22 Spices, Salt and Vinegar

22.1 Spices

Some plants with intensive and distinctive flavors and aromas are used dried or in fresh form as seasonings or spices. Table 22.1 lists the most important spice plants together with the part of the plant used for seasoning.

22.1.1 Composition

22.1.1.1 Components of Essential Oils

Most spices contain an essential or volatile oil (Table 22.2), which can be isolated by steam distillation. The main oil constituents are either

Table 22.1. Spices used in food preparation/processing

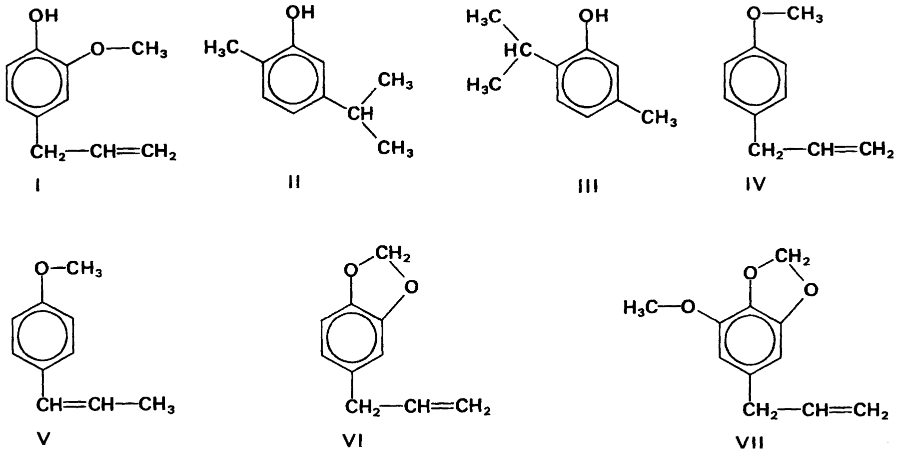
Number	Common name	Latin name	Class/order family (bot)	Cultivation region
Fruits				
1	Pepper, black	*Piper nigrum*	Piperaceae	Tropical and subtropical regions
2	Vanilla	*Vanilla planifolia* *Vanilla fragans* *Vanilla tahitensis* *Vanilla pompona*	Orchidaceae	Madagascar, Comore Island, Mexico, Uganda
3	Allspice	*Pimenta dioica*	Myrtaceae	Caribbean Islands, Central America
4	Paprika (bell pepper)	*Capsicum annuum. var. annuum*	Solanaceae	Mediterranean and Balkan region
	Chili (Tabasco)	*Capsicum frutescens*		
	Brown pepper	*Capsicum baccatum, var. pendulum*		
5	Bay tree[a]	*Laurus nobilis*	Lauraceae	Mediterranean region
6	Juniper berries	*Juniperus communis*	Cupressaceae	Temperate climate region
7	Aniseed	*Pimpinella anisum*	Apiaceae	
8	Caraway	*Carum carvi*	Apiaceae	Temperate climate region
9	Coriander	*Coriandrum sativum*	Apiaceae	
10	Dill[a]	*Anethum graveolens*	Apiaceae	
Seeds				
11	Fenugreek	*Trigonella foenum greacum*	Leguminosae	Mediterranean region, temperate climate region
12	Mustard	*Sinapsis alba*[b]	Brassicaceae	
		Brassica nigra[c]	Brassicaceae	Temperate climate region
13	Nutmeg	*Myristica fragrans*	Myristicaceae	Indonesia, Sri Lanka, India
14	Cardamom	*Elettaria cardamomum*	Zingiberaceae	India, Sri Lanka
Flowers				
15	Cloves	*Syzygium aromaticum*	Myrtaceae	Indonesia, Sri Lanka, Madagascar
16	Saffron	*Crocus sativus*	Iridaceae	Mediterranean region, India, Australia
17	Caper	*Capparis spinosa*	Capparidaceae	Mediterranean region
Rhizomes				
18	Ginger	*Zingiber officinale*	Zingiberaceae	South China, India, Japan, Caribbean Islands, Africa
19	Turmeric	*Curcuma longa*	Zingiberaceae	India, China, Indonesia

Table 22.1. (continued)

Number	Common name	Latin name	Class/order family (bot)	Cultivation region
Barks				
20	Cinnamon	*Cinnamomum zeylanicum, C. aromaticum, C. burmanii*	Lauraceae	China, Sri Lanka, Indonesia, Caribbean Islands
Roots				
21	Horseradish	*Armoracia rusticana*	Brassicaceae	Temperate climate region
Leaves				
22	Basil	*Ocimum basilicum*	Labiate	Mediterranean region, India
23	Parsley	*Petroselinum crispum*	Apiaceae	Temperate climate region
24	Savory	*Satureia hortensis*	Labiate	Temperate climate region
25	Tarragon	*Artemisia dracunculus*	Compositae	Temperate climate region, Mediterranean region
26	Marjoram	*Origanum majorana*	Lamiaceae	Temperate climate region
27	Origano	*Origanum heracleoticum, O. onites*	Lamiaceae	Temperate climate region
28	Rosemary	*Rosmarinus officinalis*	Lamiaceae	Mediterranean region
29	Sage	*Salvia officinalis*	Lamiaceae	Mediterranean region
30	Chives	*Allium schoenoprasum*	Liliaceae	Temperate climate region
31	Thyme	*Thymus vulgaris*	Lamiaceae	Temperate climate region

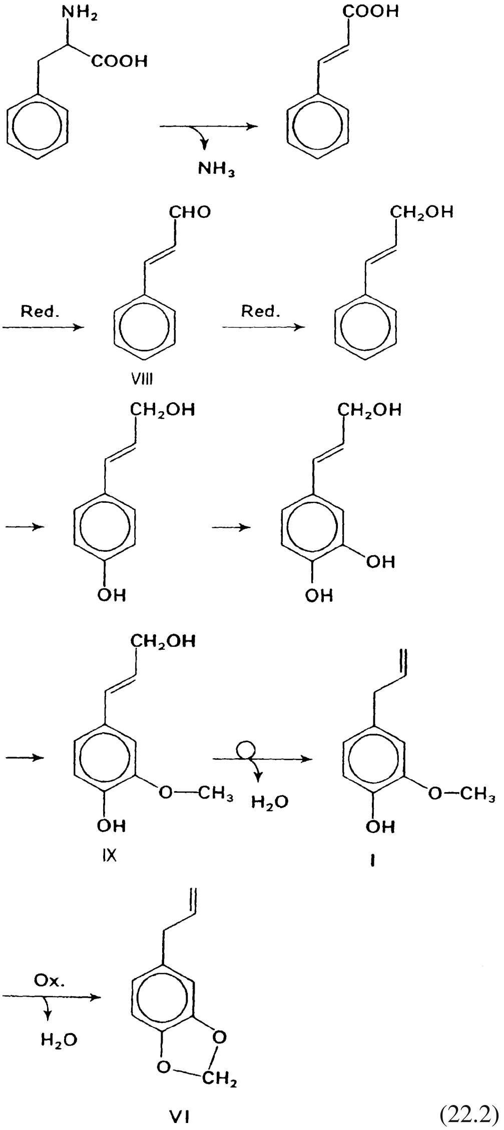
[a] Fruits and leaves, [b] white mustard, [c] black mustard.

mono- and sesquiterpenes or phenols and phenolethers. Examples of the latter two classes of compounds are eugenol (I), carvacrol (II), thymol (III), estragole (IV), anethole (V), safrole (VI) and myristicin (VII):



(22.1)

Biosynthesis of cinnamaldehyde (VIII) and also of eugenol (I) an safrole (VI) originates from phenylalanine (compare biosynthesis of other plant phenols in 18.1.2.5.1). The following reaction sequence is assumed:



(22.2)

Table 22.2. Content of essential oils in some spices[a]

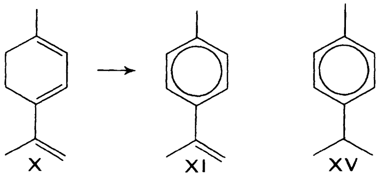
Spice	% Vol./Weight
Black pepper	2.0–4.5
White pepper	1.5–2.5
Aniseed	1.5–3.5
Caraway	2.7–7.5
Coriander	0.4–1.0
Dill	2.0–4.0
Nutmeg	6.5–15
Cardamom	4–10
Ginger	1–3
Turmeric	4–5
Marjoram	0.3–0.4
Origano	1.1
Rosemary	0.72
Sage	0.7–2.0

[a] For leaf spices, the values refer to the weight of the fresh material.

Some aromatic hydrocarbons are probably generated in spices by terpene oxidation. Examples are: 1-methyl-4-isopropenylbenzene (XI, Formula 22.3) derived from p-men-tha-1,3,8-triene (X) and (+)-ar-curcumene (XIV) from zingiberene (XII) or β-sesquiphel-landrene (XIII) [cf. Formula 22.4].

The formation of (+)-ar-curcumene from the above-mentioned precursor was detected during storage of ginger oil.

Another aromatic hydrocarbon present in significant amounts in essential oils of some spices (Table 22.3) is *p*-cymene (XV, Formula 22.3).



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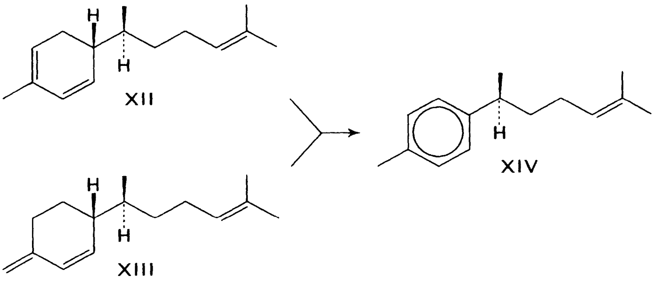


(22.4)

Table 22.3. Volatile compounds of spices[a]

Spice[b]	Components[c]
Pepper (1)	1–16% α-Pinene (XXIX*), 0.2–19% sabinene (XXV*), 9–30% β-caryophyllene (XLIX*), 0–20% Δ^3-carene (XXXII*), 16–24% limonene (IX*), 5–14% β-pinene (XXX*)
Vanilla (2)	Vanillin (1.3–3.8%, dry matter), (R)(+)-trans-α-ionone, *p*-hydroxybenzylmethylether (XVII)
Allspice (3)	50–80% Eugenol (I), 4–7% β-caryophyllene (XLIX*), 3–28% methyleugenol, 1,8-cineole (XXIII*), α-phellandrene (XI*)
Bay leaf (5)	50–70%, 1,8-Cineole (XXIII*), α-pinene (XXIX*), β-pinene (XXX*), α-phellandrene (XI*), linalool (IV*)
Juniper berries (6)	36% α-Pinene (XXIX*), 13% myrcene (I*), β-pinene (XXX*), Δ^3-carene (XXXII*)
Aniseed (7)	80–95% (E)-anethole (V)
Caraway (8)	55% (S)(+)-Carvone (XXI*), 44% limonene (IX*)
Coriander (9)	(S)(+)- and (R)(-)-Linalool (IV*), linalyl acetate, citral[d], 2-alkenales $C_{10}-C_{14}$
Dill (fruit, 10)	20–40% (S)(+)-Carvone (XXI*), 30–50% (R)(+)-limonene (IX*)
Dill (herb, 10)	70% (S)(+)-Phellandrene (XI*), 17% (3R,4S,8S)(+)-epoxy-p-menth-l-ene (XVIII), myristicin (VII), (R)-limonene (IX)
Fenugreek (11)	Linalool, 3-isobutyl-2-methoxypyrazine, 2-methoxy-3-isopropylpyrazine, 3-hydroxy-4,5-dimethyl-2(5H)-furanone (HD2F)
Nutmeg (13)	27% α-Pinene (XXIX*), 21% β-pinene (XXX*), 15% sabinene (XXV*), 9% limonene (IX*), 0.1–3.3% safrole (VI), 0.5–14% myristicin (VII), 1.5–4.2% 1,8-cineole (XXII*)2
Cardamom (14)	20–40%, 1,8-Cineole (XXIII*), 28–34% α-terpinyl acetate, 2–14% limonene (IX*), 3–5% sabinene (XXV*)
Clove (15)	73–85% Eugenol (I), 7−12% β-caryophyllene (XLIX*), 1.5–11% eugenol acetate
Saffron (16)	47% Safranal (XIV), 14% 2,6,6-trimethyl-4-hydroxy-l-cyclohexen-l-formaldehyde (XXIII)
Ginger (18)	30% (−)-Zingiberene (XLII*), 10–15% β-bisabolene (XLI*), 15–20% (−)-sesquiphellandrene (XLIII*), (+)-*ar*-curcumene (XIV), citral[c], citronellyl acetate
Tumeric (19)	30% Turmerone (XVI$_a$), 25% *ar*-turmerone (XVIb), 25% zingiberene (XLII*)
Cinnamon (20)	50–80% Cinnamaldehyde (VIII), 10% eugenol (I), 0–11% safrole (VI), 10–15% linalool (IV*), camphor (XXXIII*)
Parsley (23)	*p*-Mentha-1,3,8-triene (X), myristicin (VII), 2-sec-butyl-3-methoxypyrazine, 2-isopropyl-3-methoxypyrazine, (Z)-6-decenal, (E,E)-2,4-decadienal, myrcene (I*)
Marjoram (26)	3–18% cis-Sabinenehydrate (XXVII*), 1–7% trans-sabinenehydrate, 16–36% 1-terpinen-4-ol
Origano (27)	60% Carvacrol (II), thymol (III)
Rosemary (28)	1,8-Cineole (XXIII*), camphor (XXXIII*), β-pinene (XXX*), camphene (XXXI*)
Sage (29)	1,8-Cineole (XXIII*), camphor (XXXIII*), thujone (XXVI*)
Thyme (31)	Thymol (III), p-cymene (XV), carvacrol (II), linalool (IV*)

[a] With the exception of vanillin and dill (herb), the quantitative values refer to the composition of the essential oil.

[b] The number in brackets refers to Table 22.1.

[c] Roman numerals with an asterisk refer to the chemical structures of the terpenes presented in Table 5.33. Roman numerals without an asterisk refer to chemical structures shown in Chapter 22.

[d] A mixture of neral and geranial (cf. footnote "b" in Table 5.33).

The concentrations given in Table 22.3 are guide values which can vary greatly depending on the variety and cultivation conditions.

22.1.1.2 Aroma Substances

In some spice plants, the odor corresponds with that of the main components of the volatile fraction. These include aniseed with (E)-anethole, caraway with (S)-carvone, clove with eugenol and cinnamon with cinnamalde-hyde (cf. Table 22.3). In the case of the following spice plants, further details about the important aroma substances are known.

22.1.1.2.1 Pepper

Black and white pepper are available commercially. Black pepper is harvested before it is fully ripe and then dried. After removal of the flesh, the seed of the ripe fruit gives white pepper, which has a milder aroma.

In the concentration range of 1 to 2 mg/kg (−)-rotundone (cf. 5.3.2.4) is the key odorant of black and white pepper. Further important odorants of black pepper are given in Table 22.4. White pepper contains the same typical aroma substances, but usually in lower concentrations.

The aroma of ground pepper is not stable due to losses of important aroma substances, the extent of which is shown in Fig. 22.1.

Table 22.4. Odorants in black pepper[a]

No.	Compound	Odor threshold (mg/kg)[b]	Concentration (mg/kg)
1	Methylpropanal	0.056	1.03
2	2-Methylbutanal	0.053	1.99
3	3-Methylbutanal	0.032	4.18
4a	(−)-α-Pinene	3.4	2070
4b	(+)-α-Pinene	2.1	486
5a	(−)-Sabinene	50	4470
5b	(+)-Sabinene	6.3	285
6a	(−)-β-Pinene	2.9	3950
6b	(+)-β-Pinene	2.1	298
7	Myrcene	1.9	870
8a	(R)-α-Phellandrene	1.4	227
8b	(S)-α-Phellandrene	1.1	1390
9a	(S)-Limonene	2.8	4000
9b	(R)-Limonene	1.8	3280
10	1,8-Cineol	0.084	22.4
11	(±)-Linalool	0.069	231
12	Butyric acid	0.10	1.28
13	2-/3-Methylbutyric acid		4.27

[a] Origin: India.

[b] Odor threshold on starch.

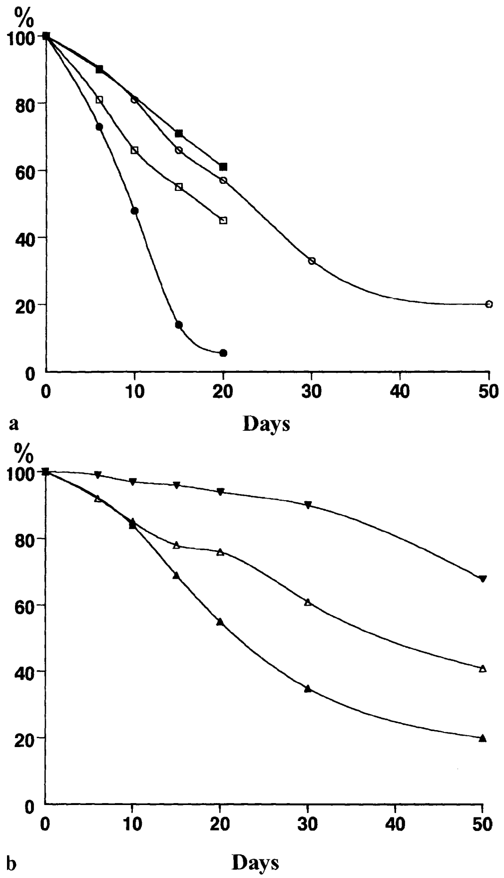


Fig. 22.1. Storage of ground black pepper at room temperature – changes in the concentrations of odorants. (a) (●–●) 3-methylbutanal, (○–○) α-pinene, (■–■) myrcene, (□–□) α-phellandrene (b) (▲–▲) limonene, (△–△) 1,8-cineol, (▼–▼) linalool

Musty/mouldy aroma defects in black pepper are caused by a mixture of 2,3-diethyl-5-methylpyrazine and 3-isopropyl-2-methoxy-pyrazine. Some samples of white pepper contain up to 2.5 mg/kg of skatole (odor threshold on starch: 0.23 μg/kg), which together with 3- and 4-methylphenol can cause a fecal aroma defect. This aroma defect arises during fermentation (degradation of amino acids, e. g., tryptophan → 3-methylindole), which is carried out to remove the flesh. On longer storage, this defect becomes more noticeable because intensive aroma substances, which disguise it in fresh white pepper, volatilize.

22.1.1.2.2 Vanilla

In the capsular fruit of vanilla, incorrectly called vanilla bean, 170 volatile compounds have been identified. However, the only fact that is certain is that apart from the main aroma substance vanillin, which is released from the glucoside on fermentation of the fruits, and (R)(+)-trans-α-ionone, the p-hydroxybenzyl-methylether (XVII) contributes to the aroma since its concentration (115–187 mg/kg) greatly exceeds the odor threshold (0.1 mg/kg, water). A mixture of 99% of sugar and 1% of ground vanilla is sold as vanilla sugar and a mixture of 98% of sugar and 2% of vanillin is sold as vanillin sugar.

22.1.1.2.3 Dill

AEDA and sensory investigations show that (S)-α-phellandrene in combination with (3S,3aS, 7aR)-3,6-dimethyl-2,3,3a,4,5,7a-hexahy-drobenzo[b]furan (XVIII, dill ether, cf. Formula 22.5) produce the aroma of dill. Both compounds are not stable and are largely lost on drying (Table 22.5).

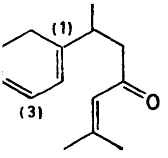
The most important aroma substance in dill fruit is (S)-carvone, which smells of caraway. In fact, dill seeds were used as a substitute for caraway in the past.

22.1.1.2.4 Fenugreek

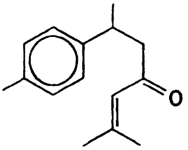
The most important odorants of seasoning (cf. 12.7.3.5) is 3-hydroxy-4,5-dimethyl-2(5H)-furanone (HD2F, XXI in Formula 22.6), 95% of which is present in the S form. This compound is also the outstanding odorant of fenugreek. Correspondingly, the seeds or the seed extract serves as the starting material for the production of seasoning. Other odorants are 3-amino-4,5-dimethyl-3,4-dihydro-2(5H)-furanone (XX in Formula 22.6), 1-octen-3-one, linalool and eugenol.

The concentration of HD2F varies in fenugreek between 3 and 12 mg/kg. However, this aroma substance is absent in *Trigonella* varieties.

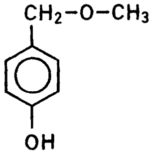
If an extract of fenugreek is heated (100 °C, 60 min) at pH 2.4, there is a ca. 10 fold increase in the HD2F concentration. Under these conditions, the precursor (2S,3R,4S)-4-hydroxy-



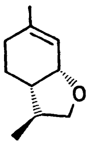
XVIa



XVIb

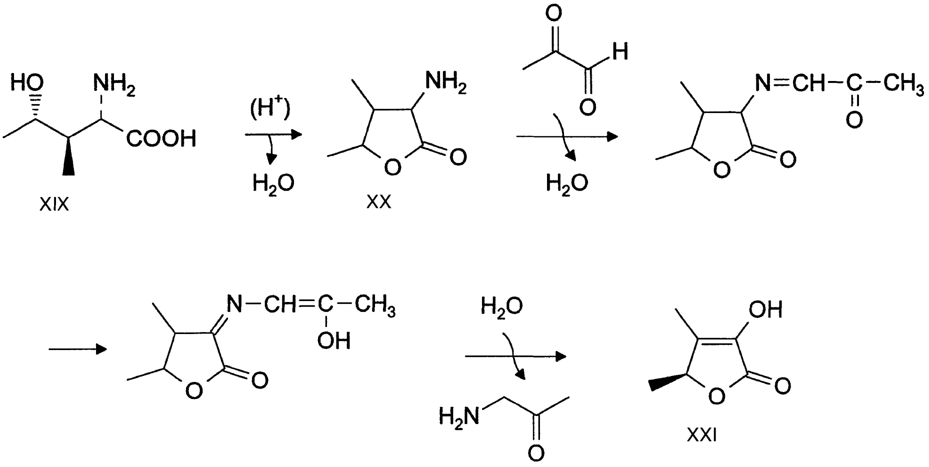


XVII



XVIII

(22.5)



(22.6)

Table 22.5. Changes in aroma substances in the drying of dill (leaves)

		Dried (air)		Freeze dried	
	Fresh	25 °C/4 h	50 °C/4 h	−25 °C/59 h	−25 °C/65 h
Water (w/w %)	90	11	12	16	2
Volatile compounds[a]	326	49	37	188	83
			Volatile compounds[a]		
α-Pinene	5.8	1.2	1.4	3.1	0.6
α-Phellandrene[b]	198.1	13.3	8.1	41.6	14.9
Limonene	10.0	0.7	0.4	2.0	0.7
β-Phellandrene	27.5	2.2	1.1	6.5	1.8
p-Cymene	5.5	1.1	0.4	4.0	0.1
3,9-Epoxy-p-ment-1-ene[b]	39.8	0.5	Traces	8.9	1.4
Myristicin	4.4	0.6	0.3	4.3	1.5
Neophytadiene	1.0	6.3	2.6	38.2	26.0

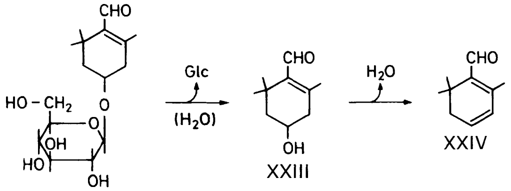
[a] Values in mg per 100 g of dry weight.

[b] Aroma substances that determine quality.

L-isoleucine (XIX in Formula 22.6) is cyclized to the amine XX, which is then converted to HD2F via the *Strecker* reaction, e. g., with methylglyoxal.

22.1.1.2.5 Saffron

In aroma extract dilution analyses (cf. 5.2.2), a compound with a saffron and hay-like odor, which could be 2-hydroxy-4,4,6-tri-methyl-2,5-cyclohexadien-l-one, gave the highest FD factor. This was followed by the terpene aldehyde safranal and an unknown compound, both of which have a saffron odor. Safranal (XXIV) is probably obtained from the bitter substance picrocrocin (XXII) by hydrolysis and elimination of water (Formula 22.6).



XXII (22.6)

22.1.1.2.6 Mustard, Horseradish

Mustard and horseradish contain glucosinolates (Table 22.6) which, after cell rupture, are exposed to the action of a *thioglucosidase* enzyme (cf. 17.1.2.6.5), yielding isothiocyanates (mustard oil). Allyl isothiocyanate is obtained from the glucoside sinigrin, a compound responsible for the pungent burning odor and taste of both spices. *p*-Hydroxybenzyl isothiocyanate obtained from sinalbin is only slightly volatile and contributes significantly to the sharp pungent taste of mustard.

The aroma of horseradish is also influenced by methyl, ethyl, isopropyl and 4-pentenyl iso-thiocyanates which, however, are present only in very small amounts in comparison to allyl isothiocyanate.

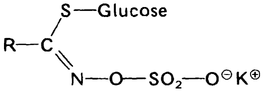
22.1.1.2.7 Ginger

The fresh ginger root has a citrus and camphor-like, flowery, musty, fatty and green odor. In a column chromatographic preliminary separation of an extract, the characteristic aroma substances appeared in the fraction of the oxidized hydrocarbons. The highest FD factors in dilution analyses were obtained for geraniol, linalool, geranial, citronellyl acetate, borneol, 1,8-cineol and neral.

22.1.1.2.8 Basil

The aroma profile of basil is characterized by green/fresh, flowery, clover- and pepper-

Table 22.6. The most important glucosinolates of mustard and horseradish



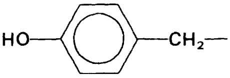
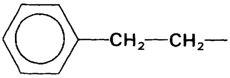
R	Name	Occurrence
	Sinalbin	Mustard
$H_2C{=}CH{-}CH_2{-}$	Sinigrin	Mustard, horseradish
	Gluconasturtiin	Horseradish

Table 22.7. Concentrations of odorants in fresh and dried basil

Compound	Concentration[a]		
	Fresh	Freeze-dried	Dried at 60 °C
(Z)-3-Hexenal	124	0.5	<0.01
1,8-Cineol	640	112	610
4-Mercapto-4-methylpentan-2-one	0.10	0.006	<0.01
Linalool	602	33	1210
4-Allyl-1,2-dimethoxybenzene	4950	1600	9540
Eugenol	890	214	391
3a,4,5,7a-Tetrahydro-3,6-dimethyl-benzofuran-2(3)-one (Winelactone)[b]	0.034	0.015	n.a.
Methylcinnamate	25	n.a.	n.a.
Estragol	12	n.a.	n.a.
α-Pineol	18	14.2	11.9
Decanal	0.39	n.a.	n.a.

[a] In mg/kg solids.
[b] cf. 5.2.5.
n.a: not analyzed.

like/spicy notes. The compounds given in Table 22.7 produce the aroma, which has been reproduced by a successful simulation. Omission experiments (cf. 5.2.7) show that eugenol, (Z)-3-hexenal, α-pinene, 4-mercapto-4-methylpentan-2-one, linalool and 1,8-cineol make the largest contributions to the aroma.

Drying damages the aroma considerably. (Z)-Hexenal and 4-mercapto-4-methylpentan-2-one are still detectable in freeze-dried basil (Table 22.7) and the green/fresh note is still perceptible. This note is absent in an air-dried sample, and the increase in linalool (Table 22.7), possibly through the enzymatic hydrolysis of the corresponding glycosides, causes the flowery note to become undesirably evident. The intensity of the pepper-like/spicy note also greatly decreases on drying.

22.1.1.2.9 Parsley

The most important odorants of parsley leaves are listed in Table 22.8. Sensory evaluations have shown that p-mentha-1,3,8-triene (X in Formula 22.3) and myrcene contribute to the characteristic aroma. (Z)-6-Decenal and (Z)-3-hexenal are responsible for the green notes. Myristicin, 2-*sec*-butyl-3-methoxypyrazine, (E,E)-2,4-decadienal, methanethiol and β-phellandrene also

Table 22.8. Concentrations of potent odorants in fresh and dried parsley[a]

Compound	Concentration[b]		
	Fresh		Dried[c]
	Cultivar I[d]	Cultivar II[d]	Cultivar II[e]
Methanthiol	1.2	0.972	0.067
Myrcene	83.6	133.8	135
2-Methoxy-3-isopropylpyrazine	0.007	0.01	n.a.
2-*sec*-Butyl-3-methoxypyrazine	0.036	0.056	0.085
Myristicin	269	991	2770
1-Octen-3-one	0.014	0.047	0.010
p-Mentha-1,3,8-triene	1829	313	1026
(Z)-3-Hexenal	0.93	1.378	0.139
(Z)-3-Hexenylacetate	0.763	0.328	n.a.
(Z)-1,5-Octadien-3-one	0.005	0.005	<0.001
(E,E)-2,4-Decadienal	4.9	4.7	0.27
(Z)-6-Decenal	27.4	16.5	2.75
Linalool	3.2	1.6	0.42
β-Phellandrene	949	1026	200
2-Methylbutanal	n.a.	n.a.	2.0
3-Methylbutanal	n.a.	n.a.	1.3
Methylpropanal	n.a.	n.a.	2.5
Dimethylsulfide	n.a.	n.a.	22.5
Methional	n.a.	n.a.	0.065
Acetaldehyde	n.a.	n.a.	8.0
Propanal	n.a.	n.a.	19.0
3-Methyl-2,4-nonandione	n.a.	n.a.	0.029

[a] Only those aroma substances which showed high FD factors in dilution analyses were quantified.
[b] In mg/kg based on solids.
[c] Dried at 70 °C (80 to 120 min), then stored for 3 months at −20 °C in nitrogen.
[d] Cultivar I: Hamburger cut, cultivar II: "Mooskrause".
[e] The fresh and dried cultivar II are of different origin.

exhibit high aroma values. The two cultivars of parsley compared in Table 22.8 differ considerably in the concentrations of some aroma substances, e. g., cultivar I contains 6 times more p-mentha-1,3,8-triene.

Drying of parsley on exposure to air leads to a large decrease in (Z)-3-hexenal and (Z)-6-decenal (Table 22.8), resulting in a reduction of the green note. In addition, sulfurous/cabbage-like and hay-like aroma defects appear due to the formation of dimethylsulfide and 3-methyl-2,4-nonandione. If drying proceeds at a higher temperature, methylpropanal, 2- and 3-methylbutanal, which do not play a role in the aroma of fresh parsley, also increase to such an extent that their malty aroma quality can assert itself in the aroma profile.

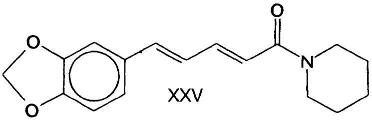
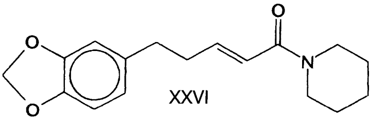
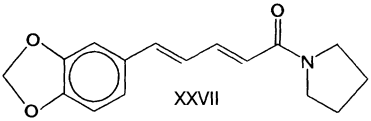
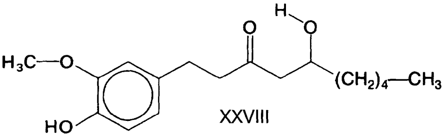
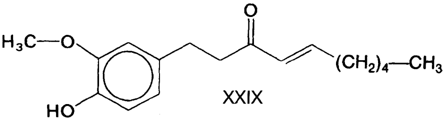
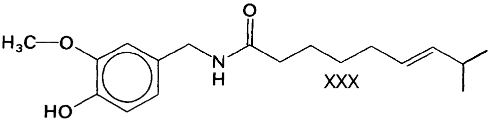
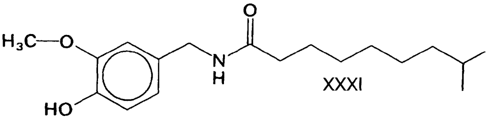
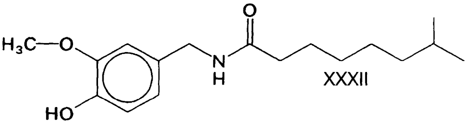
22.1.1.3 Substances with Pungent Taste

The hot, burning pungent taste of paprika (red pepper), pepper (black pepper) and ginger is caused by the nonvolatile compounds listed in Table 22.9.

Black pepper contains 3–8% of piperine (XXV) as the most important pungent substance. Pepper is sensitive to light since the trans,trans-diene system of piperine isomerizes to the cis,trans-diene system of the almost tasteless isochavicin on exposure to light.

In the processing and storage of ginger, gingerol easily dehydrates to shogaol, increasing the pungency (Table 22.9). A retroaldol cleavage of shogaol can also occur with the formation of sweet-spicy zingerone and hexanal (Formula 22.7). Above a certain concentra-

Table 22.9. Compounds present in spices causing a hot burning organoleptic perception

Name	Structure	Occurrence[a]	Relative pungency[b]
Piperine[c]	 XXV	Pepper (1)	1.0
Piperanine	 XXVI	Pepper (1)	0.5
Piperylin	 XXVII	Pepper (1)	0–1[d]
Gingerol	 XXVIII	Ginger (17)	0.8
Shogaol	 XXIX	Ginger (17)	1.6
Capsaicin	 XXX	Capsicum (4; 7)	150–300[d]
Dihydro-capsain	 XXXI	Capsicum (4; 7)	like Capsaicin
Nordihydro-caicin	 XXXII	Capsicum (4; 7)	75% Capsaicin

[a] The numerals in brackets refer to Table 22.1.

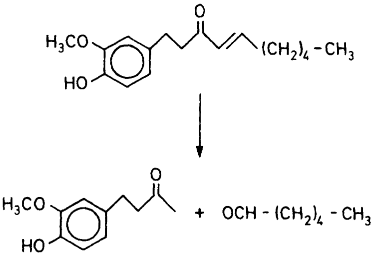
[b] Reference: pungency of piperine = 1.

[c] The corresponding *cis,trans*-compound is devoid of pungent taste.

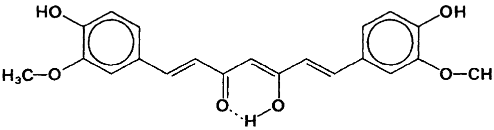
[d] Literature data are within the range of values presented.

tion, hexanal causes an aroma defect in ginger oleoresins.

The concentration of the capsaicinoids XXX, XXXI, and XXXII (Table 22.9) in the fruits of capsicum or in various other pepper plants depends on the variety, cultivation, drying and storage conditions, and varies between 0.01 and 1.2%. These compounds are the most pungent spice constituents. Their concentrations are at the upper limit in chillies and tobasco varieties and at the lower limit in sweet varieties.



(22.7)



(22.8)

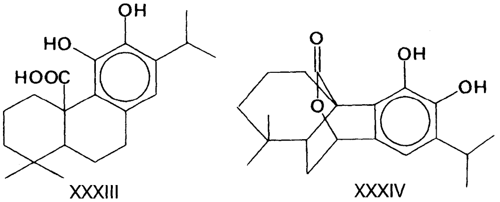
Investigations of the structure/effect relationship show that the intensity of the pungency does not change when 8-methyl-*trans*-6-nonenoic acid in capsaicin is replaced by nonanoic acid (9:0). However, it decreases when shorter, e. g., 8:0 (75%), 7:0 (25%), 6:0 (5%), or longer fatty acids, e. g., 10:0 (50%), 11:0 (25%), are introduced.

22.1.1.4 Pigments

Paprika (red pepper) and curcuma pigments are used as food colorants. Paprika pigments are carotenoids, with capsanthin as the main compound (cf. 3.8.4.1.2 and Fig. 3.47). Curcumin (cf. Formula 22.8) is the main pigment of curcuma, a tropical plant of the ginger family.

22.1.1.5 Antioxidants

Extracts of several spices, particularly of sage and rosemary, have the ability to prevent the autoxidation of unsaturated triacylglycerols. Among the most effective antioxidant constituents of both spices, the cyclic diterpene diphenols, carnosolic acid (XXXIII in formula 22.9) and carnosol (XXXIV) have been identified.



XXXIII XXXIV

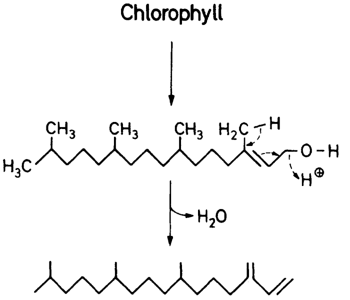
(22.9)

The high antioxidative activity of the two compounds is probably based on the fact that they are o-diphenols (cf. 3.7.3.2.1).

22.1.2 Products

22.1.2.1 Spice Powders

Spices are marketed unground or as coarsely or finely ground powders. The flavor is improved when the spices are ground using a cryogenic mill. After grinding the shelf life of the spices is limited. Favorable storage conditions are the absence of air, a relative humidity less than 60% and a temperature less than 20 °C. Crushed spices rapidly lose their aroma and absorb aromas from other sources. Leaf and herb spices are dried before they are crushed. The loss of aroma substances depends on the spice and on the drying conditions (for examples, see 22.1.1.2.3, 22.1.1.2.8 and 22.1.1.2.9). In comparison with air-drying at a raised temperature, there are no changes in aroma caused by the *Maillard* reaction in freeze-drying. However, gentle drying leads to increased hydrolysis of chlorophylls and to dehydration of the phytol released to phytadienes, e. g., to neophytadiene (7,11,15-trimethyl-3-methylene-1-hexadecene):



(22.10)

Contamination of spice powders with microorganisms is often very high, hence the addition of ground spices to food preparations may accelerate microbial food spoilage.

22.1.2.2 Spice Extracts or Concentrates (Oleoresins)

Spice extracts are being used in increasing amounts in industrial-scale food preparation since they are easier to handle than spice powders and are free of microorganisms. The production of these extracts is outlined in 5.5.1.2. The flavor quality depends on the solvent used and also on the raw material.

22.1.2.3 Blended Spices

Specially blended spices are offered commercially for some food preparations, such as liver sausage which uses a spice blend consisting of sweet marjoram, mace, nutmeg, cardamom, ginger, pepper and a little cinnamon.

Smoked, saveloy sausage spice blend consists of coriander, ginger, mustard kernels, paprika and pepper. Common spices for bread are aniseed, fennel and caraway. Gingerbread spice blend consists of aniseed, clove, coriander, cardamom, allspice and cinnamon.

22.1.2.4 Spice Preparations

Spice preparations are obtained by the addition of spices and blended spices to other substances, such as salt, sugar, glutamate, yeast extract and starch flour.

22.1.2.4.1 Curry Powder

A spice preparation containing a spice blend of turmeric as the main ingredient and paprika, chili, ginger, coriander, cardamom, clove, allspice and cinnamon, mixed together with up to 10% legume meal, starch and glucose, and with less than 5% salt.

22.1.2.4.2 Mustard Paste

A dark yellow paste used as a pungent seasoning for food. It is made from finely ground, often defatted mustard seeds, mixed into a slurry with water, vinegar, salt, oil and some other spices (pepper, clove, coriander, curcuma, ginger, paprika, etc.) and ground repeatedly or refined. During processing, lasting 1–4 h at a temperature not exceeding 60 °C, the mustard oil is released from its glucoside, as outlined in 22.1.1.2.6. "Extra strong" mustard is primarily made from dehulled black mustard seed, while the "medium hot" or "hot" types are made from seeds with hull, using varying proportions of black and white mustards.

22.1.2.4.3 Sambal

A spice preparation from Asia used for seasoning rice dishes. Its base is Sambal oelek, which consists mainly of crushed or pulverized saltpreserved chili.

22.2 Salt (Cooking Salt)

Common salt occupies a special position among the spices. Salt is used in greater amounts than all other spices to enhance the flavor and taste of food. Also, some foods are preserved when salted with large amounts of NaCl (cf. 0.3.1).

Humans require a certain constant level of intake of sodium and chloride ions to maintain their vital concentrations in plasma and extracellular fluids. The daily requirement is about 5 g of NaCl; an excessive intake is detrimental to health.

The salty taste is stimulated by ions. In comparison with the sour taste (cf. 8.10), the cation and the anion are significantly involved. The pure salt taste is only produced by NaCl. In fact, the very next chemical relative, KCl, has a sour/bitter aftertaste.

22.2.1 Composition

Common (cooking or kitchen) salt is nearly entirely NaCl. Impurities are moisture (up to 3%)

and other salts, not exceeding 2.5% (magnesium and calcium chloride; magnesium, calcium and sodium sulfates). Salt also contains trace elements.

22.2.2 Occurrence

Salt is abundant in sea water (2.7–3.7%) and in various landlocked seas (7.9% in the Dead Sea; 15.1% in the Great Salt Lake in Utah) and also in salt springs (Lueneburg, Reichenhall) and, above all, in salt beds formed in various geological periods, e. g., the European Zechstein salt deposits.

22.2.3 Production

In Germany salt is mainly mined as rock salt. It is selected, crushed and finely ground. Salt springs are also an important source. Saturated brine is recovered by tapping underground brine springs or by dissolving the salt out of beds with freshwater. For purification, magnesium is first eliminated as the hydroxide with lime milk and then calcium is removed as calcium carbonate with soda. Gypsiferous brine is treated with sodium sulfate containing mother liquor from the evaporation process. Evaporative crystallization occurs in multistage systems at 50–150 °C. The salt is centrifuged and dried. Salt obtained in such a manner is called "boiling" salt.

In warm countries sea water is concentrated in shallow flat basins by the sun, heat and wind until it crystallizes ("solar salt").

The addition of 0.25–2.0% calcium or magnesium carbonate, calcium silicate, or silicic acid improves the flowability. Indeed, 20 ppm of potassium ferrocyanide prevents the formation of lumps in the salt. The latter compound modifies the crystallization process of NaCl during the evaporation of salt spring water. In the presence of potassium ferrocyanide, the salt builds dendrites, which have strongly reduced volume, density and inclination to agglomerate.

In 1975 the worldwide production of NaCl was 162.2×10^6 t and 240×10^6 t in 2006. In 1974 only 5% of the NaCl produced in FR Germany was used for consumption; the remainder, 95%, was used in industry or trade (raw materials, salt for regeneration of ion-exchange resins, etc.).

22.2.4 Special Salt

Iodized salt is produced as a preventive measure against goiter, a disease of the thyroid gland (cf. 17.1.2.9.3). It contains 5 mg/kg of sodium-, potassium- or calcium iodide.

Nitrite salts are used for pickling and dry curing of meat (cf. 12.6.2.4). They consist of common salt and sodium nitrite (0.4–0.5%), with or without additional potassium nitrate.

22.2.5 Salt Substitutes

Some human diseases make it necessary to avoid excessive intake of sodium ions, so attempts have been made to eliminate the use of added salt as a spice or flavoring, without attempting to achieve completely salt-free nutrition. This "low salt" nutrition is actually only related to reduced sodium levels, hence a "low sodium" diet is a more relevant designation.

The compounds listed in Table 22.10 are used as salt substitutes. Their blends are marketed as "diet salts". Peptide hydrochlorides with a salty taste are discussed in Section 1.3.3.

22.3 Vinegar

Vinegar was known in old Oriental civilizations and was used as a poor man's drink and later as a remedy in ancient Greece and Rome. Vinegar is the most important single flavoring used to

Table 22.10. Substitutes for common salt

Potassium, calcium and magnesium salts of adipic, succinic, glutamic, carbonic, lactic, hydrochloric, tartaric and citric acids;
Monopotassium phosphate, adipic and glutamic acids and potassium sulfate;
Choline salt of acetic, carbonic, lactic, hydrochloric, tartaric and citric acids;
Potassium salt of guanylic and inosinic acids

provide or enhance the sour, acidic taste of food (cf. 8.12.5).

22.3.1 Production

Vinegar is produced microbiologically from ethanol or by dilution of acetic acid.

$$CH_3CH_2OH + O_2 \longrightarrow CH_3COOH + H_2O + 494\,\text{kJ} \quad (22.11)$$

22.3.1.1 Microbiological Production

Acetobacter species are cultivated in aqueous ethanol solution or, to a lesser extent, in wine, fermented apple juice, malt mash or fermented whey. Ethanol, as shown in Fig. 22.2, is dehydrogenated stepwise to acetic acid; the resulting reduced form of the cosubstrate methoxatin ($PQQH_2$) is oxidized via the respiratory chain. Part of the energy formed by oxidation is released as heat which has to be removed by cooling during the processing of vinegar. If there is an insufficient supply of oxygen, the microorganisms disproportionate a proportion of the acetaldehyde, the intermediate compound (cf. Fig. 22.2) in this aerobic reaction pathway:

$$2CH_3CHO \longrightarrow CH_3COOH + CH_3CH_2OH \quad (22.12)$$

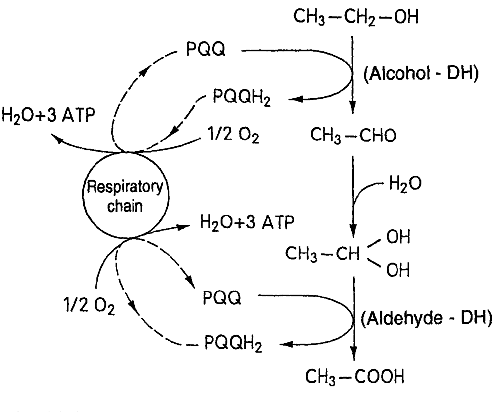


Fig. 22.2. Oxidation of ethanol to acetic acid by *Acetobacter* species (according to *Rehm*, 1980)

Fermentation of ethanol is conducted as a top fermentation and increasingly as a submerged oxidative process. In top fermentation the bacteria are cultivated on spongy, porous laminated carriers (usually beechwood shavings) with the alcoholic solution trickling down over carrier surfaces while a plentiful supply of air is provided from below. The fermentation is stopped at a 0.3% by volume residual ethanol level to avoid overoxidation, i. e., oxidation of acetic acid to CO_2 and water.

22.3.1.2 Chemical Synthesis

Acetic acid is usually synthesized by catalytic oxidation of acetaldehyde:

$$CH_3CHO + \tfrac{1}{2}O_2 \xrightarrow{\text{cat.}} CH_3COOH \quad (22.13)$$

Acetaldehyde is obtained by the catalytic hydration of acetylene or by the catalytic dehydrogenation of ethanol. Formic acid and formaldehyde are by-products of acetic acid synthesis. They are removed by distillation. Chemically pure acetic acid is diluted with water to 60–80% by volume to obtain the vinegar essence. The essence is a strongly corrosive liquid and is sold with special precautions. It is diluted further with water for production of food grade vinegar.

22.3.2 Composition

There are 5–15.5 g acetic acid in 100 g of vinegar. The blending (or adulteration) of fermented vinegar with synthetic acid can be detected by mass spectrometric determination of the $^{13}C/^{12}C$-isotope ratio (cf. 18.4.3); fermented vinegar has 5‰ more ^{13}C isotope than acetic acid synthesized petrochemically. In addition fermented vinegar can be distinguished from synthetic vinegar by analyzing the accompanying compounds. With this method fermented vinegars of different origin can also be distinguished from each other; e. g. spirit vinegar (fermented from aqueous ethanol) from wine, apple, malt and/or whey vinegar. The fermented vinegars contain metabolic by-products of *Acetobacter* strains, such as amino acids, 2,3-butylene glycol and acetyl methyl carbinol, in addition to substances derived from the raw materials used in vinegar production.

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