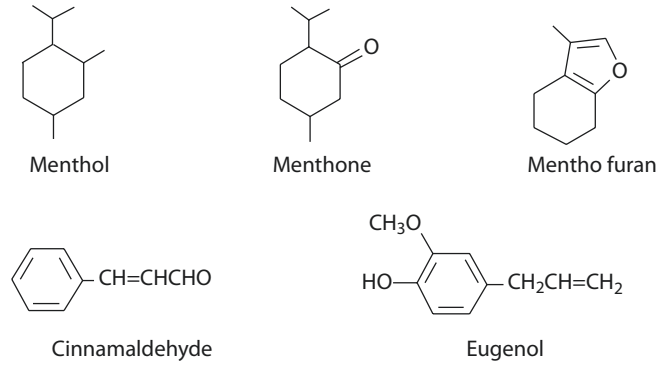


Fig. 6.21 Flavor compounds in peppermint and cinnamon

6.10.6 Cinnamon

The spice cinnamon is obtained from commercial species *Cinnamomun cassia* (China) and *C. zeylanicum* Blume (Ceylon). The traditional commercial cinnamon is the "quills" – rolled pieces of peeled bark. Essential oils are produced by distillation of bark oil or leaf oil. Cinnamaldehyde and eugenol are two main flavor compounds in the oil (Fig. 6.21).

6.11 Fruits and Vegetables

The most important category of flavor ingredients obtained from fruits, especially citrus, is included in the essential oils. An essential oil is an oil substance obtained from a plant material, and it retains the characteristic flavor of that material.

There are two common processes for the production of essential oils of citrus fruits. Most of the oil is found in the rind of the fruit. Citrus fruits that contain high concentrations of essential oil (>3%) include orange, lemon, lime, tangerine, mandarin, and grapefruit. Commercially, the oil is obtained as a byproduct of fruit juice production. When juice is pressed from the fruit, the oil is also carried through. It is removed by centrifugation and becomes what is known as cold-pressed peel oil. The essential oils used in industry are the distilled oil obtained as a by-product of various types of essence recovery processes.

The natural essence of citrus fruits is obtained when the fruit juice is concentrated in high-temperature evaporators. Approximately 25% of the juice water is removed. The volatile flavors carried in the vapor are recovered and concentrated in the essence units (fractionation stills with condensers). The flavor components collected are separable into an aqueous (aroma) and oil phase (essential oil). Essence is a common name that includes fractions of both aroma and essence oil. Since essence oil is distilled oil, it lacks the nonvolatile components and, therefore, many natural antioxidants found in cold-pressed oils. For this reason, essence oil is relatively less stable than cold-pressed oil.

6.11.1 Fruit Flavor

Citrus essential oils consist mainly of aldehydes, ketones, esters, alcohols, and acids (Table 6.3). Many of these are isoprenoids, with smaller amount of phenylpropanoids or short-chain aliphatics and their derivatives.

Table 6.3 Components of orange (valencia) oil

Compound	Concentration
Ethanol	0.1%
Ethyl acetate	50 ppm
Acetal	20 ppm
Hexanal	200 ppm
Ethyl butyrate	0.1%
Trans-2-hexenal	50 ppm
α-Pinene	0.4%
Sabinene	0.4%
Myrcene	1.8%
Octanal	0.5%
δ-Limonene	93.6%
Linalool	0.5%
Decanal	0.6%
Neral	0.2%
Geranial	0.1%
Valencene	1.7%

From Johnson and Vora [22]

The cyclic terpene δ-limonene is one of the abundant constituents (~90%) present in oranges and other citrus oils. It possesses the flavor characteristic of lemon, orange, and caraway [22]. Another major sesquiterpene present in orange oil is valencene (1–2%). Nootkatone, the character-impact compound of grapefruit, is chemically synthesized from valencene (Fig. 6.22). Another compound, α-*p*-menthene-8-thiol, has been

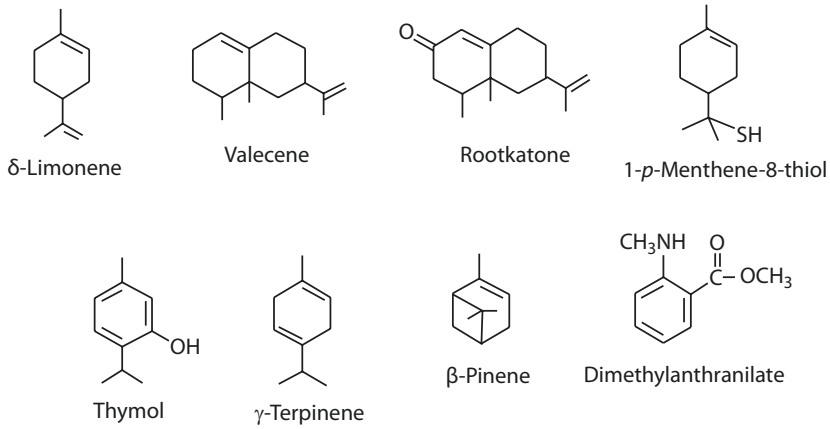


Fig. 6.22 Isoprenoids in fruit flavor

Table 6.4 Major components of tangerine and mandarin oil

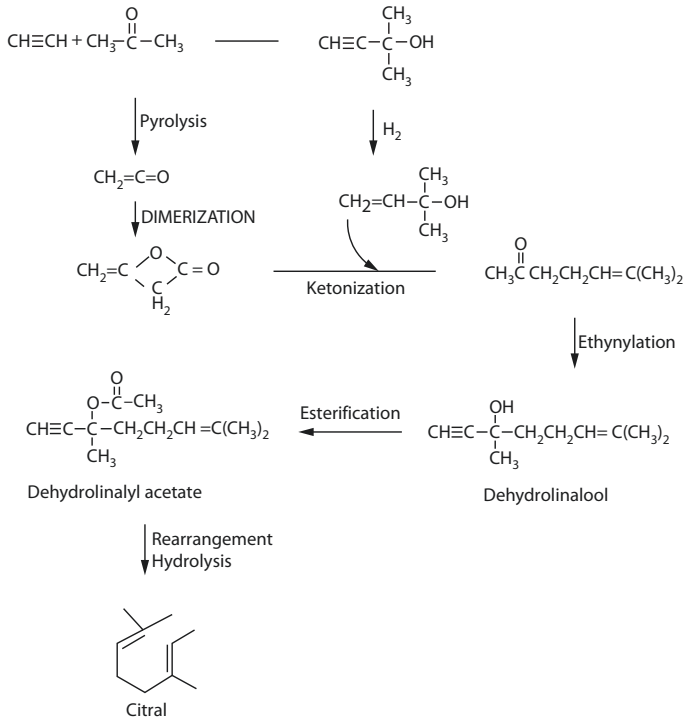
Component	Tangerine oil (WT%)	Mandarin oil (WT%)
Thymol	0.022	0.182
Methyl-*N*-methylanthranilate	0.072	0.652
γ-Terpinene	1.74	14.0
β-Pinene	0.17	1.8

From Wilson and Shaw [51]

isolated which also displays a character aroma of fresh grapefruit juice. Its flavor threshold is in the range of 1×10^{-4} ppb in water, among the lowest detection thresholds for naturally occurring flavor compounds [14].

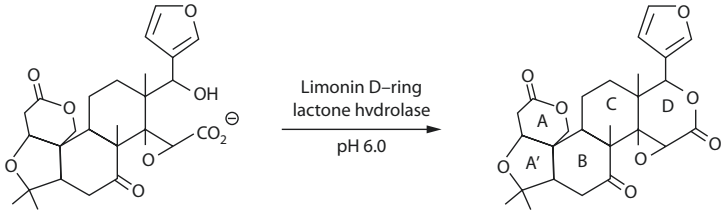
Essential oils of tangerine and mandarin contain thymol, dimethylanthranilate, γ-terpinene, and β-pinene (Table 6.4). The latter two compounds are shown to contribute to the flavor of mandarin oranges as distinct from other oranges [51].

Citral, a terpene aldehyde with a powerful lemon flavor, is present in the essential oils of lemon, lemon grass, and lime. Citral is commercially synthesized from acetylene and acetone (Eq. 6.26).



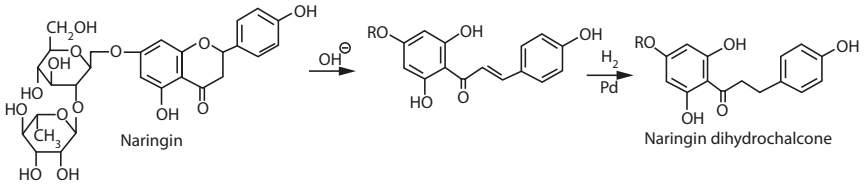
(6.26)

The bitterness of citrus fruits is ascribed to flavonoid compounds, especially naringin and limonin. Limonin belongs to a class of triterpene derivatives known as limonoids. It consists of two lactone rings, one of which has a furan substituent and an epoxide group. Limonin is the cause of the problem known as delayed bitterness, in which citrus fruit juice turns bitter after extraction. This is due to the conversion of the major natural limonoate A-ring lactone to limonin catalyzed by the enzyme limonin D-ring lactone hydrolase [18] (Eq. 6.27).



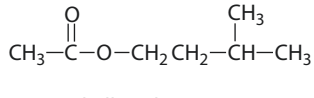
(6.27)

Another bitter compound is naringin, a flavanone neohesperidoside. The aglycone part is the flavanone naringentin, and the disaccharide part is neohesperidose, which is 2-*O*-α-L-rhamnosyl-β-D-glucose [20]. Alkaline hydrolysis of naringin converts it to the intensely sweet dihydrochalcone (Eq. 6.28). (See ▶ Chap. 7 for a detailed discussion.)

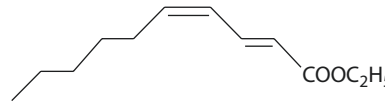


(6.28)

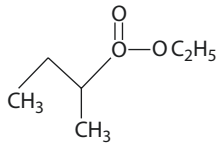
The typical flavor compounds of noncitrus fruits such as banana, pears, peaches, and apples are produced during the climacteric rise. Many aliphatic acids and amino acids in the unripe fruit are converted to esters, alcohols, and ethers that are mostly responsible for the characteristic fruit odor [33]. Esters, especially acetates and butyrates, are most abundant in bananas, and so are some phenol ethers. The main component that gives a banana aroma is isobutyl acetate (Fig. 6.23). In Barlett pears, ethyl *trans*-2-*cis*-4-decandienoate is identified as the important flavor compound. Ethyl 2-methylbutyrate in apple, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone in pineapple and strawberry, and γ-decalactone in peaches are some more examples of character-impact compounds.



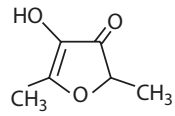
3-Methylbutyl acetate



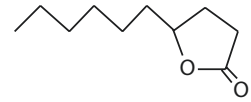
Ethyl trans - 2 - cis - 4 - decadienoate



Ethyl 2-methylbutyrate



2,5-Dimethyl-4-hydroxy-3(2H)-furanone



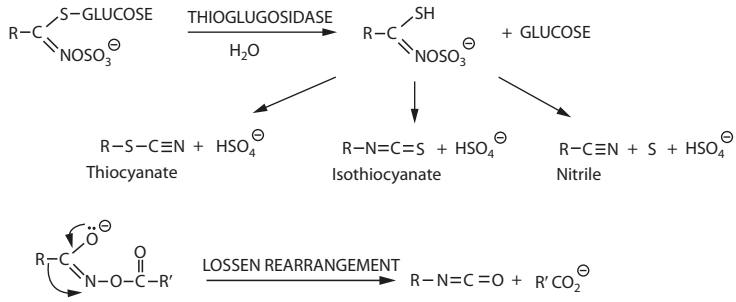
γ - Decalactone

Fig. 6.23 Character-impact compounds in some noncitrous fruits

6.11.2 Vegetables

Cruciferous vegetables, such as cabbage, cauliflower, brussels sprouts, turnips, and mustards, contain glucosinolates that can be enzymatically degraded to yield the pungent sulfur compound isothiocyanate.

The formation of isothiocyanate involves a process similar to the Lossen rearrangement in which the alkyl group of a hydroxamic acid salt migrates from the carbon to the nitrogen (Eq. 6.29) (See ▶ Chap. 8).



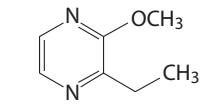
(6.29)

More than 90 glucosinolates have been identified. Some of the more important ones are listed in Table 6.5 (with only the side group R shown).

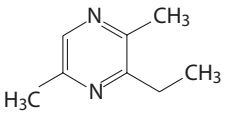
Alkoxyalkylpyrazines are widespread in vegetables, especially in pea, pepper, bean, asparagus, beetroot, carrot, and lettuce. These compounds possess a notably green odor. Bell pepper contains 20,000 ppm of 3-isobutyl-2-methoxypyrazine and 1400 ppm of 3-isopropyl-2-methoxypyrazine (Fig. 6.18) [42].

Table 6.5 Structures and occurrence of selected glucosinolates

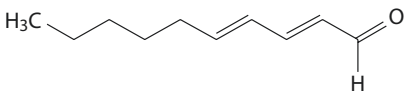
Side chain	Glucosinate (common name)	Occurrence
CH_2=CHCH_2–	Sinigrin	Brown or black mustard
HO–⟨⟩–CH_2–	Sinalbin	White mustard
OH CH_2= CHCH_2–	Progoitrin	Turnip
CH_2–⟨⟩N H	Glucobrassicin	Cabbage



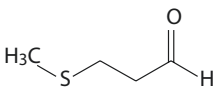
2-Ethyl-3-methoxypyrazine



2-Ethyl-3,6-dimethylpyrazine



(E,E)-2,4-decadienal

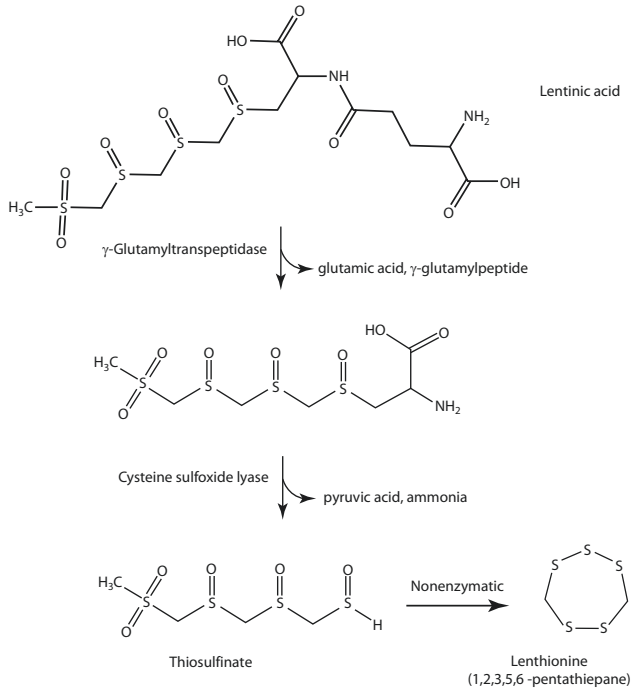


Methional

Fig. 6.24 Aroma compounds in raw and processed potatoes

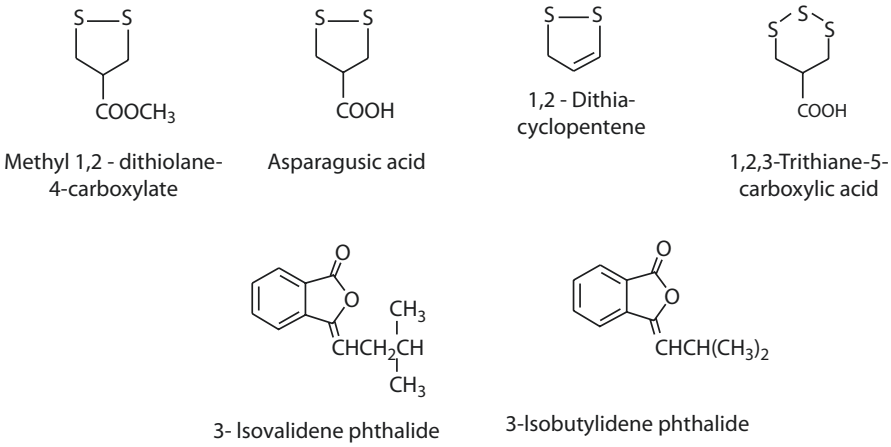
The earthly aroma of raw potato is attributed to 2-ethyl-3-methoxypyrazine. An important aroma in baked potato flavor has been identified to be 2-ethyl-3,6-dimethylpyrazine (Fig. 6.24). The alkylpyrazines, 2-isobutyl-3-methylpyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine, taken as a mixture, have a characteristic baked-potato flavor [34]. In potato chips and fries, the key character-impact compound is (*E*,*E*)-2,4-decadienal thermally generated from frying oils. Another notable aroma in potato chips is methional, a degradation product of methionine. The compound is also found in both boiled and baked potatoes.

In mushroom, the characteristic volatile flavor is associated with the unsaturated alcohol and ketone, 1-octen-3-ol and 1-octen-3-one. The latter occurs in increasing amounts in cooked mushroom and also has been related to metallic or mushroom off-flavors in dairy products [28]. The predominant sulfur compounds, bis(methylthio)methane and 1,2,4-trithiolane, are responsible for the characteristic aroma of truffles [35]. Lenthionine (1,2,3,5,6-pentathiepane, a cyclic polysulfide is known to possess the characteristic aroma of black mushroom (Shiitake, *Lentinus edodes*). This distinct aroma intensifies upon drying of the mushroom due to enzymatic conversion of lentinic acid to lenthionine. γ-Glutamyl transpeptidase removes the glutamyl moiety from lentinic acid, and *S*-alkyl-L-cysteine sulfoxide lyase acts next to produce an unstable intermediate which is spontaneously converted to the polythiepane (Eq. 6.30) [52].



(6.30)

Asparagus consists of sulfur-containing acids and esters as principal flavor compounds. The strong concentrated (~7 ppm) component, methyl 1,2-dithiolane-4-carboxylate, possesses an aroma characteristic of raw asparagus. During cooking of asparagus, the asparagusic acid (1,2-dithiolane-4-carboxylic acid) is decomposed to 1,2-dithiacyclopentene and 1,2,3-trithiane-5-carboxylic acid (Fig. 6.25) [46]. Besides the breakdown products of asparagusic acid, methyl disulfide has also been suggested to be a major aroma constituent (2–10 ppm) in cooked asparagus, formed by thermal fragmentation of *S*-methylmethionine.



Methyl 1,2 - dithiolane-4-carboxylate

Asparagusic acid

1,2 - Dithia-cyclopentene

1,2,3-Trithiane-5-carboxylic acid

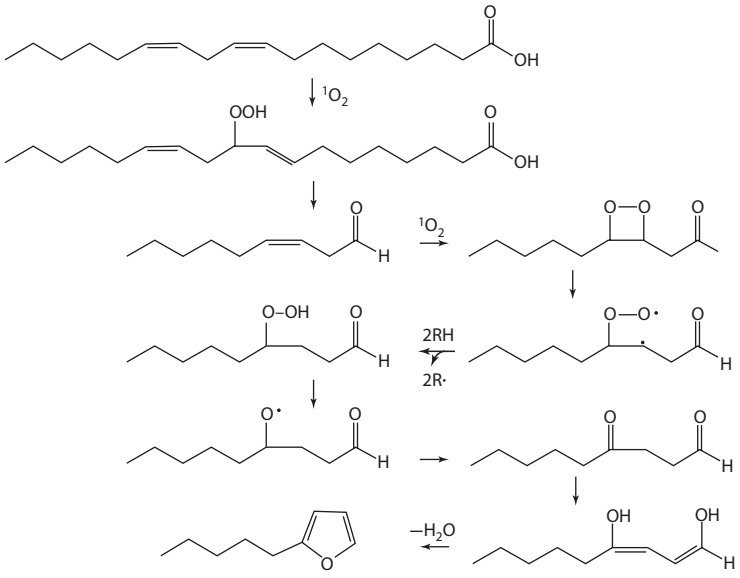
3- Isovalidene phthalide

3-Isobutylidene phthalide

Fig. 6.25 Sulfur-containing compounds and phthalides

Phthalides and their derivatives are implicated in the characteristic odor of celery. These are the 3-isovalidene phthalide, 3-isobutylidene phthalide, and their dihydro-derivatives [15] (Fig. 6.25).

The undesirable beany off-flavor in soybean products, especially in soybean oil, has been attributed to 2-pentylfuran and 2-pentenylfuran (Eq. 6.31). These products are formed by oxidation of linoleic and linolenic acids by singlet oxygen. Traces of chlorophyll acting as sensitizer may be involved [31].



(6.31)

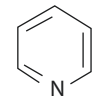
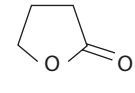
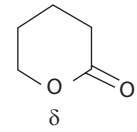
6.12 Meat Flavor

The chemistry of meat flavor represents the utmost complexity in flavor research. Meat must be cooked before it develops flavor, and numerous reactions can occur during the process.

There are well over 200 volatile compounds identified in cooked (boiled, roasted) beef. It is generally believed that the heterocyclic compounds are the important components in meat flavor. Table 6.6 list classes of volatile compounds in beef aroma [27]. The Maillard reaction and the Strecker degradation contribute to several important classes of flavor compounds: furans, pyrazines, pyrroles, oxazoles, thiophenes, thiazoles, and other heterocyclic compounds. Thermal degradation of lipids is another major source contributing to meat flavor, especially alkypyridines, alkythiophenes, trithiolanes, and alkyl-substituted heterocyclic compounds.

Furans and thiophenes with a thiol group in the 3- and 4-positions, and related disulfides, possess strong meat-like aromas with very low odor threshold values. 2-Methyl-3-furanthiol and its corresponding disulfide, bis-(2-methyl-3-furanyl) disulfide, are major contributors to the meaty aroma of cooked beef (Fig. 6.26). The odor threshold of the

Table 6.6 Classes of volatile heterocyclic compounds of beef aroma

Thiophene		Furan	
Thiazole	 Thiazole  Thiazoline	Oxazole	 Oxazole  Oxazoline
Thiopane		Pyrrole	
Pyrazine		Pyridine	
Benzenoid		Lactone	 γ  δ

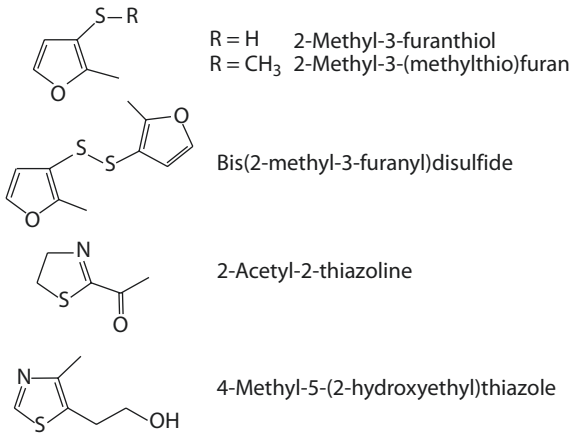
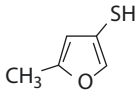
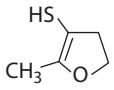
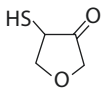
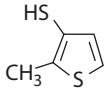
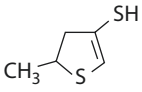
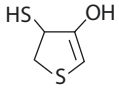


Fig. 6.26 Furans and thiophenes contributing to meaty aroma in cooked beef

disulfide has been reported to be 0.02 ppb (ng/kg) [32]. 2-Acetyl-2-thiazoline is a potent aroma of cooked chicken and broth.

The compound 4-hydroxy-5-methyl-3(2*H*)-furanone (DMHF) and its 2,5-dimethyl homologs have been detected in beef broth. These are α-dicarbonyl compounds that can thermally react with H_2S to form a whole array of compounds with meaty flavors in model systems (Table 6.7). Mercapto-substituted furans and thiophenes identified with meaty

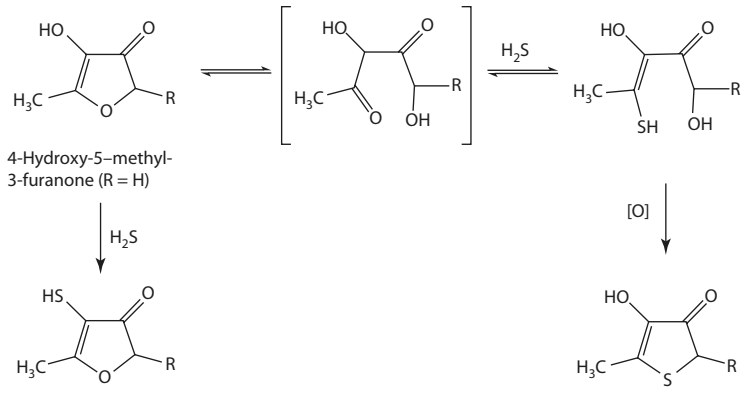
Table 6.7 Meaty flavors formed in the reaction of 4-hydroxy-5-methyl-3(2*H*)-furanone with hydrogen sulfide

4-Mercapto-2-methylfuran		Green, meaty
3-Mercapto-2-methyl-4,5-dihydrofuran		Roasted meat
4-Mercapto-3-oxo-tetrahydrofuran		Green, meaty
3-Mercapto-2-methyl-thiophene		Roasted meat
4-Mercapto-2-methyl-2,3-dihydrothiophene		Rubbery, meaty
3-Mercapto-4-hydroxy-2-methyl-2,3-dihydrothiophene		Meaty, savory

From Mottram [32], Van den Ouwedand and Peer [49]

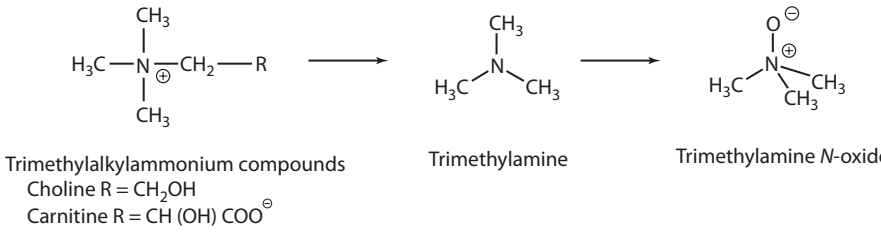
flavors may derive from this reaction pathway [49]. The reaction between dihydrofuranone and hydrogen sulfide involves substitution of the ring oxygen by sulfur to give thio analogs, via the intermediate, 2,4-diketone (Eq. 6.32). Study of the reaction using cysteine also results in the formation of roasted meat flavor.

The off-flavor, known as warm-over flavor, which develops in reheating cooked and refrigerated meats is formed by the autoxidation of lipids, primarily the phospholipids in the meat. This is the major cause of rancidity during frozen storage of meat and meat products. The autoxidation is catalyzed by heme and nonheme irons, followed by decomposition to secondary products. Of these compounds, hexanal and *trans*-4,5-epoxy-(*E*)-2-decenal contribute most strongly to the warm-over flavor of refrigerated cooked beef [23].

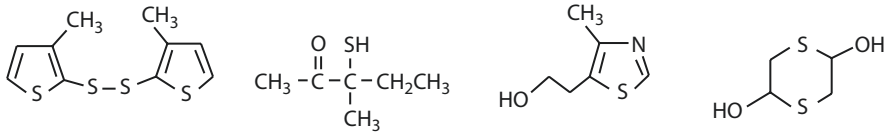


(6.32)

Fish meat has short shelf life due to the development of unpleasant odor from the breakdown of trimethylalkyammonium compounds to trimethylamine (TMA) by bacteria in the fish gut. The TMA is converted to TMAO by a monooxygenase (trimethylamine oxidase) in the digestive gland or liver, to be transported to the tissues, accumulated or excreted (■ Fig. 6.27). In addition, bacterial actions on amino acids in the tissue also produce biogenic amines, such as histamine, putrescine, and cadaverine. TMAO and biogenic amines are common indicators for freshness of fish meat.



■ **Fig. 6.27** Formation of trimethylamine and trimethylamine *N*-oxide



Bis-(2-methyl-3-furyl) disulfide

3-Mercapto-3-methylpentan-2-one

4-Methyl-5-(2-hydroxyethyl) thiazole

2,5-Dihydroxy-1,4-dithiane

Fig. 6.28 Synthetic flavoring compounds

6.12.1 Simulated Meat Flavors

Most simulated meat flavorings have been produced by thermal possessing a mixture of "precursor" compounds, some of which are listed below.
Amino acids – cysteine, cystine, methionine, glutamic acid, glycine, valine
Proteins – glycoproteins, hydrolyzed vegetable, yeast, animal proteins
Nucleotides – adenosine-5′-monophosphate, guanosine-5′-monophosphate
Carbohydrates (reducing sugars) – ribose, glucose, xylose, ribose-5-phosphate
Acids – α-ketobutyrate, succinate, lactate, aliphatic carboxylic acid
Vitamins – thiamin
Sulfur compounds – thiols, sulfides, furanones, sulfur amino acids

In general, the reaction mixture always contains: (1) an amino-containing compounds (such as amino acid), (2) a sulfur-containing compound (such as cystine, thiamin), and (3) a reducing sugar or carbonyl compound. Other flavor chemicals are sometimes added to the reaction mixture to improve the meaty flavor. These meat flavor chemicals include many of the naturally occurring flavor compounds that are not replaced as naturally occurring meat. Some of these are listed in Fig. 6.28 [50].

6.13 Microencapsulation of Flavors

There are increasing numbers of food products containing microencapsulated flavors and ingredients. The flavor ingredients are coated with edible film matrix. The coated particle has a size of less than 5000 μ. The coating materials include the following:

1. Polysaccharides, such as gum arabic, starch
2. Maltodextrin
3. Protein – gelatin
4. Hydrolyzed gelatin
5. Modified proteins – succinylated gelatin, alkylated starch

Microencapsulation has the advantages of: (1) converting liquid flavor concentrate to solid or powder form, (2) protecting flavor loss during food processing and storage, and (3) controlling the rate of release of volatiles and nonvolatiles into a food system. An example of the last is the use of slow-release capsules of ascorbic acid and calcium peroxide in bread making.

References

1. Amoore JE (1964) Current status of the steric theory of odor. Ann NY Acad Sci 116:457–476
2. Assadi-Porter FM, Maillet EC, Radeh JT, Quijada J, Markley JL, Max M (2010) Key amino acid residues involved in multi-point binding interactions between Bazzein, a sweet protein and the TIR2-TIR3 human sweet receptor. J Mol Biol 398:584–599
3. Beets MGJ (1971) Relationship of chemical structure to odor and taste. In: Proceedings third international congress on food science and technology. Institute of Food Technologists, Chicago
4. Belitz H-D, Chen W, Jugel H, Stempfl H, Treleano R, Wieser H (1983) Quantitative structure activity relationships of bitter tasting compounds. Chem Ind 3:23
5. Block E (1985) The chemistry of garlic and onions. Sci Am 252(3):114–119
6. Block E (1992) The organosulfur chemistry of the genus *Allium* – Implications for the organic chemistry of sulfur. Angew Chem Int Ed Engl 31:1135–1178
7. Boelens M, deValois PJ, Wobben HJ, van der Gen A (1971) Volatile flavor compounds from onion. J Agric Food Chem 19:984–991
8. Buck L, Axel R (1991) A novel multigene family may encode odorant receptors: a molecular basis for odor recognition. Cell 65:175–187
9. Buttery RG, Seifert RM, Guadagni DG, Ling LC (1969) Characterization of some volatile constituents of bell peppers. J Agric Food Chem 17:1322–1327
10. Cascales JJL, Costa SDO, de Groot BL, Walters DE (2010) Binding of glutamate to the umani receptor. Biophys Chem 152:139–144
11. Chandrashekar J, Hoon MA, Ryba NJ, Zuker CS (2006) The receptors and cells for mammalian taste. Nature 444:288–294
12. Connell DW (1970) The chemistry of the essential oil and oleoresin of giner (*Zingiber officinale* Roscoe). Flavor Industry 1(10):677–693
13. David C, Henze A, Frank O, Glabasnia A, Rupp M, Buning K, Orlikowski D, Bader M, Hofmann T (2012) Structural and sensory characterization of key pungent and tingling compounds from black pepper (*Piper nigrum* L). J Agric Food Chem 60:2884–2895
14. Demole E, Enggist P, Ohloff G (1982) 1-*p*-Menthene-8-thiol. A powerful flavor impact constituent of grapefruit juice (*citrus paradisi* Macfayhden). Helv Chim Acta 65:1785–1794
15. Gold HJ, Wilson CW (1963) The volatile flavor substances of celery. J Food Sci 28:484–488
16. Govindarajan VS (1977) Pepper-chemistry, technology, and quality evaluation. CRC Crit Rev Food Sci Nutr 9:115–225
17. Gunst F, Verzele M (1978) On the sunstruck flavor of beer. J Inst Brew 84:291–292
18. Hasegawa S, Maier VP (1983) Solutions to the limonin bitterness problem of citrus juices. Food Technol 37(6):73–77
19. Ho C-T, Zheng X, Li S (2015) Tea aroma formation. Food Sci HumWellness 4:9–27
20. Horowitz RM, Gentili B (1979) Taste and structure relations of flavonoid compounds. In: Chiba H (ed) Proceedings of the fifth international congress of food science and technology. Elsevier Scientific Publishing Co., New York
21. Imai S, Akita K, Tomotake M, Sawada H (2006) Identification of 2 novel pigment precursors and a reddish-purple pigment involved in the blue-green discoloration of onion and garlic. J Agric Food Chem 54:843–847
22. Johnson JD, Vora JD (1983) Natural circus essences. Food Technol 37(12):92–93. 97
23. Kerler J, Grosch W (1996) Odorants contributing to warmed-over flavor (WOF) of refrigerated cooked beef. J Food Sci 61:1271–1275
24. Kuninaka A (1967) Flavor potentiator. In: Schultz HW (ed) The chemistry and physiology of flavors. AVI, Westport
25. Kuninaka A (1981) Taste and flavor enhances. In: Teranish R, Flath RA, Sugisawa H (eds) Flavor research, recent advances. Marcel Dekker, New York
26. Liman ER, Zhang YV, Montell C (2014) Peripheral coding of taste. Neuron 81:984–1000
27. MacLeod G, Seyyedain-Ardebili M (1981) Natural and simulated meat flavors (with particular reference to beef). CRC Crit Food Sci Nutr 14:308–437
28. Maga JA (1981) Mushroom flavor. J Agric Food Chem 29:1–4
29. Malnic B, Hirono J, Sato T, Buck LB (1999) Combinatorial receptor codes for odors. Cell 96:713–723
30. Miles FD, Baker BG, Hodge JE (1969) Amadori compounds as nonvolatile flavor precursors in processed foods. J Agric Food Chem 17:723–727

31. Min DB, Callison AL, Lee HO (2003) Singlet oxygen oxidation of 2-pentylfuran and 2-pentenylfuran in soybean oil. J Food Sci 68:1175–1178
32. Mottram DS (1998) Flavour formation in meat and meat products: a review. Food Chem 62:415–424
33. Nursten HE (1978) Flavor chemistry of fruits and vegetables. In: Teranishi R (ed) Agricultural and food chemistry: past present, future. AVI, Westport
34. Pareles SR, Chang SS (1974) Identification of compounds responsible for baked potato flavor. J Agric Food Chem 22:339–340
35. Pelusio F, Nilsson T, Montanarella L, Tilio R, Larsen B, Facchetti S, Madsen JO (1995) Headspace solid-phase microextraction analysis of volatile organic sulfur compounds in black and white truffle aroma. J Agric Food Chem 43:2138–2143
36. Rizzi GP (1969) The formation of tetramethylpyrazine and 2-isopropyl-4,5-dimethyl-3-oxazoline in the Strecker degradation of DL-valine with 2,3-butanedione. J Org Chem 34:2002–2004
37. Rizzi GP (1972) A mechanistic study of alkylpyrazine formation in model systems. J Agric Food Chem 20:1081–1085
38. Sanderson GW, Co H, Gonzalez JG (1971) Biochemistry of tea fermentation: the role of carotenes in black tea aroma formation. J Food Sci 36:231–236
39. Sanderson GW, Graham HN (1973) On the formation of black tea aroma. J Agric Food Chem 21:576–585
40. Siebert TE, Wood C, Elsey GM, Pollnitz AP (2008) Determination of rotundone, the pepper aroma impact compound, in grapes and wine. J Agric Food Chem 56:3745–3748
41. Simian H, Robert F, Blank I (2004) Identification and synthesis of 2-heptanethiol, a new flavor compound found in bell peppers. J Agric Food Chem 52:306–310
42. Takken HJ, van der Linde LM, Boelens M, van Dort JM (1975) Olfactive properties of a number of polysubstituted pyrazines. J Agric Food Chem 23:638–642
43. Takken HJ, van der Linde LM, deValois PJ, van Dort HM, Boelens M (1976) Reaction products of α-dicarbonyl compounds, aldehydes, hydrogen sulfide, and ammonia. In: Phenolic, sulfur, and nitrogen compounds in food flavors. ACS symposium series, vol 26. American Chemical Society, Washington, D.C.
44. Todd PH Jr, Bensinger MG, Biftu T (1977) Determination of pungency due to capsicum by gas-liquid chromatography. J Food Sci 42:660–680
45. Tressl R, Silwar R (1981) Investigation of sulfur-containing components in roasted coffee. J Agric Food Chem 29:1078–1082
46. Tressl R, Bahri D, Holzer M, Kossa T (1977) Formation of flavor components in asparagus. 2. Formation of flavor components in cooked asparagus. J Agric Food Chem 25:459–463
47. Tressl R, Friese L, Fendesack F, Koppler H (1978) Gas chromatographic – mass spectrometric investigation of hop aroma constituents in beer. J Agric Food Chem 26:1422–1426
48. Tressl R, Rewicki D, Helak B, Kamperschroer H (1985) Formation of pyrrolidines and piperidines on heating L-proline with reducing sugars. J Agric Food Chem 33:924–928
49. van den Ouwedand GAM, Peer HG (1975) Components contributing to beef flavor. Volatile components produced by the reactions of 4-hydroxy-5-methyl-3(2*H*)-furanone and its thio analog with hydrogen sulfide. J Agric Food Chem 23:501–505
50. Wilson RA, Katz I (1974) Synthetic meat flavors. Flavor Industry 5(30–35):38
51. Wilson CW III, Shaw PE (1981) Importance of thymol, methyl N-methyl-anthranilate, and monoterpene hydrocarbon to the aroma and flavor of mandarin cold-pressed oils. J Agric Food Chem 29:494–496
52. Yasumoto K, Iwami K, Mitsuda H (1971) Enzyme-catalyzed evolution of lenthionine from lentinic acid. Agric Biol Chem 33:2070–2080
53. Zhang F, Klebansky B, Fine RM, Xu H, Pronin A, Liu H, Tachdjian C, Li X (2010) Molecular mechanism for the umami taste synergism. Proc Natl Acad Sci U S A 105:20930–20934