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Volatile compounds of fresh and processed garlic (Review)

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Abstract. Garlic is used as a spice in cooking due to its unique aroma. The unique aroma of garlic has attracted considerable attention from scientists. The cloves contain large amounts of sulfur-based substances, which as a consequence of their reactive properties, are converted easily to a variety of volatile compounds during processing. The volatile profiles of processed garlic are influenced by processing conditions, such as temperature, pH and solvent. Numerous studies on these changes in volatile compounds that occur during processing have been reported, with a number of types of sulfur-containing volatile compounds being identified in fresh and processed garlic. This review summarizes the volatile components of fresh and processed garlic, particularly those produced by heating and aging. The pungent odor of fresh garlic is contributed mainly to thiosulfinates and their degradation products. During the heating process of garlic, thiosulfinates are mainly decomposed, and nitrogen-containing volatile compounds, such as pyridines and pyrazines are generated. Aldehydes are dominant compounds in black garlic, while esters and phenols are key aroma compounds in aged garlic extract. The slight variations in chemical reactions during the aging process may lead to differences in the aroma of the two types of garlic.

Contents

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1. Introduction

Garlic (*Allium sativum* L.) is a bulbous plant that is used widely as an ingredient in traditional cooking and also for medicinal purposes, as it is a rich source of carbohydrates and protein, and contains large amounts of sulfur-based substances (1). Garlic was used by the Egyptians in several therapeutic formulas, and by the Greeks and Romans as a healing agent (2).

The first scientific studies on garlic were reported by Louis Pasteur, who attributed the plant as having anti-bacterial properties (2). Studies have also reported that garlic extracts have antioxidant (3), anti-microbial (4) and anti-asthmatic effects (5), with current attention focusing on its cancer preventive properties (6-8).

The unique aroma of garlic has also attracted considerable attention from scientists. Fresh garlic contains alliin [*S*-3-(2-propenylsulfinyl)-$_{L}$-alanine-], an odorless derivative of cysteine. When fresh garlic is crushed, alliinase can convert alliin to allicin (*S*-allyl 2-propene-1-sulfinothioate), that represents the characteristic odor of crushed fresh garlic (9). Other precursors of fresh aroma, such as *S*-methylcysteines *S*-oxide, *S*-(*E*)-1-propenylcysteine *S*-oxide and γ-glutamylalk(en)ylcysteines are found in intact garlic cloves (10-16). During the storage of the cloves, these γ-glutamylalk(en)ylcysteines can be converted into related alk(en)ylcistein *S*-oxides (14), and following disruption, these alk(en)ylcistein *S*-oxides are converted enzymatically into related alk(en)yl thiosulfinates, the primary aroma compounds of raw garlic.

This review summarized the volatile components of fresh garlic and changes in their composition and characteristics during thermal processing. The aroma of aged garlic, induced by soaking in ethanol at a low temperature, as well as the storage of bulbs at high temperatures under moisture-controlled conditions are also discussed.

2. Volatile components of raw garlic cloves

Table I presents the volatile compounds in raw and heated garlic cloves obtained by various extraction methods. A total of 85 sulfur containing compounds and 40 non-sulfur-containing have been reported in different studies. Thiosulfinates, such as allicin are reactive molecules and can undergo a number of transformations, including organosulfur compounds, such

Table I. Volatile components in fresh garlic and heated garlic.

Compound	Fresh garlic (Refs.)	Heated garlic (Refs.)
Thiols		
Allylthiol	(44,45,47,51,52)	(38,45,51,54)
1,3-Benzedithiol	(47)	
1,2-Dimercaptocyclopentane	(17)	(54)
Methanethiol	(45)	(38,45)
1-Methylimidazole-2-thiol	(51)	(51)
Thiosulfinates		
Methane methyl thiosulfinate	(46)	
Monosulfides		
Allyl 2,3-epoxypropylsulfide	(49)	
Allyl methyl sulfide	(17,24,44-47,50,51)	(38,45,51,53,54)
Allyl 1-propenyl sulfide	(44)	
Allyl propyl sulfide	(50)	(38,53)
Butyl 1-propenyl sulfide	(47)	
Cyclopentyl hexyl sulfide	(47)	
Diallyl sulfide	(17,24,44,46,47,49-51)	(34,38,51,53,54)
Dimethyl sulfide	(44-46)	(45)
Di(1-propenyl) sulfide	(44)	(38)
Dipropyl sulfide		(38)
Ethyl vinyl sulfide	(49)	
Methyl allyl thioacetate	(47)	
3-Methyl-1,1-bis(methylthio)-1,3-butadiene	(47)	
Methyl 2-propynyl sulfide	(24)	
Methylthiocyclohexane	(47)	
Methylthiocyclopentane	(47)	
3-(Methylthio)penta-2,4-dione	(47)	
5-(Methylthio)-4-penten-2-ol	(47)	
3-Methylthio propanal	(49)	
N-Morpholinomethyl isopropyl sulfide	(47)	
1-Propenyl propyl sulfide	(24)	
Disulfides		
Allyl methyl disulfide	(17,46-52)	(38,51,53,54)
Allyl 1-propenyl disulfide	(44,50)	
Allyl propyl disulfide	(17)	(38,54)
Diallyl disulfide	(17,24,26,44-52)	(34,38,45,51,53,54)
Dimethyl disulfide	(17,24,44-47,49,50)	(38,45,51,54)
Di(1-propenyl) disulfide	(44)	
Methyl 1-propenyl disulfide	(17,44,47,50)	(38,54)
Methyl propyl disulfide	(17,24,45-47,49)	(38,54)
Polysulfides		
Allyl methyl trisulfide	(17,44,46-51)	(38,51,54)
Allyl 1-propenyl trisulfide	(50)	
Diallyl tetrasulfide	(24,44,46,48,49)	
Diallyl trisulfide	(17,24,26,44,46-52)	(34,38,51,53,54)
Dimethyl tetrasulfide	(47,49,50)	
Dimethyl trisulfide	(17,44,46-50)	(38)
Dipropyl trisulfide	(50)	
Methyl butyl trisulfide	(49)	
Methyl 1-propenyl trisulfide	(50)	
Methyl propyl trisulfide	(50)	

Table I. Continued.

Compound	Fresh garlic (Refs.)	Heated garlic (Refs.)
Cyclic sulfides		
Benzothiophene	(47)	
Cyclopentathiazole	(47)	
3,5-Diethyl-1,2,4-trithiolane	(17,47-50)	(54)
4,5-Dimethylisothiazole	(47)	
2,4-Dimethylthiazole	(51)	
2,4-Dimethylthiophene	(47)	
2,5-Dimethylthiophene		(38)
3,4-Dimethylthiophene	(51)	(51)
3,5-Dimethyl-1,2,4-trithiolane		(53)
1,2-Dithiacyclopentane	(49)	(38)
1,3-Dithiane	(17,24,44,51)	(51,54)
1,2-Dithiolane	(24)	
1,3-Dithiolane	(24)	
2-Ethyl-1,3-dithiane	(47)	
2-Ethylidene-1,3-dithiane	(47)	
Ethyl-2-thiopheneacetate	(47)	
2-Methyl-3,4-dihydro-2*H*-thiopyran	(51)	(51)
5-Methyl-1,2,3,4-tetrathia-cyclohexane	(51)	(51)
5-Methyl 1,2,3-thiadiazole	(24)	
4-Methyl-5-vinylthiazole	(17)	(54)
2-(1-Propenylthio)thiophene	(47)	
Propylene sulfide	(17,24)	(54)
Tetrahydro-2,5-dimethylthiophene	(17)	(54)
2-(1-Thia-2-cyclohexen-6-yl)-1,3-dithia-cyclohex-5-ene	(49)	
3-(2-Thia-4-pentenyl)-1-thiacyclohex-5-ene	(49)	
Thiazole	(47)	
Thiirane	(24)	
2-Thiophenecarboxaldehyde	(47)	
3-(2,3,4-Trithia-5-heptenyl)-1-thia-cyclohex-5-ene	(49)	
1,3,5-Trithiane	(47,51)	(51)
3-Vinyl-1,2-dithiacyclohex-4-ene	(44,47,51)	(51)
2-Vinyl-1,3-dithiane	(47,48)	
3-Vinyl-1,2-dithiane	(48)	
2-Vinyl-4*H*-1,3-dithiine	(17,24,26,46,48-50)	(34,38,53,54)
3-Vinyl-4*H*-1,2-dithiine	(17,24,26,44,46-51)	(38,51,54)
2-Vinylthiophene	(49)	(38)
Other compounds		
Acetaldehyde		(38)
Acetone	(44)	
Allyl alcohol	(17,44)	(38,54)
Aniline	(17)	(54)
2-Butenal	(44,47)	
2,4-Dimethylfuran	(17)	(54)
2,3-Dimethylpyrazine		(38)
2,5-Dimethylpyridine	(47)	
2,5-Dimethylpyrazine		(38)
2,6-Dimethylpyrazine		(38)
2-Ethyl-2-butenal	(44)	
Ethylpyrazine		(38)
Heptadecene	(49)	

Table I. Continued.

Compound	Fresh garlic (Refs.)	Heated garlic (Refs.)
4-Heptenal	(24,44)	(38,53)
2,4-Hexadienal	(44,47)	
Hexanal	(44)	
1-Hexanol	(17)	
2-Hexanol	(44)	
5-Hexenal	(44)	
5-Hexen-2-one	(44)	
1-Hydroxy-4-methyl-2,6-di-tert-butylbenzene	(51)	(51)
Isobutyl isothiocyanate	(17)	(54)
Methoxymethyl isothiocyanate	(47)	
2-Methylbenzaldehyde	(17)	(54)
3-Methylbutanal	(44)	
2-Methyl-2-butenal	(47)	(38)
3-Methyl-2-cyclopentene-1-thione	(17)	(38,54)
2-Methyl-5-ethylpyridine		(38)
2-Methylene-4-pentenal	(44,47)	
2-Methylfuran	(47)	
2-Methyl-3-pentanol	(24)	
2-Methyl-4-pentenal	(44,47)	
2-Methylpyridine		(38)
3-Methylpyridine	(47)	
1-Methyl-3-pyrrolin-2-one	(51)	(51)
Pentadecene	(49)	
2-Pentenal	(47)	
3-Penten-2-one	(44)	
Phenylethyl butyrate	(51)	(51)
Propene	(17)	
2-Propen-1-ol	(51)	(51)
Pyridine		(38)
Sulfur dioxide	(51)	(51)
Trimethylpyrazine		(38)

as diallyl, methyl allyl, and diethyl mono-, di-, tri-, tetra-, penta- and hexasulfides, vinyldithiins, and (*E*)- and (*Z*)-ajoene (13,14,17).

Analytical methods markedly influence the results of the composition and number of compounds detected. Auger's study group used several different methods for isolating the compounds, including extraction, trapping techniques and hyphenated chromatographic procedures (18-23). According to their reports, allium odors contain only thiopropanal *S*-oxide and thiosulfinates as sulfur volatiles (23). Lee *et al* (2003) reported a comparison of the flavor composition of cut garlic obtained by either steam distillation (SD), simultaneous distillation and solvent extraction (SDE), solid-phase trapping solvent extraction (SPTE), or headspace solid-phase microextraction (HS-SPME) (24). Diallyl disulfide, allylsulfide and diallyl trisulfide were the predominant flavor components of SDE extract, whereas only diallyl disulfide was dominant in the SD, SPTE and HS-SPME extracts. The data were also analyzed to examine the association of fresh garlic aroma and considered not only diallyl disulfide, but also dithiin and allicin. Quantitative HPLC analysis of SD extracts and acetonitrile from commercial garlic, identified 20 different organosulfur compounds, including minor compounds such as 3-vinyl-4*H*-1,2-dithiin and 2-vinyl-4*H*-1,3-dithiin. Another analysis of oil-macerated garlic revealed that the samples contained (*E*)- and (*Z*)- ajoene, 3-vinyl-4*H*-1,2-dithiin and 2-vinyl-4*H*-1,3-dithiin as the major compounds (25). Abu-Lafi *et al* subsequently confirmed these results using experimental data obtained by GC-MS and HPLC chromatograms, and concluded that 3-vinyl-4*H*-1,2-dithiin and 2-vinyl-4*H*-1,3-dithiin were the major components of fresh garlic (26). However, it has been reported that these two sulfur cyclic compounds are artifacts formed from allicin during thermal gas chromatographic (GC) analysis (15,27). In our study, although these dithiins were detected as artifacts on GC analysis, we could not deny the possibility that they contributed to the fresh odor of garlic (Abe *et al*, unpublished data). Allicin is converted by water into organosulfur compounds at room

Table II. Comparison of volatile components between black garlic and aged garlic extract.

Compound	Black garlic[a] (%)	Aged garlic extract[b] (mg/l)
Sulfur containing compounds		
2-Acetylthiazole	-	0.03
Allyl mercaptane	1.1	-
Allyl methyl disulfide	-	0.66
Allyl methyl sulfide	18.2	1.37
Allyl methyl trisulfide	1.5	0.50
Allyl propyl disulfide	-	0.04
Allyl propyl sulfide	0.15	-
Benzothiazole	0.33	-
Diallyl disulfide	0.84	1.88
Diallyl sulfide	1.4	6.29
Diallyl tetrasulfide	0.11	-
Diallyl trisulfide	0.86	1.39
Dimethyl disulfide	0.65	0.02
Dimethyl trisulfide	1.0	0.06
1,3-Dithiane	0.92	-
Methional	-	0.03
5-Methyl-2-thiophenecarboxaldehyde	-	0.15
2-Vinyl-4*H*-1,3-dithiin	-	0.19
3-Vinyl-4*H*-1,2-dithiin	0.13	-
Acids		
Octanoic acid	-	0.03
Esters		
Ethy acetate	-	7.00
Ethyl butanoate	-	0.03
Ethyl 2-butenoate	-	0.07
Lactones		
3-Hydroxy-4,5-dimethyl-2(*5H*)-furanone	-	0.03
γ-Octalactone	-	0.01
Aldehydes		
Benzaldehyde	0.62	0.18
Benzeneacetaldehyde	12	-
Furfural	17.3	-
Hexanal	0.16	-
5-Hexanal	0.29	-
2-Methylene-4-pentenal	14.9	-
2-Methylpropanal	2.8	-
3-Methylbutanal	8.8	-
3-Methylbutanal	3.0	-
5-Methylfurfural	0.53	-
Nonanal	-	0.02
Vanillin	-	0.54
Ketones		
Acetone	6.4	-
2-Acetylfuran	0.15	-
2,3-Butanedione	0.91	-
2-Hydroxy-3-methyl-2-cyclopentenone	-	0.03
1-Hydroxy-2-propanone	0.74	-
3-Penten-2-one	0.42	-

Table II. Continued.

Compound	Black garlic[a] (%)	Aged garlic extract[b] (mg/l)
Alcohols		
Phenylethyl alcohol	-	0.05
2-Propen-1-ol	0.82	-
Phenols		
4-Ethylphenol	-	0.01
Eugenol	-	0.03
2-Methoxyphenol	-	0.17
Nitrogen containing compounds		
2,3-Dimethylpyrazine	-	0.02
Trimethyloxazole	-	0.07
Trimethyl pyrazine	-	0.10

[a]Relative concentration of volatile compounds in black garlic (44). [b]Concentrations of the majority of the odor active compounds in aged garlic extract (Abe *et al*, unpublished data).

temperature or heating (28,29), which may result in the aroma of fresh garlic changing more rapidly than expected.

GC methods are generally used for the analysis of the volatile compounds. Due to their reactive characteristics, some aroma compounds of garlic may be converted to artifacts during GC analysis. However, sensory-guided studies, such as GC-olfactometry (GC-O) are a useful tool for the analysis of key aroma compounds in a food matrix (30,31). We analyzed the SDE of fresh garlic using aroma extract dilution analysis (AEDA) by GC-O equipped with a cool-on column, which prevents the decomposition of volatiles in the GC injection port to characterize the aroma active components. We identified 18 aroma compounds with a flavor dilution factor (FD factor) ≥1 (Abe *et al*, unpublished data). The highest FD factor was obtained for 2-vinyl-4*H*-1,3-dithiin (pungent, FD=65536). The FD factors of the other odorants ranged from 1,024 to 128 as follows: Unknown compound (potato, earthy, FD=1,024), *S*-methyl methanethiosulfinate (radish, FD=256), unknown compound (aniseed-like, FD=256), methional (cooked potato, FD=128) and 3-vinyl-4*H*-1,2-dithiin (garlic, FD=128). Of these compounds, with the exception of the thiosulfinates, only methional was shown to have a high FD factor. Based on these results, although the pungent odor of fresh garlic can be attributed mainly to thiosulfinates, their degradation products also seemed to be contributors of fresh garlic aroma as well.

3. Nature of volatile compounds in garlic cloves during heating

Garlic is used worldwide in the home and in the industry in several types of products, such as garlic oil, garlic powder, garlic salt, garlic paste and garlic flakes. These products are prepared by various cooking treatments, including soaking in water or oil, roasting, steaming, or drying. The products may undergo further changes during cooking when used as spices or seasoning in dishes. This section focuses on how the aroma of fresh garlic is altered or transformed by processing, particularly heating.

There are several reports on the analysis of volatile components in cooked garlic samples (32,33). Locatelli *et al* described the profiles of organosulfur compounds, including allicin, *E* or *Z*-ajoene, dithiins, diallyl sulfide, diallyl disulfide and diallyl trisulfide, in the solvent extraction of pre-cooked (chopped, sliced and whole cloves) and cooked (simmering, rolling boiled and stir-fried) garlic with dichloromethane using HPLC analysis (34). Their results indicated that the allicin content could be determined in pre-cooked samples, while cooking significantly influenced the diallyl disulfide and diallyl trisulfide levels. These two compounds exhibited the highest levels with an increased treatment temperature (rolling boil and stir-fried). It has been previously reported that thisulfinates are very unstable and are transformed into polysulfides in water or into vinyldithiins in hexane, ether or vegetable oil (35-37).

Yu *et al* (1993) investigated the volatile compounds in the SD-solvent extraction of deep-oil fried, microwave-heated and oven-baked sliced garlic with using normal GC analysis (38). They reported that thiosulfinates, which contribute to and are precursors of the fresh aroma of raw garlic, were destroyed by these heating processes, and that thermally-treated garlic aroma consisted of i) acrylic sulfur-containing compounds, such as thiol and sulfide; ii) cyclic sulfur-containing compounds, such as thiophenes and vinyldithiins; iii) nitrogen-containing compounds, pyridine and pyrazine which contain one and two nitrogen atoms on the benzene ring; and iv) oxygen-containing compounds, such as aldehydes and alcohols. Diallyl disulfide and diallyl trisulfide were found to be the dominant compounds in baked and microwave-baked garlic samples. Diallyl disulfide was also found to be the dominant compound in fried, oil-cooked and microwave-fried garlic samples; however, the content of diallyl trisulfide was very low. In addition, the levels of vinyldithiins, allyl alcohols and oxygen-containing and nitrogen-containing volatile compounds were higher in fried samples than in baked samples. It has been reported that vinyldithiins are transformed from allicin into a non-polar solvent (37) and therefore, it would be expected that the level of these compounds would be increased in oil-cooked samples.

During the heating process of garlic, it is postulated that sulfur containing compounds are mainly decomposed and/or rearranged to products of alk(en)yl thisulfinates, and nitrogen-containing volatile compounds, such as pyridines and pyrazines. These compounds never exist in fresh cloves and are formed in fried or baked garlic as a result of the Maillard reaction that occurs during high temperature thermal treatment.

4. Comparison of volatile components between black garlic and aged garlic extract

The aging process provides a number of benefits to improve functional properties. Garlic is no exception to this process; black garlic is produced by the thermal processing of fresh garlic for several months at 60-80˚C under controlled humidity without additives (39). Aged garlic extract (AGE) and other aged types of garlic prepared by soaking sliced cloves in an aqueous ethanol solution or the extraction of cloves aged for several months at an ambient temperature are also available in markets (40). The diverse bioactivities of the aged garlic which were prepared by those two conditions have been described in many scientific reports (41-43). Below, the volatile compounds of AGE are shown and compared to those of black garlic in order to clarify the effects of the aging process on the formation of these compounds.

Table II presents the composition of volatile compounds in black garlic obtained by fermentation in a closed chamber for 5 weeks under high humidity at 60-80˚C (44), and AGE prepared by soaking sliced garlic cloves in an aqueous ethanol solution, or the extraction of cloves aged up to 10 months at room temperature in an air tight container (Abe *et al*, unpublished data). The volatile compounds in black garlic were analyzed by headspace-GC-MS. On the other hand, AGE was distilled by solvent-assisted flavor evaporation to separate the volatiles from the non-volatile material. The key aroma compounds in AGE were identified by AEDA and quantified by GC-MS using cold on-column injection method.

For sulfur-containing compounds, the aroma components in AGE revealed a similar trend as the volatile profile of black garlic. Allyl methyl sulfide was dominant in black garlic (18.2%), followed by allyl methyl trisulfide (1.5%), diallyl sulfide (1.4%) and several organosulfur compounds. Diallyl sulfide was dominant in AGE (6.29 mg/l), followed by diallyl disulfide (1.88 mg/ml), diallyl trisulfide (1.39 mg/l) and several organosulfur compounds. These pungent smelling sulfides were considered to have been formed by the decomposition of thiosulfinates during the processing of fresh garlic. On the other hand, for non-sulfur-containing odorants, the aroma components of AGE differed markedly from those of black garlic. Aldehydes, such as furfural (17.3%), 2-methylene-4-pentenal (14.9%) and benzeneacetaldehyde (12%) were the dominant compounds in black garlic, but were not the key aroma compounds in AGE. Furfural was detected by GC-MS in the volatile extract of AGE, but not by AEDA with a FD≥1. These findings indicated that furfural was not a key aroma component in AGE. Phenols, esters and nitrogen containing compounds were identified as key aroma components in AGE. These compounds were generated by aging, and exceeded their respective concentration which detectable by human nose. Three fruity-smelling esters (ethyl acetate, 7.00 mg/l; ethyl 2-butenoate, 0.07 mg/l; and ethyl butanoate, 0.03 mg/l) were not detected in black garlic, but were identified as key aroma components in AGE. It is likely these esters were produced by the esterification of ethanol, which was used as a solvent during the aging process. Nutty or green-smelling nitrogen containing compounds (trimethyl pyrazine, 0.10 mg/l; trimethyloxazole, 0.07 mg/l; and 2,3-dimethylpyrazine, 0.02 mg/l) that were not detected in black garlic were identified as key aroma components in AGE. These odorants are likely produced by the Maillard reaction during the aging process.

5. Conclusion

This review summarized the volatile components of fresh and processed garlic. The pungent odor of fresh garlic can be attributed mainly to thiosulfinates, as well as their degradation products seemed to be contributors for fresh garlic aroma. Although the volatile components of aging processed garlic were mainly consisted of sulfur-containing compounds, non-sulfur-containing compounds also associated with their aroma, which compositions and contents were different in type of aging process. Taken together, the findings of studies mentioned in this review indicate that slight variations in chemical reactions during the aging process may lead to differences in the aroma of two types of garlic, black garlic and AGE samples.

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Authors' contributions

KA collected the data and constructed the tables. YH designed the study and revised the manuscript. TM designed the study and wrote the manuscript. All authors have read and approved the final manuscript.

Ethics approval and consent to participate

Not applicable.

Patient consent for publication

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Competing interests

The authors declare that they have no competing interests.

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