

Food Flavors

Chemical, Sensory and Technological Properties

EDITED BY

Henryk Jeleń



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Henryk Jeleń



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Preface

Flavor is one of the main food sensory attributes of crucial importance for consumers acceptance of food. Therefore, it attracts the attention of not only food technologists, but also psychologists and neurophysiologists. Flavor compounds are challenging ones to investigate for chemists and biochemists.

This book was intended to provide a concise one volume selection of flavor topics especially important for food technologists and students in food technology/chemistry, who are main target reader groups, and all those who want to have a starting point in a more in-depth exploration of the field of food flavors.

Having this in mind, the book chapters can be grouped into five areas generally focused on the following aspects: *i*) introductory information on flavor compounds and odor and taste perception; *ii*) basics of aroma compounds formation; *iii*) flavor compounds specificity in food technology; *iv*) examples of flavors of selected foods; and *v*) analytical approaches to characterize food flavor compounds.

Chapters 1 and 2 provide an introduction into the chemistry of food odorants and food tastants, whereas Chapter 3 covers the area of flavor perception and provides fundamentals, as well as recent accomplishments in this field. Chapters 4 through 6 are organized based on flavor precursors (lipids, carbohydrates, and aminoacids), presenting universal mechanisms and pathways in aroma compounds biogenesis or formation of process flavors. This gives readers a broad outlook of the common points in the formation of flavors and should help to understand the process of flavor formation in technological processes. Chapter 7 is related to interaction of food matrix with aroma compounds in the process of their binding and release, whereas Chapter 8 describes an significant issue of flavor suppression and enhancement, important especially in functional food production and flavor perception. To guide reader through the legislative meanders of food flavors and flavorings, Chapter 9 provides important data in this respect. Chapters 10 and 11 are also helpful for food technologists, providing information on spices and essential oils, and functional properties of flavor compounds. Chapters 12 through 15 provide insight into various food products and their characteristic aroma. Because of the ample variety of food products with a distinct flavor and, simultaneously, because of the limited space in the book, a choice of products must be a compromise. Cheese flavors, flavor characterization of meat, odorants in wines, and formation of flavor in bread and bakery products represent diversified character of flavor and aroma compounds, their formation, sensory implication, and the roles of microorganisms and technological processes in their formation. Chapter 16 describes the problems of food taints and off-flavors, their origin in foods, and the strategy for their identification. The last part of the book, comprising four chapters, is devoted to analytical aspects. Chapter 17 describes the use of volatile compounds in food authenticity and traceability testing, whereas Chapter 18 presents analytical approach to the determination of key aroma and taste compounds that play a crucial role in formation of food flavor. This chapter links results of instrumental analysis with sensory impressions. Chapter 19

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is focused on the techniques used in the sensory characterization of food, whereas Chapter 20 provides the idea, theory, and instrumentation of machine olfaction.

The chapters in this book have been written by specialists from academia and industry based on their teaching and research experience and contain both fundamentals, required to understand basic processes in flavor chemistry/biochemistry and flavor perception and the evaluation of literature to present recent trends in flavor research.

I hope that information provided in the book shall give an outlook of the various aspects of flavor chemistry to the novices in the field, as well as useful information for more experienced readers, and can be a concise starting book for all interested in a role of flavors in food industry.

Editor

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1 Specificity of Food Odorants

Henryk Jeleń

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1.1 INTRODUCTION

Food is one of the main stimuli to our senses in everyday life. Apart from providing nutritious constituents during consumption, food engages the human senses: not only taste and smell, but also sight, hearing, and touch. Sensory properties resulting from the involvement of all senses provide a wholesome picture of food, which is either accepted or rejected by a consumer. Food appearance, texture, and mainly food flavor are the sensory properties that influence food acceptance. Among the sensory properties, flavor is usually the decisive factor for the choice of a particular product.

According to the *New Oxford American Dictionary*, flavor (Brit. *flavour*) is the distinctive quality of a particular food and drink as perceived by the taste buds and the sense of smell. The origin in late Middle English (in the sense fragrance, aroma) is from Old French *flaor*, perhaps based on a blend of Latin flatus "blowing" and foetor "stench." It can be assumed that flavor is the sensation produced by material taken in the mouth perceived principally by the senses of taste and smell, and also by the general pain, tactile, and temperature receptors in the mouth.

Food flavor is of cardinal importance not only for consumers at the moment of choosing a particular product, but also an important feature for breeders of fruit and vegetable varieties and in selection of raw materials used for food production. Flavor is an issue for food technologists, when developing new products, meeting consumers' requirements, and controlling it during processing and storage. Finally, flavor

is one of the main factors that determine the shelf life of a particular food product. Development of off-flavors as a result of enzymatic, chemical, or microbial changes can make food products unpalatable. Therefore, maintaining the proper flavor of food products is in the interest of both consumers and producers.

1.2 FOOD VOLATILES AND FOOD ODORANTS

Odorants have to be volatile to reach the human olfactory system; therefore, it is accepted that, generally, odorants are molecules characterized by relatively high vapor pressures of molecular weight lower than 300 Da, although there are odorants that are relatively nonvolatile [5 α -androst-16-en-3-one—mammalian pheromone having sweaty, ruinous, unpleasant woody odor; odor threshold (OT) = 0.00062 mg/kg; vapor pressure = 4.22×10^{-3}]. The vapor pressure of odorants can vary over several orders of magnitude. Majority of volatiles are also relatively nonpolar (hydrophobic) compounds, which favors their partition in aqueous media.

A differentiation should be made between volatile and odoriferous compounds. More than 11000 volatile compounds have been identified in food. They have been compiled as a database accessible on the Internet (VCF Volatile Compounds in Foods, 2010, www.vcf-online.nl) and fill 18 different chemical classes (hydrocarbons, aldehydes, ketones, esters, acids, lactones, halogens, sulfur compounds, etc.). However, it is estimated that only 5%–10% of them play a significant role in the formation of specific aromas of food products. The importance of particular compounds in flavor formation is related to their concentration and their odor thresholds. Volatile compounds influence the odor of a particular food when present in concentrations higher than their odor threshold, or they can also influence the flavor when present in mixtures that exceed these odor thresholds as a result of additive or synergistic effects.

Increasing the potential of separation techniques, and developments in gas chromatography especially comprehensive gas chromatography (GC × GC) allow the detection of hundreds or even thousands of peaks. Therefore, among the bulk of volatile compounds, key odorants of a product are of special importance in flavor analysis. As a consequence, although profiles of volatile compounds are useful in metabolomic or authenticity/traceability testing (Chapter 17), the analysis of food aroma compounds should be sensory guided. In analysis of food odorants, gas chromatographyolfactometry (GC-O) allows selection of aroma important compounds from numerous volatiles (van Ruth 2001). This approach to the analysis of food odorants and tastants is discussed in detail in Chapter 18.

1.3 ODOR THRESHOLDS AND AROMA DESCRIPTION

Odoriferous compounds are present in food in very low concentrations, usually in milligram per kilogram amounts, but very often in much lower concentrations—microgram per kilogram or even nanogram per kilogram of the product. Our olfactory system is able to detect some odorants present in extremely low concentrations. Odoriferous molecules are sensed by the olfactory epithelium located in the nasal cavity, which can be reached entering a nasal passage via the nose (orthonasal) or via the mouth (retronasal path). In humans, introduction of an odorant above a certain

threshold into the nasal cavity triggers a response to the stimulus (see Chapter 3). Odor threshold can be defined as the lowest concentration of a compound in a specified medium that is sufficient for the recognition of a particular odor. In flavor description, two thresholds are used: detection threshold defined as the lowest physical intensity at which a stimulus is perceptible, and the recognition threshold (odor threshold), which is the lowest intensity in which the stimulus can be correctly defined or identified.

To characterize aroma compounds and their contribution to food flavor, odor thresholds need to be determined. Traditionally, this has been carried out in air using olfactometers; however, for food products, a more reasonable solution is to determine odor thresholds in water (Buttery 1999). This is based on the assumption that in determining a water threshold, the odor threshold of a compound in air, where the compound is at equilibrium between the water solution and air, is determined (Buttery et al. 1973). Odor threshold in air (T_a) can be determined from the following equation:

$$T_{\rm a} = T_{\rm w} \times K_{\rm aw}$$

where $T_{\rm w}$ is a threshold concentration in water and $K_{\rm aw}$ is the air-to-water partition of the compound at the testing temperature. Similarly, threshold in oil can be calculated as follows:

$$T_{\rm ol} = T_{\rm w} \times (K_{\rm aw}/K_{\rm aol})$$

where K_{aw}/K_{aol} is equal to the oil-to-water partition.

To quantify the influence of a particular odor compound on the aroma of a product, aroma values (AV) are calculated by integrating the concentration of a particular compound and its odor threshold—AV is the ratio of a compound's concentration to its odor threshold (Rothe and Thomas 1963). An example of such approach is shown in Table 1.1. Furthermore, the log of concentration/threshold ratios is used to express the contribution of a compound to a product's overall aroma.

Basic tastes can be relatively easily described (sweet, salty, sour, bitter, and with umami being classified as the fifth basic taste). Contrary to this, description of odors is often extremely difficult to do in unequivocal terms. Complex mixtures are difficult to describe unless there is one dominant compound that influences flavor. Odors are described using adjectives comparing odors with known products/impressions (e.g., hay-like, fruity). Many terms describing odors include animal (musk, civet), camphoraceous, citrus, earthy, fatty, floral, green, herbaceous, medicinal, resinous, spicy, waxy, or woody. For complicated (from a flavor point of view) products, such as whisky, wine, or beer, flavor wheels have been constructed to help in describing main and additional odors and notes associated with a product (Figure 1.1).

1.4 CHEMICAL PROPERTIES AND PERCEPTION OF ODORANTS

Perception of food odorants is related to the nature of food product from which an aroma compound is released (food matrix) and the chemical/spatial nature of

| • | • | |
|-------------------|---------------------|--------------------------|
| Compound | Concentration (ppm) | Aroma Value ^a |
| Ethanol | 1100 | 110 |
| Acetaldehyde | 23 | 25 |
| Acetoin | 1 | 1 |
| Diacetyl | 1.3 | 330 |
| 2/3-Methylbutanal | 15 | 1900 |
| Pyruvic aldehyde | 9 | 20 |
| 2-Methylpropanal | 6 | 6000 |
| Furfural | 19 | 300 |

TABLE 1.1
Aroma Compounds in Rye Bread Crust

Source: Rothe, M., and Kruse, H.-P., in Flavor Chemistry. Thirty Years of Progress, ed. R. Teranishi, E.L. Wick, and I. Horstein, 367–375, Kluwer Academic/ Plenum Publishers, New York, 1999. With permission.

the odorant molecule. Aroma compounds interact with food macro constituents—proteins, lipids, and carbohydrates. The interactions influence release of aroma compounds from the matrix, resulting in partition coefficients that in consequence influence the levels of aroma compounds in the headspace. Odor threshold values of 2,4,6-trichloroanisol vary substantially in matrices of different viscosity and composition: in water, it is estimated at 7.6×10^{-8} ; in beer, 7×10^{-6} ; in edible oil, 7×10^{-3} ; and in egg yolk, 2.4×10^{-3} (Maarse et al. 1987).

The food macroconstituents can govern aroma binding and release in various ways: the presence of polysaccharides can alter partition of volatiles due to modified viscosity or formation of inclusion complexes. Binding of flavor compounds to proteins is dependent on protein type. The nature of aroma binding to protein molecules can be reversible, based on hydrogen bonding and hydrophobic interactions, or can be irreversible, such as in the case of sulfur compounds reacting with proteins. Lipids influence partition of volatile compounds in foods to a great extent. In emulsions, even a low level of fat can substantially influence absorption of volatiles (Roberts and Pollien 2000). The process of aroma release was discussed in detail in several review papers (Druaux and Voilley 1997; Guichard 2002). The problem is of high importance for food manufacturers especially considering the trends for production of fat-free or low-fat products. Binding and release of aroma compounds are discussed in detail in Chapter 7.

The chemical nature of odorants influences the way they are perceived. Functional groups position influences odor threshold. As an example, isomers of trichloroanisole—2,4,6-trichloroanisole and 2,3,6-trichloroanisole can be cited having odor thresholds of 0.03 and 0.0003 ppb, respectively (Maarse et al. 1987). Size and character of the functional groups may also influence odor thresholds via the influence of

^a Concentration (ppm)/threshold in water (ppm).



FIGURE 1.1 Whisky flavor wheel. (From Lee, K.-Y.M., Paterson, A., Piggot, J.R., *J. Inst. Brewing* 107, 287–313, 2001. With permission.)

odorant receptor spatial interaction. A good example showing the influence of functional groups on odor thresholds are alkylpyrazines. Werner and coworkers studied the structure–odor activity relationships of 80 alkylpyrazines. Tetramethylpyrazine had an odor threshold of >2000 ng/L, whereas trimethylpyrazine had a substantially lower odor threshold of 50 ng/L (in air). When one of the methyl groups was

OT = 50 ng/L

5-Ethyl-2,3-dimethylpyrazine OT = 200 ng/L

3-Ethyl-2,5-dimethylpyrazine OT = 3.6 ng/L

2-Ethyl-3,5-dimethylpyrazine OT = 0.011 ng/L

FIGURE 1.2 Structures of selected alkylpyrazines and their odor thresholds.

TABLE 1.2 Odor Properties of Selected Chiral Compounds

| Compound | Odor Description |
|-------------|----------------------------------------------------------|
| Linalool | (+): Sweet, petigrain |
| | (–): Woody, lavender |
| Carvone | (+): Caraway |
| | (–): Spearmint |
| Nootkatone | (+): Grapefruit |
| | (–): Woody, spicy |
| Nerol oxide | (+): Green, floral |
| | (-): Green, spicy, geranium |
| Menthol | (+): Dusty, vegetable, less minty, less cooling than (-) |
| | (-): Sweet, fresh minty, strong cooling effect |
| Limonene | (+): Orange |
| | (–): Turpentine |

Source: Brenna, E., Fuganti, C., Serra, S., Tetrahedron: Asymmetry 14, 1–42, 2003. With permission.

replaced with the ethyl group in positions 3 and 2, a decrease in odor thresholds was observed; in the case of 2-ethyl-3,5-dimethylpyrazine, a decrease to 0.01 ng/L was observed (Figure 1.2). However, 5-ethyl-2,3-dimethylpyrazine showed a higher odor threshold of 200 ng/L. When propyl or butyl groups replaced the ethyl group in 2-ethyl-3,5-dimethylpyrazine, the volume of the functional group became too bulky, resulting in an increase of odor thresholds to 23 and 180 ng/L, respectively. Moreover, based on the investigated compounds and their sensory properties, it is evident that a specific spatial configuration is required to induce earthy/roasty odor, and a model receptor for it could be proposed (Werner et al. 1999).

Enantiomers exhibit different behaviors when interacting with organisms, which is of immense importance in pharmacology, physiology, and also in odorants perception. Biogenesis of odoriferous compounds in nature yields specific enantiomers (for compounds possessing chiral centers). Enantiomers of the same compound can exhibit different odor notes (Table 1.2). Odor thresholds of enantiomers of the same compound may vary: they may have the same odor, or some of the enantiomers can be nonodoriferous: (1R,2R)-(-)-methyl-(Z)-jasmonate and its diastereoisomer (1R,2S)-(+)-methyl-(Z)-jasmonate are the key odorants in jasmine flower oil (Jasminum grandiflorum L.) and occur in the proportion of 97:3. They both have floral, jasmine, slightly fruity odor with odor thresholds of 70 and 3 µg/ml, respectively, whereas their enantiomers (Figure 1.3) are almost odorless (Acree et al. 1985).

1.5 FORMATION OF AROMA COMPOUNDS IN FOOD

Food is a complex matrix rich in flavor precursors. Food flavors (aromas) can be divided based on the origin/nature of compounds into three main categories: primary aromas, secondary aromas, and off-flavors (Figure 1.4). Such classification reflects to a certain extent the pathways of formation of odorants. Primary aromas are produced mainly in enzyme-catalyzed reactions in raw foods, whereas secondary aromas are those comprising products of thermal reactions in food processing and also compounds obtained as a result of microbial activity in fermentation processes. "Off-flavors" is a term related to compounds of various origins and nature, which impairs the natural flavor of food.

Characteristic pathways of formation of particular flavor compounds are unique for a given food, although the pool of precursors is very often similar.

1.5.1 Primary Aromas

Primary aromas are usually associated with enzymatic reactions in raw materials. They are the most characteristic for plants, fruits, and vegetables.

In the formation of aroma compounds in fruits, the main precursors are lipids, carbohydrates, and amino acids. Moreover, mevalonic acid (terpene metabolism) and cinnamic acid metabolism is involved in the formation of fruit flavors. In fruits and vegetables, many flavor compounds are released from their nonvolatile precursors in the process of enzymatic hydrolysis. The main groups of compounds forming primary aromas are esters, alcohols, aldehydes, and terpenes. The formation of

COOMe

(1R,2R)-(-)-Methyl-(Z)-jasmonate [OT > 70
$$\mu$$
g/L]

COOMe

(1R,2S)-(+)-Methyl-(Z)-jasmonate [OT = 3 μ g/L]

COOMe

(1S,2S)-(-)-Methyl-(Z)-jasmonate [odorless]

FIGURE 1.3 Enantiomers of methyl-(Z)-jasmonate: (1S,2S) and (1S,2R) isomers are odorless; (1R,2R) and (1R,2S) isomers have jasmine odor.

(1S,2R)-(+)-Methyl-(Z)-jasmonate [odorless]

aroma compounds from fatty acid precursors as a result of lipoxygenase activity is presented for tomatoes, olives, and cucumbers in Chapter 4.

An important group of compounds in essential oils, spices, and many fruits are of terpenes. Monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20), triterpenes (C30), and tetraterpenes (C40) are formed in plants; however, only monoterpenes, and to a lesser extent, sesquiterpenes, play an important role in the formation of

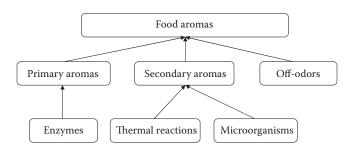


FIGURE 1.4 Classification of food flavors (aromas) and their main categories of origin.

flavor. Terpenes are formed in plants from an isoprene C5 unit via the head-to-tail addition (Ruzicka et al. 1953). The biosynthesis of terpenes commences from acetyl-CoA via acetate and mevalonate pathway (Bach et al. 1999). The independent pathway for formation of isoprenoids in plants is the deoxyxylulose phosphate/methylerythritol phosphate pathway (Lichtenhalter et al. 1997, 1998). Plants form volatile monoterpenes and sesquiterpenes as main constituents of their essential oils in specialized cells of *Lamiaceae*, *Myrtaceae*, *Pinaceae*, *Rosaceae*, *Umbelliferae* and others. Terpenes form a vast group of compounds—mainly hydrocarbons, alcohols, and aldehydes that are relatively labile and can undergo oxidations and transformations. Chapter 10 describes in detail terpenes present in essential oils and spices.

1.5.2 SECONDARY AROMAS

Secondary aromas according to the classification provided in this chapter are those formed as a result of microbial activity, mainly in fermentation processes (i.e., alcoholic beverages), controlled enzymatic reactions, and in thermal reactions (mainly Maillard reaction). There are a number of fermented foods in which microorganisms cause the formation of characteristic odoriferous compounds. Pure cultures of microorganisms are used (starter cultures) or microorganisms native to raw material with their specific enzyme profile. In cheese, starter cultures contribute to their characteristic smell and produce flavor compounds from lactose, citrate, proteins, and lipids (Marilley and Casey 2004). Depending on a cheese type, different pathways prevail and microorganisms form distinct compounds (methyl ketones in blue-veined cheese, volatile fatty acids, and sulfur compounds in Cheddar). Chapter 12 describes the aroma of cheese in detail. In traditional yeast fermentations used in the production of bread and alcoholic beverages, a number of volatile compounds, mainly alcohols, esters, and aldehydes are formed. Saccharomyces cerevisiae form compounds characteristic for yeast leavened bread: lower alcohols, acetaldehyde, propanal, pentanal, furfural, and ethyl esters lactic and acetic acid.

Heat-generated aroma compounds form the biggest group of odorants obtained in technological processes. Thermal processes that lead to heat-generated aromas not only include coffee and cocoa roasting, boiling, frying, grilling of meat, baking, but also milder processes, such as pasteurization of milk. The number of compounds obtained as a result of thermal processing is estimated at 3500–4500. Heating of foods that contain proteins, peptides, and amino acids with reducing sugars forms a vast array of volatile compounds as a result of Maillard reaction. It is one of the most important sets of reactions in food chemistry and technology and yields, apart from flavor compounds, nonvolatiles and characteristic brown pigments (melanoidins) (Hodge 1953). Maillard reaction is a source of many compounds produced from a limited number of precursors. Although it is a source of numerous volatiles, the number of odoriferous compounds is much lower. Flavor compounds produced in thermal reactions include Strecker aldehydes, oxidation products formed in free radical lipids auto-oxidation, and heterocyclic compounds being secondary products of Maillard reaction/carbohydrate degradation products. In heated foods, flavor

FIGURE 1.5 Formation of 2-pentylpyridine, 2-hexylthiophene, and 2-pentyl-2*H*-thiapyran from decadienal, ammonia, and hydrogen sulfide. (From Mottram, D.S., *Food Chemistry* 62, 415–424, 1998. With permission.)

compounds may interact with each other. As an example, interactions of volatile compounds formed in Maillard reactions with fatty acids oxidation products can be shown (Figure 1.5). This example shows an array of heterocyclic compounds obtained in the reaction of reactive cysteine degradation products (ammonia and hydrogen sulfide) with decadienal.

Heterocyclic compounds formed in thermal reactions include furanones, pyranones, thiazoles, pyridines, pyroles, and pyrazines. Examples of heterocyclic compounds found in foods are shown in Figure 1.6. Furanones are compounds that result from carbohydrates degradation and usually have a caramel odor note, besides various other characteristic notes. Heteroatomic compounds containing nitrogen(s) atoms are usually formed in heated foods; however, some can be formed in enzymatic reactions or in biological systems in a combination of enzyme-catalyzed and nonenzymatic reactions. Pyridines can be formed in a reaction of unsaturated aldehydes with ammonia or primary amines. Pyrazines are formed in heat-treated foods by nonenzymatic reactions, or in a combination of nonenzymatic and enzymatic reactions. Alkylpyrazines are usually associated with heat-treated foods, formed in

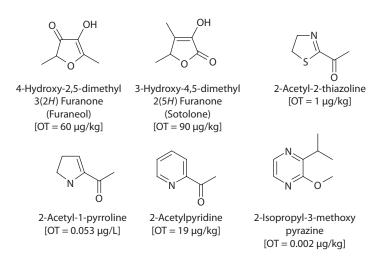


FIGURE 1.6 Selected heterocyclic odor compounds in foods.

a chemical reaction from hydroxyacetone or related hydroxycarbonyls, ammonia/aminoacetone (Rizzi 1988). On the contrary, methoxy pyrazines are usually associated with living organisms and fermented foods and their number in food products is limited to the main odorants: 2-methoxy-3-isopropyl, 2-methoxy-3-isobutyl, and 2-methoxy-3-secbutylpyrazine. Their biosynthesis was studied in *Bacillus subtilis*, *Aspergillus oryzae*, and *Pseudomonas* spp., indicating amino acids as precursors (Rizzi 2002).

2-Acetyl-1-pyrroline has been associated with the aroma of white bread crust and contributes to the popcorn flavor compound and identified in wheat bread crust, cooked beef, and corn tortillas. It is formed in Maillard reaction using 2-oxopropanal (formed in the degradation of reducing sugars) or 1-pyrroline (which can be formed from ornithine and/or proline) (Hoffmann and Schieberle 1998). However, 2-acetyl-1-pyroline can be also microbially formed in cheeses and airdried sausages.

Sulfur-containing compounds are an important group of compounds found in heated foods. They are aliphatic thiols, sulfides, and mainly heterocyclic compounds. Heterocyclic aroma compounds often contain sulfur in conjunction with nitrogen. Sulfur-containing compounds comprise more than 250 volatiles and are abundant in meat. The main precursors of sulfur-containing aroma compounds are sulfur-containing amino acids cysteine and methionine. Strecker degradation of cysteine leading to formation of hydrogen sulfide, ammonia, and acetaldehyde provides intermediates for many interactions especially with lipids (Figure 1.5). The important pathway in the formation of sulfur-containing compounds is thermal degradation of thiamine-yielding thiazoles, furanthiols, and thiophenes. Excellent reviews of sulfur odor compounds in foods have been provided in the literature (Mottram and Mottram 2002; Vermeulen et al. 2005).

1.5.3 Off-Odors

Off-odors in food are associated with the presence of compounds that either migrate into food products from external sources (taints), or are formed from food constituents as a result of chemical, biological, or microbial deterioration (off-flavors). They generate problems in food processing that affect the whole food chain. Chapter 16 is devoted to off-flavors and taints in food. There are also entire books on taints and off-odors in foods (Saxby 1993; Baigrie 2003).

Off-odorants are represented by haloanisoles, halophenols, phenolics, sulfur compounds, carbonyls, esters, amines, and fatty acids. They can be classified according to their origin—microbially derived; compounds originating from packagings, cleaning agents, and disinfectants; and compounds formed in auto-oxidation or other reactions taking place in stored foods.

One of the most important groups of off-odorants comprises compounds that contribute to musty and earthy off-odors in foods. They include geosmin, methylisoborneol, chloro-, bromoanisoles, octa-1,3-diene, 4,4,6-trimethyl-1,3-dioxan, 2,6-dimethyl-3methoxypyrazine, and 2-methoxy-3-isopropylpyrazine. Chloroanisoles were detected as compounds responsible for musty taint first time in eggs and broilers (Engel et al. 1966); 2,4,6-trichloroanisol is responsible for a Rio off-flavor in coffee (Spadone et al. 1990) and corky taint in wine (Buser et al. 1982). Geosmin and/or 2-methylisoborneol mainly produced by Strepromyces, Nocardia, Oscillatoria, and various Penicillium species (Bőrjesson et al. 1993; Mattheis and Roberts 1992) are compounds related to the occurrence of muddy-musty off-flavor in water (Watson et al. 2000), fish (Conte et al. 1996), stored grain (Jeleń et al. 2003), and in red beet (Lu et al. 2003). Phenolic compounds form an important group of off-odorants in foods contributing to smoky odors (guaiacol, 4-ethylphenol, 4-ethyl guaiacol) or pharmaceutical odors (4-vinylphenol and 4-vinylguaiacol) (Saxby 1993). They contribute to Brett defect in wines described as barnyard or band aid odor (Licker et al. 1998). Sulfur compounds, besides contributing to the characteristic flavor of many vegetables, fruit, meat, and cheeses, can be a potent group of off-flavors: 3-methyl-2-butene-thiol (MBT) in beer, possessing a skunky odor, is derived from photochemical degradation of iso-α-acids in beer exposed to light. Volatile lipid oxidation products, which are also an important group of off-odorants, are responsible for the rancid off-flavor (1-octene-3-one is responsible for the off-flavor of rancid butter), whereas 1-pentene-3-one has a characteristic fishy off-flavor (Badings 1970; Belitz et al. 2008). Offflavors in fat-containing foods are also related to the presence of methyl ketones, which are responsible for the ketonic rancidity-musty, stale off-flavor of desiccated coconut (Kellard et al. 1985), caused by oxidation of medium-chain fatty acids by molds (Kochar 1993).

1.6 BOUND FLAVOR COMPOUNDS

Aroma compounds exist in plants in their free form; however, in many plants, they also exist in the form of glycoconjugated precursors. There are about 50 plant families in which glycoconjugated aroma compounds have been detected. Moreover, the pool of glycosidically bound compounds exceeds in some cases the free flavor

compounds fraction in a ratio range of 2:1 to 10:1 (Winterhalter et al. 1999). Bound aroma compounds are characteristic to fruits and vegetables and do not contribute to food aroma until released. Odoriferous aglycons are bound as glycosides with mainly monosaccharides and disaccharides. Aglycons may be released from carbohydrates as a result of tissue disruption, during maturation, storage, processing, and aging. The aglycon release is usually catalyzed by enzymes, acids, or heat. Examples of bound aroma compounds are glucosinolates in *Cruciferae*, bound terpenes, norisoprenoids, and phenolic compounds in grapes and other fruits.

Glucosinolates are metabolites in *Cruciferae* family that include among others radish, horseradish, cabbage, cauliflower, kale, and wasabi. The enzyme that catalyzes the hydrolysis of thioglucosidic bond in glucosinolates is myrosinase (Figure 1.7). Myrosinase gains access to glycosinolates in tissue damage, as both the enzyme and a substrate are located within vacuoles, although in different cell types and subcellular structures. Of the presented hydrolysis compounds, isothiocyanates are the most important in forming the sharp and pungent flavor of *Cruciferae* plants. However, epitiospecific proteins that influence the formation of glucosinolates hydrolization products favor the formation of nitriles and thiocyanates, which are less toxic than isothiocyanates.

Since the first studies on bound aroma compounds—geraniol in rose flowers (Francis and Allock 1969)—investigations have focused mainly on grapes, and also on other fruits—apricot, peach (Krammer et al. 1991), passiflora (Chassagne et al. 1996), nectarines (Aubert et al. 2003), mango (Ollé et al. 1998), strawberries (Roscher

FIGURE 1.7 Formation of aroma compounds released by myrosinase in *Cruciferae*.

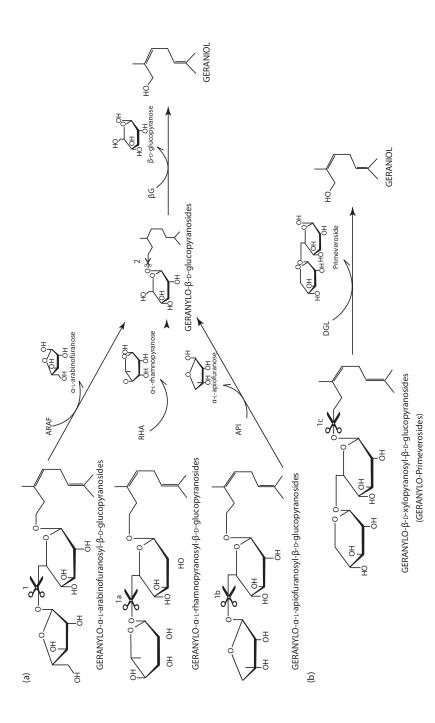


FIGURE 1.8 Structures of glycosidic monoterpene precursors from grape berries and their hydrolysis by specific enzymes (geraniol shown as aglycone). (From Dziadas, M., and Jeleń H., Acta Sci. Pol. Technol. Aliment., 10, 7–17, 2011. With permission.)

et al. 1997), cape gooseberry (Mayorga et al. 2001) and saffron (Straubinger et al. 1998).

The odoriferous aglycons of glycosides in plants include monoterpenes, C13-norisoprenoids, benzene derivatives, and alcohols. The sugar moieties are usually glucose or disaccharides in $6-O-\alpha$ -L-arabino-pyranosyl- β -D-glucopyranosides (vicianosides), $6-O-\alpha$ -L-arabinofuranosyl- β -D-glucopyranosides, $6-O-\alpha$ -L-rhamno-pyranosyl- β -D-glucopyranosides (rutinosides), $6-O-\beta$ -D-apiofuranosyl- β -D-glucopyranosides (primeverosides), and $6-O-\beta$ -D-glucopyranosyl- β -D-glucopyranosides (gentibiosides) (Stahl-Biskup et al. 1993; Vasserot et al. 1995; Cabaroglu et al. 2003).

Grape varieties, rich in monoterpenes, are used for white wine production; in particular, Muscat and aromatic varieties such as Gewürtztraminer, Riesling, and Sylvaner provide rich floral aromas because of the presence of monoterpene odoriferous alcohols, which exist in free and bound forms (Güth 1997; Mateo and Jimenez 2000). In the winemaking process, volatile compounds from glycosides can be released by enzyme or acid hydrolyses (Williams et al. 1982; Ibarz et al. 2006; Tamborra et al. 2004; Günata and Sarry 2004; Mateo and Jimenez 2000; Mateo and Maicas 2005). The acid hydrolysis progresses relatively slowly in winemaking conditions, being dependent on the pH and temperature of the medium and on the structure of the aglycone moiety. Sequential reactions take place in the enzymatic hydrolysis of diglycosides involving several glycosidases specific for the sugar moiety of the substrates (Cabaroglu et al. 2003) (Figure 1.8).

1.7 CONCLUSION

Food volatiles are thousands of compounds that represent different chemical classes. Among them, odoriferous compounds form a smaller (5%–10% of compounds) group, which is responsible for food aroma. Food odorants are present in concentrations ranging from milligram per kilogram down to nanogram per kilogram. Key odorants also represent diverse chemical classes, are very often unstable, and react with various other compounds. Formation of aroma compounds is a very dynamic process in heated foods as well as in enzyme-catalyzed reactions. Understanding the formation of aroma compounds and their chemical and sensory properties allows better understanding of the technological processes and reactions involved during food manufacturing and storage.

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2 Important Tastants and New Developments

Jakob Ley, Katharina Reichelt, Katja Obst, Gerhard Krammer, and Karl-Heinz Engel

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2.1 INTRODUCTION

Taste and odor are among the most important factors influencing the selection of food by humans. Tastants are perceived mainly in the oral cavity, especially on the tongue and the soft palate (Smith and Margolskee 2001). Here, a food is "analyzed" for the last time before being swallowed to avoid the intake of tainted food or toxic compounds. Five basic tastes are distinguished: sweet, sour, salty, bitter, and umami. Salty taste is involved in regulating ion and water homeostasis in the body, whereas sweet and umami tastes are responsible for estimating the energy content of food (especially carbohydrates and amino acids). Both sour and bitter tastes may act as warning mechanisms to avoid the consumption of unripe fruits or the intake of toxins (Glendinning 1994; Lindemann 1996). In addition, sour taste is considered to be a protection against immoderate acid intake to avoid mismatches in acid/base balance in the body (Roper 2007).

Apart from the five basic tastes, a number of further taste qualities are under discussion. Among them are fat taste (Laugerette et al. 2007), calcium taste (Tordoff and Sandell 2009), and kokumi taste, standing for mouthfulness, mouth feel, and richness of taste (Dunkel et al. 2007; Schlichtherle-Cerny et al. 2003; Toelstede and Hofmann 2009; Ueda et al. 1997).

Another important taste-related impression is the perception of pain caused by a number of compounds, responsible for cold, hot, and spicy taste of a food. Many traditionally used spices, such as chilli, pepper, paracress, mustard, or ginger, contain pungent, tingling, or "heating" compounds. Cooling sensations are caused by compounds such as (–)-menthol. Astringency is a very important (off-) taste quality. It is heavily discussed whether it may be mainly a physical effect, which is caused by precipitation of saliva proteins by astringent compounds, or a real taste or trigeminal quality, or even a combination of both (Bajec and Pickering 2008).

In this short review, it is not possible to cover all known tastants, and therefore we will focus on a selection of the most important compounds of each category and some highlights found just recently. Flavor- and/or taste-modifying compounds are reviewed in Chapter 8 of this book.

2.2 BITTER TASTANTS

In contrast to most other taste qualities, the number of bitter-tasting molecules is very high and shows a wide structural variance. For food bitterness, some common polyphenols such as the widely distributed catechins (e.g., epigallocatechin gallate from green tea) and the lower molecular weight proanthocyanidins (e.g., procyanidine B2 from roasted cocoa nibs) (Stark et al. 2006); phenolic glycosides such as naringin and neohesperidin from citrus pericarps; β -amygdalin from bitter almonds; terpenoids such as thujone from sage oils; limonin from citrus fruits; curcubitacins occurring in the family of *Cucurbitaceae*; *iso*- α -acids such as *cis*-isohumolone from hop (Fritsch and Shellhammer 2008); iridoids, for example, oleuropein from olives; alkaloids such as caffeine from coffee or tea; and theobromine from cocoa are important examples (Figure 2.1). Over the centuries, one of the intentions of plant selection, cultivation, breeding, and processing has been to reduce the content of these bitter compounds. In contrast to these undesired compounds, certain bitter principles are added to food or beverages for taste reasons, for example, quinine to bitter lemon soft drinks, and hop extracts to beer.

Another class of bitter components are the small hydrophobic peptides. These peptides, especially the ones with hydrophobic amino acids, such as leucine, isoleucine, valine, or proline at the N or C terminus, frequently exhibit a bitter taste and are often generated during aging or fermentation processes starting from larger proteins, for example, during cheese maturing (Maehashi and Huang 2009; Solms 1969; Toelstede and Hofmann 2008). As a recent example, the pentapeptide Asn-Ala-Leu-Pro-Glu isolated from soybean glycinine shows a bitter threshold of 74 μ mol/L (Kim et al. 2008).

Unlike other taste-active compounds, bitter-tasting molecules often show low thresholds to avoid poisoning by high concentrations of toxins (Roper 2007). Examples for extremely bitter-tasting compounds are denatonium benzoate with a taste threshold of 0.01 µmol/L (Meyerhof 2005), quinine (1.6 µmol/L), limonin (2.1 µmol/L) (Glendinning 1994), and *cis*-isohumolone (10 µmol/L) (Intelmann et al. 2009), whereas caffeine (133 µmol/L) (Stevens et al. 2001) and epigallocatechin gallate (190 µmol/L) (Stark et al. 2006) are moderate bitter taste-eliciting substances.

Identification of new bitter components in raw or processed foods is also very important to support quality assurance and to prevent taste defects. The bitter off-taste observed in some batches of carrots that can deteriorate carrot-based baby food

FIGURE 2.1 Typical bitter-tasting molecules that occur naturally or are added to foods.

was identified by using taste dilution analysis (TDA) to be falcarindiol (Czepa and Hofmann 2003, 2004) (Figure 2.2). Some chlorogenic acid-derived lactones (e.g., 5-O-caffeoyl-muco- γ -quinide, detection threshold 29 μ mol/L) could be detected to contribute significantly to the bitter taste of coffee brew (Frank et al. 2008). The cyclic octapeptide cyclolinopeptide E was found to contribute to the bitter off-taste of some linseed oil qualities after storage (Brühl et al. 2008). Some 1-oxo-2,3-di-hydro-1H-indolizinium-6-olates could be identified via TDA as very potent bitter (threshold 0.25 μ mol/kg water) compounds of Maillard reactions based on xylose, rhamnose, and alanine (Frank et al. 2003).

2.3 SWEET TASTANTS

In food preparations, carbohydrates, especially sucrose, glucose, and fructose, are widely used because of their sweet taste and mouth feel. However, not only carbohydrates evoke sweet taste in humans but also a number of structurally diverse compounds, showing high sweet intensities at low levels of use. These high intensity sweeteners (HIS) can be both artificial and of natural origin, their structures ranging from small molecules such as saccharin to highly complex proteins, such as

FIGURE 2.2 New bitter compounds found in foods by modern approaches of taste analysis.

thaumatin or monellin (Duffy et al. 2004; Kinghorm and Soejarto 1986). Commonly used artificial HIS (Figure 2.3) include saccharin (approved as food additive in United States and the European Union [EU]), which was the first commercially used artificial HIS; cyclamate (EU only); aspartame (United States, EU); acesulfame K (United States, EU); and sucralose (United States, EU).

FIGURE 2.3 Important HIS approved as food additives by FDA and/or European Commission.

Saccharin is considered to be 450 times sweeter than a 10% sucrose solution, but a typically bitter taste occurs at higher saccharin concentrations, which can be detected only by about 25% of the European population (Helgren et al. 1955). Cyclamate is 40 times sweeter than a 2% sucrose solution. Aspartame shows a 340 times higher sweet intensity in comparison to a 0.34% iso-sweet sucrose solution (Belitz et al. 2007) and is described to have a clean sweet taste without any bitter or metallic off-notes. The new high-potency sweetener neotame (United States only), a derivative of aspartame, is considered to be 30–60 times sweeter than aspartame. Because of its lower use levels, it can also, unlike aspartame, be consumed by patients with phenylketonuria (Stargel et al. 2001). Sucralose is approximately 750 times sweeter compared to a 2% sucrose solution, while the taste is perceived similar to that of sucrose: sweet without any off-tastes (Goldsmith and Merkel 2001). Other HIS include neohesperidine dihydrochalcone and alitame, a representative of the series of L-aspartyl-D-alanine amides.

HIS, however, are not only obtained as artificial compounds, but occur also naturally (Kim and Kinghorn 2002; Kinghorn and Compadre 2001). Currently, glycyrrhicinic acid from the rhizomes and roots of licorice (*Glycyrrhiza glabra* L. Fabaceae), thaumatin from the fruit of *Thaumatococcus daniellii* (Bennett) Benth (Marantaceae), and rebaudioside A from *Stevia rebaudiana* (Carakostas et al. 2008) are the most important naturally occurring HIS of commercial interest.

2.4 UMAMI AND KOKUMI TASTANTS

Until recently, only the amino acids glutamic acid and to a lesser extent aspartic acid and their corresponding salts, especially the monosodium glutamate (MSG), and some peptides were described as umami tastants. Some nucleotides such as guanosine 5′-monophosphate or inosine 5′-monophosphate also show a weak intrinsic umami taste, but more important is their ability to enhance synergistically the umami taste of MSG. In the past 5 years, several new high intensity umami-tasting compounds were found; recently, a review regarding the newest developments was given (Winkel et al. 2008), but meanwhile some new structures were published (Looft et al. 2008a, 2008b). In contrast to MSG (umami threshold about 0.2 mmol/L; Kaneko et al. 2006) and all other known umami tastants, these particular molecules are much stronger in activity (100–1000 times compared to MSG) and exhibit umami taste without any additional sodium ions or other peptides. Examples are shown in Figure 2.4.

Some new peptide-like kokumi-tasting compounds were described recently (Figure 2.4). Starting from earlier reports that glutathione-rich foods (Ueda et al. 1997) as well as some seasonings containing fermented peptides (Yamanaka 2006) exhibit a "kokumi" taste quality, some γ -glutamyl peptides such as γ -glutamylcysteine- β -alanine occurring in beans were found to contribute to this taste direction (Dunkel et al. 2007). Furthermore, γ -glutamyl dipeptides such as γ -Glu–Met in mature Gouda cheese (Toelstede et al. 2009) and other cheeses produced or ripened by *Penicillium roqueforti* (Toelstede and Hofmann 2009) imparting kokumi taste could be identified. From dry scallop, (*R*)-strombine was isolated as a component contributing to the dry mouth feel of umami taste (Starkenmann 2009).

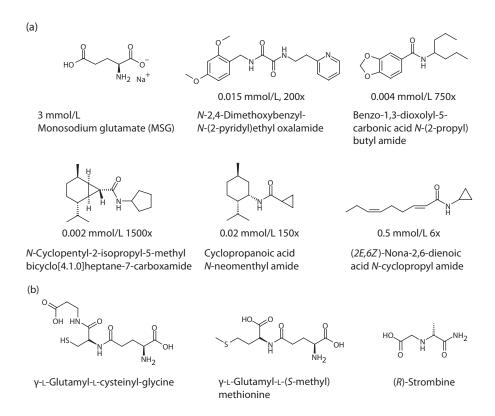


FIGURE 2.4 Umami tastants. (a) Concentrations given are those exhibiting nearly the same umami impression as 3 mmol/L MSG. (b) New kokumi tastants.

2.5 SALTY AND SOUR COMPOUNDS

A clean salt taste can only be found for sodium chloride, the most intense salty-tasting salt. LiCl and NH₄Cl are also salty but cannot be used for human consumption because of safety concerns or off-tastes, respectively. Therefore, KCl as the next relative is often used as a NaCl replacer, but shows strong bitter and other off-tastes. In the literature, reports can be found about salty-tasting compounds such as glycine ethyl ester (Kawai et al. 2008) or choline chloride (Locke and Fielding 1994), but in general, the compounds do not intrinsically taste salty but in fact enhance saltiness of sodium salts.

There are no reliable reports about molecules exhibiting a sour taste without being protic acids. Various studies, however, showed that naturally occurring weak organic acids, such as citric, succinic, malic, or lactic acid, are perceived as more sour in the oral cavity than hydrochloric acid at the same pH (Ganzevles and Kroeze 1987; Makhlouf and Blum 1972). This leads to the conclusion that undissociated acids are also involved in the sour taste perception of organic acids. Unlike pH value, titratable acidity involves both free and bound hydrogen ions in a solution (Da Conceicao Neta et al. 2007). It was shown that sourness intensity is positively correlated with

increasing titratable acidity at a given pH (Makhlouf and Blum 1972). The perceived sourness of different organic acids is positively correlated with their dissociation constant. Titration experiments with several organic acids showed correlations with the rank order of the perceived sourness (Ganzevles and Kroeze 1987).

2.6 HEATING, PUNGENT, AND TINGLING COMPOUNDS

Warming, heating, or pungent sensations are caused mostly by substances influencing the vanilloid receptor TRPV1 or the pain receptor TRPA1 expressed on free nerve endings of the trigeminal nerve system (Patapoutina et al. 2003). These effects are not elicited by real increase in physical temperature but by lowering the temperature threshold of the free nerve endings. As a result, the nerves are firing at body temperature and not only at moderate or noxious heat as in the nonactivated state. The exact description of the so-called chemestethic effects depends on the compound and its concentration; whereas low amounts of, for example, capsicum extract elicits only a mild and pleasant warming effect, the sensation caused by higher concentrations is described as "pungent," "hot," or even "burning like fire." The most important flavor compounds showing these effects (Figure 2.5) are capsaicin and nonivamide from Capsicum extracts (Capsicum ssp.); piperine from pepper (Piper nigrum) (Szallasi 2005); [8]-gingerole and related compounds from ginger (Zingiber ssp.) and related species (Banno and Mukaiyama 1976; Kikuzaki 2000); [6]-paradol from "Grains of Paradise" (Aframomum melegueta) (Fernandez et al. 2006); some alkamides such as cis-pellitorine from tarragon (Artemisia dracunculus) (Ley et

FIGURE 2.5 Typical heating, pungent, and tingling compounds found in nature.

al. 2004); terpenoidal dialdehydes such as polygodial from hydropiper (*Polygonum hydropiper*) (Starkenmann et al. 2006); mioganal from *Zingiber mioga* (Abe et al. 2008); and isothiocyanates such as the lachrymator allyl isothiocyanate from Brassicacea (Jordt et al. 2004).

The alkamides *trans*-pellitorine (found in, e.g., *P. nigrum*; Subehan et al. 2006), spilanthol (found in, e.g., paracress, *Spilanthes acmella*; Ramsewak et al. 1999), and alpha-hydroxy sanshool (from *Zanthoxylum schinifolium*; Iseli et al. 2007) show a so-called "tingling" effect on the tongue. It is more an irritating sensory experience and accompanied by a numbing feeling. In addition, they can induce salivation (Ley and Simchen 2007).

2.7 COOLING COMPOUNDS

The most important flavor compound exhibiting a physiological cooling effect is (–)-menthol. Similar to heating, the cooling effect is not caused by a real physical decrease in temperature but by increasing the temperature threshold of the coolsensitive free nerve endings of the trigeminal nerve (or the corresponding nerves of the dorsal root ganglion for the lower parts of the body) (Zanotto et al. 2007) resulting in activation of the nerves at body temperature. This pseudo-cooling effect can be caused by binding of (–)-menthol to the ion channel TRPM8 (Patapoutina et al. 2003).

(–)-Menthol is broadly used for mint-flavored products such as toothpaste, chewing gum, and mouthwash. Unfortunately, it is difficult to apply to non-mint-flavored products because the threshold for its aroma value (0.1–0.2 mg/kg water) is roughly 10 times lower compared to the threshold for its cooling effect (0.9–1.9 mg/kg water) (Ottinger et al. 2001). Consequently, cooling compounds with a much weaker aroma value but with a comparable cooling effect were developed during the past decades. Several comprehensive reviews about the most important cooling compounds were given in recent years (Eccles 1994; Erman 2004; Leffingwell 2009; Pringle and Brassington 2007; Watson et al. 1978). Therefore, only the most important cooling compounds as well as the established natural alternatives to menthol and some new developments are shown in Figure 2.6.

The menthol derivatives menthyl lactate and menthyl glycerol ether (Cooling Agent 10), and menthyl carbonates such as the propylene glycol carbonate (Frescolat MGC) are established cooling compounds as well as the menthone ketal of glycerol (Frescolat MGA). The menthane carbonic acid amides and some structural related hindered carbonic acid amides (WS compounds) were developed in the 1970s and show a very low aroma value and an increased cooling strength compared to menthol (Watson et al. 1978). Icilin was found to elicit a strong cooling effect in vitro and in vivo (Chuang et al. 2004) but was never commercially used. By using TRPM8 assays and structure—activity concepts, the cooling strength of the menthane carbonic acid amides could be potentiated, and as a result, the menthane carbonic acid 4-cyanomethylphenyl amide (Evercool 180) was found (Furrer et al. 2008).

Apart from (–)-menthol, only a small number of cooling compounds were found in nature: menthyl lactate isomers were described to occur in fermented *Mentha piperita* leaves (Gassenmeier 2006), menthyl succinate in *M. piperita* and *Lycium*

FIGURE 2.6 Important cooling compounds including natural alternatives to (–)-menthol (first row).

barbarum (Hiserodt et al. 2004; Marin and Schippa 2006), and menthyl glutarate in Litchi chinesis (Hiserodt et al. 2004). Cubebol is known as a constituent of fruits of false cubeb (*Piper lowong*) (De Rosa 1994; Velazco et al. 2000).

2.8 ASTRINGENCY

The perception of astringency is still not well understood: it may be caused by a more macroscopic event via precipitation of saliva proteins and subsequent alteration of the lubrication property of the saliva, binding and cross-linking of proteins by astringent compounds to the surface of the mucous membrane, or even binding of the compounds to still unknown receptors or ion channels (Bajec and Pickering 2008; Rossetti et al. 2009). Typical astringents are alumina, ferrous and zinc salts; catechol- and especially gallate-type polyphenols such as epigal-locatechin gallate; gallic acid esters of carbohydrates (ester type tannins such as tannic acid, hamameli tannins); condensed catechins such as proanthocyanidine A2 (Haslam 2007); and flavonol glycosides such as rutin (Scharbert and Hofmann 2005) (Figure 2.7).

The detection thresholds differ widely for several well-known astringent compounds. Rutin shows a very low threshold of 1 μ g/kg (Scharbert et al. 2004), a concentration at which the protein precipitation cannot play any significant role. In contrast, epigallocatechin gallate has a threshold of 87 mg/kg (Scharbert et al. 2004) and is also able to cause protein aggregation (Nayak and Carpenter 2008). Further astringent substances with low thresholds and uncommon structures are shown in Figure 2.8. As examples, 3-carboxymethyl-indole-1*N*- β -D-glucopyranoside (1 μ mol/L) and 3-methylcarboxymethyl-indole-1*N*- β -D-glucopyranoside (0.3 μ mol/L), and the

FIGURE 2.7 Polyphenolic astringent compounds.

non-cyanogenic nitriles 2-(4-hydroxybenzoyloxymethyl)-4-β-D-glucopyranosyloxy-2(*E*)-butenenitrile (5.9 mmol/L) and 2-(4-hydroxy-3-methoxybenzoyloxymethyl)-4-β-D-glucopyranosyloxy-2(*E*)-butenenitrile (1.2 mmol/L) were isolated from red currant (Schwarz and Hofmann 2007). Cinnamic acid amides of amino acids such as clovamide (9.3 mg/kg) could be identified in cocoa nibs (Stark et al. 2006; Stark and Hofmann 2005).

ROOC

$$R = H, CH_3$$
 HO
 OH
 HO
 OH
 HO
 OH
 HO
 OH
 HO
 OH
 HO
 OH
 O

FIGURE 2.8 Newly found astringent compounds with considerably low taste thresholds.

2.9 CONCLUSION AND OUTLOOK

Most tastants do not occur as neat compounds in nature, but in mixtures and even as single molecules, they can exhibit more than one taste (or even aroma) quality. Consequently, the detection and structure elucidation of newly found tastants is still a challenge for analytical and flavor chemists. Nevertheless, there are still surprising new compounds as exemplified for the class of high intense umami-tasting molecules that were not known until several years ago. Whereas detection of bitter molecules is crucial for the identification of off-flavors and especially off-tastes, the finding of new high intensity sweet, umami, or other taste qualities is of high importance for the development of new flavorings. Additionally, the discussion is ongoing whether further taste qualities and their specific tastants can be found and unequivocally be described.

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3 Smell, Taste, and Flavor

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3.1 INTRODUCTION

During food consumption, we experience dynamic stimulations through the gustatory, olfactory, and trigeminal sensory systems. Accordingly, the International Standards Organization (ISO 1992, 2008) has defined flavor as a "complex combination of the olfactory, gustatory and trigeminal sensations perceived during tasting.

The flavor may be influenced by tactile, thermal, painful and/or kinesthetic effects." In addition, many studies have demonstrated that visual or auditory cues also influence flavor perception (Verhagen and Engelen 2006; Zampini et al. 2007, 2008; Shankar et al. 2009, 2010). That is, flavor perception is a multisensorial and dynamic sensation.

In this chapter, we will try to explain how flavors are perceived. First, the basic anatomy and physiology of three main sensory systems involved in flavor sensation (i.e., gustatory, trigeminal, and olfactory system) will be explored. Next, the two olfactory pathways will be introduced: ortho- and retronasal olfaction. In fact, during food consumption, aromatic volatile compounds of foods are delivered via both ortho- and retronasal pathways, but odors from either nose or mouth are perceived differently. Finally, interactions between olfactory and gustatory stimuli will be addressed.

3.2 CHEMOSENSORY SYSTEM

3.2.1 GUSTATORY SYSTEM

3.2.1.1 Human Taste

In many cases, people use the word "taste" to describe sensations during eating and drinking. However, from the biological point of view, taste is restricted to sensations mediated by an anatomically and physiologically defined gustatory system (Bachmanov and Beauchamp 2007). As one of the basic sensory modalities, the sense of taste is essential to evaluate whether foods or drinks are safe or poisonous. Broadly speaking, sweet taste reflecting calorie or energy is accepted, whereas bitter taste signaling toxic or hazardous substances is rejected. In particular, a sense of taste (gustation), in addition to a sense of smell (olfaction), is closely related to food consumption. For example, a large portion of people with taste loss or distortion report that their eating behavior and/or nutritional status is altered (Kokal 1985; Mattes-Kulig and Henkin 1985; Mattes et al. 1990; Langius et al. 1993; Ritchie et al. 2002; Aschenbrenner et al. 2008b). In addition, a line of studies have demonstrated the association between eating disorder and gustatory function (Casper et al. 1980; Nakai et al. 1987; Tóth et al. 2004; Frank et al. 2006; Aschenbrenner et al. 2008b; Wagner et al. 2008; Wöckel et al. 2008). Specifically, people with eating disorders (e.g., anorexia nervosa and bulimia nervosa) show lower gustatory sensitivity than healthy controls, and they prefer sweet taste, but not fat stimuli (Casper et al. 1980; Nakai et al. 1987; Aschenbrenner et al. 2008b; Wöckel et al. 2008). Furthermore, compared to healthy controls, people with eating disorders show a different pattern of neural processing for the taste stimulation in the electroencephalogram (Tóth et al. 2004) and brain imaging (Frank et al. 2006; Wagner et al. 2008). For example, using functional magnetic resonance imaging (fMRI), Wagner et al. (2008) reported differences of neural activation for sucrose or water stimulation between women recovered from restricting-type anorexia nervosa and healthy control women. Specifically, in the primary gustatory cortical region (e.g., insular), neural activation was significantly lower in women who recovered from restricting-type anorexia nervosa than in healthy controls.

The current consensus is that human taste sensation is divided into five taste qualities labeled as sweet, sour, salty, bitter, and umami [or savory; the prototypical substance is the sodium salt of the amino acid glutamate (monosodium glutamate or MSG) and 5′-ribonucleotides, e.g., inositol monophosphate or guanidine monophosphate] (Bachmanov and Beauchamp 2007; Ninomiya and Beauchamp 2009). Human neonates seem to discriminate those taste qualities (Steiner 1974; Rosenstein and Oster 1988; Bergamasco and Beraldo 1990). For example, neonates show differential facial expressions depending on the taste quality presented (Steiner 1974; Rosenstein and Oster 1988; Bergamasco and Beraldo 1990). However, taste qualities are still dependent on experience; for example, the term "umami" is still unfamiliar to most people in the Western Hemisphere, although they are able to perceive and discriminate umami-tasting substances (Singh et al. 2010).

Moreover, there is growing evidence that "fat taste" is another basic taste quality (Khan and Besnard 2009; Mattes 2009a). Previous studies have demonstrated that dietary fat and its metabolites activate somatosensory, olfactory, and gustatory systems (Mattes 2005; Bachmanov and Beauchamp 2007; Khan and Besnard 2009; Mattes 2009a). Esterified fatty acids (e.g., triacylglycerol fatty acids) are not effective as gustatory stimuli (Mattes 2009a). However, in the oral cavity, lingual lipase hydrolyzes triglycerides and releases free fatty acids, which can access taste receptor cells and inhibit the delayed rectifying potassium channels in rats (Gilbertson et al. 1997; Bachmanov and Beauchamp 2007). Additionally, in mice and rats, the fatty acid transporter CD36 that is localized along the apical side of taste buds of foliate and circumvallate papillae, has a high affinity for longchain fatty acids and is expressed in taste receptor cells (Laugerette et al. 2005; Bachmanov and Beauchamp 2007; Gaillard et al. 2008). That is, free fatty acids appear to be effective as gustatory stimulus (Mattes 2009a). It has been shown that humans may detect free fatty acids varying in saturation and chain length (C6–C18) in the condition designed to minimize nongustatory sensory cues (Chale-Rush et al. 2007; Mattes 2009a, 2009b). However, there is individual variability in detection of free fatty acids and there is little evidence for the existence and function of fatty acid transduction systems on human taste receptor cells (Mattes 2009a). In addition, data verify that free fatty acids are effective stimuli only for the gustatory system, but not for other related sensory systems (Mattes 2009a). Taken together, it is still debatable whether "fat taste" constitutes a sixth primary taste—further study is needed to clarify this issue.

The taste qualities seem to interact at central nervous levels (e.g., cognition) as well as at peripheral levels (e.g., perception) in terms of enhancement/suppression or synergy/masking (Keast and Breslin 2002; Breslin and Huang 2006). Keast and Breslin (2002) suggested three levels of taste interaction that must be considered when examining interaction of taste mixture: (1) chemical interaction between tasting components in the mixture; (2) oral physiological interaction between one of mixture components and the taste receptor/transduction of the other component; and (3) cognitive interactions between different taste qualities being perceived together. Typically, interactions between same taste qualities are fitted to a sigmoidally shaped psychophysical function, with expansive, linear, and compressive phases (Keast and Breslin 2002). Rather, when two taste compounds eliciting the same quality