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Food & Nutrition

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FLAVOR, FRAGRANCE, AND ODOR ANALYSIS
second edition

There are many advantages to stir bar sorptive extraction (SBSE) for isolating and concentrating flavor-active chemicals from foods, including its simplicity and wide application appeal. Written from a practical, problem-solving perspective, the second edition of **Flavor, Fragrance, and Odor Analysis** highlights this powerful technique and emphasizes the range of applications available.

Topics discussed include

- Sequential SBSE, a novel extraction procedure
- A simplified method for switching from one-dimensional to two-dimensional GC-MS
- How analytical sensitivity and recovery of phenolic compounds can be improved using aqueous acylation prior to SBSE GC-MS
- Analyzing and combating off-flavors caused by metabolites from microorganisms
- A technique for measuring synergy effects between odorants
- The identification of the characterizing aroma-active compounds of tropical fruits with high economic potential
- The parameters utilized during the production of aqueous formulations rich in pyrazines
- How spectral deconvolution can be used to speciate the subtle differences in essential oil content and track key ingredients through the manufacturing process

The final chapter summarizes chemical identities of characterizing aroma chemicals in fruits, vegetables, nuts, herbs and spices, and savory and dairy flavors. It also provides a brief compendium of the characterization of off-flavors and taints that are reported in foods.

With contributions from a distinguished panel of international experts, this volume provides chemists and researchers with the latest techniques for analyzing and enhancing food flavor and fragrance.

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Ray Marsili

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FLAVOR, FRAGRANCE, and ODOR ANALYSIS

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chapter nine

Character-impact flavor and off-flavor compounds in foods

Robert J. McGorrin

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Introduction

Aroma substances that comprise food flavors occur in nature as complex mixtures of volatile compounds. However, a vast majority of volatile chemicals that have been isolated from natural flavor extracts do not elicit aroma contributions that are reminiscent of the flavor substance. For instance, *n*-hexanal is a component of natural apple flavor [1]; however, when smelled in isolation its odor is reminiscent of "green, painty, rancid oil." Similarly, ethyl butyrate provides a nondescript "fruity" aroma to blackberries, raspberries, and pears, but it does not distinctly describe the flavor quality of any of these individual fruits. It has long been the goal of flavor chemists to elucidate the identity of pure aroma chemicals that possess the unique flavor character of the natural fruit, vegetable, meat, cheese, or spice from which they were derived. Frequently, these unique flavor substances are referred to as "character-impact compounds" [2].

A character-impact compound is a unique chemical substance that provides the principal sensory identity of a particular flavor or aroma.

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Often, character impact is elicited by a synergistic blend of several aroma chemicals. When tasted or smelled, the character-impact chemical, or group of chemicals, contributes a recognizable sensory impression even at the low concentration levels typically found in natural flavors (e.g., vanillin in vanilla extract and diacetyl in butter) [3,4]. In some instances, flavor concentration and food context are very important. For example, although at high concentrations 4-mercapto-4-methyl-2-pentanone (cat ketone) has an off-odor associated with cat urine, when it is present in reduced levels in the context of a Sauvignon Blanc wine it conveys the typical flavor impression of the Sauvignon grape [5].

For many foods, character-impact flavor compounds are either unknown or have not been reported to date. Examples of such foods include cheddar cheese, milk chocolate, and sweet potatoes. For these foods, the characterizing aroma appears to comprise a relatively complex mixture of flavor compounds rather than one or two aroma chemicals.

The intent of this chapter is to summarize and update a previous review [6] regarding what is generally known about the chemical identities of characterizing aroma chemicals in fruits, vegetables, nuts, herbs and spices, and savory and dairy flavors. A brief compendium of characterizing off-flavors and taints that have been reported in foods is also discussed.

Character-impact flavors in foods

More than 6000 compounds have been identified in the volatile fraction of foods [7]. The total concentration of these naturally occurring components varies from a few parts per million (ppm) to approximately 100 ppm, with the concentration of individual compounds ranging from parts per billion (ppb) to parts per trillion (ppt). A majority of these volatile compounds do not have significant impact on flavor. For example, more than 800 compounds have been identified in the flavor of coffee, but in general only a small proportion of these substances have a significant contribution to its sensory flavor profile [8].

The ultimate goal of flavor research is to identify and classify unique aroma chemicals that contribute to the characteristic odor and flavor of foods. This knowledge enables the flavor industry to better duplicate flavors through nature-identical or biosynthetic pathways and can facilitate better quality control of raw materials by screening appropriate analytical target compounds.

In recent studies, potent aroma compounds have been identified using various gas chromatography–olfactometry (GC–O) techniques, such as combined hedonic aroma response measurements (CHARM) analysis, and aroma extract dilution analysis (AEDA) [9,10]. The flavor compounds identified by these methods are significant contributors to the sensory profile.

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In some cases, these sensory-directed analytical techniques have enabled the discovery of new character-impact compounds. However, in other instances key aroma chemicals have been identified that, while potent and significant to flavor, do not impart character impact. For example, in dairy products, chocolate, and kiwifruit, these flavor types appear to be produced by a complex blend of noncharacterizing key aroma compounds.

Knowledge of character-impact compounds enables flavor chemists to use these materials as basic "keys" to formulate enhanced versions of existing flavors. As analytical techniques improve in sensitivity, flavor researchers continue their quest to discover new character-impact flavors that will enable them to develop the next generation of improved flavor systems.

Herb, spice, and seasoning flavors

The original identifications of character aroma compounds were from isolates of spice oils and herbs. Many of these early discoveries paralleled developments in synthetic organic chemistry [11]. The first identifications and syntheses of character flavor molecules include benzaldehyde (cherry), vanillin (vanilla), methyl salicylate (wintergreen), and cinnamaldehyde (cinnamon). A listing of the character-impact compounds found in herb and spice flavors is presented in Table 9.1.

Table 9.1 Character-Impact Compounds in Herbs, Spices, and Seasonings

Character-impact compounds	Chemical Abstracts Services (CAS) Registry number	Occurrence	Reference
trans-p-Anethole	[4180-23-8]	Anise	4
Methyl chavicol (estragole)	[140-67-0]	Basil	12
(S)-(+)-Carvone	[2244-16-8]	Caraway	14
trans-Cinnamaldehyde	[104-55-2]	Cinnamon	4
Eugenol	[97-53-0]	Clove	4
Eugenyl acetate	[93-28-7]	Clove	12
D-Linalool	[78-70-6]	Coriander	4
trans-2-Dodecenal	[20407-84-5]	Coriander	18
Cuminaldehyde	[122-03-2]	Cumin	12
p-1,3-Menthadien-7-al	[1197-15-5]	Cumin	12
(S)-α-Phellandrene	[99-83-2]	Fresh dill	12
3,9-Epoxy-*p*-menth-1-ene	[74410-10-9]	Fresh dill	21
1,8-Cineole (eucalyptol)	[470-82-6]	Eucalyptus	14
Sotolon	[28664-35-9]	Fenugreek	15

(*Continued*)

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Table 9.1 Character-Impact Compounds in Herbs, Spices, and Seasonings (*Continued*)

Character-impact compounds	Chemical Abstracts Services (CAS) Registry number	Occurrence	Reference
Benzenemethanethiol	[100-53-8]	Garden cress	28
Diallyl disulfide	[2179-57-9]	Garlic	22
Diallylthiosulfinate (allicin)	[539-86-6]	Garlic	22
1-Penten-3-one	[1629-58-9]	Horseradish	4
4-Pentenyl isothiocyante	[18060-79-2]	Horseradish	22
O,S-Diethyl thiocarbonate	[3554-12-9]	Indian cress	29
Allyl isothiocyanate	[57-06-7]	Mustard	4
Propyl propanethiosulfonate	[1113-13-9]	Onion, raw	22
3-Mercapto-2-methylpentan-1-ol	[227456-30-6]	Onion, raw	26
Allyl propyl disulfide	[2179-59-1]	Onion, cooked	22
2-(Propyldithio)-3,4-dimethylthiophene	[126876-33-3]	Onion, fried	22
Carvacrol	[499-75-2]	Oregano	12
Rotundone	[18374-76-0]	Pepper, black	20
L-Menthol	[89-78-1]	Peppermint	4
t-4-(Methylthio)-3-butenyl isothiocyanate	[13028-50-7]	Radish	22
Verbenone	[80-57-9]	Rosemary	14
(R)-(–)-Carvone	[6485-40-10]	Spearmint	14
Safranal	[116-26-7]	Saffron	17
ar-Turmerone	[532-65-0]	Turmeric	16
Thymol	[89-83-8]	Thyme	14
Methyl salicylate	[119-36-8]	Wintergreen	4

A major contributor to the flavor of basil is methyl chavicol (estragole), which provides tealike green, hay, and minty notes [12]. In Italian spice dishes, basil is complemented by oregano, for which carvacrol is a character-impact aroma. Thyme comprises the dried leaves of *Thymus vulgaris*, a perennial of the mint family, for which thymol provides a warm, pungent, and sweetly herbal note with contributions from carvacrol [13]. Interestingly, with fennel (*Foeniculum vulgare*) seed and oil, the essential flavor character is not a single primary compound but is provided by a combination of *trans*-anethole (anise, licorice), estragole (basil, anise), and fenchone (mint, camphor) [13]. In a classic example of the effect of chiral isomers on flavor character, (S)-(+)-carvone imparts caraway flavor, whereas (R)-(–)-carvone provides spearmint flavor [14].

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Toasted and ground fenugreek seed is an essential ingredient of curry powders. Sotolon (3-hydroxy-4,5-dimethyl-2(5H)furanone) was recently established as a character-impact flavor component in fenugreek on the basis of its "seasoning-like" flavor note [15]. Its aroma characteristic changes from caramel-like at low concentration levels to currylike at high concentrations. The sensory impact of sotolon is attributed to its extremely low detection threshold (0.3 mg/L in water) and the fact that its concentration in fenugreek seeds is typically 3000 times higher than its threshold.

Turmeric is also primarily used as a spice component in curry dishes, and as a coloring agent in dried and frozen foods. The character-impact compound for turmeric is reported as *ar*-turmerone [16]. Saffron, the dried red stigmas of *Crocus sativus* L. flowers, is utilized to impart both color and flavor, which is described as "sweet, spicy, floral, with a fatty herbaceous undertone." Safranal (2,6,6-trimethyl-1,3-cyclohexadiene-1-carboxaldehyde) is generally considered the character-impact compound of saffron; however, a recent investigation has identified two other potent compounds, 4,4,6-trimethyl-2,5-cyclohexadien-1-one and an unknown compound, possessing "saffron, stale, dried-hay" aroma attributes [17]. Representative structures for spice impact compounds are shown in Figure 9.1.

A key component of both chili powder and curry powder, cumin is the dried seed of the herb *Cuminum cyminum*, a member of the parsley family. Cuminaldehyde is the principal contributor of aroma and flavor to the spice, which imparts a strong musty/earthy character with green grassy notes contributed by *p*-1,3- and 1,4-menthadienals. *trans*-2-Dodecenal, possessing a persistent fatty-citrus-herbaceous odor, is a character-impact component of coriander, along with *d*-linalool [18].

Sesquiterpenes are important contributors to natural flavors. Previously, the aroma of black pepper was attributed to sensory interactions of terpenes and other flavor components [19]. Recently, rotundone was identified as the key aroma-impact compound for black pepper with a strong, spicy peppercorn character, and it is also a source of the peppery, spicy aroma in Shiraz wines [20]. Its aroma detection thresholds were measured as 8 ng/L in water and 16 ng/L in red wine. (+)-α-Phellandrene, the main constituent of dill (*Anethum graveolus* L.), greatly contributes to the sensory impression of the dill herb [12]. However, fresh dill character impact appears to be a synergistic relationship contributed primarily by (+)-α-phellandrene with a modifying effect from "dill ether," 3,9-epoxy-*p*-menth-1-ene [21].

The *Allium* genus includes garlic, onion, leek, and chive. All comprise sulfur-containing character-impact compounds. The aroma-impact constituents of garlic are diallyl disulfide and the corresponding thiosulfinate derivative (allicin), which are enzymatically released from a sulfoxide flavor precursor (alliin) during the crushing of garlic cloves [22].

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The flavor chemistry of sulfur compounds in onion is quite complex [23,24]. Polysulfides and thiosulfinates that were initially reported to be flavor significant were later demonstrated to be thermal artifacts from gas chromatographic analysis [25]. Character-impact sulfur compounds have been proposed for fresh, boiled, and fried onion. In raw, fresh onion,

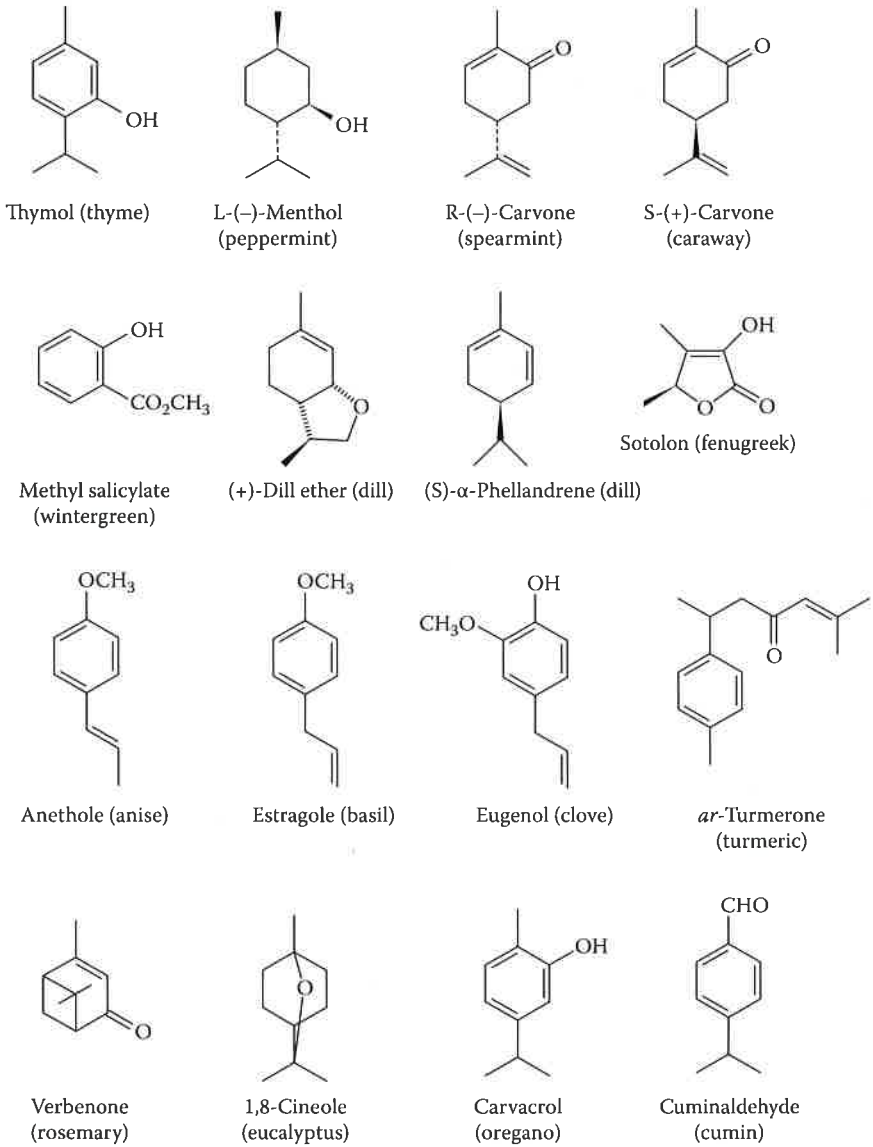

Figure 9.1 Flavor compounds: Representative herb and spice character-impact flavor compounds.

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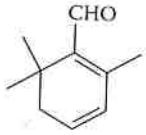
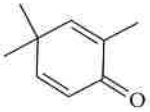
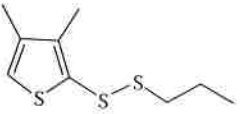


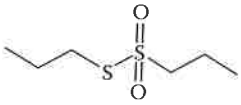
Safranal (saffron)



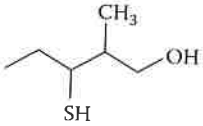
4,4,6-Trimethyl cyclohexadienone (saffron)



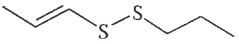
2-(Propyldithio)-3,4-dimethyl-thiophene (fried onion)



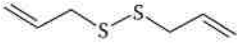
Propyl propanethiosulfonate (raw onion)



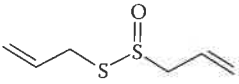
3-Mercapto-2-methyl-pentan-1-ol (raw onion)



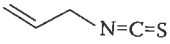
1-Propenyl propyl disulfide (boiled onion)



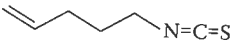
Diallyl disulfide (garlic)



Diallyl thiosulfinate (garlic)

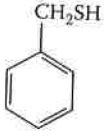


Allyl isothiocyanate (mustard)

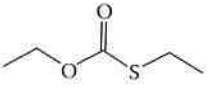


4-Pentenyl isothiocyanate (horseradish)

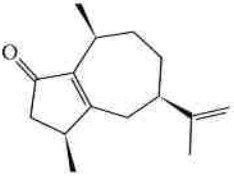
t-4-(Methylthio)-3-butenyl isothiocyanate (radish)



Benzenemethanethiol (garden cress)



O,S-Diethyl thiocarbonate (Indian cress)



Rotundone (black pepper)

Figure 9.1 *(Continued)*

the impact contributors are propyl propanethiosulfinate, propenyl propanethiosulfinate, thiopropanal S-oxide, and propyl methanethiosulfinate [22,23]. Several compounds contribute to the aroma character of cooked onion, among which dipropyl disulfide and allyl propyl disulfide show key impact [22]. Fried onion aroma is formed by heating the latter compound and is characterized by 2-(propyldithio)-3,4-dimethylthiophene, which has an odor threshold of 10–50 ng/L in water. More recently, a new, highly potent aroma compound, 3-mercapto-2-methylpentan-1-ol, was identified in raw onions [26]. The flavor impact of this thiol is strongly dependent on concentration; at 0.5 ppb it provides a pleasant brothlike, sweaty, onion, and leeklike flavor, whereas at high levels it provides a

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strong, unpleasant onionlike quality. Higher concentrations are formed in cooked onions, and it was also found in other *Allium* species including chives, onions, and leeks but not garlic [27].

Isothiocyanates are character-impact constituents that provide pungency and typical flavor to mustard (allyl isothiocyanate), radish (*trans*-4-(methylthio)-3-butenyl and *trans*-4-(methylthio)butyl isothiocyanate), and horseradish (4-pentenyl and 2-phenylethyl isothiocyanate) [22]. Garden cress (peppergrass) is classified in the *Brassica* (*Cruciferae*/mustard) family, and its leaves and seeds were historically used as salad greens and as a spicy condiment because of their peppery flavor. Benzenemethanethiol was identified as the character-impact compound for the unique flavor of garden cress (*Lepidium sativum*) seed, and it also occurs in the volatile extracts of potatoes [28]. Recently, a novel sulfur volatile, *O,S*-diethyl thiocarbonate, was identified in Indian cress (*Tropaeolaceae* family), providing a "red fruity-sulfury" character [29].

Fruit flavors

The aroma constituents of essential oils from fruits such as lime, lemon, and orange were among the first character-impact compounds identified by flavor chemists. Fruit flavors are a subtle blend of characterizing volatile compounds, supported by fruit sugars, organic acids, and noncharacterizing volatile esters. Fruit aromatics tend to be present in concentrations of greater abundance (< 30 ppm) than other foods, which facilitated early analytical studies. The volatile composition of fruits is extremely complex, and noncharacterizing flavor esters are common across species. A compilation of the character-impact compounds found in fruit flavors is given in Table 9.2.

The combination of ethyl 2-methyl butyrate, β-damascenone, and hexanal is important for the characteristic flavor note of red apples [30,31]. The blend of character-impact flavors combines "apple ester" and "green apple" notes, which fluctuate with apple ripeness and seasonality. β-Damascenone is an unusually potent aroma compound having a threshold of 2 pg/g in water, and it also occurs in natural grape and tomato flavors [31].

Two important character-impact compounds of strawberry flavor are the furanones 2,5-dimethyl-4-hydroxy-2H-furan-3-one (*Furaneol*) and 2,5-dimethyl-4-methoxy-2H-furan-3-one (mesifuran) [32]. However, at various concentrations Furaneol can simulate other flavors, for example, pineapple [14] or Muscadine grape [33] at low levels and caramel at high levels. Mesifuran exhibits a caramel, sherrylike aroma and is a contributor to pineapple, raspberry, and mango. Other important character-impact compounds of strawberry flavor are methyl cinnamate and ethyl 3-methyl-3-phenylglycidate, a synthetic aroma chemical [4,34].

Table 9.2 Character-Impact Flavor Compounds in Fruits

Character-impact compounds	CAS Registry number	Occurrence	Reference
Ethyl-2-methyl butyrate	[7452-79-1]	Apple	4
β-Damascenone	[23696-85-7]	Apple	4, 27
iso-Amyl acetate	[123-92-2]	Banana	4
4-Methoxy-2-methyl-2-butanethiol	[94087-83-9]	Black currant	22
8-Mercapto-*p*-menthan-3-one	[38462-22-5]	Black currant (synthetic)	47
iso-Butyl 2-butenoate	[589-66-2]	Blueberry	4
Benzaldehyde	[100-52-7]	Cherry	4
p-Tolyl aldehyde	[1334-78-7]	Cherry	4
Ethyl heptanoate	[106-30-9]	Cognac brandy	4
3,5-Dimethyl-1,2,4-trithiolane	[23654-92-4]	Durian	61
Methyl anthranilate	[134-20-3]	Grape, Concord	22
Ethyl-3-mercapto-propionate	[5466-06-8]	Grape, Concord	35
Linalool	[78-70-6]	Grape, Muscat	38
4-Mercapto-4-methyl-2-pentanone	[19872-52-7]	Grape, Sauvignon	5
		Green tea (sencha)	42
		Hops	43
		Grapefruit	44
Nootkatone	[4674-50-4]	Grapefruit	4
1-*p*-Menthene-8-thiol	[71159-90-5]	Grapefruit	48
Citronellyl acetate	[150-84-5]	Kumquat	52
Citral (neral + geranial)	[5392-40-5]	Lemon, lime	4
α-Terpineol	[98-55-5]	Lime	4
2,6-Dimethyl-5-heptenal	[106-72-9]	Melon	14
Z-6-Nonenal	[2277-19-2]	Melon	30
Methyl N-methyl-anthranilate	[85-91-6]	Orange, mandarin	51
Thymol	[89-83-8]	Orange, mandarin	51
3-Mercapto-1-hexanol	[51755-83-0]	Passion fruit	57, 58
2-Methyl-4-propy-1,3-oxathiane	[67715-80-4]	Passion fruit	22
γ-Undecalactone	[104-67-6]	Peach	4
6-Pentyl-2H-pyran-2-one	[27593-23-3]	Peach	4

(*Continued*)

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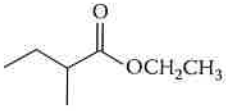
Table 9.2 Character-Impact Flavor Compounds in Fruits (*Continued*)

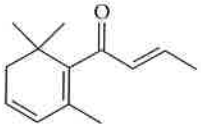
Character-impact compounds	CAS Registry number	Occurrence	Reference
Ethyl *trans*-2, *cis*-4-decadienoate	[3025-30-7]	Pear, Bartlett	4
Allyl caproate	[123-68-2]	Pineapple	14
Ethyl 3-(methylthio) propionate	[13327-56-5]	Pineapple	62
Allyl 3-cyclohexylpropionate	[2705-87-5]	Pineapple	14
4-(*p*-Hydroxyphenyl)-2-butanone	[5471-51-2]	Raspberry	4, 53, 54
trans-α-Ionone	[127-41-3]	Raspberry	4, 53, 54
Ethyl 3-methyl-3-phenylglycidate	[77-83-8]	Strawberry	4
Furaneol	[3658-77-3]	Strawberry, Muscat	32, 33
		Guava	60
Mesifuran	[4077-47-8]	Strawberry, mango	32
		Guava	60
(Z,Z)-3,6-Nonadienol	[53046-97-2]	Watermelon	30

Representative chemical structures for fruit flavor-impact compounds are shown in Figure 9.2.

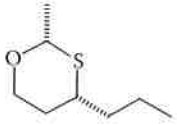
The character-impact component for Concord (*Vitis labrusca*) grape has long been known as methyl anthranilate. Subsequently, ethyl 3-mercaptopropionate was identified in Concord grape, and it possesses a pleasant and fruity fresh grape aroma at low ppm levels [35]. 2-Aminoacetophenone and mesifuran are also significant contributors in Concord to its "foxy" and "candylike" notes, respectively. Ethyl heptanoate elicits an odor reminiscent of cognac brandy [4]. These aroma characters contrast significantly with those resulting from grape varieties (*Vitis vinifera*) used for the production of table wines, whose flavors derive from the specific variety of grape, vinification, maturation, and aging conditions. It is a well-established fact that characteristic wine flavors are produced from secondary metabolites of grapes and yeast during the fermentation process, which increase the chemical and aroma complexity of wines [36]. For example, in Pinot Noir wines, there is no single compound that characterizes the wine's fruity "plum, cherry, ripe blackberry" aroma but rather a complex blend of odorants including 2-phenylethanol, ethyl butyrate, 3-methylbutyl alcohol/acetate, and benzaldehyde, among others [37]. However, other wines made from certain *vinifera* grape varieties possess unique flavor-impact compounds, including "flowery, muscat" character from linalool in Muscat



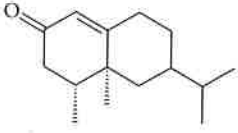
Ethyl-2-methyl butyrate
(apple)



β-Damascenone
(apple, grape)

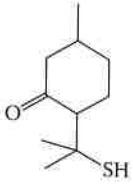


(+)-*cis*-Tropathiane
(passion fruit)

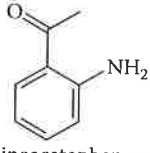


Nootkatone
(grapefruit)

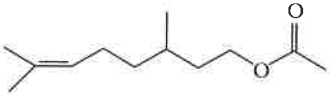
R-(+)-1-*p*-Menthene-8-thiol
(grapefruit)



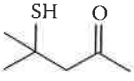
8-Mercapto-*p*-menthan-3-one
(black currant—synthetic)



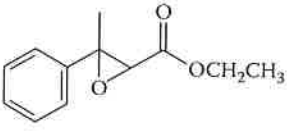
o-Aminoacetophenone
(Concord grape—foxy,
Labruscana wine)



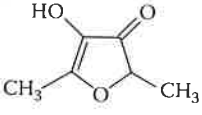
Citronellyl acetate
(kumquat)



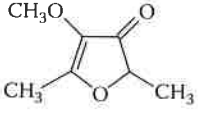
Cat ketone
(Sauvignon grape, hops,
green tea, grapefruit)



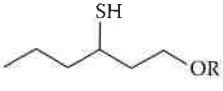
Ethyl-3-methyl-3-phenylglycidate
(stawberry—artificial)



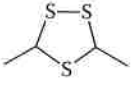
Furaneol
(strawberry, pineapple,
muscat, guava)



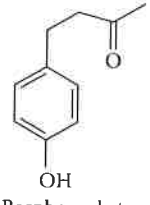
Mesifuran
(strawberry, grape,
mango, guava)



R=H 3-Mercaptohexan-1-ol
R=Ac 3-Mercaptohexyl acetate
(passion fruit, grapefruit, wine, guava)



3,5-Dimethyl-1,2,4-trithiolane
(durian)



Raspberry ketone
(raspberry)

Figure 9.2 Representative fruit character-impact flavor compounds.

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wine; "green pepper, earthy" from 3-isopropyl- and 3-isobutyl-2-methoxy pyrazines in Sauvignon Blanc wine; foxy from 2-aminoacetophenone in Labrusca wine; "floral, lychee" from *cis*-rose oxide in Gewurztraminer; and "sulfury" character from 3-mercaptohexan-1-ol, 3-mercaptohexyl acetate, 2-furfurylthiol, and benzyl mercaptan in Grenache, Merlot, and Cabernet wines [38,39, and references cited therein]. Red Tannat wines, produced in southern Uruguay and frequently described as spicy and mintlike, contain 1,8-cineole (eucalyptol) as a flavor character. In Tannat fermentations, 1,8-cineole is produced by chemical rearrangements of limonene or α-terpineol, and levels can be increased by heating to 45°C at wine pH (3.2) [40]. As discussed in the "Introduction" section, 4-mercapto-4-methyl-2-pentanone (cat ketone) provides "catty" character in Sauvignon Blanc (and also Scheurebe) wine at an aroma perception threshold below 3 ppt [5,41]. It is also a characteristic flavorant in Japanese green tea (sencha) [42], a main contributor to the fruity aroma in beer made with certain hops [43], and a significant contributor to the flavor of hand-squeezed grapefruit juice [44].

The mechanism of thioketone formation involves an aldol condensation between two molecules of acetone to yield 4-hydroxy-4-methyl-2-pentanone as shown in Figure 9.3 (**1** in the figure). Dehydration of this intermediate results in 4-methyl-3-penten-2-one (mesityl oxide; **2** in the figure). Hydrogen sulfide (from the degradation of cysteine and methionine amino acids in proteins) can readily undergo a Michael-type addition to the enone moiety of mesityl oxide to generate the thioketone (**3** in Figure 9.3) [45].

Black currant flavor is very popular in Europe and is associated with numerous health-related functional foods and alcoholic drinks (cassis liqueur). The key aroma component in black currant is 2-methoxy-4-methyl-4-butanethiol [22]. The "catty/ribes" flavor of black currant (*Ribes nigrum*) was earlier attributed to cat ketone, but it was more recently

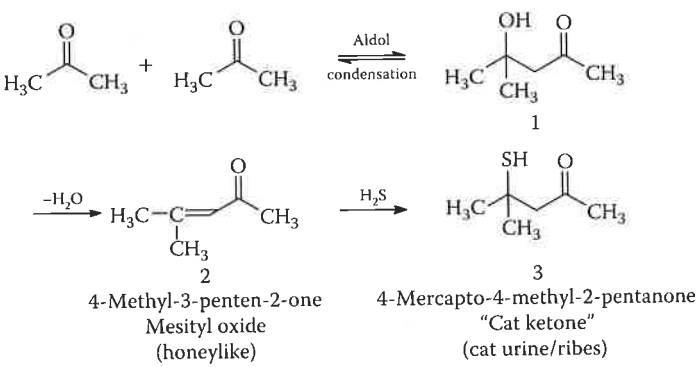

Figure 9.3 Mechanism for the formation of 4-mercapto-4-methyl-2-pentanone (cat ketone).

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shown to be absent during flavor and sensory analysis of black currant juice concentrates [46]. The flavor chemical 8-mercapto-*p*-menthan-3-one contributes a powerful black currant, cassis, and cattylike aroma character; however, it has not been identified in the natural fruit [47].

Two character-impact compounds have been proposed for grapefruit flavor, the first being nootkatone, a sesquiterpene. The fresh juicy note of grapefruit juice is attributable to 1-*p*-menthene-8-thiol. This compound has a detection threshold of 10^{-1} ppt, which is among the lowest values reported for aroma chemicals [48]. The (+)-R-isomer was found to have a lower aroma threshold in water than the racemic mixture, and it imparts a pleasant, fresh grapefruit juice character as opposed to the extremely obnoxious sulfur note contributed by the (–)-S-epimer. 3-Mercapto-1-hexanol and its acetate were recently reported to contribute "grapefruit, passion fruit, box tree–like" aromas in fresh grapefruit juice [49].

Among other citrus flavors the basic flavor-impact compound of lemon is citral, a mixture of neral and geranial isomers that together comprise the aroma impression. The flavor character of lime results from a combination of α-terpineol and citral, even though limonene is the most abundant, but sensorially immaterial, volatile in lime and other citrus oils. In contrast to other citrus flavors, orange flavor lacks a specific character-impact compound, and the current belief is that orange flavor is the result of a complex mixture of C_9–C_{13} aldehyde, terpene, and norisoprenoid volatiles blended in specific proportions [50]. For mandarin and tangerine flavors, methyl-*N*-methyl anthranilate and thymol are associated with character impact, with additional contributions from β-pinene and γ-terpinene [51].

Kumquat (*Fortunella japonica* Swingle) is another fruit in the citrus genus that contains characteristic terpene compounds found in other citrus oils. The flesh is quite sour and the peel is often consumed with the flesh. Two sensorially significant diterpene esters, citronellyl formate and citronellyl acetate, were identified in kumquat peel oil by organoleptic evaluation with GC–O. However, citronellyl acetate was found to possess the sensory character that contributes the most to the aroma of kumquat [52].

Lactones have characteristic aromas that are attributable to peach, coconut, and dairy flavors and occur in a wide variety of foods. The γ-lactones, specifically γ-undecalactone and lesser for γ-decalactone, possess intense peachlike odors [14]. A doubly unsaturated δ-decalactone, 6-pentyl-2H-pyran-2-one, also has an intense peach character [4]. As a point of distinction, the C_{10}–C_{12} δ-lactones, particularly the "creamy coconut" note of δ-decalactone, are flavor constituents of coconut as well as cheese and dairy products [14]. Wine lactone (3a,4,5,7a-tetrahydro-3,6-dimethylbenzofuran-2(3H)-one), which conveys an intense "coconut-like, woody, sweet" aroma, has been reported as a background note in Gewurztraminer and Scheurebe white wines [41].

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In addition to the character-impact compound of raspberry, 4-(4-hydroxyphenyl)-butan-2-one (raspberry ketone), α- and β-ionone, geraniol, linalool, Furaneol, maple furanone, and other furaneols were concluded to be of importance to raspberry aroma [53,54]. The odor threshold of raspberry ketone was measured at 1–10 μg/kg. The ionones are similar in chemical structure and potencies to β-damascenone [14].

The aroma profiles of Evergreen, Marion, and Chickasaw blackberries are complex, as no single volatile was unanimously described as being characteristically "blackberry" [55,56]. Flavors of importance include ethyl butyrate, Furaneol and other furanones, linalool, and β-damascenone. Blackberry aroma character was shown to differ for the same variety, depending on the growing region [56].

The "tropical" category is one of the most important areas for new discoveries of key flavor impact compounds. Analyses of passion fruit have identified many potent sulfur aroma compounds [22]. Among these is tropathiane, 2-methyl-4-propyl-1,3-oxathiane, which has an odor threshold of 3 ppb [18]. 3-Mercapto-1-hexanol is a powerful odorant reminiscent of citrus and tropical fruit. It was first isolated from passion fruit and contributes to its character impact [57,58]. It has been extensively studied in wine flavor and identified as one of the key aroma compounds in Sauvignon Blanc, Riesling, Gewurztraminer, Cabernet Sauvignon, and Merlot wines [59]. In pink guava fruit, 3-mercapto-1-hexanol (grapefruit aroma) and 3-mercaptylhexyl acetate (black currant aroma) provide tropical character in a nearly racemic ratio, and both the mercaptohexanol enantiomers have extremely low odor thresholds of 70–80 pg/L [60]. These two thiols, in combination with Furaneol, sotolon, mesifuran, and other esters, contribute significantly to the strong and characteristic tropical fragrance of fresh guava fruits. In Indonesian durian fruit, sulfur volatiles dominate the overall aroma perception. From flavor extract dilution analysis, 3,5-dimethyl-1,2,4-trithiolane was identified as the most potent odorant in durian [61]. For pineapple, 2-propenyl hexanoate (allyl caproate) exhibits a typical pineapple character [14]; however, Furaneol, ethyl 3-methylthiopropionate, and ethyl-2-methylbutyrate are important supporting character-impact compounds [62]. The latter ester contributes the background apple note to pineapple flavor. Another character-impact compound, allyl 3-cyclohexylpropionate, has not been discovered in nature, but it provides a sweet, fruity pineapple flavor note [14].

Characterizing flavors for melons include (Z)-6-nonenal, which contributes a typical melon aroma impression, and (Z,Z)-3,6-nonadienol for watermelon rind aroma impact [30]. 2,6-Dimethyl-5-hepten-1-al (Melonal) has not been identified in melon, but it provides a melonlike note in compounded flavors [14]. A more recent study confirmed that the flavor chemistry of muskmelons is more complex, with methyl 2-methylbutyrate and ethyl 2-methylbutyrate providing noncharacterizing "fruity, sweet,

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and cantaloupe-like" aromas and ethyl 3-(methylthio)propionate contributing "green, fresh melon" notes [63]. Although an important constituent to both varieties, the flavor of sweet cherries (*Prunus aviium*) is less dominated by the character-impact compound benzaldehyde than is the flavor profile of sour cherries (*P. cerasus*) [64].

Vegetable flavors

Recent aroma research has been devoted to the identification of key flavor compounds in vegetables and is the subject of several contemporary reviews [62,65,66]. Cucumbers, sweet corn, and tomatoes are botanically classified as fruits; however, for flavor considerations they are regarded as vegetables, since they are typically consumed with the savory portion of the meal. Overall, the knowledge base of character-impact compounds for vegetables is much smaller than that for other flavor categories and warrants further investigation.

Identifying flavor-impact compounds in vegetables depends considerably on how they are prepared (cutting, blending) and the form in which they are consumed (raw vs. cooked). For example, the character impact of fresh tomato is delineated by 2-*iso*-butylthiazole and (Z)-3-hexenal, with modifying effects from β-ionone and β-damascenone [62]. Alternatively, dimethyl sulfide is a major contributor to the flavor of thermally processed tomato paste [62,65]. Dimethyl sulfide is also a flavor-impact compound for both canned cream and fresh corn, whereas 2-acetyl-1-pyrroline provides a "corn chip" character. Hydrogen sulfide, methanethiol, and ethanethiol may further contribute to the aroma of sweet corn due to their low odor thresholds [66]. A summary of character-impact compounds for vegetable flavors is outlined in Table 9.3.

The character-impact compound of green bell pepper, 2-isobutyl-3-methoxypyrazine, was the first example of a high-impact aroma compound because of its exceptionally low odor threshold of 2 ppt [18]. A compound with a similarly low odor threshold, geosmin is the character impact of red beets and is detectable at a concentration of 100 ppt. Recently, characteristic cooked red bell pepper notes were attributed to (E)-3-heptene-2-thiol (sesame, green, bell peppers, fresh note) and (E)-4-heptene-2-thiol (sesame, coffee, bitterness of peppers) [67]. The flavor of raw peas and peapods is attributed to 2-*iso*-propyl-3-methoxypyrazine [65]. The importance of C_9 aldehydes to the character impact of cucumber flavor was recently confirmed by calculating their odor unit values (ratio of concentration to odor threshold). (E,Z)-2,6-Nonadienal and (Z)-2-nonenal were determined to be the principal odorants of cucumbers [68].

Tomatillo (*Physalis ixocarpa* Brot.) is a solanaceous fruit vegetable similar in appearance to a small green tomato, which is used to prepare green salsas in various Mexican dishes. The character-impact compounds in

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Table 9.3 Character-Impact Flavor Compounds in Vegetables

Character-impact compounds	CAS Registry number	Occurrence	Reference
Dimethyl sulfide	[75-18-3]	Asparagus	4
1,2-Dithiacyclopentene	[288-26-6]	Asparagus, heated	65
Geosmin	[19700-21-1]	Red beet	65
4-Methylthiobutyl isothiocyanate	[4430-36-8]	Broccoli	66
Dimethyl sulfide	[75-18-3]	Cabbage	65
S-Methyl methane-thiosulfinate	[13882-12-7]	Sauerkraut	71
2-*sec*-Butyl-3-methoxypyrazine	[24168-70-5]	Carrot (raw)	65
3-(Methylthio)propyl isothiocyanate	[505-79-3]	Cauliflower	66
3-Butylphthalide	[6066-49-5]	Celery	66
Sedanolide	[6415-59-4]	Celery	66
(Z)-3-Hexenyl pyruvate	[68133-76-6]	Celery	4
Dimethyl sulfide	[75-18-3]	Corn	66
2-Acetyl-2-thiazoline	[29926-41-8]	Corn, fresh	66
(E,Z)-2,6-Nonadienal	[557-48-2]	Cucumber	68
(E)-2-Nonenal	[2463-53-8]	Cucumber	68
2-*iso*-Butyl-3-methoxypyrazine	[24683-00-9]	Green bell pepper	65
(E)-3-Heptene-2-thiol	[1006684-17-8]	Red bell pepper	67
(E)-4-Heptene-2-thiol	[1006684-18-9]	Red bell pepper	67
1-Octen-3-ol	[3391-86-4]	Mushroom	65
1-Octen-3-one	[4312-99-6]	Mushroom	65
p-Mentha-1,3,8-triene	[18368-95-1]	Parsley	76
2-*iso*-Propyl-3-methoxypyrazine	[25773-40-4]	Pea (raw)	65
2-*iso*-Propyl-3-methoxypyrazine	[25773-40-4]	Potato (earthy)	65
3-Methylthiopropanal	[3268-49-3]	Potato (boiled)	21
2-Ethyl-6-vinylpyrazine	[32736-90-6]	Potato (baked)	65
(Z)-3-Hexenal	[6789-80-6]	Tomatillo	69
(E,E)-2,4-Decadienal	[25152-84-5]	Tomatillo	69
2-*iso*-Butylthiazole	[18640-74-9]	Tomato (fresh)	21
(Z)-3-Hexenal	[6789-80-6]	Tomato (fresh)	62
Bis(methylthio)methane	[1618-26-4]	Truffle	74, 75
1,2,4-Trithiolane	[289-16-7]	Truffle	74

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tomatillo were recently established as (Z)-3-hexenal; (E,E)-2,4-decadienal; and nonanal, which impart the fruit vegetable's dominant "green" flavor [69]. Similar to tomato flavor, β-ionone and β-damascenone provide modifying effects in tomatillo; however, tomatillo does not contain 2-*iso*-butylthiazole, a key character-impact compound of tomato.

Among the cruciferous vegetables, cooked cabbage owes its dominant character-impact flavor to dimethyl sulfide. In raw cabbage flavor, allyl isothiocyanate contributes sharp, pungent horseradish-like notes [66]. *S*-Methyl methanethiosulfinate was observed to provide the character impact of sauerkraut flavor, and it occurs in Brussels sprouts and cabbage [70,71]. Compounds likely to be important to the flavor of cooked broccoli include dimethyl sulfide and trisulfide, nonanal, and erucin (4-(methylthio)butyl isothiocyanate) [65]. Cooked cauliflower contains similar flavor components as broccoli, with the exception that 3-(methylthio)propyl isothiocyanate is the characterizing thiocyanate in the former [65]. Key volatile sulfur compounds were identified in the flavor of cooked asparagus [72]. Representative structures for vegetable flavor-impact compounds are presented in Figure 9.4.

Potato flavor is greatly influenced by methods of cooking or preparing the vegetable. Raw potato contains the characteristic "earthy aroma" component, 2-*iso*-propyl-3-methoxypyrazine. A character-impact compound common to boiled and baked potatoes is methional (3-(methylthio) propanal). Baked potatoes contain Maillard products such as 2-ethyl-3-methylpyrazine (earthy, nutty) and 2-ethyl-6-vinylpyrazine (buttery, baked potato) [65]. In potato chips and French-fried potatoes, the potato flavor character of methional is modified by volatile aromatics from frying oils, such as (E,E)-2,4-decadienal, and thermally generated alkyl oxazoles possessing lactonelike flavors [65,73].

Aroma-impact compounds that are universal to all varieties of mushrooms include 1-octen-3-ol (threshold of 1 ppb) and 1-octen-3-one (threshold of 0.05 ppb), both of which have been described as having a fresh, wild-mushroom aroma [18]. However, 1-octen-3-one also possesses a metallic odor, particularly in the context of oxidized oils [65].

The predominant sulfur component in black and white truffle aroma is dimethyl sulfide; however, bis(methylthio)methane and 1,2,4-trithiolane are reported to be unique to white truffle aroma [74]. 1-(Methylthio) propane and 1-methylthio-1-propene were newly identified in black truffle [75].

The characteristic compound for raw carrot is 2-*sec*-butyl-3-methoxypyrazine, which has an extremely low (2-ppt) threshold value. Its sniffing port aroma in GC–O has been described as "raw carroty" [65]. Unsaturated aldehydes contribute to the flavor of cooked carrot, the most significant being (E)-2-nonenal (fatty-waxy) [65].

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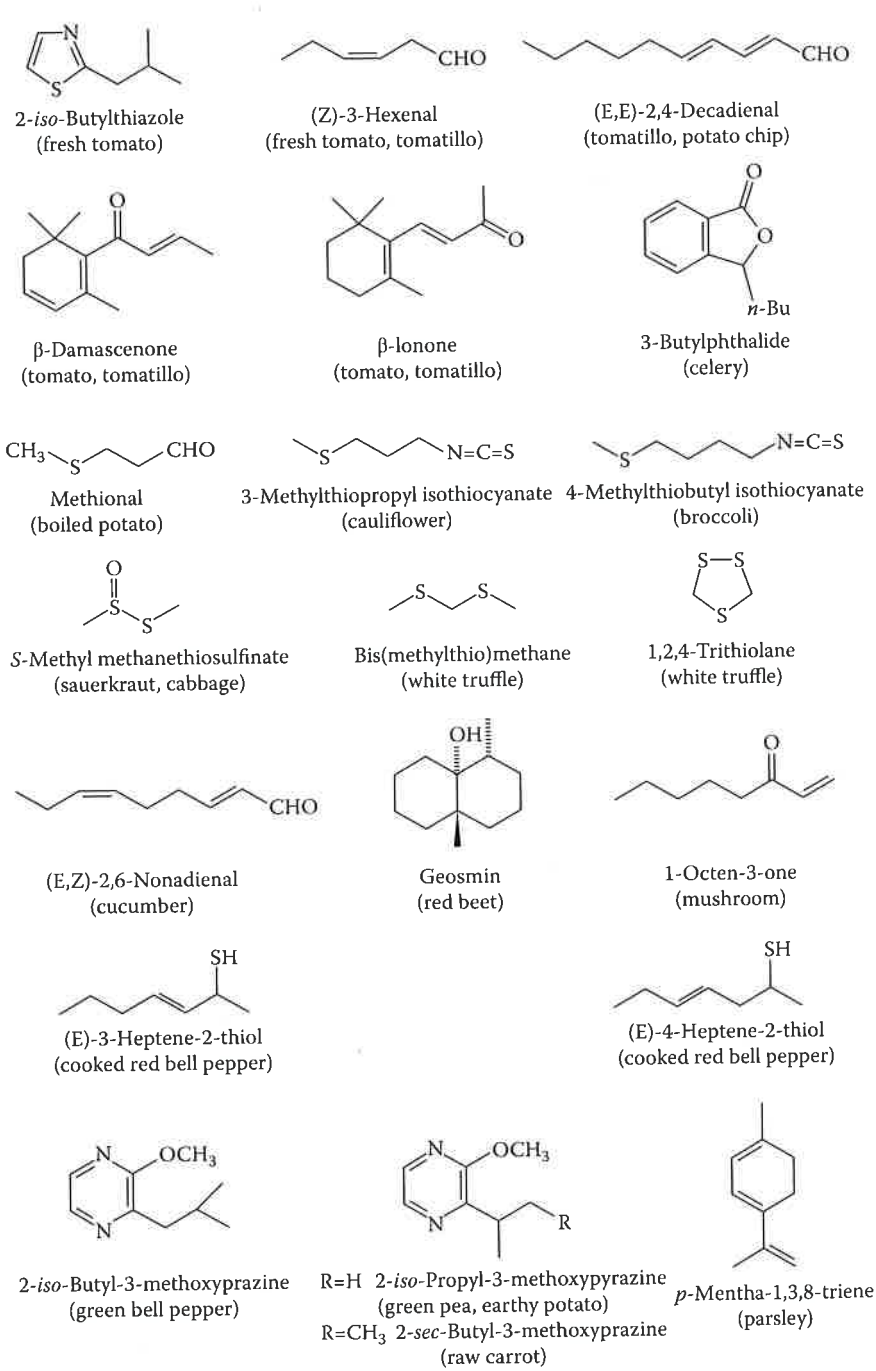

Figure 9.4 Representative vegetable character-impact flavor compounds.

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Compounds important to the aroma of celery include two lactones, 3-butylphthalide and sedanolide (3-butyl-3a,4,5,6-tetrahydrophthalide), which provide impact at low concentrations (< 3 ppm). Other terpene hydrocarbons such as β-selinene and limonene are present in greater abundance, but they do not contribute significantly to celery flavor. A recent assessment of its odor threshold by Takeoka [66] suggests that 3-butylphthalide is the most significant character-impact compound for celery.

Key parsley aroma compounds have been reported [76]. The primary flavor contributors were found to include *p*-mentha-1,3,8-triene (terpeny, parsleylike); myrcene (metallic, herbaceous); 2-*sec*-butyl-3-methoxypyrazine (musty, earthy); myristicin (spicy); linalool (coriander); (Z)-6-decenal (green, cucumber); and (Z)-3-hexenal (green).

Maillard-type, brown, and cereal flavors

The flavor characteristics of heated sugar compounds that possess caramel, burnt sugar, and maple notes include a family of structures containing a methyl enol-one group [77]. As discussed in the section *Fruit flavors*, Furaneol (2,5-dimethyl-4-hydroxy-(2H)-furan-3-one) has a sweet, caramel-like, burnt sugar flavor with appreciable fruitiness and occurs in thermally processed foods such as beer, arabica coffee, cocoa, and white bread crust [78]. Maltol (3-hydroxy-2-methyl-4H-pyran-4-one) exhibits a sweet, burnt sugar, caramel note similar to Furaneol, but not as strong or fruity. Ethyl maltol does not occur in nature; however, it possesses a very intense sweet, caramel-like odor, which is four-to-six times more potent than the odor of maltol [14]. Cyclotene (3-methyl-2-cyclopenten-2-ol-1-one) has a strong maple-caramel flavor. 2-Methyltetrahydrofuran-3-one has a very pleasant, sweet-caramel character [18]. Sotolon (4,5-dimethyl-3-hydroxy-2(5H)-furanone) was identified as a potent flavor-impact compound from raw cane sugar. At low concentrations, its aroma character is caramel, maple syrup, and burnt sugar, typical of unrefined cane sugar [79]. At high concentrations, it has the typical seasoning-like aroma of fenugreek or curry. A summary of character-impact compounds for thermally generated flavors is given in Table 9.4.

Characteristic heated flavor compounds arise via the Maillard pathway, the thermally induced reaction between amino acids and reducing sugars. Aroma constituents in chocolate, coffee, toasted cereal grains, wheat bread crust, and popcorn are products of Maillard reactions, in addition to flavors in roasted nuts and meats, which are discussed in "Nut flavors" and "Meat and seafood flavors" sections, respectively. Guaiacols occur as pyrolysis products of carbohydrates or lipids in smoked and charbroiled meats.

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Table 9.4 Character-Impact Flavor Compounds in Cooked Flavors and Maillard-Type Systems (Chocolate, Coffee, Caramelized Sugar)

Character-impact compounds	CAS Registry number	Occurrence	Reference
5-Methyl-2-phenyl-2-hexenal	[21834-92-4]	Chocolate	99
2-Methoxy-5-methyl-pyrazine	[2882-22-6]	Chocolate	4, 100
iso-Amyl phenylacetate	[102-19-2]	Chocolate	4, 100
2-Furfurylthiol	[98-02-2]	Coffee	80
		Wine (barrel-aged)	83
Furfuryl methyl disulfide	[57500-00-2]	Coffee (mocha)	18
2-Methyl-3-furanthiol	[28588-74-1]	Wine (barrel-aged)	83
Furaneol	[3658-77-3]	Fruity, burnt sugar	78
Sotolon	[28664-35-9]	Brown sugar	79
Phenylacetaldehyde	[122-78-1]	Honey	100
3-Methylbutanal	[590-86-3]	Malt	88
Maltol	[118-71-8]	Cotton candy	14
Ethyl maltol	[4940-11-8]	Caramel, sweet	14
2-Hydroxy-3-methyl-2-cyclopenten-1-one	[80-71-7]	Maple	14
2-Acetyl-1,4,5,6-tetrahydropyridine	[25343-57-1]	Cracker (saltine)	87
(E,E,Z)-2,4,6-Nonatrienal	[100113-52-8]	Oat flake	95
2-Acetyl-1,4,5,6-tetra-hydropyridine	[25343-57-1]	Popcorn	85, 86
2-Acetyl-1-pyrroline	[85213-22-5]	Popcorn	85, 86
2-Propionyl-1-pyrroline	[133447-37-7]	Popcorn	85
2-Acetylpyrazine	[22047-25-2]	Popcorn	85
2-Acetyl-2-thiazoline	[22926-41-8]	Roasty, popcorn	97
5-Acetyl-2,3-dihydro 1,4-thiazine	[164524-93-0]	Popcorn (model system)	89
3-Thiazolidineethanethiol	[317803-03-5]	Popcorn (model system)	90
2-Acetyl-1-pyrroline	[85213-22-5]	Wheat bread crust	86, 88
		Rice (basmati)	86, 88
2-Ethyl-3,5-dimethyl-5-pyrazine	[13925-07-0]	Potato chip	97
2,3-Diethy-5-methyl-pyrazine	[18138-04-0]	Potato chip	97
2-Vinylpyrazine	[4177-16-6]	Roasted potato	97

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Table 9.4 Character-Impact Flavor Compounds in Cooked Flavors and Maillard-Type Systems (Chocolate, Coffee, Caramelized Sugar) (*Continued*)

Character-impact compounds	CAS Registry number	Occurrence	Reference
(Z)-2-propenyl-3,5-dimethylpyrazine	[55138-74-4]	Roasted potato	97
Guaiacol	[90-05-1]	Smoky	4
4-Vinylguaiacol	[7786-61-0]	Smoky	18

2-Furfurylthiol is the primary character-impact compound for the aroma of roasted arabica coffee [80]. It has a threshold of 5 ppt and smells like freshly brewed coffee at concentrations between 0.01 and 0.5 ppb [81]. At higher concentrations, it exhibits a stale coffee, sulfury note. Other potent odorants in roasted coffee include 5-methylfurfurylthiol (threshold of 0.05 ppb), which smells meaty at 0.5–1.0 ppb and changes character to a sulfury mercaptan note at higher levels [81]. Furfuryl methyl disulfide has a sweet mocha coffee aroma [18]. Whereas other sulfur compounds such as 3-mercapto-3-methylbutyl formate and 3-methyl-2-buten-1-thiol were previously thought to be important factors for coffee aroma, recent studies have confirmed that the flavor profile of brewed coffee is primarily contributed by 2-furfurylthiol, 4-vinylguaiacol, and "malty"-smelling Strecker aldehydes, among others [80,82]. For wines and champagnes aged in toasted oak barrels, 2-furfurylthiol and 2-methyl-3-furanthiol have been identified as providing "roast-coffee" and "cooked meat" aroma characters, respectively [83].

Cereal grains, including wheat, rice, corn, and oats, have characteristic "toasted, nutty" flavors (pyrazines, tetrahydropyridines, pyrrolines, etc.) that are thermally generated through Maillard pathways [84]. The principal impact aroma compounds of freshly prepared popcorn were determined by Schieberle [85] as 2-acetyltetrahydropyridine, 2-acetyl-1-pyrroline, and 2-propionyl-1-pyrroline [86]. The crackerlike aroma of tetrahydropyridine, which exists in two tautomeric forms (2-acetyl-1,4,5,6- and 2-acetyl-3,4,5,6-tetrahydropyridine), was previously identified as the character compound of saltine crackers [87]. The decrease of these compounds during storage was directly correlated with staling flavor. Another "popcornlike" odorant, 2-acetylpyrazine, was determined to have a minor contribution to the aroma of fresh popcorn because of its considerably lower odor activity [88]. Two novel, highly intense "roasty, popcornlike" aroma compounds were recently identified in Maillard model systems: (1) 5-acetyl-2,3-dihydro-1,4-thiazine (odor threshold of 0.06 ppt) from the reaction of ribose with cysteine [89] and (2) *N*-(2-mercaptoethyl)-1,3-thiazolidine (3-thiazolidineethanethiol) (odor threshold of 0.005 ppt) from the reaction of fructose with cysteamine

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[90]. Neither of these characteristic popcorn flavor compounds has been reported in food aromas to date.

The flavor formed by the cooking of fragrant rice (e.g., basmati rice) is described as popcornlike; hence it is not surprising that 2-acetyl-1-pyrroline is the character-impact volatile [88]. In masa corn tortillas, 2-aminoacetophenone provides the character impact resulting from the lime treatment of corn [91], whereas in corn chips its contribution is modified by 2-acetyl-1-pyrroline and unsaturated aldehydes [92].

In addition to Maillard pathways, cereal-like flavor character is provided by trace volatiles formed through lipoxygenase oxidation of unsaturated lipids, such as linoleic and linolenic acids. One of the first studies on oat flavor by Heydanek and McGorrin [93,94] established the importance of C_8–C_{10} unsaturated aldehydes and ketones as key contributors to the flavor of dried oat groats. Recently, Schuh and Schieberle [95] identified the character-impact compound (E,E,Z)-2,4,6-nonatrienal as eliciting the typical "cereal, sweet" aroma of rolled oat flakes. This odorant exhibits an extremely low odor threshold (0.0002 ppt), and the value is among the lowest reported to date. Representative chemical structures for thermally generated flavor-impact compounds are shown in Figure 9.5.

Two compounds that create characteristic odor notes in the pleasant aroma of wheat bread crust have been identified as the popcornlike 2-acetyl-1-pyrroline and 2-acetyltetrahydropyridine [88]. The aroma of the bread crumb portion is principally due to the presence of lipid-derived unsaturated aldehydes such as (E)-2-nonenal and (E,E)-2,4-decadienal, which create stale aromas at high levels. The malty notes that predominate in yeast and sourdough breads are attributed to 2- and 3-methylbutanal and Furaneol [88,96].

"Potato chip" aroma is associated with the pyrazines 2-ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine, whereas 2-vinylpyrazine and (Z)-2-propenyl-3,5-dimethylpyrazine provide an intense "roasted potato" odor [97]. A combination of methional, 2-acetyl-1-pyrroline, phenylacetaldeyde, and butanal are important flavor characters for extruded potato snacks [28].

Cocoa and chocolate represent a highly complex flavor system for which no single character impact has been identified. Vanillin and Furaneol contribute to the sweet, caramelized background character of milk chocolate, whereas 3-methylbutanal provides its malty flavor [98]. 5-Methyl-2-phenyl-2-hexenal provides a "deep bitter, cocoa" note and is the aldol reaction product from phenylacetaldehyde and 3-methylbutanal, two Strecker aldehydes formed in chocolate [99]. 2-Methoxy-5-methylpyrazine and *iso*-amyl phenylacetate have "chocolate, cocoa, nutty" and "cocoalike" notes, respectively, and both are used in synthetic chocolate flavors [100]. Systematic studies of key odorants in milk chocolate were performed using AEDA; however, character-impact compounds unique to chocolate flavor were not reported [98,101].

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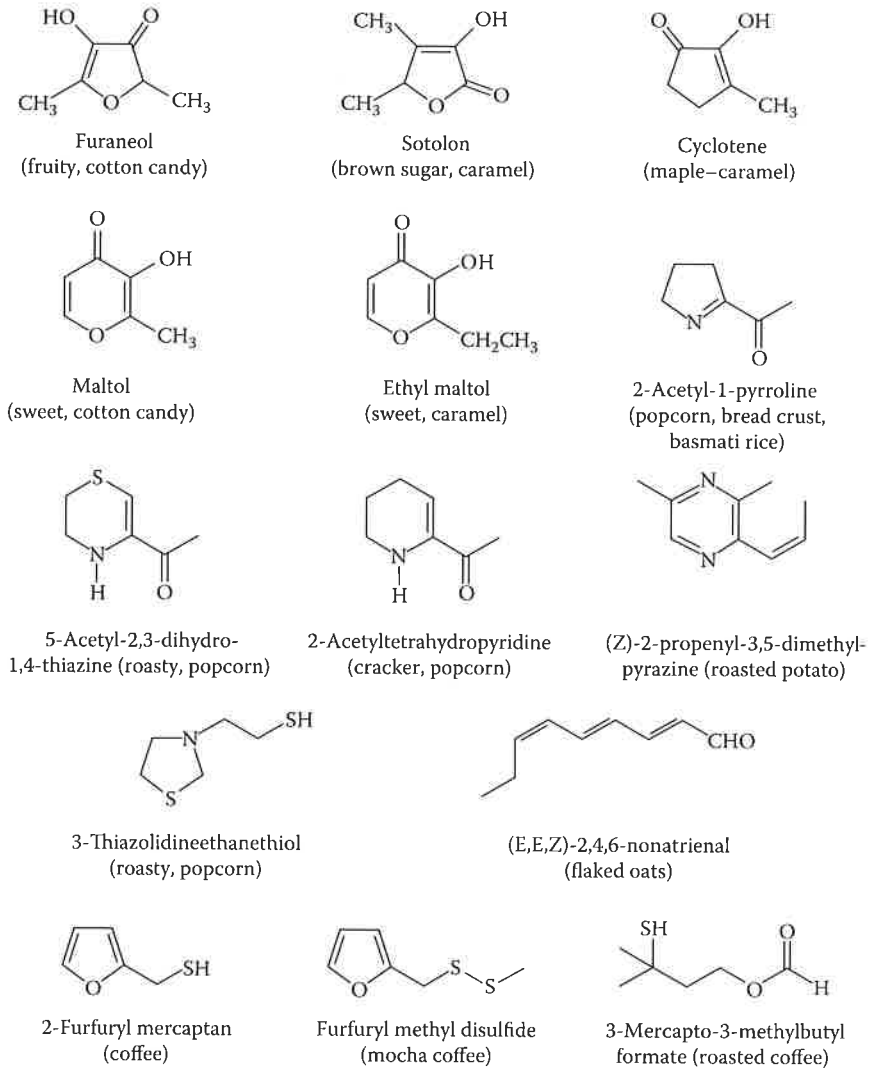

Figure 9.5 Representative Maillard-generated and cereal-like character-impact flavor compounds.

Nut flavors

Pyrazines are the major compound classes in peanuts, formed by the thermally induced Maillard reaction (with the exception of methoxy pyrazines) [102]. Two pyrazines that represent peanut flavor character are 2,5-dimethylpyrazine (nutty) and 2-methoxy-5-methylpyrazine (roasted nutty); they are listed in Table 9.5.

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Benzaldehyde has long been known as the character-impact compound of oil of bitter almond. It possesses an intense almondlike flavor in the context of savory applications; in sweet systems, it becomes cherrylike. 5-Methyl-2-thiophene-carboxaldehyde also provides almond flavor character, and occurs naturally in roasted peanuts [100].

The character-impact compound of hazelnuts, (E)-5-methyl-2-hepten-4-one (filbertone), undergoes isomerization during the roasting process [103]. Of the four possible geometric and enantiomeric isomers formed, all exhibit the typical hazelnut aroma, but the *trans*-(S)-isomer has the strongest impact. 5-Methyl-4-heptanone also contributes a fruity, hazelnut-like aroma. Structures are presented in Figure 9.6.

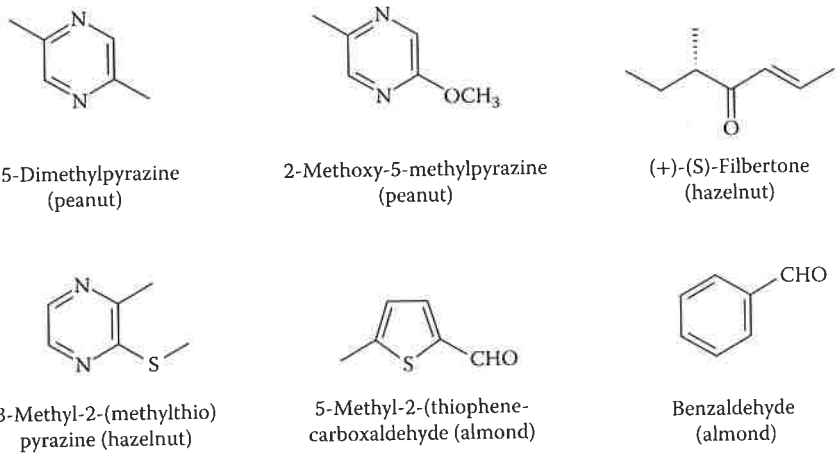

Figure 9.6 Representative character-impact flavor compounds in peanuts and tree nuts.

Table 9.5 Character-Impact Flavor Compounds in Nuts

Character-impact compounds	CAS Registry number	Occurrence	Reference
Benzaldehyde	[100-51-6]	Almond	4
5-Methyl-2-thiophenecarboxal	[13679-70-4]	Almond	4, 100
γ-Nonalactone	[104-61-0]	Coconut	102
δ-Decalactone	[705-86-2]	Coconut	102
(E)-5-Methyl-2-hepten-4-one	[81925-81-7]	Hazelnut	103
5-Methyl-4-heptanone	[15726-15-5]	Hazelnut	103
2,5-Dimethylpyrazine	[123-32-0]	Peanut	4
2-Methoxy-5-methylpyrazine	[68358-13-5]	Peanut	4

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As discussed in the section titled *Fruit flavors*, δ-lactones (e.g., δ-decalactone and δ-octalactone) possess a coconut flavor character. However, γ-nonalactone has the most intense coconut-like aroma as an individual character-impact compound, but it occurs only in artificial coconut flavors [102]. As the side-chain length increases, the character of γ-lactones changes to a peachlike aroma [14].

Meat and seafood flavors

Sulfur-containing heterocyclic compounds are associated with meaty characteristics. Two compounds with the most potent meaty characteristics include 2-methyl-3-furanthiol (threshold of 1 ppt) and the corresponding dimer bis-(2-methyl-3-furyl) disulfide (threshold of 0.02 ppt) [22]. Both substances have been identified in cooked beef and chicken broth, and they have a strong meaty quality upon dilution. 2-Methyl-3-furanthiol also occurs in canned tuna fish aroma [104]. The disulfide has a recognizable aroma character of "rich, aged beef, prime rib" [18]. Both compounds are produced from the thermal degradation of thiamin [105]. A related compound, 2-methyl-3-(methylthio)furan, is the character-impact compound for roast beef [22]. Other potent modifiers, such as 2-acetyl-2-thiazoline, impart a potent "roasty, popcorn" note, which enhances the meaty and roast flavor [106]. 2-Ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine also contribute potent roasty notes to roast beef flavor [107]. 2-Acetyl-2-thiazoline was subsequently detected as a potent odorant of chicken broth and cooked chicken [108]. A summary of character-impact compounds for meat and seafood flavors is shown in Table 9.6.

A brothy compound associated with boiled beef 4-methyl-5-(2-hydroxyethyl)thiazole (sulfurol) is a "reaction flavor" product from the hydrolysis of vegetable protein. It is suspected that a trace impurity (2-methyltetrahydrofuran-3-thiol) in sulfurol is the actual "beef broth" character-impact compound [18]. Another reaction product flavor chemical is 2,5-dimethyl-1,4-dithiane-2,5-diol (the dimer of mercaptopropanone); it has an intense chicken-broth odor. 2-Pyrazineethanethiol, a synthetic pyrazine, provides excellent pork character [18].

Lipid components associated with meat fat, especially unsaturated aldehydes, play a significant role in species-characterization flavors. For example, (E,Z)-2,4-decadienal exhibits the character impact of chicken fat and freshly boiled chicken [108]. (E,E)-2,6-Nonadienal has been suggested as the component responsible for the tallowy flavor in beef and mutton fat [105]. 12-Methyltridecanal was identified as a species-specific odorant of stewed beef and provides a tallowy, beeflike flavor character [109]. While aldehydes provide desirable flavor character to cooked meat, they can contribute rancid and "warmed-over" flavors at high concentrations, resulting from the autoxidation of lipids [110].

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Table 9.6 Character-Impact Flavor Compounds in Meat and Fish

Character-impact compounds	CAS Registry number	Occurrence	Reference
Dimethyl sulfide	[75-18-3]	Clam, oyster	111
Methional	[3268-49-3]	Boiled clam	117
		Crustaceans	118, 119
Pyrrolidino-2,4-dimethyl-dithiazine	[116505-60-3]	Roasted shellfish	120
2-Acetylthiazole	[24295-03-2]	Boiled clam	117
2-Acetyl-2-thiazoline	[22926-41-8]	Roast beef	106
		Cooked chicken	108
		Crustaceans	118, 119
4-Methylnonanoic acid	[45019-28-1]	Lamb	105
4-Methyloctanoic acid	[54947-74-9]	Lamb	105
2-Pentylpyridine	[2294-76-0]	Lamb	105
4-Methyl-5-(2-hydroxyethyl)thiazole	[137-00-8]	Roasted meat	18
2-Methyl-3-(methylthio) furan	[63012-97-5]	Roast beef	22
2-Ethyl-3,5-dimethyl-pyrazine	[13925-07-0]	Roast beef	107
2,3-Diethyl-5-methyl-pyrazine	[18138-04-0]	Roast beef	107
2-Methyltetrahydrofuran-3-thiol	[57124-87-5]	Brothy, meaty	18
2-Methyl-3-furanthiol	[28588-74-1]	Meat, beef	22
		Canned tuna fish	
Bis-(2-methyl-3-furyl) disulfide	[28588-75-2]	Aged, prime-rib	22
12-Methyltridecanal	[75853-49-5]	Beef, stewed	109
(E,E)/(E,Z)-2,4-Decadienal	[25152-84-5]	Cooked chicken	18, 108
2,5-Dimethyl-1,4-dithiane-2,5-diol	[55704-78-4]	Chicken broth	18
Pyrazineethanethiol	[35250-53-4]	Pork	18
(Z)-1,5-Octadien-3-one	[65767-22-8]	Salmon, cod	114
(E,Z)-2,6-Nonadienal	[557-48-2]	Trout, boiled	115
(Z,Z,Z)-5,8,11-Tetradecatrien-2-one	[85421-52-9]	Shrimp, cooked	116
2,4,6-Tribromophenol	[118-79-6]	Shrimp, ocean fish	121

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Two fatty acids, 4-methyloctanoic and 4-methylnonanoic acid, provide the characteristic flavor of mutton [105]. 2-Pentylpyridine has been identified as the most abundant alkylpyridine isolated from roasted lamb fat. This compound has a fatty, tallowy aroma at an odor threshold of 0.6 ppb and is suspected to negatively impact the sensory acceptance of lamb and mutton [105].

The "fishy" aroma of seafood is incorrectly attributed to trimethyl amine. Flavor formation in fresh- and saltwater fish results from complex enzymatic, oxidative, and microbial reactions of ω-3 polyunsaturated fatty acid precursors (e.g., eicosapentaenoic acid) [111–113]. Hence, fish flavor is primarily composed of noncharacterizing "planty" or "melonlike" aromas from lipid-derived unsaturated carbonyl compounds. Examples are (Z)-1,5-octadien-3-one (geranium-like aroma) in boiled cod [114] and (E,Z)-2,6-nonadienal (cucumber-like aroma) in boiled trout [115]. 5,8,11-Tetradecatrien-2-one exhibits a distinct seafood aroma character described as "cooked shrimplike" or "minnow bucket" [116].

Three notable sulfur volatiles in boiled clam were determined by AEDA: (1) 2-acetyl-2-thiazoline (roasted aroma), (2) 2-acetylthiazole (popcorn aroma), and (3) methional (boiled potato aroma) [117]. Methional and 2-acetyl-2-thiazoline also contribute to the meaty and nutty/popcorn aroma notes in cooked crustaceans such as crab, crayfish, lobster, and shrimp [118,119]. An extremely potent odorant in cooked shellfish, including shrimp and clam, was identified as pyrrolidino[1,2-e]-4H-2,4-dimethyl-1,3,5-dithiazine [120]. This dithiazine contributes a roasted character to boiled shellfish and has the lowest odor threshold recorded to date, 10^{-5} ppt in water. 2,4,6-Tribromophenol and other bromophenol isomers have been associated with the ocean-, brine-, and iodine-like flavor character in seafood such as Australian ocean fish and prawns. The source of bromophenols is thought to be polychaete worms, which form an important part of the diet for many fish and prawn species [121]. Dimethyl sulfide is reported to be the character aroma of stewed clams and oysters [111]. Representative structures for meat and seafood flavor-impact compounds are shown in Figure 9.7.

Cheese and dairy flavors

With a few exceptions, many of the known important flavors in dairy products do not provide characterizing roles. This is especially true for milk, cheddar cheese, and cultured products, such as sour cream and yogurt. δ-Lactones are important flavors in butter, buttermilk, and cheeses, which are derived from triglycerides containing hydroxyl fatty acids. Although they do not directly contribute as dairy character-impact compounds, lactones play key supporting roles in dairy flavors. The subject of key odor-active compounds in milk and dairy flavors has been recently reviewed [122–126]. A summary of character-impact compounds for cheese and dairy flavors is presented in Table 9.7.

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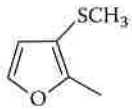
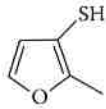
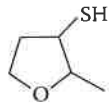


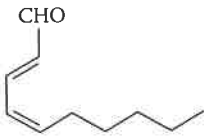
2-Methyl-3-(methylthio)furan
(roast beef)



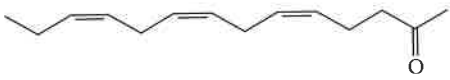
2-Methyl-3-furanthiol
(roast beef, canned tuna)



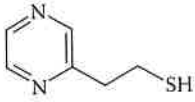
2-Methyltetrahydrofuran-3-thiol (brothy, boiled meat)



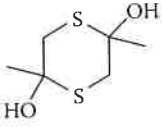
(E,Z)-2,4-Decadienal
(chicken fat)



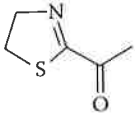
(Z,Z,Z)-5,8,11-Tetradecatrien-2-one
(cooked shrimp)



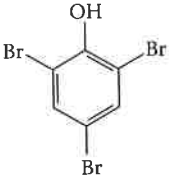
2-Pyrazineethanethiol
(pork)



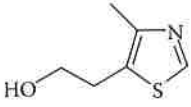
Mercaptopropanone dimer
(chicken broth)



2-Acetyl-2-thiazoline
(cooked beef, chicken, lobster)



2,4,6-Tribromophenol
(shrimp, prawns)



4-Me-5-(2-hydroxyethyl)thiazole
(roasted meat)

Pyrrolidino-(2,4-dimethyl)-dithiazine (roasted shellfish)

Figure 9.7 Representative meat and seafood character-impact flavor compounds.

Urbach [127] discusses the formation of volatile flavor compounds in different varieties of cheeses and provides a compilation of important aroma compounds. A recent qualitative assessment by Sable and Cottenceau [128] surveys the significant flavor volatiles that have been identified in soft mold-ripened cheeses including Camembert, Brie, blue, Gorgonzola, Munster, and Limburger among others. Octen-3-ol, 2-phenylethanol, and 2-phenylethyl acetate are character-impact components in Camembert-type cheese; these compounds together with sulfur compounds, 1-octen-3-one, and δ-decalactone are reported to be the key

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Table 9.7 Character-Impact Flavor Compounds in Cheese and Dairy Products

Character-impact compounds	CAS Registry number	Occurrence	Reference
2,3-Butanedione	[431-03-8]	Butter	141, 146
δ-Decalactone	[705-86-2]	Butter	141, 145, 146
6-Dodecen-γ-lactone	[156318-46-6]	Butter	141, 145
		Cheese, cheddar	134, 135
2-Heptanone	[110-43-0]	Cheese, blue	127
1-Octen-3-ol	[3391-86-4]	Cheese, Camembert	128
Butryric acid	[107-92-6]	Cheese, cheddar	134
2-Acetyl-2-thiazoline	[22926-41-8]	Cheese, cheddar	134, 135, 138
Tetramethylpyrazine	[1124-11-4]	Cheese, cheddar	138
Methional	[3268-49-3]	Cheese, cheddar	134
		Cheese, Parmigiano Reggiano	131–133
Skatole	[83-34-1]	Cheese, cheddar	134, 138
2-Acetyl-1-pyrroline	[85213-22-5]	Cheese, cheddar	134, 138
		Whey protein concentrate	144
2,6-Dimethylpyrazine	[108-50-9]	Parmigiano Reggiano	132
		Whey, dried	143
4-Mercapto-4-methyl-2-pentanone	[19872-52-7]	Cheese, cheddar	139
4-Mercapto-3-methyl-2-pentanone	[385766-53-0]	Cheese, cheddar	139
Homofuraneol	[110516-60-4]	Cheese, Swiss	147
		Cheese, cheddar	134, 135
Propionic acid	[79-09-4]	Cheese, Swiss	147
Ethyl-3-mercapto-propionate	[5466-06-8]	Camembert, Munster	129
4-Methyloctanoic acid	[54947-74-9]	Cheese, goat	130
4-Ethyloctanoic acid	[16493-80-4]	Cheese, goat	130
(Z)-4-Heptenal	[6728-31-0]	Cream	4
		Cheese, cheddar	135
(E,E)-2,4-Nonadienal	[5910-87-2]	Cream	122
1-Nonen-3-one	[24415-26-7]	Yogurt, milk	148
Furaneol	[3658-77-3]	Milk, nonfat dry	142
		Whey protein concentrate	143, 144
		Butter, heated	145, 146

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aroma substances for Camembert. A thiolester ethyl 3-mercaptopropionate was reported for the first time in Munster and Camembert cheeses [129]. This sulfur volatile was described at low concentrations as having pleasant "fruity, grapy, rhubarb" characters. 4-Methyl- and 4-ethyloctanoic acids contribute the "waxy/animal" character in fresh chèvre-style goat cheese flavor [130]. 2-Heptanone, 2-nonanone, and short- and moderate-chain fatty acids are the dominant character compounds of blue cheese flavor. Sulfur compounds, especially methanethiol, hydrogen sulfide, and dimethyl disulfide, contribute to the strong garlic/putrid aroma of soft-smear or surface-ripened cheeses. Key aroma compounds in Parmigiano–Reggiano cheese were recently reported, including 3-/2-methylbutanal, 2-methylpropanal, dimethyltrisulfide, diacetyl, methional, ethyl C_4–C_8 fatty acid esters, and C_2–C_8 fatty acids [131–133]. In the basic fraction, 2,6-dimethylpyrazine and 6-ethyl-2,3,5-trimethylpyrazine had very strong nutty, baked characters and the highest flavor intensities among the six pyrazines detected [132].

By a wide margin, cheddar is the most popular cheese flavor in North America. Although its flavor is described as "sweet, buttery, aromatic, and walnut," there is no general consensus among flavor chemists about the identity of individual compounds or groups of compounds responsible for cheddar flavor. At present, it is thought to arise from a unique balance of key volatile components rather than a unique character-impact compound. Sensory-guided flavor studies concluded that butyric acid, acetic acid, methional, homofuraneol (5-ethyl-4-hydroxy-2-methyl-(2H)-furan-3-one), (E)-2-nonenal, (Z)-4-heptenal, (Z)-1,5-octadien-3-one, and 2-acetyl-1-pyrroline are primary contributors to the pleasant mild flavor of cheddar cheese [134,135]. Important contributors to cheddar aroma are 2,3-butanedione, dimethyl sulfide, dimethyl trisulfide, and methanethiol [134]. Two recent studies confirmed that concentrations of hydrogen sulfide and dimethyl disulfide increased only during the initial stages of cheddar cheese aging, whereas those of dimethyl sulfide, dimethyl trisulfide, and methanethiol continued to increase throughout the aging process [136,137]. A desirable nutty flavor supports "sulfur" and "brothy" characters in a quality aged cheddar cheese sensory profile. 2-Acetyl-2-thiazoline [134] and 2-acetyl-1-pyrroline [134,135] contribute "roasted, corny" flavors, which were suggested to be related to the nutty cheddar flavor. In an effort to characterize the nutty flavor in cheddar cheese, a comprehensive sensory–analytical study concluded that Strecker aldehydes (2-methylpropanal; 2- and 3-methylbutanal), which individually are "green, malty, chocolate," provide an enhanced overall nutty flavor when added to cheddar cheese [138]. Novel polyfunctional thiols were recently reported in aged cheddar cheese. Among these were 4-mercapto-4-methyl-2-pentanone (catty note) and 4-mercapto-3-methyl-2-pentanone (cooked milk, sweet note) [139]. In the case of cheddar cheese powders, dimethyl sulfide imparts a desirable "creamed corn" flavor [140].

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The most aroma-active compound in fresh, sour-cream butter was reported as the character-impact compound diacetyl, with supporting contributions from δ-decalactone, (Z)-6-dodeceno-γ-lactone, and butyric acid [141].

Key aroma-active compounds have been reported in dried dairy products including nonfat milk and whey powders. Furaneol is the primary contributor to the sweet, caramelized aroma character of nonfat dry milk, with supporting contributions from heat-generated sotolon, maltol, vanillin, and (E)-4,5-epoxy-(E)-2-decenal [142]. Compounds important to dried sweet whey from cheddar cheese manufacture include butyric and hexanoic acids; maltol; Furaneol; dimethylpyrazines; 2,3,5-trimethylpyrazine; and several lactones [143]. Additional flavor-impact compounds identified in whey protein concentrate and whey protein isolate were butyric acid (cheesy note); 2-acetyl-1-pyrroline (popcorn note); 2-methyl-3-furanthiol (brothy/burnt note); Furaneol (maple/spicy note); 2-nonenal (fatty note); (E,Z)-2,6-nonadienal (cucumber note); and (E,Z)-2,4-decadienal (fatty/oxidized note) [144].

A summary of potent flavor compounds in dairy products is presented in Table 9.7. Representative structures of significant dairy flavorants including homofuraneol in heated butter [145,146], mild cheddar cheese [134], and Swiss cheese [147]; δ-decalactone in butter and buttermilk [141]; (Z)-6-dodecen-γ-lactone in butter [145,146] and mild cheddar cheese [134,135]; and 1-nonen-3-one in milk and yogurt [148] are shown in Figure 9.8.

Characterizing aromas in off-flavors

Flavor defects, so-called taints, malodors, or off-flavors, are sensory attributes that are not associated with the typical aroma and taste of foods and beverages. These defects can range from subtle to highly apparent and are often significant detractors to food quality. Off-flavors can be produced due to several possible factors: contamination (air, water, packaging, or shipping materials); ingredient mistakes in processing; or generation (chemical or microbial) in the food itself. In the latter instance, generation of off-flavors in foods may result from oxidation, nonenzymatic browning, chemical reactions between food constituents, light-induced reactions, microbial fermentations, or enzymatic pathways.

Over the past 15 years, numerous complete and detailed reviews have discussed the occurrence of off-flavors in food and packaging systems [149–153]. The intent of this section is to summarize recent highlights and off-flavorants of significance, without striving for comprehensiveness.

Lipid-derived volatile compounds play an important role in many food flavors. These compounds contribute to the characteristic and desired flavor attributes of foods, but they can also cause off-flavors depending on their concentrations relative to other sensorially relevant odorants.

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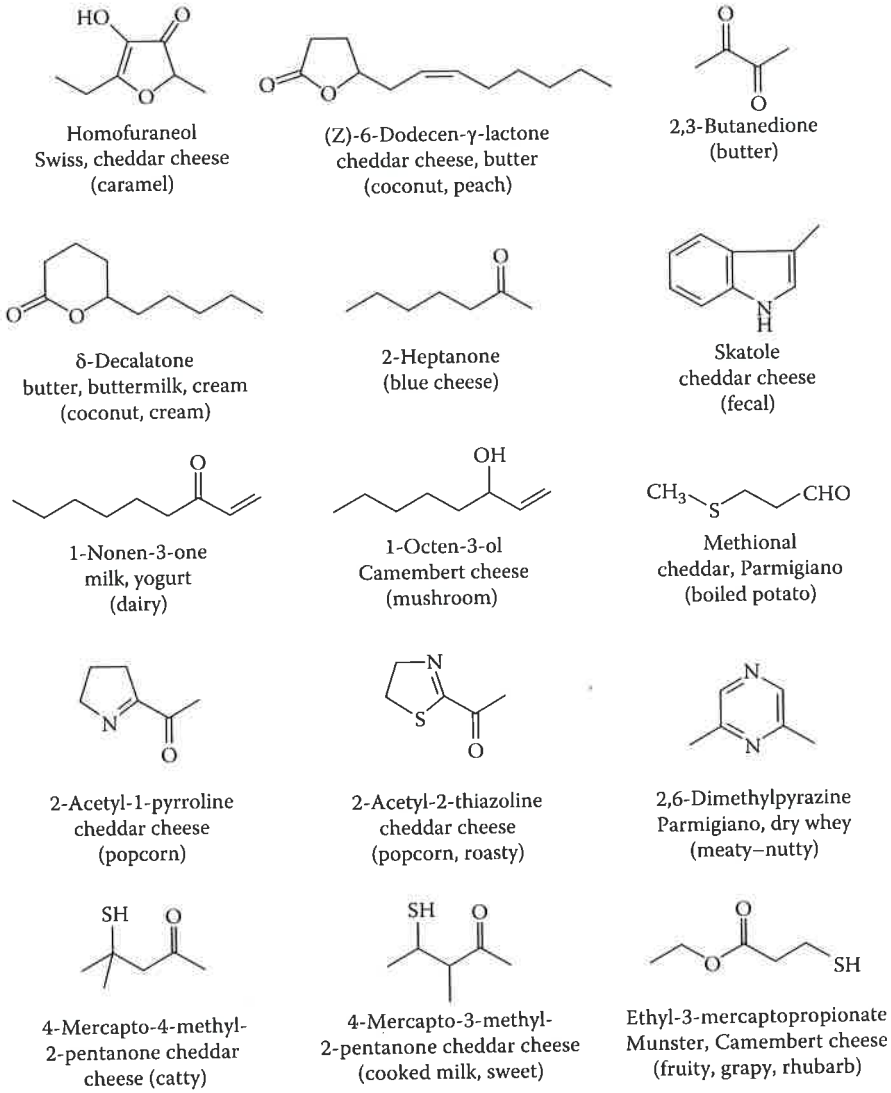

Figure 9.8 Representative cheese and dairy character-impact flavor compounds.

For example, the "cardboard" off-flavor of butter oil is primarily related to the presence of (E)-2-nonenal, which is formed by the autoxidation of palmitoleic acid [154]. Carbonyl compounds formed by lipid peroxidation were identified in cooked beef, which develops a warmed-over flavor from reheating after 2 days of refrigerated storage [110]. Warmed-over flavor is principally caused by the formation of (E)-4,5-epoxy-(E)-2-decenal (metallic note) and hexanal (green note), which are not present in freshly

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cooked beef. Similarly, for boiled chicken "green/cardboardlike/metallic" off-odors were formed during refrigerated storage and reheating, primarily from a sevenfold increase in hexanal [108]. These and other unsaturated carbonyl compounds, including (E,E)-2,4-decadienal (deep-fried note) and 1-octen-3-one (mushroomlike/beany note), are primarily responsible for the rancid off-flavors in soybean and canola oils, which are caused by the oxidation of linoleic and linolenic acids [155]. The light-induced compound 3-methyl-2,4-nonanedione (strawy, lard-like, beany note) strongly contributes to the reverted off-flavor of oxidized soybean oil, because of its extremely low odor threshold (0.007–0.014 ppt) [156]. Melon odors are associated with foods cooked in partially hydrogenated soybean oils that have undergone oxidative deterioration during heating. 6-Nonenal (cucumber/melon note) from (Z,Z)-9,15-linoleic acid is reported to be a character flavor associated with these deteriorated oils [157]. (Z)-3-Hexenal and (Z,Z)-3,6-nonadienal were shown to contribute substantially to the fatty, "fishy" off-flavor of boiled trout, which was in frozen storage for several months before cooking [115]. Other carbonyl compounds that are likely to contribute to characteristic "fishy" off-flavors in oxidized seafood because of their low odor thresholds include 2,6-nonadienal and 1,5-octadien-3-one [111]. A summary of off-flavor impact compounds for foods, beverages, and packaging materials is presented in Table 9.8, and the representative chemical structures are given in Figure 9.9.

The characteristic odor-active components in cardboard packaging material are *cis*- and *trans*-2-nonenal, along with an unidentified "woody smelling" constituent [158]. *trans*-2-Nonenal is considered the characteristic volatile responsible for a "stale, cardboard" off-flavor in aged packaged beer. Mechanistic studies using labeled nonenal confirmed that cardboard off-flavor in finished beer arises from lipid autoxidation during wort boiling and not from lipoxygenase activity during the mashing step [159]. Studies also revealed that 2-furfuryl ethyl ether is responsible for an astringent, stale off-flavor in beer [160]. The stale flavor was reproduced by adding furfuryl ether and *trans*-2-nonenal to fresh beer, but not by adding either compound individually. Recently, 4-vinylsyringol (3,5-dimethoxy-4-hydroxystyrene) was identified as a contributor to stale beer odor in naturally aged beer [161]. Its odor character from GC–O was described as "smoky, tobacco, old beer." The chemically similar 4-vinylguaicol contributes "phenolic, medicinal, or clove" off-flavors at higher levels from wheat beers brewed with certain yeast strains [162]. Lipid-derived (E,E)-2,4-decadienal, in addition to hexanal, (E)-2-octenal, and (E)-2-nonenal, was shown to be the most potent off-flavor compound in precooked vacuum-packaged potatoes [163]. In dry raw spinach, (Z)-1,5-octadien-3-one and methional are responsible for a "fishy" off-flavor when they are present in a 1:100 ratio. 3-Methyl-2,4-nonanedione produces a "haylike" off-flavor character from the oxidative degradation of furanoid fatty acids in dry spinach [164] and in dry parsley [165].

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Table 9.8 Off-Flavor Impact Compounds in Food and Beverage Products

Impact compounds	CAS Registry number	Off-flavor descriptors	Occurrence	Reference
Geosmin	[19700-21-1]	Musty, earthy	Catfish, wheat, water	185, 192
2,4,6-Trichloroanisole	[87-40-1]	Musty, moldy	Coffee, wine corks, raisins	191, 192, 188
2,4,6-Tribromoanisole	[607-99-8]	Musty, moldy	Casein, wine corks, wine	189, 187
2-Methylisoborneol	[2371-42-8]	Earthy, musty	Coffee, catfish, beans	191, 185, 192
2-*iso*-Propyl-3-methoxypyrazine	[25773-40-4]	Peasy	Coffee, cocoa beans	191, 151
Ethyl formate	[109-94-4]	Fermented	Coffee, roasted	184
4,4,6-Trimethyl-1, 3-dioxane	[1123-07-5]	Musty	Packaging film	195
8-Nonenal	[39770-04-2]	Smoky, plastic	Polyethylene packaging	196
Iodocresol	[16188-57-1]	Medicinal	Lemon cake mix	194
(E)-2-Nonenal	[2463-53-8]	Cardboard, stale	Beer, packaged	166
		Cardboard	Oxidized butter	154
		Cardboard	Soybean lecithin	155
		Cardboard	Cardboard packaging	158
(E)-4,5-Epoxy-(E)-2-decenal	[134454-31-2]	Metallic	Warmed over (beef)	110
		Metallic	Oxidized soybean oil	155
		Metallic	Butter	78
(E,Z)-2,6-Nonadienol	[7786-44-9]	Metallic	Buttermilk	205
1-Octen-3-one	[4312-99-6]	Metallic, mushroom	Butterfat	200
		Beany	Rancid soybean oil	155
Hexanal	[66-25-1]	Green grass	Rancid soybean oil	155
		Rancid	Warmed over (beef)	110
(E,E)-2,4-Decadienal	[25152-84-5]	Deep fried	Rancid soybean oil	155

2,3-Diethyl-5-methylpyrazine	[18138-04-0]	Roasty, earthy	Soybean lecithin	155
6-Nonenal	[6728-35-4]	Cucumber, melon	Partially hydrogenated soy oil	157
(Z)-3-Hexenal	[6789-80-6]	Fatty, fishy	Aged trout	115
(Z,Z)-3,6-Nonadienal	[21944-83-2]	Fatty, fishy	Aged trout	115
5α-Androst-16-en- 3-one	[18339-16-7]	Urine	Boar meat	151, 213
Skatole	[83-34-1]	Fecal like	Boar meat, potato chips	213, 151
		Medicinal	Beef	214
2-Furfuryl ethyl ether	[6270-56-0]	Stale, astringent	Beer	160
3-Methyl-2-butene-1-thiol	[5287-45-6]	Skunky	Beer (light-struck)	166, 167
S-Methyl hexanethioate	[2432-77-1]	Cabbagy, rubbery	Beer	169
4-Vinylsyringol	[28343-22-8]	Old beer, tobacco, smoky	Beer	161
4-Vinylguaiacol	[7786-61-0]	Medicinal, clove	Beer, wort	162
		Rotten, old fruit	Orange juice, apple juice	216, 217
4-Mercapto-4-methyl-2-pentanone	[19872-52-7]	Cat urine, ribes	Beer	170
Methional	[3268-49-3]	Worty	Beer (alcohol-free)	176
		Cooked vegetables	Oxidized white wine, orange juice	172, 173, 174
		Potato	UHT-processed milk	178, 210, 211
Dimethyl disulfide	[624-92-0]	Sunlight off-flavor	Milk, skim	179
(E)-1,3-Pentadiene	[504-60-9]	Kerosene	Cheese (sorbic acid)	151, 206

(*Continued*)

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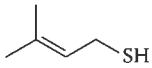
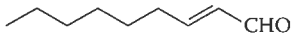
Table 9.8 Off-Flavor Impact Compounds in Food and Beverage Products (*Continued*)

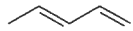
Impact compounds	CAS Registry number	Off-flavor descriptors	Occurrence	Reference
2,4,5-Trimethyloxazole	[20662-84-4]	Melon, kiwifruit	Dried sour cream	140
Tetradecanal	[124-25-4]	Sickening, aldehydic	Milk powder	207
β-Ionone	[79-77-6]	Haylike	Milk powder	207
Benzothiazole	[95-16-9]	Sulfuric, quinoline	Milk powder	207
2,6-Dimethylpyrazine	[108-50-9]	Cooked milk	UHT-processed milk	210
2-Ethyl-3-methylpyrazine	[15707-23-0]	Cooked milk	UHT-processed milk	210
2-Aminoacetophenone	[551-93-9]	Gluey, glutinous	Milk powder, casein	197, 198, 208
		Untypical aging (UTA)	White wine	199
3-Methyl-2, 4-nonanedione	[113486-29-6]	Strawy, beany	Soybean oil (light-induced)	156
		Haylike	Dried spinach, parsley	164, 165
(Z)-1,5-Octadien-3-one	[65767-22-8]	Fishy	Dried spinach, old fish	164, 111
Bis(2-methyl-3-furyl)disulfide	[28588-75-2]	Vitamin B_1 odor	Thiamin degradation	203
4-Methyl-2-isopropylthiazole	[15679-13-7]	Vitamin, cabbage	Orange juice (Vitamin B_2)	180
Sotolon	[28664-35-9]	Burnt, spicy	Citrus soft drink	202
2-Methyl-3-furanthiol	[28588-74-1]	Aged flavor	Orange juice	174, 175
(S)-(+)-Carvone	[2244-16-8]	Woody, terpeny	Oxidized orange juice	215



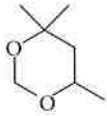
3-Methyl-2-butene-1-thiol
light-struck beer



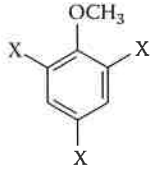
(E)-2-Nonenal
cardboard (beer, butter, packaging)



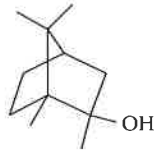
1,3-Pentadiene
kerosine (sorbate/cheese)



4,4,6-Trimethyl-1,3-dioxane
musty packaging film

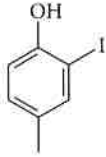


X=Cl 2,4,6-Trichloroanisole
X=Br 2,4,6-Tribromoanisole
musty (coffee, wine corks, casein)

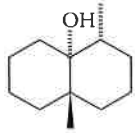


2-Methylisoborneol
earth–musty (coffee, catfish)

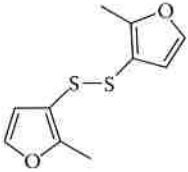
trans-4,5-Epoxy-(E)-2-decenal
metallic (warmed-over flavor beef; soybean oil)



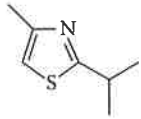
Iodocresol
medicinal (lemon cake mix)



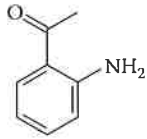
Geosmin
musty–earthy (fish, water)



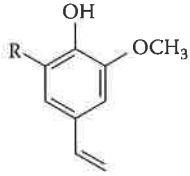
Bis-(2-methyl-3-furyl)disulfide
vitamin B_1 (thiamin)



4-Methyl-2-iso-propylthiazole
vitamin B_2 (fortified orange juice)

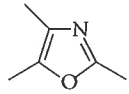


2-Aminoacetophenone
gluey (milk, wine)



R=H 4-Vinylguaiacol
rotten (orange); clove (beer)
R=OCH_3 4-Vinylsyringol
old beer, tobacco, smoky (beer)

8-Nonenal
smoky plastic (oxidized polyethylene)



2,4,5-Trimethyloxazole
melonlike (dried cream)

Figure 9.9 Representative off-flavor character-impact compounds.

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Exposure of beer to light has been shown to produce 3-methyl-2-butene-1-thiol, which produces a skunky off-flavor in "sun-struck" or "light-struck" ales [166,167]. This mercaptan has a sensory threshold of 0.05 ppb in beer. It results from complex light-induced degradations of isohumulones (hop-derived bitter *iso*-acids) to form free-radical intermediates, which subsequently react with the thiol group of cysteine. The light-struck off-flavor can be controlled in beer through the use of improved packaging technology (colored glass bottles), chemically modified hop bitter acids, or antioxidants or its precipitation with high-molecular-weight gallotannins by the addition of zinc salts [168]. In addition to dimethyl sulfide, thioesters have been reported to contribute a cabbagy, rubbery off-note; they sometimes are derived from hops in beer, the most significant being *S*-methyl hexanethioate, which has a detection threshold of 1 ppb [169]. Diacetyl can produce an undesirable buttery off-character in beer through accelerated fermentation, whereby brewer's yeast does not convert all the diketone intermediates to flavor-inactive acetoin and 2,3-butanediol [166]. Another staling off-flavor in beer is described as catty/ribes, whose character comes from 4-mercapto-4-methyl-2-pentanone (cat ketone). This off-flavor can develop rapidly in beers that are packaged and stored with a high air content in the headspace [170]. A similar catty/ribes off-flavor in aged lager beer was attributed to 3-mercapto-3-methylbutyl formate [171].

Strecker aldehydes are a frequent source of off-flavors in fermented products. Development of off-flavors in oxidized white wines typically marks the end of shelf life for these wines. Methional (3-methylthiopropionaldehyde) was identified as producing a "cooked vegetables" off-flavor character in a young white wine that had undergone spontaneous oxidation [172]. Methional levels increased in wines spiked with methionol or methionine, suggesting its formation via direct peroxidation or Strecker degradation of methionine. The importance of methional in the development of characteristic oxidation notes in white wine was further demonstrated [173]. Methional and 2-methyl-3-furanthiol are purported off-flavor components in stored orange juice [174]. Methanethiol, 1-*p*-menth-1-ene-8-thiol, 2-methyl-3-furanthiol, and dimethyl trisulfide contributed atypical "tropical fruit/grapefruit" character to canned orange juice [175]. Methional was shown to impart a worty off-flavor in alcohol-free beer, with more sensory significance than was previously attributed to 3-methyl- and 2-methylbutanal for this off-taste [176]. In an alcohol-free beer medium, perception of worty off-flavors is strengthened by the absence of ethanol and by the higher level of sugars. Methional, methanethiol, and dimethyl sulfide are the sources of sulfur and cooked off-flavors in ultrahigh-temperature (UHT)–processed soy milks [177]. Similar to the off-flavor in UHT-processed cow's milk, 2-acetyl-1-pyrroline, 2-acetylthiazole, and carbonyl compounds also contributed to the cooked flavor impact [178]. Methional was initially thought to be responsible for the "sunlight" off-flavor in photooxidized

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milk exposed to high-intensity fluorescent light or sunlight. This cardboardlike off-flavor is generated via photooxidation of methionine in the presence of riboflavin as a sensitizer. More recently, dimethyl disulfide was identified as the source of the light-induced off-flavor in skim milk [179]. Another vitamin-derived off-odor problem was recently described in which a pineapple fruit juice beverage was fortified with riboflavin. The "vitamin, cabbage, brothy, vegetable soup" off-odor was characterized as 4-methyl-2-isopropylthiazole, which resulted from riboflavin-sensitized Strecker degradation of valine, cysteine, and methionine followed by reaction of the resulting aldehydes with ammonia and hydrogen sulfide [180].

Sulfur compounds present in wine can have a detrimental effect on its aroma character, producing odors described as "garlic, onion, and cauliflower" or the so-called Boeckser aromas. This sulfurous character is correlated with 2-methyl-3-hydroxythiophene, 2-methyl-3-furanthiol, and ethanethiol, and their concentrations in wine are influenced by winery practices and the use of certain winemaking yeasts [181]. Off-flavors in European wines were associated with the nonvolatile bis(2-hydroxyethyl) disulfide, a precursor to the "poultrylike" character of 2-mercaptoethanol and hydrogen sulfide [182].

Other undesirable "Brett" off-flavors are produced in wines due to contamination in grape musts and wineries with *Brettanomyces* yeast strains, named after their original discovery in British beers. These off-flavors are typically described as "Band-Aid," "barnyard," "horse sweat," "plastic," and "wet animal." A recent study identified the key character compounds in high-Brett wines as isovaleric acid, 4-ethyl guaiacol, and 4-ethyl phenol; however, a potent, plastic note was not characterized in this study [183].

The quality of coffee is influenced by many factors including its variety, agricultural and postharvest conditions, roasting parameters, and brewing. Recently, ethyl formate was identified as being responsible for the characteristic "fermented" off-note, which is occasionally perceived in the aroma of roasted and ground coffee [184]. As this fermented off-flavor is a well-known issue for coffee growers and the coffee trade, ethyl formate is useful as a quality marker for coffee.

Musty aromas and flavors are a major problem in a variety of foods and packaging materials, and many of the causative character-impact materials show powerful impact [185]. For example, 2,4,6-trichoroanisole is a highly odorous metabolite of a fungus that attacks wood, paperboard packaging, and wine corks [150,151]. Trichloroanisole has a musty, haylike odor and possesses an extremely low odor threshold (~0.05 ppt). Tricholoroanisoles, tribromoanisoles, and their corresponding phenols can provide musty off-flavor character to foods [186], wine corks/wine [187], process water, and raisins [188]. 2,4,6-Tribromoanisole was recently reported to impart a musty flavor defect to calcium caseinate and is formed from the fungal conversion of 2,4,6-tribromophenol contaminants in wood freight containers and

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plastic slip sheets [189]. It was present in tainted caseinate at concentrations of 2–560 ppb, with a sensory threshold of 20 ppt in 10% aqueous solution. About 20% of Brazilian coffee production exhibits the so-called Rio defect, which is characterized by a strong off-flavor that is often described as "medicinal, phenolic, or iodine-like" [190]. Occasionally, this defect also occurs in coffees of other origins. 2,4,6-Trichloroanisole in concentrations ranging from 1 to 100 ppb was identified as the most likely key compound for the Rio off-flavor as analyzed by capillary GC, GC–sniffing, and GC–MS. 2,4,6-Trichlorophenol, the probable precursor, was also found in most of these samples. Adding trichloroanisole to freshly brewed coffee imparted to it the same off-flavor notes as described in actual Rio coffee. Its perception threshold in coffee brew was found to be 8 ppt by aroma and 1–2 ppt for taste [190]. In Robusta coffees, 2-methylisoborneol provides an "earthy, tarry" character at 5 ppt and it must be removed during processing to approach the flavor of arabica coffees [191]. Geosmin (1,10-dimethyl-9-decalol) imparts an earthy musty off-odor to drinking water and a "muddy" odor to catfish and tilapia fish, which live in brackish water [185,192,193]. It is produced from *Actinomycetes* microorganisms in soil, planktonic algae, and fungi. 2-Methylisoborneol also provides an earthy musty character to catfish [192]. A medicinal off-flavor was produced in a lemon-flavored cake mix by the reaction between two minor ingredients of the cake, *p*-cresol from the lemon flavor and iodine from iodized salt. The resulting iodocresol was shown to possess a medicinal character at 0.2 ppb aroma threshold [194]. McGorrin, Pofahl, and Croasmun [195] studied a musty off-odor in printed plastic film, which was not a phenol as expected but was identified as 4,4,6-trimethyl-1,3-dioxane. It was formed during film manufacture as a reaction product of 2-methyl-2,4-pentanediol, a solvent coating to facilitate ink adhesion, and formaldehyde, a component of the ink.

Another common source of packaging-derived off-flavors is polyethylene packaging materials, which occasionally transfer undesirable off-flavors to foods stored in them. So-called plastic or "smoky-poly" off-flavors can be generated by minor plasticizer components in the resin or by oxidation of the polyolefin during polymerization and subsequent thermal extrusion into films, sheets, or containers. Polyethylene films that are manufactured under high-temperature conditions are more likely to contribute such off-flavors. Recently, a previously unidentified, potent plastic off-flavorant in oxidized polyethylene films was identified as 8-nonenal, which contributes a characteristic plastic off-flavor to corn chips packaged in the films [196].

Compounds that have positive character impact in some foods can become off-flavors in different food contexts. For example, indole and skatole in cheddar cheese flavor become fecal in the context of potato chips [151]. 2-Aminoacetophenone, having foxy character in Concord grape, imparts a "gluey" flavor in milk powder and casein through the degradation of tryptophan [197,198]. In white wines (such as Riesling),

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it contributes an "untypical aging" (UTA) note, presumably from oxidative degradation of the tryptophan metabolite indole-3-acetic acid after the sulfuration step in wine making [199]. 1-Octen-3-one (mushroom) imparts an undesired metallic flavor in dairy products and oxidized vegetable oils [200]. A recent study identified two key metallic odorants generated in aqueous ferrous sulfate solutions in which 1-nonen-3-one provides a 10-fold more potent metallic-smelling character relative to 1-octene-3-one [201]. Sotolon, the furanone character-impact flavor of fenugreek (Table 9.1) was recently shown to cause a "burnt, spicy" off-flavor in citrus soft drinks, generated by the reaction of ascorbic acid with ethanol [202]. Whereas 2-isopropyl-3-methoxy pyrazine contributes to pea an earthy potato flavor character, it provides an undesirable "peasy" off-flavor to Rwandan coffee [191] and fermented cocoa beans [151]. Although bis(2-methyl-3-furyl) disulfide contributes a desirable aged, prime-rib flavor in beef, it is the principal "vitamin B" off-odor resulting from thiamin degradation [203].

Character compounds that contribute to positive flavor impact at low levels can become off-flavors when they occur at higher concentrations. For example, dimethyl sulfide provides an appropriate "cornlike" background character to beer flavor at low levels, whereas it contributes a highly undesirable cooked vegetable or cabbagelike malodor to beer when present at levels significantly above its sensory threshold (30–45 ppb) [204]. Similarly, for cheddar cheese flavor it imparts a rotten vegetable taste when present at high levels [135].

Off-flavors in dairy products have been reviewed much in the literature [151,152]; however, there have been several recent developments. In sour-cream buttermilk, the key odorant responsible for a metallic off-flavor was identified as (E,Z)-2,6-nonadienol [205]. During cream fermentation, its formation occurs from the peroxidation of α-linolenic acid to generate the 2,6-nonadienal precursor, with subsequent reduction to dienol by starter culture reductases that remain active during storage. Metallic off-flavors are not formed readily in fermented sweet-cream buttermilk due to the presence of significantly lower concentrations of α-linolenic acid [205]. The common use of sorbic acid or potassium sorbate as a mold inhibitor in commercial dairy products often produces an off-flavor described as "kerosene, plasticlike, or paintlike," which may incorrectly be attributed to packaging materials. The source of the taint is (E)-1,3-pentadiene, which results from the decarboxylation of sorbates by lactic acid bacteria in yogurt, cheese, and margarine [151,206]. A "melon, ripe kiwifruit" off-flavor in spray-dried cultured dairy products was identified as 2,4,5-trimethyloxazole, a product of the Maillard reaction between diacetyl and arginine (whey source) or acetaldehyde and ammonia [140].

Other significant dairy taints studies include studies on the characteristic off-flavor in spray-dried skim milk powder, which was related to contributions from tetradecanal (sickening, aldehydic note), β-ionone

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(haylike note), and benzothiazole (sulfuric, quinoline note) at low-ppb levels [207]. The cause of an intense "musty, stale" off-flavor was identified as 2-aminoacetophenone in micromilled milk powder [208]. A recent AEDA study of the characteristic aroma components of dried rennet casein indicated that although 2-aminoacetophenone is a potent odorant, sensory reconstitution confirmed that hexanoic acid, indole, guaiacol, and *p*-cresol were the principal factors behind rennet casein's typical "animal/wet dog" odor [209]. In three studies of UHT-processed milk, the "UHT-milk-flavor" character is contributed by methional, δ-decalactone, 2-acetyl-1-pyrroline, and 2-acetylthiazole; 2,6-dimethylpyrazine; 2-ethylpyrazine; and 2-ethyl-3-methylpyrazine were also significant contributors [178,210]. Additionally, dimethyl sulfide, diacetyl, 2-heptanone, 2-nonanone, 2-methylpropanal, 3-methylbutanal, nonanal, and decanal were reported as significant flavor components of UHT milk off-flavor [211]. Formation of the UHT off-flavor was shown to be inhibited by the addition of 0.1% epicatechin during milk processing [178]. Fruity (pineapple-like) off-flavors in pasteurized milk indicate the presence of high levels of ethyl butyrate, ethyl hexanoate, ethyl octanoate, and ethyl decanoate esters, whereas rancid, soapy tastes arise from the presence of decanoic and dodecanoic acids [212].

As previously discussed in the section titled *Meat and seafood flavors*, lipid oxidation is generally related to flavor deterioration in meat and meat products. However, "boar taint," an intense urinelike off-odor, is attributed primarily to the flavor synergy between two compounds in boar fat, androstenone (5-α-androst-16-ene-3-one) from testes and the "fecal-like" skatole (3-methyl indole) from tryptophan breakdown [213]. Generally, women tend to be more sensitive to the odor than men. Skatole has also been implicated in a medicinal off-odor in beef [214].

Off-flavors in citrus oils such as orange oil have been related to autoxidation of limonene to (S)-carvone (caraway; Figure 9.1) and carveol, producing "woody, turpeny" off-flavors [215]. Other off-flavors in orange juice arise from the presence of 4-vinylguaiacol, which contributes an "old fruit" and "rotten" character via decarboxylation of ferulic acid [216]. Conversion of ferulic acid to 4-vinylguaiacol by yeast contaminants, with corresponding off-flavor development, has been reported in unpasteurized apple juice [217] and in beers and worts [162]. Thermal abuse during processing or high-temperature storage of orange and grapefruit juices produces Furaneol, which contributes a "sweet, pineapple" defect [216].

Conclusion

The objective of this chapter is to provide an updated review of character-impact compounds in flavors and off-flavors. Particular emphasis is placed on compounds that have been identified in natural flavor systems.

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The summarized data can be applied in creative flavor-compounding efforts to replicate and monitor the production of flavors and in food processing to ensure flavor quality.

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