Volatile Character-Impact Sulfur Compounds and their Sensory Properties

By Mans H. Boelens, Boelens Aroma Chemical Information Service, The Netherlands and Leo J. van Gemert, TNO Biotechnology and Chemistry Institute, The Netherlands

Volatile organic sulfur compounds are important constituents for the flavor of food, beverages and natural isolates. Character-impact sulfur compounds have been found in foods (bread, potato and prepared meat), beverages (beer and coffee), vegetables (allium species, truffle and radish), fruits (grapefruit, pineapple, grape, tomato, melon, passionfruit and black currant) and natural isolates like essential oils, absolutes and oleoresins (rose, hop, galbanum, absinth, cassia, patchouli, pepper, helichrysum and geranium). These character-impact sulfur compounds are, often in a certain low concentration, characteristic for the sensory properties of the material. Although these facts are generally accepted in the flavor and fragrance industry, still some questions can be put forward, namely:

- What are the identities of these compounds?
- What are their sensory properties? That is, what is their odor and flavor character and in which concentration can they be perceived?

In this article we will try to answer these questions as much as possible mainly based on a survey of the available literature.

Occurrence of Volatile Sulfur Compounds in Food

Until 1991 up to 6,200 volatile compounds had been detected in foods and beverages.[1] As shown in Table I, 633 of these compounds, or about 10%, are sulfur compounds.

It may be expected that in the forthcoming years some hundreds of new sulfur compounds will be detected in foods and beverages. This expectation is based on the fact that a lot of sulfur compounds, which can be derived from the existing ones, have not yet been detected. For instance on the basis of the occurrence of 40 thiols one could expect 820 disulfides, where 820 = n(n + 1)/2 when n = 40. Up to

Table I. Volatile sulfur compounds detected in food as of 1991[1]

Thiols and sulfides		**172**
Thiols/mercaptans	40	
Monosulfides	53	
Disulfides	51	
Trisulfides	20	
Tetrasulfides	8	
Thiophenes		**78**
Normal thiophenes	62	
Dihydrothiophenes	9	
Tetrahydrothiophenes	7	
Thiazoles		**91**
Normal thiazoles	73	
Thiazolines	5	
Benzothiazoles	13	
Thianes		**52**
Dithianes	27	
Trithianes	7	
Tetrathianes	14	
Pentathianes	4	
Thiocyanates		**44**
Normal thiocyanates	8	
Isothiocyanates	36	
Thiolanes		**24**
Dithiolanes	7	
Trithiolanes	17	
Alkane-thio acid esters		**22**
Dithiines and dithiazines		**18**
Other bifunctional methylthio-derivatives		**42**
Miscellaneous		**90**
Total		**633**

0272-2666/93/0003-0029$04.00/0—© 1993 Allured Publishing Corp.

now only 51 have been found.

Of course not all the 40 thiols occur in one and the same food, beverage or natural isolate, in which all the possible disulfides could be formed. Nevertheless, a lot more disulfides will be proved to exist.

Another aspect regarding the number of natural sulfur compounds is the frequency of the occurrence of the methylthio group in heterocyclic molecules, such as pyrazines and thiazoles. For instance, from the 155 pyrazines detected in food[1] only one contains a methylthio substituent; it will be clear that several more should exist and will be found in the future. Most of the volatile sulfur compounds are essential constituents of the material. That means they are necessary for the sensory quality, but that they are not characteristic. A small number of the sulfur compounds, however, are characteristic compounds, which are recognized by experts as representing a great deal of the sensory quality of the material. These are the so-called character-impact compounds (Table II).

Table II. Character-impact sulfur compounds in foods and beverages (except Allium species)

Food/ beverage	Character-impact compound	*Threshold* value ng/l of water	Reference
Bread	2-[(methyldithio)methyl]furan	40*	3
	2-acetyl-2-thiazoline	1,300*	61
Meat	2-methyl-3-(methylthio)furan	50*	15
	bis-(2-methyl-3-furyl)disulfide	0.02*	62
Potato	3-(methylthio)propanal	200*	13
Coffee	furfurylmercaptan	5*	15
Beer	3-methyl-2-butene-1-thiol	0.2**	16
Tomato	2-isobutylthiazole	3,500*	22
Grapefruit	(+)-(R)-1-p-menthene-8-thiol	0.02**	24
	(–)-(S)-1-p-menthene-8-thiol	0.08**	24
Passionfruit	3-(methylthio)hexanol	unknown	
	2-methyl-4-propyl-1,3-oxathiane	unknown	
Grape	ethyl 3-thiol-propanoate	200,000**	27
Black currant	1-methoxy-3-methyl-3-butanethiol	30-60***	32
Buchu leaf	p-menthan-3-one-8-thiol	unknown	
Truffle	bis(methylthio)methane	<300**	63
Radish	(E)-4-(methylthio)-3-butenyl isothiocyanate	unknown	
Horseradish	4-pentenyl isothiocyanate	unknown	
Watercress	2-phenylethyl isothiocyanate	6,000**	64

* = odor; ** = flavor; *** = odor threshold in sunflower oil

Structure-Activity Relationships of Volatile Organic Sulfur Compounds

The structure-activity relationships of volatile organic sulfur compounds are rather complicated because the qualitative sensory properties of the compounds often are strongly dependent on their concentration.

This olfactive dependence on stimulant concentration may be caused by the so-called multiplicity of the compound. Multiplicity of a compound is its ability to trigger different receptor sites at various concentrations.

From an olfactive point of view the volatile organic sulfur compounds can reveal various qualities, depending on the accessibility of the sulfur-atom in the whole molecule.

High sulfur concentration: Sulfur compounds smelled at relatively high concentration, for instance in 0.1-1.0% solution in water, may show the following qualities:

- Sulfurous (alliaceous): lower alkylthiols, mono-, di- and tri-sulfides
- Olefinic (benzenoid): bifunctional monosulfides, substituted thiophenes
- Camphoraceous: bulky substituted sulfides, such as di-tert-butylsulfide.

It is generally known[2] that benzene has some odor resemblance with thiophene. This resemblance is even more pronounced with the odors of p-xylene and 2,5-dimethylthiophene.

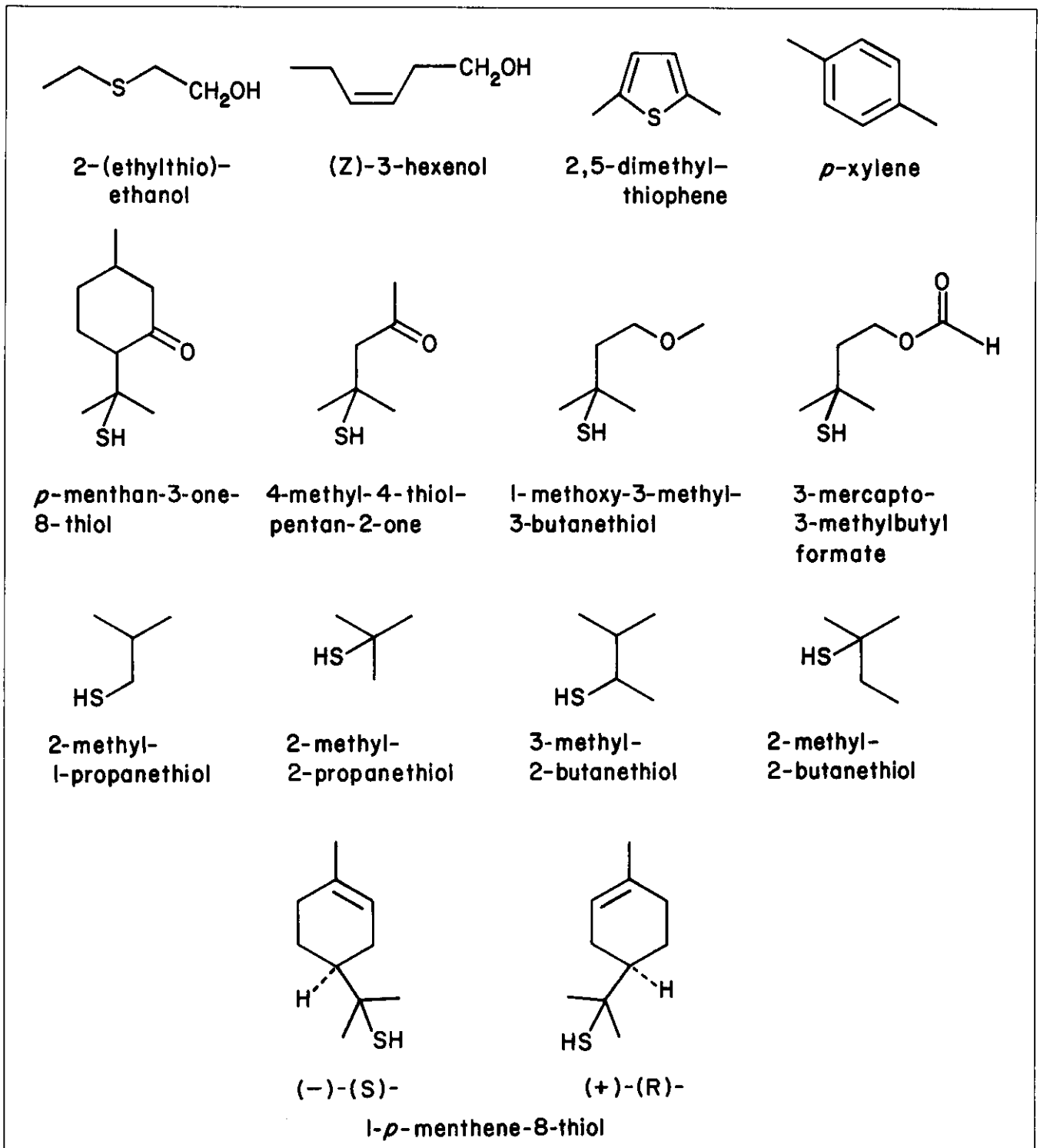
Probably the odor-character does not change a lot if one substitutes a sulfur atom for a cis carbon-carbon double bond. A nice example of this substitution is demonstrated by a cis-3-hexenyl derivative and replacement of its double bond by a sulfur atom.[2] See Scheme 1 for examples.

Low sulfur concentration: Another aspect of organic sulfur compounds is the influence of other functional group(s) in the molecule on the overall olfactive or sensory quality. This influence often is demonstrated at rather low concentration (<1 ppm). In this type of sulfur compound one often encounters a proton-releasing (-SH) group and at a certain distance a proton-attracting group (-C=O or -C-O-C-) more or less according to the Shallenberger principle for the sweetness of organic compounds.

Examples of this type of sulfur compound are: p-menthan-3-one-8-thiol (so-called buchu-thiol); 4-methyl-4-thiolpentan-2-one (so-called cassis-body); 1-methoxy-3-methyl-3-butanethiol (black currant compound); and 3-thiol-3-methylbutyl formate (coffee and beer). See Scheme 1.

All these compounds contain a tertiary thiol group. One can notice a significant difference between the threshold values of primary or secondary thiols on the one side and tertiary thiols on the other side. See Table III. The threshold values of tertiary thiols are a factor of 300-3000 lower than those of primary and secondary thiols. (In this article

Case No.: IPR2023-00207
U.S. Patent No. 11,224,241



Scheme 1. Structure-activity relationships of sulfur compounds

all threshold values are given in nanogram per liter or nanogram per kilogram, indicated as ng/l or ng/kg.)

Character-Impact Sulfur Compounds in Food

A list of character-impact sulfur compounds is shown in Table II. See Scheme 2 for examples.

Bread: 2-[(Methyldithio)methyl]furan or methyl furfuryl disulfide has been detected in bread crust by Mulders et al.[3] They proposed that the compound was responsible for the "golden brown" crust aroma of white bread. This observation was based on its aroma quality and its odor threshold value in water of 40 nanograms per liter (ng/l).

Motif Exhibit 1119, Page 3 of 11

Folkes and Gramshaw[4] mentioned that 2-acetyl-2-thiazoline could also contribute to the crust aroma of bread. The compound has an odor threshold value in water of 1,300 ng/l.[61]

Meat: Two excellent reviews on the compounds with meat flavor have been written by MacLeod[5] and Mottram.[6]

The odor properties of a number of furans with thiol and methylthiol substituents have been shown to have meaty characteristics. MacLeod and Ames[7] identified 2-methyl-3-(methylthio)furan as a character-impact compound generated during the cooking of beef. The compound has been reported to have an odor threshold of 50 ng/l and a meaty aroma at concentrations below 1,000 ng/l, becoming thiamin-like at higher levels.[15]

Two compounds that showed the highest aroma values and meaty aromas were identified as 2-methyl-3-furanthiol and its disulfide bis-(2-methyl-3-furyl) disulfide. The thiol also had a very low threshold value, estimated to be 2,500 times lower than that of its methylated derivative 2-methyl-3-(methylthio)-furan. The latter compound was also found in the beef flavor extract, but it had only a low aroma value, and the authors[7] considered that it was of relatively minor importance in the aroma of cooked beef compared with the methylfuranthiol and its disulfide.[9-11]

Baines and Mlotkiewicz[8] noticed that the 2-thio-substituted furans and thiopenes appear to have burnt or sulfurous characteristics, while compounds with thio-substituents in the 3- and 4-positions have more meat-like qualities.

Gasser and Grosch[9-11] confirmed the presence of 2-methyl-3-furanthiol and bis-(2-methyl-3-furyl) disulfide in cooked beef and chicken broth. They mentioned that both products had a meat-like quality and determined the odor threshold value in air of 2-methyl-3-furanthiol as 0.0025-0.001 ng/l, and of bis(2-methyl-3-furyl) disulfide as 0.0006-0.0028 ng/l.

Kubota et al.[12] identified pyrrolidino[1,2-e]-4H-2,4-dimethyl-1,3,5-dithiazine in prepared shellfish species, such as cooked shrimp, clam and corbicula. They mentioned that the compound could be formed during heating of the shellfish from 1-pyrroline, ethanol and hydrogen sulfide. The pyrrolidinodimethyldithiazine, which consists of two enantiomers, contributes a roasted odor to the taste of boiled corbicula, and has an odor threshold value of 0.00000001 ng/l in water. To the best of our knowledge this is by far the lowest threshold value ever found for a flavor component. This threshold value means that very low levels of impurities of this and, perhaps, related compounds can have a very large contributing effect on threshold values determined so far. To check on odor purity of compounds for which threshold values are to be determined is thus very important.

Potato: Buttery et al.[13] found that 3-(methylthio)propanal (methional) was a character-impact compound of boiled and baked potatoes. The odor threshold value in water of this compound was published as 200 ng/l.

Table III. Flavor threshold values of some primary, secondary and tertiary thiols, in nanograms per liter

Thiol	Flavor in	threshold value ng/l	Reference
1-Butanethiol (primary)	beer	700	19
2-Butanethiol (secondary)	beer	600	19
2-Methyl-1-propanethiol (primary)	beer	2,500	19
2-Methyl-2-propanethiol (tertiary)	beer	80	19
3-Methyl-2-butanethiol (secondary)	beer	200	19
2-Methyl-2-butanethiol (tertiary)	beer	0.07	19
(+)-(R)-1-p-Menthene-8-thiol (tertiary)	water	0.02	24
(–)-(S)-1-p-Menthene-8-thiol (tertiary)	water	0.08	24

Coffee: A thorough review of sulfur compounds in coffee has been made recently by Flament.[14]

Tressl and Silwar[15] estimated the odor threshold value in water of furfurylmercaptan at 5 ng/l, smelling like freshly roasted coffee at concentrations of 10-500 ng/l, but exhibiting the aroma of stale coffee with a sulfury note at values of 1,000 to 10,000 ng/l.

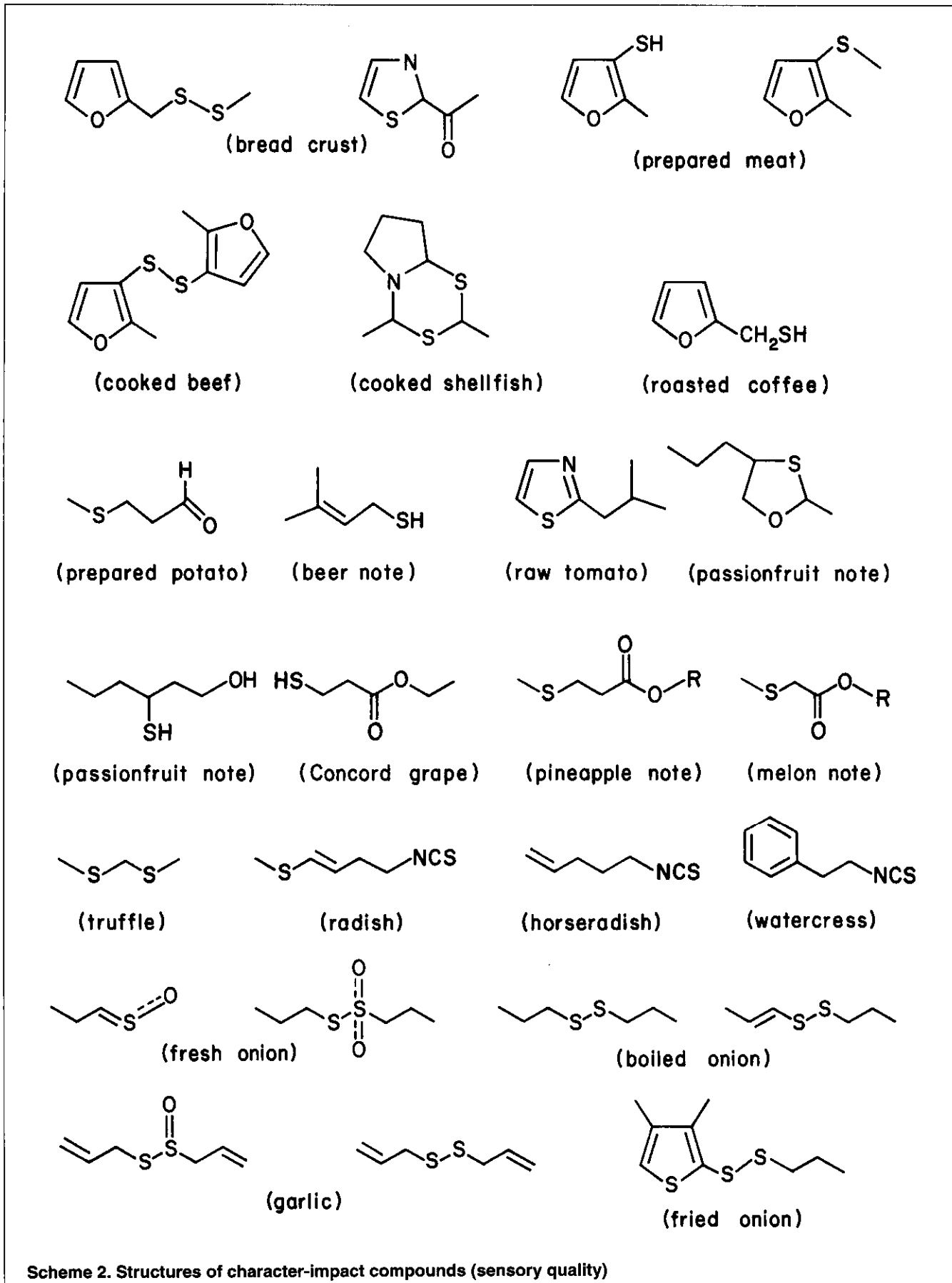
5-Methylfurfurylmercaptan has an odor threshold in water of 50 ng/l and delivers also a sulfury note above 5,000 ng/l. Both compounds are formed during roasting of coffee and increase 5 to 10 fold during storage.[15]

Very recently Holscher et al.[16] and Blank et al.[17] identified 3-methyl-2-butene-1-thiol (prenylmercaptan), 3-thiol-3-methylbutanol and its formate in roasted coffee. 3-Methyl-2-buten-1-ol (prenyl alcohol) was mentioned as a common precursor for the sulfur compounds.

3-Thiol-3-methylbutyl formate could be identified as an aroma-potent constituent of roasted coffee flavor with an odor threshold value in air of 0.0002-0.0004 ng/l[17] and with an odor threshold value in water of 2-5 ng/l.[16]

Beer: Angelino[18] recently wrote that sulfur compounds are flavor-active constituents in beers. Dimethyl sulfide has been mentioned as responsible for the sulfury note in beer. He also mentioned that one particular compound in beer has been traced back to its very origin and chemical pathway. It concerns the cause of so-called sunstruck or lightstruck flavor in beer due to exposure to ultraviolet light.[18] 3-Methyl-2-butene-1-thiol (prenyl mercaptan) is considered to be responsible for this "off-flavor." The composition of the sunstruck flavor substance and the mechanism of its evolution were studied by Kuroiwa and Hashimoto.[20] They published a flavor threshold value in beer of less than 3×10^4 ng/1; Holscher et al.,[16] however, found a flavor threshold in water of 0.2-0.3 ng/l.

Prenyl mercaptan has been mentioned as causing an off-flavor in beer, but a minimum concentration of about 100



Scheme 2. Structures of character-impact compounds (sensory quality)

ng/l in beer seems to be necessary for its characteristic flavor. More recently Schieberle[21] also detected 3-thiol-3-methylbutyl formate, with its catty and ribes-like odor, in pale lager beer (see also Hop oil).

Tomato: Buttery et al.[22] made a quantitative study of the fresh tomato aroma volatiles. One of the compounds considered to be most important for the raw tomato flavor is 2-isobutylthiazole with a threshold value in water of 3,500 ng/l.

McGlasson et al.[23] mentioned that dimethyl trisulfide was an important tomato aroma component.

Grapefruit: The two character-impact compounds proposed for the grapefruit flavor are nootkatone and 1-p-menthene-8-thiol.

Demole et al.[24] isolated 1-p-menthene-8-thiol and 2,8-epithio-cis-p-menthane from grapefruit juice. 1-p-Menthene-8-thiol consisted of two enantiomers, (+)-(R) and (–)-(S), which were separated. For the flavor detection threshold values in water, the authors found 0.02 ng/l for the (+)-(R) isomer and 0.08 ng/l for the (–)-(S) isomer. Qualitatively, there was no significant difference between the sensory properties of the racemic mixture and of the optically active (+)-(R), while the (–)-(S)-enantiomer appears to have a somewhat more fruity and natural aroma than its antipode; the mixture behaved just like a mixture of both forms.

Table IV. Olfactive qualities of enantiomers of p-menthan-3-one-8-thiol[34]

p-Menthan-3-one-8-thiol Stereoisomer	Odor Quality
1R,4R	onion-like, weak fruity, tropical, dirty
1S,4S	stronger than (1R,4R)-isomer, tropical, sulfurous, pronounced Buchu leaf oil note
1R,4S	rubber, mercaptan-note, isopulegone-note, burnt, sulfurous, disagreeable
1S,4R	black currant leaf, tropical note of passionfruit, intensive fruit note

Mosandl[25] more recently determined the sensory qualities of the two enantiomers of 1-p-menthene-8-thiol. He found for the (R)-(+)-isomer a pleasant, fresh grapefruit juice character and for the (S)-(–) an extremely obnoxious sulfur note.

Passionfruit: Winter and coworkers[26] identified two new sulfur compounds in passionfruit. They are 3-(methylthio)hexanol with a green, fatty sulfury note and 2-methyl-4-propyl-1,3-oxathiane with a green slightly burnt connotation. They are considered to be key flavor components in the yellow fruit.

Grape: In 1983 Kolor[27] identified an important new flavor compound in Concord grape: ethyl 3-thiol-propanoate. He mentioned that it is well recognized in the flavor industry that variations in the concentration of certain chemicals can have a dramatic effect on their flavor characteristics. Ethyl 3-thiol-propanoate, which has a flavor threshold in water of 2×10^5 ng/l, is a very good example of this phenomenon. At low concentration levels it has a very pleasant, fruity, grape character, while at higher concentrations its aroma takes a skunky or foxy, animal-like note.

Black currant: The catty note of black currant bud has always been of interest for the flavorist. This note can also be achieved with synthetic compounds, such as 4-methyl-4-thiol-2-pentanone or p-menthan-3-one-8-thiol, a constituent of buchu leaf oil.[28] In 1986 Rigaud et al.[29] and later Le Querre and Latrasse[30] identified and synthesized 1-methoxy-3-methyl-3-butane-thiol, a character-impact sulfur constituent from black currant.

From this compound in black currant bud extract, Joulain and Laurent[31] found several derivatives, for instance the dimer. More recently Guth and Grosch[32] detected 1-methoxy-3-methyl-3-butanethiol, with a black currant-like odor, in virgin olive oils. They mentioned that the compound had a threshold value in air of 0.00008-0.00030 ng/l.

Buchu leaf oil: Because buchu leaf oil is often used as an enhancer for black currant flavor, it seems worthwhile here to mention its character-impact compound, p-menthan-

Fleurchem, Inc.

Essential Oils, Flavors, Fragrances, Natural and Synthetic Chemicals

Natural Chemicals

Acetal
Acetaldehyde (100%, 50%, 10% in ethanol)
Acetaldehyde ex orange oil
Acetic acid
Acetone
Acetoin (Kosher)
Acetyl propionyl
Alcohol C-6 (see Green Fort. 1800)
Aldehyde C-5 (see Valeraldehyde)
Aldehyde C-6
Aldehyde C-7
Aldehyde C-8
Aldehyde C-10
Aldehyde C-14
Allyl caproate (see Pineapple 2500)
Allyl isothiocyanate (Mustard oil)
Almond, bitter
Amyl acetate
Amyl alcohol
Amyl butyrate
Amyl hexanoate
Anethole
Anisic aldehyde
Anisyl acetate
Anisyl alcohol
Apple cider vinegar (200 grains)
d-Arabinose
l-Arabinose
d-Arabitol
l-Arabitol

Benzaldehyde
Benzyl acetate
Benzyl butyrate
Benzyl propionate
Bitter almond oil (ex Apricot kernel oil)
n-Butyl acetate
n-Butyl alcohol
n-Butyl isovalerate
n-Butyl lactate
n-Butyraldehyde
Butyric acid

Capric acid (Kosher)
Caproic acid (Kosher)
Caprylic acid (Kosher)
4-Carvomenthenol
d-Carvone
Caryophyllene
Cinnamic acid
Cinnamic alcohol
Cinnamic aldehyde
Cinnamyl acetate
Cinnamyl cinnamate
Citral (Std, Extra, ex Lemongrass)
Citronellal
l-Citronellol
Citronellyl acetate
Citronellyl butyrate
Citronellyl propionate
Cocolactone
Cocotone 7500 (CO_2 extraction)
Cocotone 9700 (CO_2 extraction)
Cocotone 9800 (CO_2 extraction)

γ-Decalactone
γ-Undecalactone (Aldehyde C-14)
Decanal (50% and 90%)
Decanoic acid
Diacetyl
Dihydro cuminyl aldehyde
Dimethyl anthranilate
2,5-Dimethyl-3-(2H)-furanone (10% and 20%)
Dimethyl pyrazine
Dimethyl sulfide

Estragole
Ethyl acetate
Ethyl benzoate
Ethyl butyrate
Ethyl butyrate ex orange oil
Ethyl caprate
Ethyl caproate
Ethyl caprylate
Ethyl cinnamate
Ethyl decanoate
Ethyl heptanoate
Ethyl hexanoate
Ethyl isobutyrate
Ethyl isovalerate
Ethyl lactate
Ethyl laurate
Ethyl levulinate
Ethyl-2-methyl butyrate
Ethyl myristate
Ethyl octanoate
Ethyl oleate
Ethyl oxyhydrate (see Rum ether)
Ethyl palmitate
Ethyl propionate
Ethyl pyruvate
Eucalyptol
Eugenol (ex Bay, Ex Clove)

d-Fenchone
Fermentaberry
Furaniol (see Strawberry furanone)
Furfural

d-Galactose
Geraniol
Geraniol (ex Citronellal)
Geranyl acetate "C"
Geranyl acetate "D"
Geranyl butyrate
Geranyl caprate
Geranyl caproate
Geranyl caprylate
Geranyl isovalerate
Geranyl propionate
Grapefruit 001 "5X
Grapefruit 002 "5X

Heptanal
2-Heptanone (Methyl amyl ketone)
Heptyl acetate
t-2-Hexenal
t-2-Hexenyl acetate (see Green 5050)
Hexanol
Hexyl acetate
Hexyl butyrate
Hexyl-2-methyl butyrate
cis-3-Hexenol
cis-3-Hexenyl acetate
cis-3-Hexenyl butyrate
cis-3-Hexenyl caproate
cis-3-Hexenyl isovalerate
cis-3-Hexenyl lactate
cis-3-Hexenyl-2-methyl butyrate

Ionone α,β (60:40)
Ionone α 50% in alcohol
Ionone β 50% in alcohol
Isoamyl acetate
Isoamyl alcohol
Isoamyl butyrate
Isoamyl caprate
Isoamyl caproate
Isoamyl caprylate
Isoamyl cinnamate
Isoamyl isobutyrate
Isoamyl isovalerate
Isoamyl laurate
Isoamyl propionate
Isobutyraldehyde
Isobutyl acetate
Isobutyl alcohol
Isobutyl butyrate
Isobutyl caprate
Isobutyl caproate
Isobutyl caprylate
Isobutyl isovalerate
Isobutyl laurate
Isobutyl propionate
Isobutyric acid
Isopulegone
Isovaleraldehyde
Isovaleric acid

Ketonarome

Lactic acid
Lauric acid
Leaf alcohol
Lemon aldehyde
Lime aldehyde
d-Limonene
l-Linalool
Linalool (ex BDR, Ho)
Linalool ex Orange (regular and extra)
Linalyl acetate (ex BDR, petitgrain)

Maltol
Maltone
d-Mannose
Maple lactone
Massoia lactone
p-Mentha-1,8-dien-7-al
l-Menthol
l-Menthone
Menthyl acetate
Methanol
Methyl amyl ketone
Methyl anthranilate
Methyl benzoate
Methyl butanal
2-Methyl butyraldehyde
Methyl butyrate
2-Methyl butyric acid
Methyl cinnamate
Methyl cyclopentenelone
Methyl heptanoate
Methyl heptenone
Methyl heptyl ketone
Methyl isobutyrate
Methyl-n-methyl anthranilate
Methyl nonyl ketone
Methyl salicylate
Methyl sulfide
Morin dihydrate
Mustard oil (Allyl isothiocyanate)
Myristic acid

Naringen
Neral
Nerolidol
2-Nonanone (Methyl heptyl ketone)
Nootkatone

Ocimene
Octanal (50% and 90%)
3-Octanol
Octyl acetate
Octyl butyrate
Octyl isovalerate
Oleic acid
Orange aldehydes
Orange carbonyls

Palmitic acid
Perilla aldehyde
α-Phellandrene
α-Pinene
β-Pinene
d-Piperitone
Propionic acid
Propyl acetate
Propyl alcohol
Propyl butyrate
Propyl caprate
Propyl caproate
Propyl caprylate
Propyl laurate
Propyl propionate
Pulegone
Pyrazines
Pyruvic acid

l-Rhamnose
Rhodinol
d-Ribose
Rum ether

Sclareol
Sinensal
d-Sorbitol

Tannic acid
Tartaric acid
α-Terpineol
Terpinyl acetate
Tetramethyl pyrazine
Thymol, natural

Valencene
Vanilla absolute (CO_2 extraction)
Vanillin
d-Xylose

New Items Currently Being Worked On:

δ-Decalactone
2,6-Dimethoxyphenol (Syringol)
Ethyl formate
Ethyl pelargonate
Formic acid
Guaicol
γ-Heptalactone
Methyl acetate
Raspberry ketone

Kosher for Passover:

(will be available by the end of 1992)

Ethyl acetate
Ethyl butyrate
Ethyl formate
Ethyl propionate

Natural Fortifiers

Apple	#4900
Apple	7000
Apple	7400
Apricot	2600
Blueberry	1000
Blueberry	1700
Cherry	1000
Cherry	1400
Cherry	9600
Cocoa flavor	1000
Cranberry	8500
Fermented flavor	2000
Grape	4000
Green note	1295
Green note	1800
Green note	3100
Green note	5050
Green note	9000
Malt fortifier type	3000
Peach	2000
Peach	2100
Pineapple	2500
Pineapple	7100
Praline	4000
Raspberry	1100
Raspberry	1120
Raspberry	1600
Raspberry	1605
Raspberry	2600
Raspberry	2610
Raspberry	3600
Raspberry	3615
Strawberry	3000
Strawberry	3030
Strawberry	7000
Strawberry	7025
Strawberry	7600
Strawberry	7635
Tomato	1026
Tomato	1034

P.O. Box 283, Garnerville, NY 10923-0283 • Tel. #: (914) 786-3121 • Fax #: (914) 786-3139

3-one-8-thiol.[33] Köpke and Mosandl[34] very recently isolated the four enantiomers of p-menthan-3-one-8-thiol and determined their olfactive qualities (Table IV).

Pineapple: Takeoka and coworkers[35] identified methyl 3-(methylthio)-propanoate, ethyl 3-(methylthio)propanoate and 3-(methylthio)-propyl acetate in pineapples and they mentioned that the first two appear in such concentrations that their odor unit values are of significance. The odor threshold values in water were mentioned to be 180 x 10^3 and 7 x 10^3 ng/l for methyl- and ethyl 3-(methylthio) propanoate respectively.

Melon: Sulfur-containing compounds in the aroma volatiles of melons were recently studied by Wyllie and Leach.[36] They demonstrated the occurrence of six thioether esters: methyl and ethyl (methylthio)acetate; 2-(methylthio)ethyl acetate; methyl and ethyl 3-(methylthio) propanoate; and 3-(methylthio)propyl acetate. In addition, they determined the concentrations of these compounds in a number of cultivars, varying from 1 x 10^3 ng/l up to 1.5 x 10^6 ng/l, and mentioned that some have shown to have odor values which indicate that they contribute to the overall aroma perception of the ripe fruit.

Truffle: In an excellent review on vegetables, Whitfield and Last[37] mentioned that two sulfur compounds, dimethyl sulfide and bis(methylthio)methane, are considered to be the compounds principally responsible for the characteristic aroma of truffles. These truffle compounds were detected by Fiecchi et al.[38] and Talou et al.[39]

Table V. Character-impact sulfur compounds in Allium species

Allium Species	Character-impact Compounds
Onion	
raw, fresh	thiopropanal S-oxide propyl propanethiosulfonate
cooked	dipropyl disulfide 1-propenyl propyl disulfide
fried	2-(propyldithio)-3,4-dimethyl-thiophene
Garlic	2-propenyl 2-propenethiosulfinate di-2-propenyl disulfide (diallyl disulfide)
Leek	methyl/propyl di(tri)sulfides 3,4-dimethyl-2,5-dioxo-2,5-dihydro-thiophene ? (hydrogen sulfide release)

Publications by Whitfield et al.[40] indicated that the distinct garlic-like aroma possessed by bis(methylthio) methane, which has been detected in prawns in concentrations between 1,000 ng/kg and 4,000 ng/kg and in lobsters as high as 14,000 ng/kg, is regarded as an off-flavor in both seafoods.

Various vegetables: (Methylthio)alk(en)yl isothiocyanates are the major components in extracts from radish.[37] These isothiocyanates are mainly responsible for the typical radish flavor. Two in particular, (E)-4-(methylthio)-3-butenyl- and 4-(methylthio)butyl isothiocyanate, are present in relatively high concentrations and may be considered as character-impact constituents of radish.

Alkenyl and aryl isothiocyanates, such as 4-pentenyl- and 2-phenylethyl isothiocyanate, are major constituents from horseradish.[37] These compounds are regarded as responsible for the intensely pungent flavor of horseradish. 2-Phenylethyl isothiocyanate is considered to provide the characteristic "hot" or "burning" sensation of watercress, and 3-phenylpropanenitrile is believed to provide an important modifying effect.[37,41]

Allium Species

More than 50% of the volatile compounds isolated from the Allium species—onion, garlic, leek and chive—contain organic sulfur compounds. Thus it is not surprising that character-impact sulfur compounds have been found in the volatiles from these products (Table V).[42-47]

Recently Block et al.[65] found that after cutting or crushing, Allium plants release alliinase enzymes that convert sulfoxide precursors to intermediate sulfenic acids, which then condense to form odorous thiosulfinates. Thiosulfinates, which can be analyzed only at 0°C, contain allyl, methyl or 1-propenyl groups in garlic, elephant garlic, wild garlic, or

Chinese chive. They contain propyl, methyl, and 1-propenyl groups in onion, shallot, leek, chive and scallion.

Onion: Character-impact sulfur compounds have been proposed for raw (fresh), boiled and fried onion by Boelens.[43] In raw onion some important components are: thiopropanal-S-oxide; and alkyl alkanethiosulfonates with four or more carbon atoms, such as propyl methanethiosulfonate and propyl propanethiosulfonate. The last two compounds had odor threshold values in water of 1,700 ng/l and 1,500 ng/l, respectively.[43]

A number of compounds contribute the aroma of cooked onion. Dipropyl disulfide and cis- and trans-1-propenyl propyl disulfide have odor threshold values in water of 3,200 and 2,000 ng/l (mixture of isomers), respectively.

More than 20 years ago Boelens reported that dimethylthiophenes have a distinct fried onion aroma. These dimethylthiophenes were prepared by heating cis/trans propenyl propyl disulfide. This reaction was completely reproduced by Brandsma of the University of Utrecht,[48] with the same fried onion sensory quality of the end product. In the meantime it turned out that in spite of the fact that the obtained end product had a strong fried onion character, this character was not due to 2,4- or 3,4-dimethylthiophene[49,50] but to minor impurities (<4%), which very probably are 2-(propyldithio)-dimethylthiophenes, as very recently demonstrated by Kuo et al. and Kuo and Ho.[51,52] The flavor threshold values of dimethylthiophenes in water have been found to be 3-5 x 10^6 ng/l.[50] With an estimated concentration of 1% 2-(propyldithio)-dimethylthiophenes in the mixture and an observed odor threshold value of this mixture in water of 1,000 ng/l, the threshold value of pure 2-(propyldithio)-3,4-dimethylthiophene can be calculated as 10-50 ng/l in water.[43]

Garlic: A recent study on the volatile flavor components of garlic essential oil has been made by Pino et al.[54] They not only quantified the main constituents in the oil, but also made an odor intensity evaluation and determined the odor threshold value of new volatile compounds found in the oil. Examples of these new volatile compounds include: (Z)- and (E)-1-propenyl 2-propenyl disulfide; 1,2,3-trithi-4-ene; and 2-propenyl tetrasulfide. The most important character-impact compounds in garlic are di(2-propenyl) disulfide and di(2-propenyl) trisulfide, which are present in the oil at more than 50%.[55]

Leek: Whitfield and Last[37] mentioned that the compounds described as possessing leek aromas are propanethiol, methyl propyl disulfide, methyl propyl trisulfide, dipropyl trisulfide and 3,4-dimethyl-2,5-dioxo-2,5-dihydrothiophene. The latter compound, having an odor threshold value in

water of 7,000 ng/l, was said to have an aroma similar to that of hydrogen sulfide.[56] It seems more probable that this compound as a potential thioanhydride gives a slow release of hydrogen sulfide by hydrolysis with traces of water.

Table VI. Some essential oils with their number and concentration of sulfur compounds

Essential oil	Number of compounds	Concentration in oil (ppm)	4,5-Epithiocaryophyllene and epithiohumulenes (ppm)
Rose (Bulgarian)	20	600	500
Pepper	10	300	100
Absinth	6	200	50
Patchouli	5	100	50
Immortelle	5	50	30
Cassia	4	40	15
Clove	3	10	5

Sulfur Compounds in Natural Isolates

Sulfur compounds occur in almost every natural isolate. Some sulfur compounds may be formed during isolation, for instance disulfides during steam distillation.

Essential oils contain sulfur compounds in concentrations from part per billion (0.001 ppm) up to part per mille (1000 ppm). Often the low concentration of these materials present in the natural isolate (essential oil or extract) does not allow their detection by normal gas chromatographic techniques. Detection is only possible by the use of the inherent sensitivity and specificity of the flame photometric detector (FPD) for the determination of sulphur-containing compounds.

Table VII. Quantified sulfur compounds in rose oils (in ppm)

	Bulgarian	Turkish	Moroccan	Russian
Dimethyl sulfide	38	41	2	5
Dipropyl sulfide	49	27	124	50
4,5-Epithiocaryophyllene	480	351	120	100
Dibenzothiophene	16	21	10	10

In Table VI some essential oils are shown with their number and concentration of sulfur compounds according to unpublished observations. All these compounds were identified and quantified with a specific FPD sulfur detector.

As can be seen from this Table, 4,5-epithiocaryophyllene and epithiohumulenes (1,2- and 4,5-) are predominant sulfur compounds in the oils.

Rose oil: Nineteen sulfur compounds have been detected in various rose oils in a total concentration of up to 600 ppm.[53,57]

methanethiol
dimethyl sulfide
dimethyl disulfide
dimethyl trisulfide
dipropyl sulfide
hexyl methyl sulfide
4,5-epithiohumulene
1-methyldibenzothiophene
3-methyldibenzothiophene
3-(4-methyl-3-pentenyl)thiophene
3-methyl-2-(3-methyl-2-butenyl)thiophene
3-(4,8-dimethyl-3,7-nonadienyl)thiophene
4-(4-methyl-3-pentenyl)-1,2-dithia-4-cyclohexene
butyl methyl sulfide
β-mintsulfide
1,2-epithiohumulene
4,5-epithiocaryophyllene
2-methyldibenzothiophene
4-methyldibenzothiophene

Omata et al. reported[57] that the sulfur components of Bulgarian rose oil play an important role in its overall odor-character (Table VII). Dibenzothiophene and its methyl derivatives (dimethyl mono- and dimethyl trisulfide), dipropyl disulfide, butyl methyl disulfide, 3-(4-methyl-3-pentenyl)-thiophene, and 3-methyl-2-(3-methyl-2-butenyl)thiophene seemed to contribute to the topnote.

Omata also reported that 4-(4-methyl-3-pentenyl)-1,2-dithia-4-cyclohexene has a seaside green odor with a leathery and powdery undertone that is very long lasting. 4,5-Epithiocaryophyllene also has a seaside green odor, but it has a spicy (nutmeg-like) and powdery undertone, it possesses a great tenacity.[57] Although these compounds were present only at the ppm level in rose oil, because of their tenacity they seemed responsible for the middle and base note.

Hop oil: Peppard[58] wrote a thorough review on volatile sulfur compounds in hop and hop oils. These compounds include alkyl sulfide, polysulfides, epithio-sesquiterpenes and S-methyl thioesters. Hop oils distilled at high temperatures from sulfur-treated hops may give rise to compounds with sulfury off-flavors, whereas hop oils prepared at room temperature contain less volatile sulfur compounds.

Galbanum oil: Burrell et al.[59] isolated five thio-esters from galbanum oil and established their structures as S-isopropyl 3-methylbutanethioate, S-isopropyl 3-methyl-2-butenethioate, S-sec-butyl 2-methylbutanethioate, S-sec-butyl 3-methylbutanethioate, and S-sec-butyl 3-methyl-2-butenethioate. Although the concentration of these compounds in the oil is rather low (less than 0.01%), they contribute significantly to the overall odor of the oil.

Very recently the importance of sulfur compounds in

galbanum oil was confirmed by an investigation of Fellous et al.[60]

References

Address correspondence to Mans H. Boelens, Boelens Aroma Chemical Information Service, Groen van Prinstererlaan 21, 1272 GB Huizen, The Netherlands.

1. H Maarse et al, in *Volatile Compounds in Food* 1989-1991, TNO Biotechnology and Chemistry Institute, PO Box 360, 3700 AJ Zeist, The Netherlands
2. H Boelens and J Heydel, *Chem Zeit* **97** 6-14 (1973)
3. EJ Mulders et al, *Chem Ind* (London) 613-614 (1976)
4. DJ Folkes and JW Gramshaw, *Prog Food Nutr Sci* **5** 369-376 (1981)
5. G MacLeod, in *Developments in Food Flavours,* GG Birch and MG Lindley, eds, London: Elsevier Applied Science (1986) pp 191-223
6. DS Mottram, in *Volatile Compounds in Foods and Beverages,* H Maarse, ed, New York: Marcel Dekker Inc (1991) pp 107-178
7. G MacLeod and JM Ames, *Chem Ind* (London) 175-177 (1986)
8. DA Baines and JA Mlotkiewicz, in *Recent Advances in the Chemistry of Meat,* AJ Baily, ed, London: Royal Society of Chemistry (1984) pp 119-164
9. U Gasser and W Grosch, *Z Lebensm Unters Forsch* **186** 489-494 (1988)
10. U Gasser and W Grosch, *Z Lebensm Unters Forsch* **190** 3-8 (1990)
11. U Gasser and W Grosch, *Z Lebensm Unters Forsch* **190** 511-515 (1990)
12. K Kubota et al, *J Agric Food Chem* **39** 1127-1130 (1991)
13. RG Buttery et al, *J Agric Food Chem* **19** 969-971 (1971)
14. I Flament, in *Volatile Compounds in Foods and Beverages,* H Maarse, ed, New York: Marcel Dekker Inc (1991) pp 617-670
15. R Tressl and R Silwar, *J Agric Food Chem* **29** 1078-1082 (1981)
16. W Holscher et al, *J Agric Food Chem* **40** 655-658 (1992)
17. I Blank et al, *Z Lebensm Unters Forsch* **195** 239-245 (1992)
18. SAF Angelino, in *Volatile Compounds in Foods and Beverages,* H Maarse, ed, New York: Marcel Dekker Inc (1991) pp 581-616
19. MC Meilgaard, *Master Brew Assoc Amer Tech Quart* **12** 151-168 (1975)
20. Y Kuroiwa and N Hashimoto, *Proc Amer Soc Brew Chem,* 28-36 (1961)
21. P Schieberle, *Z Lebensm Unters Forsch* **193** 558-565 (1991)
22. RG Buttery et al, *J Agric Food Chem* **35** 540-544 (1987)
23. WB McGlasson et al, *Hort Sci* **22** 632-634 (1987)
24. E Demole et al, *Helv Chim Acta* **65** 1785-1794 (1982)
25. A Mosandl, presentation for Flavours, Regulation Control meeting, Brussels (Apr 16-17, 1991)
26. M Winter et al, *Helv Chim Acta* **59** 1613-1620 (1976)
27. MG Kolor, *J Agric Food Chem* **31** 1127-1129 (1983)
28. EH Polak, *J Agric Food Chem* **36** 355-359 (1988)
29. J Rigaud et al, *Sci Aliments* **6** 213-220 (1986)
30. JL Le Quere and A Latrasse, *J Agric Food Chem* **38**, 3-10 (1990)
31. D Joulain and R Laurent, in *Proceedings 11th Int Congr of Ess Oils, Fragrances and Flavours 1987, New Delhi, India* (1989)
32. H Guth and W Grosch, *Fat Sci Technol* **93** 335-339 (1991)
33. D Lamparsky and P Schudel, *Tetrahedron Letters* **36** 3323-3326 (1971)
34. T Köpke and A Mosandl, *Z Lebensm Unters Forsch* **194** 327-376 (1992)
35. G Takeoka et al, in *Flavor Chemistry, Trends and Development,* 223-237; eds, R Teranishi, RG Buttery and F Shahidi, eds, ACS Symposium Series 388, Washington DC: American Chemical Society (1989) pp 223-237
36. SG Wyllie and DN Leach, *J Agric Food Chem* **40** 253-256 (1992)
37. FB Whitfield and JH Last, in *Volatile Compounds in Foods and Beverages,* H Maarse, ed, New York: Marcel Dekker Inc (1991) pp 203-282
38. A Fiecchi et al, *Tetrahydron Letters* **32** 1681-1682 (1967)
39. T Talou et al, *J Agric Food Chem* **35** 774-777 (1987)
40. FB Whitfield et al, *Chem Ind* (London) 158-159 (1981)
41. AJ MacLeod and R Islam, *J Sci Food Agric* **26** 1545-1550 (1975)
42. MH Brodnitz and PV Pascale, *J Agric Food Chem* **19** 269-272 (1971)
43. M Boelens et al, *J Agric Food Chem* **19** 984-991 (1971)
44. GG Freeman and RJ Whenham, *J Sci Food Agric* **26** 1869-1886 (1975)
45. GR Fenwick and AB Henley, *CRC Crit Rev Food Sci Nutr* **22** 273-377 (1985)
46. JF Carson, *Food Rev Int* **3** 71-103 (1987)
47. JW Chen and CM Wu, in *Proceedings 9th Int Congr of Ess Oils, Singapore* (1983) pp 30-35
48. H Boelens and L Brandsma, *Rec Trav Chim Pays Bas* **91** 141-145 (1972)
49. WG Galetto and AA Bednarczyk, *J Food Sci* **40** 1165-1167 (1975)
50. WG Galetto and PG Hoffman, *J Agric Food Chem* **24** 852-854 (1976)
51. M-C Kuo et al, *J Agric Food Chem* **38** 1378-1381 (1990)
52. M-C Kuo and C-T Ho, *J Agric Food Chem* **40** 111-117 and 1906-1910 (1992)
53. K Yomogida et al, *Proceedings 11th Int Congr of Ess Oils, Singapore,* Book 2 (1983) pp 196-203
54. J Pino et al, *Acta Alimentaria* **20** 163-171 (1991)
55. G Vernin et al, *Planta Med* **2** 96-101 (1986)
56. M Albrand et al, *J Agric Food Chem* **28** 1037-1038 (1980)
57. A Omata et al, in *Flavors and Fragrances: A World Perspective,* BM Lawrence, BD Mookherjee and BJ Willis, eds, Amsterdam: Elsevier Sci Publ BV (1988) pp 707-714
58. TL Peppard, *J Inst Brew* **87** 376-385 (1981)
59. JWK Burrell et al, *Tetrahedron Letters* 2837-2838 (1971)
60. R Fellous et al, *Proceedings 12th Int Congr of Flav Frag and Ess Oils, Vienna, Austria* (Oct 4-8, 1992)
61. R Teranishi et al, in *Geruch- und Geschmackstoffe,* F Drawert, ed, Nürnberg: Verlag Hans Carl (1975) pp 177-186
62. RG Buttery et al, *J Agric Food Chem* **32** 674-676 (1984)
63. D Sloot and P Harkes, *J Agric Food Chem* **23** 356-357 (1975)
64. RG Buttery et al, *J Agric Food Chem* **24** 829-832 (1976)
65. E Block et al, *J Agric Food Chem* **40** 2418, 2431 (1992)