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REVIEW



# Flavor components, precursors, formation mechanisms, production and characterization methods: garlic, onion, and chili pepper flavors

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## ABSTRACT

There is an enormous demand in the food industry to shift toward natural flavors. However, most flavor molecules are significantly unstable outside their original sources. Moreover, limited studies are focused on the flavor formation mechanisms, regeneration methods, and stability, which could help facilitate this replacement by establishing a link between food processing conditions and flavor generation.

This scoping review summarizes major findings related to the identification of garlic, onion, and chili pepper flavors and their precursor molecules, formation mechanisms, generation of flavors and precursors, characterization methods, and precursor stability under thermal food processing conditions. The findings confirmed that the allium flavors could be generated by alliin and isoalliin precursors through thermal processing. Also, the literature lacks detailed knowledge about chili pepper flavor's precursors, and only capsaicinoids have been reported as a thermally stable chili pepper flavor.

Although numerous studies have focused on this area, there is still a lack of detailed applicable knowledge. Future investigations can be framed into (1) Development of efficient methods to generate flavors during food processing; (2) Improvement of flavors' stability; (3) Understanding the interactions of flavors and their precursors with other food ingredients and additives; and (4) Characterization of the organoleptic properties of flavors.

## KEYWORDS

Plant-based flavor; flavor precursors; thermal processing; alliin; isoalliin; capsaicinoids

## Introduction

There is considerable growth in demand for using natural ingredients in food products (Brewster 2020; Intelligence 2019; Olayanju 2019). The wide varieties of plants, one of the major food resources, make them a target for the extraction of substances such as flavor and colorant for replacing synthetic chemicals in food products. More specifically, allium products, such as onion and garlic, have gained more attention because of their distinctive flavor and health benefits (Fujisawa et al. 2008; Griffiths et al. 2002). In addition, peppers have been a center of interest for both the food and pharmaceutical industries due to their hot flavor and health benefits.

### Garlic and onion flavors

The alliums are a large genus containing about 700 species. Among alliums, garlic (*Allium sativum*) and onion (*Allium cepa* L.) are the most important vegetables that have been widely used in foods because of their distinct flavors (Griffiths et al. 2002; Randle and Lancaster 2002). Chemical components in garlic and onion such as flavonoids, phenolic compounds, and nitrogen oxides can potentially deliver

nutritional and health benefits (Agbana et al. 2020; Borlinghaus et al. 2014; Lanzotti, Scala, and Bonanomi 2014).

The sulfur-containing nonvolatile amino acid components mainly contribute to the allium's flavors (Horníková et al., 2010). The flavor components of garlic and onion mainly include S-allyl cysteine sulfoxide (allicin), S-allyl-cysteine, and the sulfides of diallyl-, methyl allyl-, and dipropyl mono-, di-, tri-, and tetra-sulfides, all of which are produced by the decomposition of sulfur-containing components (Lanzotti, Scala, and Bonanomi 2014). In general, these sulfur-containing volatile components of the allium could be released from their nonvolatile precursors, S-alkenyl cysteine sulfoxides (ACSOs), through an enzyme-mediated degradation process (Amagase 2006; Lawson 1996; Reuter 1995; Yamazaki, Sugiyama, and Saito 2002).

### Chili pepper flavors

Pepper belongs to the Solanaceae family and has been widely consumed as a spice for its pungent taste, pigments, and functional activities. There are more than 200 pepper species. In all varieties, capsaicinoids are major flavor compounds in peppers and responsible for hot taste or pungency

characteristics (Van Ruth and Roozen 1994). Moreover, capsaicinoids are found to exert multiple pharmacological and physiological effects, including analgesia, anticancer, anti-inflammation, antioxidant, and anti-obesity effects (Adler and Beuchat 2002; Lanciotti et al. 2004; Luo, Peng, and Li 2011; Moses et al. 2018).

In the food industry, flavors can be produced either through the chemical synthesis of molecules (e.g. vanillin ( $C_8H_8O_3$ , vanilla flavor)) or by direct use of flavor powder and the oil extracted mechanically from fresh products. In most synthesis methods, organic reagents (such as glyoxylic acid used in the chemical synthesis of vanillin) are not food-safe and also require extra steps to remove these reagents (Huang et al. 2013). The common extraction method for flavor (e.g. garlic and onion oils extracted by steam distillation process) is also limited, as the obtained powder and oil can be easily oxidized through the process. Moreover, the final product may not be desired as of unfavored sensory attributes of powder and oily taste (Sowbhagya et al. 2009). Moreover, during the high-temperature process, oils can produce off-flavors, which further limits their application in food thermal processes such as frying and baking (Choe and Min 2006; Piletti et al. 2019).

The food industry has been trying to promote more consumer-appealing clean label by replacing synthetic-based flavors with natural flavors (Olayanju 2019). Moreover, the addition of natural flavors could potentially reduce the need for preservatives such as sodium benzoate since many natural flavors (e.g. garlic and chili pepper flavor) have antioxidant or antimicrobial properties (Ankri and Mirelman 1999; Harris et al. 2001; Taylor, Doyle, and Webb 2018).

In this vein, this scoping review is designed to collect and review most related published papers in the field of garlic, onion, and chili pepper flavors and their precursors (Supplementary Materials: Table S1 and Figure S1). This review summarizes major findings in the areas of identifying garlic, onion, and chili pepper flavors and flavor precursor molecules, their flavor formation mechanisms, regeneration methods, and stability of the flavor precursors or flavor molecules to give an insight into the relationship between thermal processing conditions and flavor generation. The collected information in this scoping review highlights the existing gap in plant-based flavor formation mechanisms, thermal degradation of flavor precursors, and the utilization in various food applications.

## Identifying plant-based flavor components

In this section, volatile compounds responsible for garlic, onion, and chili pepper flavors are discussed.

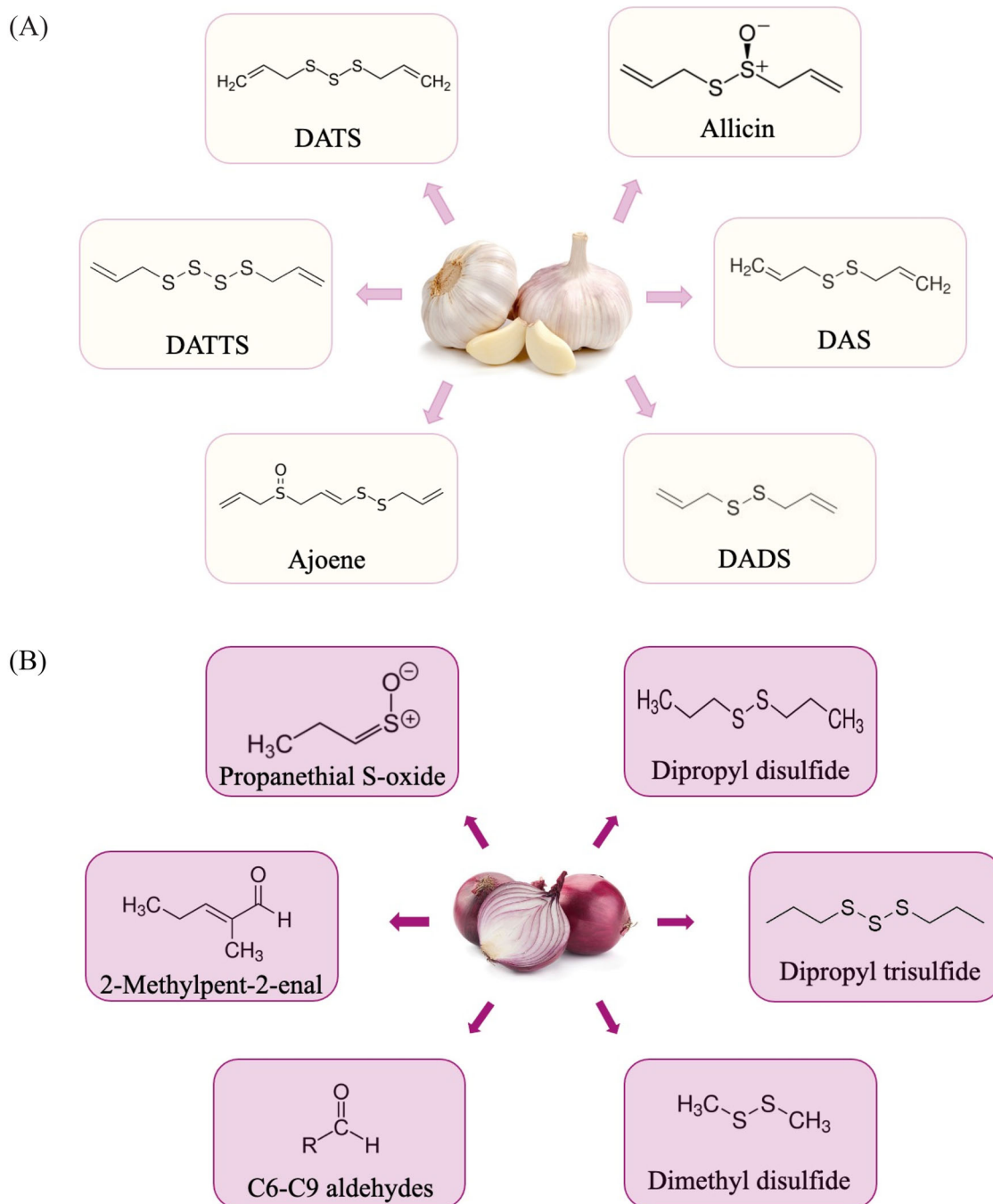
### Garlic and onion flavors

The flavors for both garlic and onion (Figure 1) are generated by enzymatically mediated degradation of their nonvolatile precursors of ACSOs facilitated by the disruption of plant tissue since the flavor precursors are stored in the cell cytoplasm, and the enzyme exists in the vacuoles within the

cell (Amagase 2006; Lawson 1996; Reuter 1995; Yamazaki, Sugiyama, and Saito 2002). It is noteworthy that planting, storage, and processing conditions (e.g. temperature, pH, and water content), affect the flavor's chemical composition and its bioactivity (Martins, Petropoulos, and Ferreira 2016).

Allicin ( $C_6H_{10}OS_2$ ) is a key molecule of garlic flavor and is responsible for the typical smell and taste of freshly cut or crushed garlic. It is released from its precursor ACSO *via* a rapid alliinase-mediated degradation (i.e. 0.3 min) at room temperature (Chu et al. 2012; Lawson and Hughes 1992). Allicin is described as a colorless or light-yellow oil with low water solubility. Generally, 1 g of fresh garlic contains approximately 2.5 mg alliin, producing at least 1 mg of allicin (Murray et al., 2012). Allicin accounted for 70% (w/w) of the total thiosulfinate compounds present or formed upon crushing the garlic cloves (Miron et al. 1998). It is very unstable and can be converted to allyl sulfides, such as diallyl sulfide (DAS), diallyl disulfide (DADS), diallyl trisulfide (DATS), and diallyl tetrasulfide (DATTS), which also contribute to the flavor of garlic products (Figure 1A) (Abe, Hori, and Myoda 2019; Kimbaris et al. 2006).

As for the different garlic flavor compounds obtained from various thermal processes, Table 1 shows the detailed information. Diallyl disulfide was the dominant volatile compound for both baked garlic and oil-treated garlic, accounts for 42–46% and 29–49%, respectively. However, other major volatile compounds generated from baked or oil-treated garlic samples were quite different. Diallyl trisulfide was the major volatile compound in baked garlic, accounting for 36–41%. Vinyl dithiins were major volatile compounds in oil-treated samples. The key generation mechanisms of diallyl trisulfide from allicin are described in two steps. First, the interactions of two molecules of allicin led to the formation of sulfonium ions. And then the addition of water to the allyl double bond followed by the electron rearrangements in this sulfonium ion formed diallyl trisulfide. However, the oil system could inhibit the interaction of allicin molecules and the reaction of the addition of water to the allyl double bond in the sulfonium ion in the oil system (Block 1992). Vinyl dithiins were found to be generated from allyl alk(en)yl thiosulfonates when these thiosulfonates were put in hexane, ether, or vegetable oil or were heated at very high temperatures under low water activity (Larry D Lawson and Hughes 1992; Yu, Wu, and Liou 1989). As a result, the high content of these vinyl dithiins found in oil-treated samples was related to the high-temperature treatment of garlic slices and the nonpolar property of vegetable oil. A relatively high amount of nitrogen-containing compounds were found in both baked and oil-treated samples, such as pyridines and pyrazines, which were proved to be generated through Maillard reaction and from the interactions between amino compounds and reducing sugars. The flavor precursors of garlic act as amino groups and react with sugar in garlic during baking or frying treatment (Yu, Wu, and Ho 1993). Black garlic is another popular product and is processed by aging fresh garlic under high temperature (65–90 °C) and high humidity (60–80%) for 60–90 days. Several key aroma-active



**Figure 1.** The main flavor components of garlic (A) and onion (B).

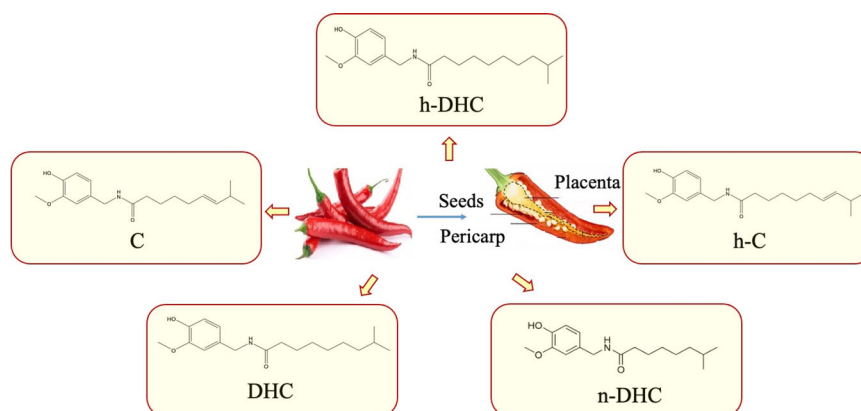
compounds, including diallyl sulfide, diallyl disulfide, diallyl trisulfide, allyl methyl trisulfide, furaneol, acetic acid, and 5-heptyldihydro-2(3H)-furanone were reported in black garlic. For these sulfur-containing products, diallyl sulfide, diallyl disulfide, diallyl trisulfide, and allyl methyl trisulfide were derived from the degradation compounds of allicin. Furaneol was derived from C5 sugars through the Maillard reaction. Acetic acid was produced by  $\alpha$ -dicarbonyl and  $\beta$ -dicarbonyl cleavage of hexose or pentose during thermal processing. Furthermore, it was reported that 5-heptyldihydro-2(3H)-furanone was a product derived from the combination of lipid oxidation and Maillard reaction (Yang et al. 2019).

Like garlic, onion is characterized by its distinctive flavor and pungent smell. Onion pungency closely correlates with its pyruvic acid content and its lachrymatory factor (LF) (Propanethial S-oxide,  $\text{CH}_3\text{-CH}_2\text{-CH=SO}$ ) (Ianni et al. 2016). The mass of enzymatically generated pyruvic acid per gram of fresh onion is often used as a measure of onion flavor (Bacon et al. 1999; Dhumal, Datir, and Pandey 2007). Pyruvic acid, as well as both volatile and nonvolatile sulfur compounds, contribute to the characteristic odor and flavor of onion (Gitin et al. 2014). There are several sulfur-containing compounds that contribute to the major flavor of onion, including thiosulfonates, mono-, di- and tri-sulfides, as well as specific compounds such as the lachrymatory or tear

**Table 1.** Flavor compounds of garlic and onion.

Plant	Process	Generated flavor compound	Stability	References
Garlic	Fresh chopped garlic	Allicin	Allicin: Stable when the temperature is below 4 °C at pH 5–6	(Chu et al. 2012; Fujisawa et al. 2008)
	Baked and microwave baked	Diallyl disulfide, diallyl trisulfide, methyl allyl trisulfide, methyl allyl disulfide, and nitrogen-containing compounds	Diallyl trisulfide, methyl allyl trisulfide: Most stable at pH 6	(Yu, Wu, and Liou 1989; Yu, Wu, and Ho 1993)
	Fried, oil-cooked, and microwave-fried garlic samples (oil-treated samples)	Diallyl disulfide, methyl allyl disulfide, allyl alcohol, vinyl dithiols, and nitrogen-containing compounds	Diallyl disulfide and methyl allyl disulfide: most stable at pH 9	(Yu, Wu, and Ho 1993)
	Black garlic (aging fresh garlic under high temperature (65–90 °C) and high humidity (60%–80%) for 60–90 days)	Diallyl sulfide, diallyl disulfide, diallyl trisulfide, allyl methyl trisulfide, furaneol, acetic acid, and 5-heptyldihydro-2(3H)-furanone	n/a*	(Yang et al. 2019)
Onion	Fresh chopped onion	Propanthial S-oxide, propyl propanethiosulfonate	n/a	(Block 1992)
	Cooked onion	Propyl and propenyl-containing di- and trisulfides	n/a	(Galletto and Bednarczyk 1975)
	Fried onion	2,4- and 3,4-dimethylthiophenes	n/a	(Boelens et al. 1971)
	Fried onion	Triethyl dihydrodithiazine	n/a	(Ledl 1975)
	Hot-air-drying and at smaller scale from pickling and boiling	Dipropyl disulfide and dipropyl sulfide	n/a	(Freeman and Whenham 1975)

\*n/a: Not Available.

**Figure 2.** Chili pepper cross-section and its main flavor compounds.

factor and thiopropanal S-oxide (Figure 1B). The sulfur compounds account for 98.30% of the total volatile compounds in fresh onion, with dipropyl disulfide making up to 77.70% of that number (Choi et al. 2017). In addition, various aldehydes (most consisting of six to nine carbons) are identified as volatiles in fresh onion (Choi et al. 2017). Table 1 shows the different onion flavor compounds obtained from various food processes.

### Chili pepper flavor

The major flavor components of hot pepper that contribute to the special hotness sensation are capsaicinoids. Capsaicinoids are accumulated in specific epidermal cells in vacuoles and eventually excrete them to the seeds and internal pericarp surface (Stewart et al. 2007). Figure 2 shows the schematic cross-section of chili pepper and the chemical structure of capsaicinoids.

Capsaicinoids mainly include capsaicin (C, 69%), dihydrocapsaicin (DHC, 22%), nordihydrocapsaicin (n-DHC,

7%), homocapsaicin (h-C, trace amount), and homodihydrocapsaicin (h-DHC, trace amount) (Cisneros-Pineda et al. 2007). As a major flavor component, capsaicin (trans-8-methyl-N-vanillyl-6-nonenamide,  $C_{18}H_{27}NO_3$ ) is crystalline, lipophilic, colorless, and odorless alkaloid. Capsaicin is soluble in fat, alcohol, and other organic solvents (Hayman and Kam 2008). It is always found as the trans isomer (Reyes-Escogido, Gonzalez-Mondragon, and Vazquez-Tzompantzi 2011). The capsaicin distribution inside the plant varies in different plant compartments. The placenta tissues and seeds of *C. chinense* are reported to have most of the capsaicin contents—62% and 37%, respectively (Cisneros-Pineda et al. 2007). Different varieties of pepper have different capsaicin contents. The variety of *C. chinense* was reported to contain higher capsaicin contents compared to the variety of *C. annuum* (Cisneros-Pineda et al. 2007).

The stability of capsaicinoids is affected by their cultivars, initial concentration, heating temperature, and pH, as shown in Table 2. The degradation rate of capsaicinoids was reported slower at higher initial concentrations ranging



**Table 2.** Stability of capsaicinoids compounds under different processing conditions.

Compounds	Degraded (%)	Temperature (°C)	Time (min)	pH	References
Capsaicin (600 ppm)	50%	100	90	7	(Si et al. 2014)
Dihydrocapsaicin (600 ppm)	70%	100	90	7	
Nordihydrocapsaicin (600 ppm)	95%	100	90	7	
Capsaicinoids (1000 ppm)	4%	100	90	7	
Capsaicinoids (600 ppm)	8%	100	90	7	(Schweiggert, Schieber, and Carle 2006)
Capsaicinoids (200 ppm)	45%	100	90	3	
Capsaicinoids (200 ppm)	42%	100	90	5	
Capsaicinoids (200 ppm)	25%	100	90	7	
Capsaicinoids (200 ppm)	40%	100	90	9	
Whole chili pepper	20–30%	80–100	5	n/a	
	(Capsaicinoids)				
Capsaicinoids	2%	160	4		(Yan et al. 2009)
Capsaicinoids	5%	160	8		

from 200 to 1000 ppm at 100 °C and pH of 7.0 for 90 min (Si et al. 2014). The study also reported that at constant initial capsaicinoids concentration (e.g. 200 ppm), the rate of degradation in capsaicinoids content in neutral pH was lower than alkaline and acidic conditions (Si et al. 2014). Also, it was reported that capsaicinoids were more stable at alkaline conditions than acidic (Si et al. 2014). The temperature had a significant effect on the retention of capsaicinoids content ( $p < 0.05$ ), and as the temperature increased from 25 to 100 °C, the degradation of capsaicinoids was more intense, especially under a lower initial concentration of 200 ppm (Si et al. 2014). In general, capsaicin is the most stable capsaicinoids, followed by dihydrocapsaicin and nordihydrocapsaicin (Schweiggert, Schieber, and Carle 2006; Si et al. 2014; Yan et al. 2009).

### Identification of flavor precursors and formation mechanisms of flavors

Flavor precursors as originators of flavors do not render flavor properties (Baines and Seal 2012). However, the identification of these precursors and understanding of their flavor generation mechanisms could potentially shed light on new applications/products in the food industry.

#### Garlic and onion flavor precursors

For the allium plant, the different flavor precursors could produce different thiosulfinates, each imparting a distinct flavor. ACSOs are the main flavor precursors of garlic and onion flavors. These compounds are odorless and nonvolatile amino acids (Krest, Glodek, and Keusgen 2000). They usually include S-allyl cysteine sulfoxide (alliin, ACSO), S-methyl cysteine sulfoxide (methiin, MCSO), S-propyl cysteine sulfoxide (propiin, PCSO), and S-propenyl-L-cysteine sulfoxide (isoalliin, 1-PeCSO), as shown in Table 3 (Jones et al. 2004). Moreover, the study showed that these four major derivatives of L-cysteine sulfoxide contributed significantly to the flavor, pungency, and lachrymatory characteristics of these plants.

More specifically, for garlic, the volatile components are released from their nonvolatile and odorless precursors. The predominant flavor precursor of garlic is alliin, with lower contributing concentrations of 1-PeCSO and MCSO and trace amounts of PCSO (Hughes et al. 2005; Ichikawa, Ide,

and Ono 2006; Ichikawa, Ide, Yoshida, et al. 2006). Garlic's alliin content is reported to be about 0.1–1.29%, which is dependent on the cultivar varieties, planting environment, and fertilizing practices (Iberl et al. 1990; Tang and Chen 2007).

For the onion, there are mainly three S-alkenyl cysteine sulfoxide flavor precursors: 1-PeCSO, MCSO, and PCSO (Table 3). Among these, 1-PeCSO usually has the highest concentration. This molecule is responsible for both pungency and the formation of pigment precursors of pink discoloration of onion. MCSO is normally present in low concentrations, and PCSO is only present in trace amounts (William Randle et al. 1995). However, a wide range of concentrations for these precursors are reported in the literature without the exact determination of onion varieties (Bacon et al. 1999; Resemann, Maier, and Carle 2004; Thomas and Parkin 1994).

#### Formation mechanisms of garlic and onion flavors

The formation mechanism of allium flavor mainly includes enzyme-mediated degradation of their nonvolatile precursors (i.e. S-alk(en)yl cysteine sulfoxides) (Ilić et al. 2011; Resemann, Maier, and Carle 2004), secondary reactions of primary flavor components (Wang et al., 2008), and thermal degradation of precursors (Kubec, Drhová, and Velíšek 1998, 1999), as shown in Figure 3.

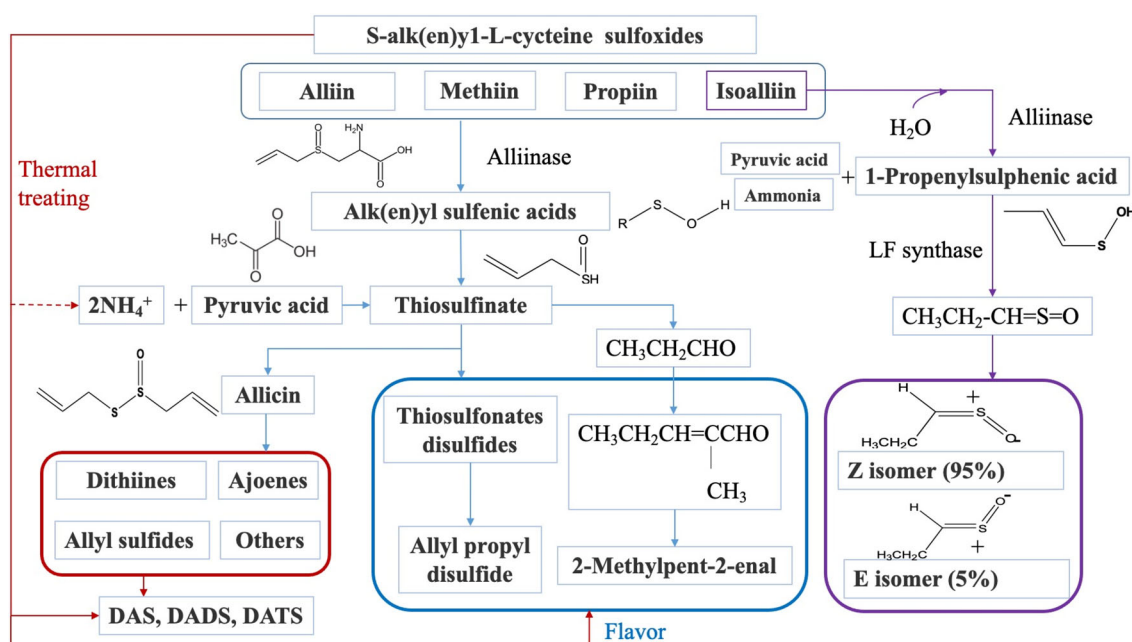
#### Enzymatic reaction of precursors

The sulfur compounds of the allium plants usually go through an enzyme-mediated degradation process with the substrate of nonvolatile precursors, including MCSO, ACSO, 1-PeCSO, and PCSO, when the allium is crushed or chopped (Amagase 2006; Koch and Lawson 1996; Reuter 1995).

As shown in Figure 3, the alliinase enzyme (EC 4.4.1.4) reacts with precursors, i.e. alliin, MCSO, PCSO, and 1-PeCSO to catalyze the  $\alpha$ ,  $\beta$ -elimination of precursors and subsequently produce alk(en)yl sulfenic acids (i.e. flavor intermediates), pyruvic acid, and ammonia. These alk(en)yl sulfenic acids are unstable and can rapidly rearrange to produce thiosulfinates, which could undergo further chemical reactions and cause the changes of alliums aroma over time (Sabiou et al. 2019).

**Table 3.** Major flavor precursors of garlic and onion.

Flavor precursor	Alternative name	Characteristic plant	Structure
S-allyl cysteine sulfoxide (ACSO)	Alliin	Garlic	
Trans-S-1-propenyl Cysteine sulfoxide (1-PeCSO)	Isoalliin	Onion	
S-methyl cysteine Sulfoxide (MCSO)	Methiin	Onion/garlic	
S-propyl cysteine Sulfoxide (PCSO)	Propiin	Onion/garlic	

**Figure 3.** The formation mechanism of allium flavors.

In garlic, alliin, the major flavor precursor of it, is catalyzed by alliinase and leads to the production of dehydroalanine and allyl sulfenic acid (2-propenesulfenic acid). Then, two molecules of allyl sulfenic acid condense spontaneously to one molecule of allicin, contributing to the characteristic flavor of fresh garlic (Ilić et al. 2011). Furthermore, allicin could undergo nonenzymic rearrangement to form the sulfides, sulfur dioxide, and thiosulfonates that affect garlic's flavor and garlic's flavor intensity (Wang et al. 2008).

In onion, the alliinase interacts with ACSOs, including MCSO, PCSO, and 1-PeCSO. 1-PeCSO is the major flavor precursor in onion and, with the help of alliinase can produce 1-propenylsulphenic acid, pyruvic acid, and ammonia.

On the one hand, 1-propenylsulphenic acid interacts with LF synthase to produce propanthial S-oxide (i.e. LF). In contrast, 1-propenylsulphenic acid is very unstable and can condense spontaneously to chiefly give thiosulfonates, 2-Methyl-2-pental, and zwiebelanes. The LF was detected only when alliinase, 1-PeCSO, and LF synthase are present in the reaction (Imai et al. 2002). Previous studies on the alliinase-mediated transformation of ACSOs showed that the levels of conversion for MCSO and 1-PeCSO are different (25–75% and 50–100%, respectively), apparently because of different environmental conditions such as temperature, time, water content, and onion cultivar (Resemann, Maier, and Carle 2004). Primary products of this reaction include

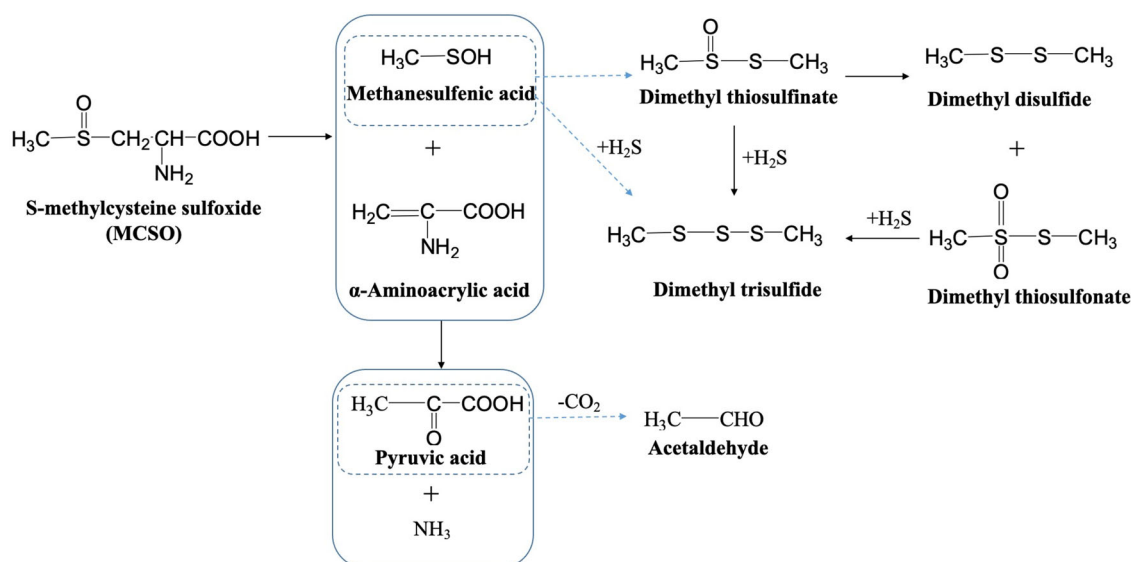


Figure 4. Thermal degradation pathway of MCSO (Kubec, Drhová, and Velíšek 1998).

intermediate alk(en)yl sulfenic acids, pyruvic acid, and ammonia (Resemann, Maier, and Carle 2004).

From the point of enzymatic reaction of precursors, more contents of flavor precursors (e.g. alliin, 1-PeCSO, PCSO) and optimum alliinase reaction conditions (e.g. 35 °C at pH 7) could enhance the flavor generation (Chhabria and Desai 2018; Krest, Glodek, and Keusgen 2000). Furthermore, the variety of garlic and onion cultivars can affect the precursors' chemical type and content (Bacon et al. 1999; Jones et al. 2004). Also, the studies confirmed that the concentration of alliin increases significantly with the extension of fertilization (Bloem, Haneklaus, and Schnug 2010, 2011).

### Degradation of primary flavor components

Due to the instability of the primary flavor compounds of allium, decomposition or condensation to secondary flavor compounds could take place. Secondary flavor compounds are those compounds derived from alk(en)yl thiosulfinates (Wang et al. 2008).

For garlic, alliin is very unstable and readily degrades to form secondary products, a variety of sulfides (e.g. diallyl disulfide and sulfur dioxide) (Amagase 2006; Iciek, Kwiecień, and Włodek 2009). The degradation of alliin depends on temperature, pH, and solvent (Fujisawa et al. 2008). Alliin is quite sensitive to higher temperatures. Studies show that alliin is stable at temperatures below 4 °C (Fujisawa et al. 2008). At higher temperatures (e.g. 20–42 °C), the alliin content decreased linearly (Fujisawa et al. 2008). Moreover, the degradation of alliin dramatically increased at temperatures higher than 50 °C (Chong et al. 2015). Also, alliin completely degrades to form sulfides after 30 min in boiling water, after 20 min stir-frying in olive oil, after 3 min in deep frying (180 °C), and after overnight heating at 75 °C (Chong et al. 2015; Prati et al. 2014). In addition, pH can influence the breakdown of alliin. Alliin is easily degraded at pH higher than 11 or lower than 1.5 (H. Wang et al. 2015). Also, studies showed that degradation rate of alliin varies in different solvents. Alliin is known to

be more stable in an aqueous solution than in an organic solvent (e.g. hexane) (Ilić et al. 2011; Lawson 1996; Lawson and Hughes 1992). Other studies showed that alliin in hexane or in vegetable oil degraded more rapidly than in ethanolic and acetone aqueous solutions (Cañizares et al. 2004; Fujisawa et al. 2008; Lawson, Wood, and Hughes 1991). The breakdown of alliin, together with other thiosulfinates contribute the most to the formation of the flavor compounds of garlic (Egen-Schwind, Eckard, and Kemper 1992; Rahman and Lowe 2006).

For the onion, the degradation products of primary flavor components are classified as oxygenated compounds, thiols, monosulfides, thiophenes, disulfides, trisulfides, and tetrasulfides. Among these secondary flavor compounds, methyl propyl disulfide, methyl propyl trisulfide, and dipropyl trisulfide were considered to play a major role in the onion flavor (Wang et al. 2008).

From the point of degradation of primary flavor components, the flavor formation of garlic and onion was related to the stability of primary flavor components (i.e. alk(en)yl thiosulfinates), which can be affected by the processing temperature, pH, and solvent (Fujisawa et al. 2008). However, there is a significant challenge to control the formation of specific flavor compounds during degradation of primary flavor components since relationships among conditions (e.g. temperature, time, and pH), flavor compounds, and sensory characteristics have not been fully understood.

### Thermal degradation of garlic and onion flavor precursors

Thermally generated products of ACSOs can significantly contribute to the aroma of allium flavors (Kubec, Drhová, and Velíšek 1998, 1999). The literature lacks detailed information on the thermal degradation mechanism of alliin and 1-PeCSO compared to MCSO. For MCSO, the thermal degradation pathway has been investigated, and it is reported that the thermal decomposition (from 80 °C to 200 °C, particularly higher than 120 °C) pathway is similar to its enzymatic decomposition pathway (Kubec, Drhová, and



**Table 4.** Thermal degradation of garlic and onion flavor precursors under different conditions.

Precursor	Flavor/volatile compounds	Temperature (°C)	pH	Water content	Time (min)	References
MCSO	Dimethyl disulfide: 102.52 mg/g Pyridine: 0.32 mg/g Dimethyl trisulfide: 11.81 mg/g	160	n/a	10%	60	(Kubec, Drhová, and Velíšek 1998)
	Dimethyl disulfide: 11.18 mg/g Dimethyl trisulfide: 1.00 mg/g No pyridine	100	n/a	10%	60	
	Dimethyl disulfide: 12.95 mg/g Dimethyl trisulfide: 6.60 mg/g	120	n/a	5%	60	
PCSO	Dipropyl disulfide Dipropyl trisulfide Propylthiol Dipropyl thiosulfonate	100–200	n/a	10–40%	60	(Kubec, Drhová, and Velíšek 1999)
Alliin	Diallyl sulfides (mono-, di-, tri-, and tetrasulfide) Allyl alcohol	80–140	n/a	In aqueous solution	4 —60	(Kubec et al. 1997)
	Diallyl sulfides (mono-, di-, tri-, and tetrasulfide) Allyl alcohol Sulfur-containing cyclic compounds, namely: 2,5-dimethyl-1,4-dithianes 2-methyl-1,4-dithiepane Dimethyl-1,2,5-trithiepanes	> 140	n/a		60	
	Dioxanes Methyl sulfides 2-acetylthiazole Methyl-1,2,3-trithiacyclopentane Methyl-1,2,3,4-tetrathiacyclohexane predominate	180	5	0.005 mol of alliin was dissolved in 100 ml distilled water	60	(Yu et al., 1993)
	Acetal 2-methylpyridine 1,2,3,4-tetrathiacycloheptane	180	3		60	
	3,5-dimethyl-1,2,4-trithiolane 2,4,6-trimethylperhydro-1,3,5-dithiazine 4-ethyl-6-methyl-1,2,3,5-tetrathiacyclohexane	180	7 or 9		60	

Velíšek 1998). The breakdown products of MCSO sulfoxide, such as dimethyl thiosulfinate, pyruvic acid, and ammonia, are similar in the thermal as well as enzymatic decomposition pathways, confirming that the thermal degradation of precursors can also contribute to the aroma (Figure 3: Dashed and solid red arrows) (Kubec, Drhová, and Velíšek 1998).

As shown in Figure 4, under thermal treatment (80–200 °C), firstly, MCSO breaks down into  $\alpha$ -aminoacrylic acid and methanesulfenic acid (Kubec, Drhová, and Velíšek 1998). The  $\alpha$ -aminoacrylic acid could be spontaneously hydrolyzed to generate ammonia and pyruvic acid, which might be further decarboxylated to acetaldehyde. The methanesulfenic acid could go through self-condensation to form dimethyl thiosulfinate, which is the key breakdown product. Dimethyl thiosulfinate can then be easily decomposed into dimethyl thiosulfonate and dimethyl disulfide. Dimethyl thiosulfonate and hydrogen sulfide can further generate dimethyl trisulfide. Dimethyl trisulfide can also be generated *via* the other two pathways: methanesulfenic acid and dimethyl thiosulfinate (Chin and Lindsay 1994). However, the most important step in producing dimethyl trisulfide is the degradation of dimethyl thiosulfinate using hydrogen sulfide, especially when the temperature is kept between 120–200 °C (Chin and Lindsay 1994; Kubec, Drhová, and Velíšek 1998).

The thermal decomposition of PCSO is similar to MCSO (Kubec, Drhová, and Velíšek 1999). During the first step of the formation of the volatile compound, PCSO cleaves into  $\alpha$ -aminoacrylic acid and propanesulfenic acid at high temperatures (80–200 °C) (Kubec, Drhová, and Velíšek 1999). Then, the hydrolyzation of  $\alpha$ -aminoacrylic acid leads to the spontaneous formation of ammonia and pyruvic acid. The self-condensation of propanesulfenic acid produces dipropyl thiosulfinate. Dipropyl thiosulfinate is reported to be an important breakdown intermediate that could further decompose into dipropyl disulfide, dipropyl thiosulfonate, and dipropyl trisulfide (Kubec, Drhová, and Velíšek 1999).

From the point of thermal degradation of flavor precursors, different types of flavor precursors (e.g. alliin, 1-PeCSO, MCSO, PCSO) can generate different flavor components under different processing conditions, including thermal temperature, time, pH, and water content (Kubec, Drhová, and Velíšek 1998, 1999; Kubec et al. 1997; Yu et al. 1994). Detailed information is explained in Section “Garlic and onion flavors generation through thermal treatment,” as shown in Table 4. However, the thermal degradation mechanisms of different precursors and the relationships between processing conditions and specific flavor compounds are not well researched and should be investigated in future work.

### Chili pepper flavor precursors

The flavor precursors of capsaicinoids are phenylalanine and branched-chain fatty acid, including (*E*)-8-methyl-6-nonenic acid and vanillylamine (Narasimha Prasad et al. 2006). Although (*E*)-8-methyl-6-nonenic acid occurs at lower concentrations compared to vanillylamine, but it is a key substrate for capsaicinoids synthesis (Narasimha Prasad et al. 2006) and consequently the hotness of chili pepper. It is worthy of mentioning that the contents of capsaicinoids in ripe pepper depend on the genotype and environment (Garcés-Claver et al. 2007; Zewdie and Bosland 2000).

### Formation mechanisms of chili pepper flavor

Capsaicinoids can be synthesized by enzymatic condensation of vanillylamine and different-sized fatty acid chains (medium-chain fatty acid), which are elongated by a fatty acid synthase (Thiele, Mueller-Seitz, and Petz 2008). The capsaicin synthase enzyme requires magnesium ion ( $Mg^{2+}$ ), adenosine triphosphate (ATP), coenzyme A, and vanillylamine for its enzymatic activity. Vanillylamine is the phenolic portion formed from phenylalanine as a product in the phenylpropanoid pathway. The fatty acid is formed from the amino acid valine or leucine (Reyes-Escogido, Gonzalez-Mondragon, and Vazquez-Tzompantzi 2011). The transamination of those amino acids to 2-oxocarboxylic acids followed by decarboxylation leads to isovalerate and isobutyrate (Thiele, Mueller-Seitz, and Petz 2008). The nature of the lateral fatty acid chain defines the structural differences among the capsaicinoids, which range from 9 to 11 carbon atoms long with a variable number of double bonds located in different positions along the chain (Reyes-Escogido, Gonzalez-Mondragon, and Vazquez-Tzompantzi 2011).

In general, there is limited study on generating chili flavor (capsaicinoids) from flavor precursors during food processes, and most of the available researches focused on extraction rather than synthesis of the capsaicinoids.

### Production of flavor precursors and the regeneration of flavors

In this section, different methods to generate flavor precursors and flavors, especially those consisted of clean-label methods, are discussed. And this may potentially help create a link between food processing and flavor generation.

### Garlic and onion flavor precursors production

There are usually three kinds of methods for the production of flavor precursors, such as tissue culture, chemical synthesis, and the extraction of the precursor from allium vegetables (Jiang et al. 2014). Tissue culture is out of the scope of this review. So, the rest two methods are discussed in detail below.

### Chemical synthesis methods

Alliin, a major precursor of garlic flavor, was first chemically synthesized in 1951. It was synthesized from L-cysteine, ethanol, sodium hydroxide, and allyl bromide. Briefly, deoxyalliin was first synthesized from L-cysteine and allyl bromide. It was then purified by recrystallization in ethanol. The obtained deoxyalliin (>95%) was finally oxidized with hydrogen peroxide to form alliin (Hakamata et al. 2015; Nikolić et al. 2012).

1-PeCSO, as a key component of the onion flavor precursor, has been synthesized by several research groups (Jayathilaka et al. 2014, 2015; Lanzotti 2006; Namyslo and Stanitzek 2006). In a recent study, the main configuration of 1-PeCSO, (+)-*trans*-1-PeCSO, was prepared by 3-step chemical synthesis and purified by reversed-phase-high performance liquid chromatography (RP-HPLC). First, L-cysteine and allyl bromide were used to form deoxyalliin, which then underwent a base-catalyzed reaction to isomerize to a mixture of *cis* and *trans* deoxyisoalliin. The *trans* form was separated by RP-HPLC afterward and oxidized by  $H_2O_2$  to form a mixture of (–)- and (+)-*trans*-1-PeCSO. Finally, RP-HPLC was used again to separate (–)- and (+)-*trans*-1-PeCSO (Jayathilaka et al. 2014).

### Extraction of flavor precursors

The extraction of flavor precursors from raw materials is a viable option to mitigate the purchase of expensive flavor precursors and obtain precursors that are not readily available in the market. Alliin can be extracted from garlic after deactivation of the enzyme alliinase (Dethier et al. 2012). However, partial deactivation of alliinase enzyme could cause alliin's degradation. Several techniques have been adapted to deactivate the enzyme (Lawson and Wang 2001; Li, Xu, and Sun 2007; Zhang et al. 2013). The blanching process (i.e. boiling in water for 20 min) was used to deactivate the alliinase (Zhang et al. 2013). Alliin was then extracted and purified by ultrafiltration and column chromatography (cation exchange resin 732,  $2.5 \times 50$  cm) from garlic. In another method, a microwave (500 W) oven was used (30 min/3 g) to deactivate the alliinase, followed by soaking the microwaved garlic in a water bath to extract alliin (Hakamata et al. 2015). As the final step, column chromatography (silica gel) was employed to purify alliin (Hakamata et al. 2015).

The precursor alliin can also be extracted from dry powder through solvent extraction. A study reported that the extracted alliin from garlic lyophilization powder (1.0 g) by  $CH_2Cl_2$ /EtOH/MeOH/ $H_2O$  (12:3:1:0.5, v/v, 10 mL) for 30 min and 30.9 mg crude residue was obtained and purified by column chromatography on silica gel ( $CH_2Cl_2$ /EtOH/MeOH/ $H_2O$ /CF<sub>3</sub>COOH, 12:3:1:0.5:0.5, v/v) to gain 14.7 mg of alliin (Hakamata et al. 2015). Moreover, in other studies, dry garlic powder was used to extract alliin by methanol-water (80:20, v/v) solution. To enhance the recovery, keeping the pH of the solution in the lower range of 3.0 was recommended (Arnault et al. 2003; Hakamata et al. 2015; Nasim et al. 2009). To increase the alliin production yield and further purification using garlic powder, a two-step

process combining aqueous two-phase extraction (ATPE) was utilized. In ATPE, 19% (w/w)  $(\text{NH}_4)_2\text{SO}_4$ , 20% (w/w) 1-propanol, at 30 °C, and pH 2.35 with 8.54% (w/w) NaCl were used. The ammonium form of sulfonic acid cation-exchange resins 001  $\times$  7 was exploited. The recovery and purity of alliin after purification were reported 76% and 80%, respectively (Jiang et al. 2014).

There is limited information on the production of flavor precursors by directly extraction from the fresh or dried garlic and onion because of the lower yield. In addition, before extraction, extra processing should be carried to deactivate the enzyme alliinase. Among these extraction solvents, ethanol and water is preferred in food applications considering the safe and environmentally friendly process (Nasim et al. 2009; Zhang et al. 2013).

It is noteworthy that chemical synthesis is usually faster, straightforward, and efficient compared to extraction methods. However, the chemical synthesis yields, unfavorably, a diastereomeric mixture of sulfoxides (sulfur and  $\alpha$ -carbon atom being *R* and *R*, or *S* and *R*) that could potentially interfere with the major precursor molecules configuration (*S* configuration of sulfur and  $\alpha$ -carbon atom) (Hakamata et al. 2015).

### Garlic and onion flavors generation through thermal treatment

Garlic and onion flavors generation usually included the extraction from garlic and onion, chemical synthesis, or thermal treatment of flavor precursors or allium vegetables. In this review, we primarily focus on the thermal method as it can be broadly integrated into various food processing. Thermal treatment of flavor precursors could be a cost-effective and readily accessible method to generate garlic and onion flavors. The thermal treatment causes the emission of volatile compounds that contribute to desired garlic and onion flavors. Table 4 shows the garlic and onion flavor precursors and their degradation process at various temperatures, pH, water content, and time.

In garlic, alliin and deoxyalliin are the major precursors and significantly contribute to the garlic flavor when treated thermally (Kubec et al. 1997; Yu et al. 1994). Alliin is less stable than deoxyalliin at high temperatures. This is due to the unstable sulfoxide bond of alliin. This generates much more volatile compounds converted from alliin compared with deoxyalliin (Kubec et al. 1997). Although the temperature is a key factor, other factors such as water activity and pH contribute to alliin and deoxyalliin degradation (Kubec et al. 1997; Yu et al. 1994; Zhang et al. 2013). Diallyl sulfides (mono-, di-, tri-, and tetrasulfide) and allyl alcohol play a major role in volatile compounds generated by thermal degradation of alliin and deoxyalliin under 80–200 °C, especially between 100 and 160 °C (Kubec et al. 1997). Other important degradation products—that are formed between 140 and 200 °C in particular—were noted as sulfur-containing cyclic compounds, namely 2,5-dimethyl-1,4-dithianes, 2-methyl-1,4-dithiepane, and dimethyl-1,2,5-trithiepanes (Kubec et al. 1997).

The thermal treatment of 1-PeCSO as a major precursor of onion has not been thoroughly discussed in the context of flavor generation. Dimethyl disulfide is the principle volatile compound formed by thermal decomposition of MCSO under the temperature range of 100–160 °C, which accounts for 60% of the total generated volatiles. Dimethyl trisulfide, the second most abundant volatile, can be generated on a considerably smaller scale, and its production can be increased when heated under 160 °C compared with 100 °C. Moreover, other minor decomposition compounds such as dimethyl thiosulfinate, dimethyl thiosulfonate, and alkyl- and alkylthio-substituted pyridines can be formed (Kubec, Drhová, and Velíšek 1998).

PCSO is a rather thermolabile amino acid containing a sulfoxide group. Like MCSO, temperature, time of heating, and water content in the reaction system can all affect the thermal degradation of PCSO. It decomposes almost completely during 1 h of heating at 120 °C in the presence of 10–40% of water. The molecule can be degraded more slowly when heated dry or in more diluted samples. The dipropyl disulfide, dipropyl trisulfide, and propanethiol are the major volatile compounds and account for greater than 79% of total volatiles when the heating temperature ranges from 100 to 200 °C. Increasing the heating temperature from 100 to 200 °C progressively increases the propanethiol content (Kubec, Drhová, and Velíšek 1999).

Some of the degradation compounds generated from the precursors in thermal treatments (Table 4) are quite like the flavor compounds generated from processed garlic and onion (Table 1). This phenomenon confirms that the products of the non-enzymatic breakdown (thermal treatment for a certain time (4–60 min), at different temperature of 80–200 °C and water activity) of ACSOs could potentially participate in the characteristic flavor of processed allium vegetables (Abe, Hori, and Myoda 2019; Kubec, Drhová, and Velíšek 1999; Kubec et al. 1997).

### Garlic and onion flavor extraction methods

Conventionally, steam distillation, enzyme-assisted extraction, and supercritical fluid extraction (SFE) have been employed for extraction of garlic and onion flavors, as shown in Table 5 (Dron et al. 1997; Lee, Kim, and Lee 2003; Salina et al. 2013). Steam distillation is the most widely used flavor extraction method. This method is simple and cost effective, but the yield and quality are usually low (Dron et al. 1997; Satyal et al. 2017; Takahashi and Shibamoto 2008). A study compared the volatile oils extracted from the bulbs of garlic by three different methods: laboratory hydrodistillation (3 h, 0.2% yield), industrial hydrodistillation (4 h, 0.22% yield), and industrial steam distillation (5 h, 0.18% yield) (Satyal et al. 2017). The results showed that the oils were dominated by allyl polysulfides, including diallyl sulfide (1.9–9.5%), diallyl disulfide (20.8–27.9%), diallyl trisulfide (16.8–33.4%), allyl methyl disulfide (4.4–8.3%), and allyl methyl trisulfide (14.5–19.2%).

In enzyme-assisted extraction, enzymes such as cellulase and pectinase are usually applied to garlic or onion before

**Table 5.** A summary of different extraction methods about garlic and onion flavors.

Plant	Extraction methods	Extraction conditions	Results	References
Garlic	Steam distillation	Finely chopped garlic bulbs, 3 h.	Diallyl sulfide (1.9%), diallyl disulfide (20.8%), diallyl trisulfide (33.4%), allyl methyl disulfide (4.4%), and allyl methyl trisulfide (19.2%).	(Satyal et al. 2017)
	Industrial hydrodistillation	Finely chopped garlic bulbs, 4 h.	Diallyl sulfide (3.4%), diallyl disulfide (25.9%), diallyl trisulfide (31.2%), allyl methyl disulfide (5.2%), and allyl methyl trisulfide (14.5%).	
	Industrial steam distillation	Finely chopped garlic bulbs, 5 h.	Diallyl sulfide (9.5%), diallyl disulfide (27.9%), diallyl trisulfide (16.8%), allyl methyl disulfide (8.3%), and allyl methyl trisulfide (17.7%).	
	Traditional simultaneous distillation extraction	Distillation time of 2 h, cooled at $-10^{\circ}\text{C}$ diethyl ether.	Yield of 0.23 g oil/100 g garlic, diallyl sulfides of 51.8%, methyl allyl sulfides of 25.6%, vinyl dithiins of 4.7%.	(Kimbaris et al. 2006)
	Microwave-assisted hydrodistillation extraction	Diethyl ether distillation time of 30 min, with LG 700 W max power household microwave oven.	Yield of 0.22 g oil/100g garlic, diallyl sulfides of 27.7%, methyl allyl sulfides of 23.2%, vinyl dithiins of 33.6%.	
	Ultrasound-assisted extraction	Diethyl ether fixed-frequency of 35 kHz, temperature of the sonicated bath was $25^{\circ}\text{C}$ , sonication time of 30 min.	Yield of 0.13 g oil/100 g garlic diallyl sulfides of 8.7%, methyl allyl sulfides of 0.7%, vinyl dithiins of 70.8.	
	Enzyme-assisted extraction	Enzyme + steam distillation 400 g crushed garlic treated with the selected enzymes (cellulose 0.5%, pectinase 0.5%, protease 0.5%, and viscozyme 1% individually). pH 4.5–5.0, incubated at $50 \pm 2^{\circ}\text{C}$ for a period of 90 min, then steam distillation at $100^{\circ}\text{C}$ for 3 h.	Yield: cellulose (0.39%), pectinase (0.51%), protease (0.50%), viscozyme (0.46%), control (0.28%). A near two-fold increase in the yield of oil compared to distillation with little change either in flavor or physicochemical properties of the oil.	
Enzyme + hydrodistillation cellulase, pectinase, protease, viscozyme distilled for 3 h		Yield: cellulose (0.45%), pectinase (0.57%), protease (0.55%), viscozyme (0.50%), control (0.31%). A near two-fold increase in the yield of oil compared to distillation with little change either in flavor or physicochemical properties of the oil.		
Onion	Supercritical fluid extraction using carbon dioxide	$35\text{--}50^{\circ}\text{C}$ , 30–40 MPa.	Yield: 1%.	(Del, Mena, and Budinich 2008)
	Steam distillation	30 g freeze-dried onion mixed with 1.5 L boiling deionized water until collecting 500 mL water distillate.	71 volatile compounds, 24 sulfur-containing volatile compounds.	
	Supercritical fluid extraction using carbon dioxide	200 g crushed onion, $35^{\circ}\text{C}$ , 20 MPa, 100- 150 STP mL/min $\text{CO}_2$ , 5 h.	28 sulfur-containing volatile compounds. Have characteristic fresh onion-like smell, different compounds detected compared with steam distillation.	(Sinha et al. 1992)
			$37^{\circ}\text{C}$ , 24.5 MPa), 0.89 g/cm $\text{CO}_2$ .	Yield: 0.0324% (weight basis). Higher yields, better quality, and unique fresh onion-like flavor.

extraction to help increase the yield of volatile compounds (Salina et al. 2013; Sowbhagya et al. 2009). The highest oil recovery (18.38%) was obtained by sample extracted with amylase and cellulase after 16 h at  $65^{\circ}\text{C}$  (Salina et al. 2013). Garlic volatile oil compounds extracted by hydrodistillation or enzyme-pretreated coupled with steam distillation/hydrodistillation were similar confirmed by GC–MS. The result showed that the enzyme pretreatment resulted in increase in the concentration of dithiins from 1.85% to 7.97% (Sowbhagya et al. 2009). However, the high cost of enzymes in industrial scale could lead to a major

limitation of this method (Salina et al. 2013; Sowbhagya et al. 2009).

SFE is another common extraction method for garlic and onion flavor compounds. Carbon dioxide is frequently used as the supercritical solvent for extraction since it is nontoxic and available in high purity at a relatively low cost (Worsfold et al. 2019). However, SFE's equipment is expensive (Worsfold et al. 2019). In the case of garlic and onion, more thermal liable flavor compounds, including allicin, diallyl thiosulfinate, and propyl methanethiosulfonate, can be extracted, resulting in a fresh garlic/onion-like flavor since



extraction temperature is controlled (e.g. 35 °C) (Del Valle, Mena, and Budinich 2008; Sinha et al. 1992). A study reported that extraction temperature (35–65 °C) and pressure (10–45 MPa) had a significant and positive effect on yield, but sulfur content was higher in extracts obtained at 10 MPa than at 30 MPa. Sulfur content also increased with process temperature in experiments carried out at 30–40 MPa (Simándi et al. 2000). Another research reported the optimum SFE-CO<sub>2</sub> conditions at 35–50 °C and 30–40 MPa based on yield and quality (Del Valle et al., 2008).

Extraction methods can significantly affect the flavor compounds. A study of traditional simultaneous distillation extraction (SDE, harsh thermal treatment), microwave-assisted hydrodistillation extraction (MWHd, short-time thermal), and ultrasound-assisted extraction (UAE, room-temperature isolation) was carried out to compare the extracted garlic volatile compounds (Kimbaris et al. 2006). The essential oils obtained by SDE contained more R-substituted polysulfides and fewer vinyl dithiin components than those isolated by the MWHd and UAE methods. The garlic oil by SDE is richer in diallyl disulfide (DADS, 28.4%), followed by diallyl trisulfide (DATS, 20.4%), methyl allyl trisulfide (MATs, 16.3%). For MWHd, DADS was the primary volatile (17.6%), followed by MATs (14.1%), 2-vinyl-[4H]-1,3-dithiin (2-VST, 17.7%), and 3-vinyl-[4H]-1,2-dithiin (3-VDT, 15.9%). For UAE, the major essential oil components were found to be 2-vinyl-[4H]-1,3-dithiin (38.1%) and 3-vinyl-[4H]-1,2-dithiin (32.7%). Generally, the difference in the flavor components is closely related to the thermal treatment intensity.

### Chili pepper flavor precursors production

Production of chili flavor precursors is suffering from a lack of detailed analysis. Vanillylamine and (*E*)-8-methyl-6-nonenic acid are the two main flavor precursors (Narasimha Prasad et al. 2006). Vanillin and 6-bromohexanoic acid are the main raw chemical compounds needed to synthesize the flavor precursors (Kaga, Miura, and Orito 1989). Although these two raw materials are available in the market, their use is not cost-effective in large-scale production. In addition, toxic condensing and catalytic agents such as chloroform and isobutylaldehyde are also needed to facilitate the process (Kaga, Miura, and Orito 1989).

### Chili pepper flavor generation

For the spicy flavor, capsaicinoids, there is not a clear definition and determination of its precursors. In the literature, there are three ways to generate capsaicinoids: chemical synthesis, extraction, and biosynthesis, the latter being out of the scope of this review. The first two methods are going to be discussed below.

### Chemical synthesis method

The chemically synthesized capsaicinoids method has been adopted by some researchers; however, procedures are quite

complicated and need some toxic agents. The study shows that 6-bromohexanoic acid, triphenylphosphine, isobutyl aldehyde, vanillin, and ammonium formate are needed for the chemical synthesis of capsaicin (Kaga, Miura, and Orito 1989). In another research, 4-hydroxy-3-methoxy benzylamine hydrochloride, undecanoic acid, and tridecanoic acid are the main chemicals needed to obtain capsaicinoids in 48–63% yields (Barbero et al. 2010). Nevertheless, their applications in food processing is restricted due to the use of non-food-grade condensing and catalytic agents such as chloroform (Barbero et al. 2010; Kaga, Miura, and Orito 1989).

### Extraction method

Capsaicinoids can be extracted from pepper by adopting a food-safe method. However, where the use of non-food-grade solvents is necessary, the separation method can be adopted by making sure to remove the residual solvents to the permissible concentration. The capsaicinoids can be extracted by organic solvents, such as hexane, ethyl acetate, acetone, chloroform, methanol, and ethanol (Barbero, Palma, and Barroso 2006; Chinn, Sharma-Shivappa, and Cotter 2011; Collins, Wasmund, and Bosland 1995). The study shows that the level of extracted capsaicinoid was in the following order: hexane > ethyl acetate > acetone > methanol; and the maximum amounts of capsaicin and dihydrocapsaicin were extracted in hexane, ranging from 35.1 to 2495 µg/g and 16.8 to 1016 µg/g, respectively (Bae et al. 2012). However, among different solvents, ethanol is preferred in food applications considering environmental risks and chemical and toxicological limitations. Also, it was reported that 96% ethanol could extract 80% of capsaicinoids which makes ethanol a promising solvent compared to hexane in large-scale production (Santamaria et al. 2000). In another study, ethanol was used to extract capsaicinoids from fresh red peppers, and the extracted materials were reported to have high concentrations of capsaicin and dihydrocapsaicin (25.15 mg/L) (Dong et al. 2014). Typically, the organic solvent extraction requires large samples (e.g. 20 g), large volumes (up to 300 ml), intensive labor work (requiring several pretreatment steps per sample), and long (2–24 h) extraction time (Williams et al. 2004).

Moreover, the extraction methods can be assisted with different techniques. It is reported that microwave-assisted extraction (MAE) yields a significantly higher concentration of extracted compounds compared to the magnetic stirring methods (Williams et al. 2004). It was also confirmed that the extraction-based MAE is a much faster method compared to traditional methods of extraction, such as magnetic stirring (Barbero, Palma, and Barroso 2006). As shown in Table 6, the study was reported that more than 95% of the quantities of capsaicinoids could be obtained with 30 min of extraction employing magnetic stirring or by 5 min MAE (Barbero, Palma, and Barroso 2006). MAE extraction method can be performed very rapidly and characterized by a huge reduction of the energy required and of the solvent consumed. However, MAE requires expensive equipment



**Table 6.** A summary of different extraction methods for Chili pepper.

Extraction method	Compounds	Extraction condition	Efficiency	Advantage	References
Microwave-assisted extraction	Capsaicin and dihydrocapsaicin	2 g pepper samples in 20 ml acetone, 150 W, 3 min	Capsaicin: 0.48 mg/g FW; dihydrocapsaicin: 0.27 mg/g FW.	Approximately double the yield compared with reflux or shaking.	(Williams et al. 2004)
	Capsaicin, DHC, n-DHC, h-DHC, h-C	0.5 g of triturated fresh peppers in 25 mL ethanol, 125 °C, 500 W, 5 min	Capsaicin: 451.6 $\mu$ mol/kg; DHC: 265.1 $\mu$ mol/kg; n-DHC: 93.8 $\mu$ mol/kg; h-DHC: 46.8 $\mu$ mol/kg; h-C: 29.6 $\mu$ mol/kg	Reduced the extraction time, 5 min MAE has similar yield compared to 30 min magnetic stirring extraction.	(Barbero, Palma, and Barroso 2006)
Ultrasound-assisted extraction	Capsaicinoids	1 g dried powder in 5 ml of 95% ethanol, 45 °C, 35 kHz, 3 h	Recovery percentage: 87.4%	Shorter extraction time compared to maceration (15 h) and Soxhlet (5), higher recovery.	(Boonkird, Phisalaphong, and Phisalaphong 2008)
	Capsaicinoids	2 g of dried <i>C. frutescens</i> L. in 200 ml ethanol, 40 kHz-ultrasonic, 20 min	Capsaicinoids: 4.01 mg/g dried samples	Required minimum energy consumption; energy consumption per capsaicinoid, ultrasound-assisted extraction: 25.411 kJ/mg; microwave-assisted extraction: 72.700 kJ/mg; Soxhlet method: 4119.779 kJ/mg.	(Chuichulcherm et al. 2013)
Supercritical fluid extraction	Capsaicin and dihydrocapsaicin	5 g freeze-dried peppers, CO <sub>2</sub> , 15 MPa, 40 °C	Capsaicin: 42 mg/g; dihydrocapsaicin: 18.5 mg/g	Higher yield.	(De Aguiar et al. 2013)
	Capsaicin and dihydrocapsaicin	Hot peppers, CO <sub>2</sub> , 15 Mpa, 40 °C	Capsaicin: 1.83 mg/g; dihydrocapsaicin: 1.00 mg/g	Yield increased up to 77%.	(Santos et al. 2015)
Enzymatic assisted-extraction process	Capsaicin	Fresh green chili, enzyme: Viscozyme L, ethanol, 45 min, pH 4.5, between 40 and 50 °C	Capsaicin efficiency: 71.2%	Higher efficiency.	(Baby and Ranganathan 2016)
	Capsaicin	Fresh green chili, enzyme: Cellulclast, ethanol, 45 min, pH 4.5, between 40 and 50 °C	Capsaicin efficiency: 70.5%		
	Capsaicin	Fresh green chili, enzyme: Pectinex, ethanol, 45 min, pH 4.5, between 40 and 50 °C	Capsaicin efficiency: 70.5%		
	Capsaicin	Fresh green chili, enzyme: Protease, ethanol, 45 min, pH 4.5, between 40 and 50 °C	Capsaicin efficiency: 70.6%		

compared to organic solvent extraction (Williams et al. 2004). Apart from the microwave power, temperature, and time, the effectiveness of MAE also depends on the capacity of the extraction solvent to absorb and transmit the microwave energy. The addition of small quantities of water to the extraction solvents improves the extracting properties since water is a very polar solvent that will be capable of absorbing a large amount of microwave energy (Barbero, Palma, and Barroso 2006). At present, MAE has not been widely used for capsaicinoids extraction, and it has been more used as a sample preparation step for HPLC analysis (Fabela-Morón et al. 2020).

Ultrasound-assisted extraction (UAE) is another simple and cost-effective assisted method to improve the extraction of capsaicinoids (Barbero et al. 2008). UAE could reduce the extraction time since the cavitation

phenomenon in UAE improves the accessibility of the solvent on the surface of the sample by imploding the bubbles; and eventually enhancing the extraction (Barbero et al. 2008). It was reported that UAE could be applied on a large scale and shorten the extraction time at a lower operating temperature compared to conventional industrial hot maceration process (Boonkird, Phisalaphong, and Phisalaphong 2008). High temperature is not beneficial for UAE, because the capsaicinoids can be damaged above 75 °C (Fabela-Morón et al. 2020). The study reported that the optimum conditions for capsaicinoid extraction from 1 g dried chili pepper powder in an ultrasonic bath with a frequency of 35 kHz, were using 5 ml of 95% (v/v) ethanol at 45 °C. The extraction efficiency was reported 85% in 3 h of extraction process (Boonkird, Phisalaphong, and Phisalaphong 2008).

In a large-scale comparative study on the extraction of capsaicinoids using MAE and UAE, it was found that although UAE is cost-effective and has a lower energy consumption, MAE extraction resulted in 30% more capsaicinoids production (Chuichulcherm et al. 2013).

The SFE using carbon dioxide can be employed for the extraction of capsaicinoids. In general, the temperature, pressure, time, co-solvent, and supercritical carbon dioxide flow rate affect the yield and purity of capsaicinoids (Fabela-Morón et al. 2020). More specifically, using the SFE technique led to getting a higher yield of C and DHC (42 mg/g and 18.5 mg/g, respectively) at pressures as low as 15 MPa (De Aguiar et al. 2013). The combination of UAE and SFE could increase the extraction yield and rate of capsaicinoids. The study shows that the yield of capsaicinoids increased up to 77% when ultrasound waves coupled with SFE process, while the variation of ultrasound parameters (such as the power of 200–360 W, time of 60–240 min) has no effect on the extract efficiency (Santos et al. 2015). Another study found that only pressure was a key factor affecting the extraction efficiency of capsaicinoids in both SFE and SFE-UAE techniques. The capsaicinoid yield was enhanced with ultrasound by 12% at the condition of SEF temperature of 40 °C, the pressure of 25 MPa, and ultrasonic power of 200 W, ultrasonic time of 40 min (Dias et al. 2016).

The enzymatic assisted-extraction process is another technique reported in the literature. For this process, various commercially available enzymes such as Olivex (Santamaria et al. 2000), Celluclast (Baby and Ranganathan 2016; Santamaria et al. 2000), Viscozyme L (Baby and Ranganathan 2016; Santamaria et al. 2000), and Peczyme 5XAL (Santamaria et al. 2000) have been reported. It was reported that the extraction rate could be improved significantly to about 87% for capsaicinoids (Salgado-Roman et al. 2008; Santamaria et al. 2000).

The different extraction methods, including organic solvents extraction, MAE, UAE, SFE, and enzymatic assisted extraction, would affect the extraction efficiency of capsaicinoids (Boonkird, Phisalaphong, and Phisalaphong 2008). The content of each capsaicinoid (e.g. capsaicin, dihydrocapsaicin, nordihydrocapsaicin, and homocapsaicin) varies with different extract methods (De Aguiar et al. 2013; Williams et al. 2004). Detailed information about different extraction methods was shown in Table 6. It is noteworthy to mention that other factors, including process safety, usage and the residual amount of organic solvent, and economic issues should also be considered in the selection of proper extraction methods.

### Characterization of flavors and their precursors

The accurate characterization of flavors and understanding of their physicochemical properties provides insights into flavor stability. Such information also sheds light on flavor precursors and flavor generation mechanisms. This section reviews the available characterization methods for flavors and their precursors.

### Characterization of garlic and onion flavors and their precursors

Although several studies have been focused on the identification of various cysteine sulfoxides sub-groups, including ACSO, MCSO, and 1-PeCSO in garlic and onion; however, the literature lacks a detailed understanding of cysteine sulfoxides characterization.

As discussed above, alliin is rapidly converted by alliinase into allicin, ammonia, and pyruvic acid (Chhabria and Desai 2018). Therefore, ammonia and pyruvic acid can be used as markers for alliin determination. This alliinase enzyme method is inaccurate and time-consuming. A direct quantitative characterization of alliin has been suggested using liquid chromatography (LC) equipped with ultraviolet (UV) detectors (Chen et al. 2017; Lee et al. 2014) and gas chromatography (GC) (Hayashi, Sano, and Ohsumi 1993).

Using chromatography techniques for allicin characterization was encountered a challenge of finding suitable (i.e. commercially available) standard chemicals due to allicin's instability. High-performance liquid chromatography (HPLC) was employed by using purified allicin to obtain the standard curve (Iberl et al. 1990). Moreover, to quantitatively determine allicin without an external standard, a spectrophotometric method based on the reaction between allicin and thiol was established (Han et al. 1995; Miron et al. 1998). Over the past few decades, the LC methods have been optimized and developed to quantitatively fill the gap in alliin and allicin characterization since the availability of commercial allicin standards (Fujisawa et al. 2008; Zhu et al. 2016).

Some other approaches, including ultra-performance liquid chromatography (UPLC), liquid chromatography coupled with mass spectrometry detection (LC-MS) (Calvey, Roach, and Block 1994; Fujisawa et al. 2008; Zhu et al. 2016), high-performance thin-layer chromatography (HPTLC), capillary electrophoresis (CE), HPLC-multiple MS without derivatization (Arnault et al. 2003; Horie and Yamashita 2006), infrared, and Raman spectroscopy have been used to characterize alliin and allicin (X. Wang et al. 2013). Table 7 shows more detailed information about characterization techniques that have been used for garlic and onion flavors and their precursors.

### Characterization of chili pepper flavor – capsaicinoids

There are many ways reported in the literature to characterize capsaicinoids. Among all, HPLC is considered to be the most reliable and accurate technique to characterize capsaicinoids. The HPLC-UV (Chen and Kang 2013; Musfiroh et al. 2013; Othman et al. 2011), HPLC-MS (Barbero et al. 2014), reverse phase HPLC/diode array detection (RP-HPLC/DAD) (Ziino et al. 2009), and HPLC-Photodiode array detection (HPLC-PAD) (Gahungu et al. 2011) are four types of HPLC techniques used for capsaicinoids characterization.

Moreover, GC has also been used to determine capsaicin content (Ha et al. 2008). The study showed that there was no significant difference in the precision and accuracy

**Table 7.** Representative extraction, purification, and determination methods of ACSOs and flavor components.

Compounds	Sample	Extraction and Purification	Characterization Technique	Concentration	References
Allicin	Garlic extracts	Homogenized in water and filtered, and then extracted with methylene chloride	Supercritical fluid chromatography with mass spectrometric identification [M + H] <sup>+</sup> : m/z 163	n/a	(Calvey, Roach, and Block 1994)
Alliin, MCSO, 1-PECSO	Extracts of plant tissues (garlic cloves, onion bulbs, leek bulbs, and cabbage leaves)	Tissues were steeped in methanol/chloroform/water and then phase-separated in chloroform/water. Then the chloroform phase was discarded, and the methanol/water phase was concentrated. Sample derivatization.	Infrared analysis HPLC-fluorescence spectrophotometer Thin-layer chromatography	MCSO: 14.7 ~ 60.4 mg/100 g FM Alliin: nd~305 mg/100 g FM 1-PECSO: nd~131 mg/100 g fresh mass (FM)	(Thomas and Parkin 1994)
Alliin	Rat plasma	Deproteinized with acetonitrile: ethanol (50:50) mixture	LC-ESI-MS [M-H] <sup>-</sup> : m/z 176	n/a	(Shin and Matsuura, 2000)
Allicin	Non-purified and purified garlic extracts	Saturated with NaCl and extracted with dichloromethane	HPLC with UV and electrochemical detection (ED) Wavelength: 254 nm Electrode set: +0.0 v and +1.7 v	Non-purified: 3.6 ~ 4.6 mg/g FM Purified: 1.7 ~ 2.1 mg/g FM	(Bocchini et al., 2001)
MCSO, 1-PECSO and BCSO	Different parts of <i>allium siculum</i>	Tissues were extracted with boiling MeOH, filtered and passed through a cation-exchange column, and then subjected to preparative HPLC	GC after derivatization with methyl chloroformate <sup>1</sup> H and <sup>13</sup> C NMR spectra UV spectra CD spectra	MCSO: 18 ~ 73 mg/100 g FW 1-PECSO: 11 ~ 64 mg/100 g FW	(Kubec et al., 2002)
Alliin, deoxyalliin, allicin, and dipeptide precursors	Garlic powder with different sulfur fertilization levels	Extracted using methanol-water (80:20, v/v)+0.05% formic acid (pH < 3)	HPLC with UV and multiple ms Wavelength: 208 nm	Alliin concentration is related to sulfur fertilization levels	(Arnault et al. 2003)
Allicin	Fresh and powdered garlic	CO <sub>2</sub> -supercritical fluid extraction (SFE)	HPLC with diode array detection (DAD)	White garlic: 3.20 ~ 4.81 mg/g FM Elephant garlic: 0.73 mg/g FM Garlic powder: 2.25 ~ 2.93 mg/g dry mass (DM)	(Rybak et al., 2004)
MCSO and alliin	Vegetables: garlic, chinese chive, cabbage, and broccoli	Dipped in water and heated in a microwave, then crushed in water and filtered	Capillary electrophoresis (CE)	Alliin concentration: Garlic gloves: 12.67 ~ 16.93 mg/g FM Garlic stems: 5.26 mg/g FM Chinese chive leaves: 1.01 mg/g FM	(Horie and Yamashita 2006)
Alliin, MCSO, isoalliin, and PCSO	16 accessions of garlic 15 varieties of onion	The freeze-dried sample was heated in methanol and then crushed and heated again. Then the extract was filtered and washed. The filtrates were evaporated.	Biosensor (based on alliinase reaction) The enzyme was immobilized and placed inside a flow-through cartridge. HPLC-MS-MS	Alliin: 0.2 ~ 2.2 g/100 g dm in garlic Isoalliin: 0.3 ~ 1.25 g/100 g dm in onion	(Ziegert et al., 2006)
MCSO, alliin, 1-PECSO, PCSO and cycloalliin	Yellow onions ( <i>allium cepa</i> L.)	A whole onion was deep-frozen, cut, heated in water, and then crushed with a homogenizer. Then cold acetone was added to the homogenate, and the mixture was stored, centrifuged, and evaporated.	HPLC and GC analyses after derivatization	HPLC MCSO: 0.22 mg/g FM; alliin: trace; 1-pecso: 1.30 mg/g FM; PCSO: n/a GC MCSO: 0.23 mg/g FM; alliin: 0.04 mg/g FM; 1-PeCSO: 1.32 mg/g FM; PCSO: n/a	(Wang et al., 2007)

(continued)

Table 7. Continued.

Compounds	Sample	Extraction and Purification	Characterization Technique	Concentration	References
Allicin	Aqueous extracts from green garlic leaf, shoot, and young bulbs	Crushed and homogenized, and sonicated in water, then the obtained mash was squeezed and centrifuged.	HPLC-UV Wavelength: 220 nm	Root bulb: 1.12 mg/ml Young bulb: 0.48 mg/ml Shoot: 0.44 mg/ml Leaves: 0.26 mg/ml	(Arzanlou and Bohlooli, 2010)
Allicin	Garlic bulb powder	Treated with cold water and then centrifuged.	UPLC-UV Wavelength: 254 nm	1.14 ~ 2.42%	(Wang et al., 2010)
Diastereoisomers of alliin	Garlic extract	Peeled and boiled in water, then crushed and boiled. The preparation was then filtered.	HPLC-UV Wavelength: 210 nm	n/a	(Dethier et al. 2012)
Allicin	Allicin obtained from garlic by supercritical CO <sub>2</sub> extraction	Purification by molecular distillation. The optimal absolute pressure, distillation temperature, and feed flow rate were 200 Pa, 50 °C, and 15 ml/min, respectively.	HPLC-UV Wavelength: 240 nm	n/a	(Liang et al., 2012)
Alliin and MCSO	n/a	n/a	Infrared spectral analysis: Range: 4000 ~ 550 cm <sup>-1</sup> Raman spectral analysis: Range: 3200 ~ 100 cm <sup>-1</sup>	n/a	(Wang et al. 2013)
Alliin	Garlic powder	A two-step process combining aqueous two-phase extraction with chromatography. The extraction process was optimized by response surface methodology. Alliin was purified with the ammonium form of sulfonic acid cation-exchange resins.	HPLC-Diode array detector Wavelength: 210 nm	n/a	(Jiang et al. 2014)
Allicin	Aqueous garlic extract	Proteins were removed by methanol. Allicin was separated using a semi-preparative C18 column, and its fractions were collected and concentrated.	HPLC-UV Wavelength: 220 nm	n/a	(Arzanlou , M., S. Bohlooli, and M. Ranjbar 2015 )
Alliin and its thermal degradation compounds	Alliin solutions	n/a	HPLC-UV Wavelength: 230 nm HPLC-MS ESI <sup>+</sup> and ESI <sup>-</sup> MS/MS ESI <sup>+</sup> UPLC-High resolution mass spectrometry (HRMS) ESI <sup>+</sup>	n/a	(Chen et al. 2017)
Allicin	Garlic	Salting-out extraction based on ethanol/ ammonium sulfate. The major parameters were optimized by response surface methodology: 23% (w/w) ethanol and 24% (w/w) salt.	HPLC-UV Wavelength: 240 nm	n/a	(Li et al., 2017)

**Table 8.** Representative characterization methods of capsaicinoids.

Compound	Sample	Characterization	Concentration	References
C, DHC, n- DHC	<i>Calabrian Capsicum annum</i> (hot pepper)	RP-HPLC/DAD	n/a	(Ziino et al. 2009)
C, DHC	Capsicum samples	HPLC	Green peppers: $1.0 \pm 0.9 \mu\text{g/g}$	(Othman et al. 2011; Thomas and Parkin 1994)
C	Red pepper	HPLC-UV	Capsaicin content: 9.48 mg/g dry weight	(Chen and Kang 2013)
C	<i>Capsicum annum L.</i>	Mobile phase: acetonitrile - acetate acid 2% (6:4), Flow rate: 1.0 ml/minute Detection wavelength: 280 nm	Chili Tanjung: 0.38% (w/w), Red Chili: 0.83% (w/w), Red Gendot: 0.87% (w/w), Green Gendot: 0.88% (w/w), Green Curry: 1.05% (w/w), Japlak Rawit: 1.09% (w/w), Red Curry: 1.14% (w/w), Red Rawit: 1.85% (w/w), Green Rawit: 2.11 % (w/w)	(Musfiroh et al. 2013)
Capsaicinoids	<i>Capsicum annum L.</i>	HPLC- MS	n/a	(Barbero et al. 2014)
Capsaicinoids	<i>Capsicum Chinese</i>	RP-HPLC/PAD	Capsaicin: 47.632 mg/g dihydrocapsaicin: 23.096 mg/g	(Gahungu et al. 2011)
C	<i>Gochujang</i>	GC	n/a	(Ha et al. 2008)
Bell-like aroma	n/a	HS-SPME GC/MS	n/a	(Ziino et al. 2009)

between the GC method and the HPLC method (Ha et al. 2008). Table 8 provides detailed information about capsaicinoids characterization.

### Relationship between chemical compounds and sensory profiles

Garlic, onion, and chili pepper have their special sensory profiles and various volatile compounds (As shown in Table 9). In terms of the similarities, dimethyl trisulfide and nonanal were found in garlic, onion, and chili pepper (Block, Putman, and Zhao 1992; Choi et al. 2017; Mazida, Salleh, and Osman 2005; Molina-Calle, Priego-Capote, and de Castro 2017; Yang et al. 2019). Except for the above compounds, garlic and onion shared other compounds, such as dimethyl disulfide and benzaldehyde (Block, Putman, and Zhao 1992; Choi et al. 2017; Molina-Calle, Priego-Capote, and de Castro 2017; Yang et al. 2019). Moreover, dipropyl disulfide, [E]-2-octenal, and hexane were found in both onion and chili pepper (Block, Putman, and Zhao 1992; Choi et al. 2017; Mazida, Salleh, and Osman 2005).

When turning into the most important volatile compounds, as for the garlic flavor, allicin, diallyl sulfide, diallyl disulfide, and diallyl trisulfide were reported to have a strong, pungent odor of fresh garlic. Allyl methyl trisulfide was reported to have a cooked garlic flavor (Yang et al. 2019). Vinyl dithiin was reported to have a pungent odor (Sun et al. 2019). As for onion flavor, dipropyl disulfide, dipropyl trisulfide, dimethyl disulfide, and dimethyl trisulfide provide onion sensory attributes. Trans-zwiebelane has a green or raw onion taste and a sweet sulfur taste (Block, Putman, and Zhao 1992). As for chili pepper flavor, 2-isobutyl-3-methoxy pyrazine gives the green pepper note, while other flavor compounds mainly linked to fruitiness, including 3-carene (fruity, rubbery), trans-2-hexenal (fruity and sweet), nonanal (fruity), and linalool (fruity) (Mazida, Salleh, and Osman 2005). Also, capsaicinoids are reported to render the spicy taste (Cisneros-Pineda et al. 2007).

### Summary and future perspective

Plant-based flavors are widely used in the food and pharmaceutical industries because of their preferable flavoring properties and potential health benefits (Ayseli and Ayseli 2016). Among plant flavors, the allium and chili pepper classes are important due to their distinctive flavor and aroma (Fujisawa et al. 2008; Griffiths et al. 2002). However, most flavor components are significantly unstable during food processing or preservation. As a result, a better understanding of formation mechanisms and optimum production of plant-based flavor compounds, which helps improve their stability and quality, has become an important issue for the food industry.

In this scoping review, the related studies in the areas of flavor components and precursor molecules of garlic, onion, and chili pepper, their flavor formation mechanisms, regeneration methods, and stability of the flavor precursors or flavor molecules were summarized. Presenting this information would yield insights to the food industry to better utilize plant-based flavors and promote clean label in a broader range of products. Alliin and 1-PeCSO are the major flavor precursors in garlic and onion, respectively (Jones et al. 2004; William Randle et al. 1995). The formation mechanism of garlic and onion flavor mainly included the enzymatic reaction of precursors, degradation of primary flavor components, and thermal degradation of flavor precursors. Considering of the instability and oily quality of the current flavor products in the market, we found that allium flavor produced by its precursors through thermal degradation should be further investigated as a new concept for flavor regeneration, especially for thermal food processes. For chili pepper flavor, the major flavor components are capsaicinoids, and its flavor precursors are phenylalanine and branched-chain fatty acid (Narasimha Prasad et al. 2006). Capsaicinoids are mainly produced by enzymatic reactions. Considering the lack of research in flavor precursors and formation mechanisms, the direct extraction of the flavor, capsaicinoids, can be an accessible method. Also, the studies



**Table 9.** Detailed information between chemical compounds and sensory profiles.

Compound	Odor description	Fresh garlic <sup>a</sup>	Aged garlic <sup>b</sup>	Onion <sup>c</sup>	Died onion <sup>d</sup> (50 °C)	Chili pepper <sup>e</sup>
Allyl mercaptan	Sulfury and burnt	+	+	—	—	—
Allyl methyl disulfide	Fresh garlic	+	—	—	—	—
Allyl methyl trisulfide	Sulfury and eggy	+	+	—	—	—
Allyl propyl disulfide	Fresh garlic	+	—	—	—	—
Diallyl sulfide	Pungent and fresh garlic	—	+	—	—	—
Diallyl disulfide	Pungent and fresh garlic	+	+	—	—	—
Diallyl trisulfide	Pungent and garlic	+	+	—	—	—
Dimethyl disulfide	Sulfury and onion	+	+	+	+	—
Dimethyl trisulfide	Cabbage and onion	+	+	—	+	+
Dipropyl disulfide	Strong raw onion, sulfury, and fresh leek	—	—	+	+	+
Dipropyl trisulfide	Onion	—	—	+	+	—
Methyl propyl disulfide	Rotten, fried onions, and sour cabbage	—	—	+	+	—
Propanethial S — oxide	Trans: Green or raw onion taste and sweet sulfur taste. Cis: sweet or brown “sauté” taste with liver, hydrogen sulfide notes	—	—	+	—	—
Nonanal	Fruity	—	+	—	+	+
Methional	Cooked potato	+	+	—	—	—
Benzaldehyde	Almond and fruity	—	+	—	+	—
2-acetylthiazole	Popcorn-like	—	+	—	—	—
5-methylmethanethiosulfinate	Radish	+	+	—	—	—
3-vinyl-4H-1,2-dithiin	Garlic	+	—	—	—	—
2-vinyl-4H-1,3-dithiin	Pungent and garlic	+	+	—	—	—
2,5-Dimethylthiophene	Spring onion and fresh onion	—	—	+	+	—
3,4-Dimethylthiophene	Wood and dry smell	—	—	+	+	—
2-Methyl-2-pentenal	Green, grassy, and herbal	—	—	+	+	—
[E]-2-Octenal	Soap and raw leek	—	—	—	+	+
Hexane	Green aroma, grassy, and herbal	—	—	+	+	+
2-isobutyl-3-methoxypyrazine	Grassy aroma and green bell pepper	—	—	—	—	+
2,3-butanedione	Fruity and caramel	—	—	—	—	+
3-carene	Fruity and rubbery	—	—	—	—	+
1-penten-3-one	Pungent/spicy	—	—	—	—	+
Trans-2-hexenal	Fruity and sweet	—	—	—	—	+
Linalool	Fruity	—	—	—	—	+

a: (Molina-Calle, Priego-Capote, and de Castro 2017; Yang et al. 2019)

b: (Molina-Calle, Priego-Capote, and de Castro 2017; Yang et al. 2019)

c: (Block, Putman, and Zhao 1992)

d: (Choi et al. 2017)

e: (Mazida, Salleh, and Osman 2005).

showed that the capsaicinoids have acceptable stability under thermal treatment, which broadens the application in thermal food processing (Si et al. 2014).

However, the stability of flavors and flavor precursors is a function of the environment and process conditions (Weerawatanakorn et al. 2015). Flavor and flavor precursors' stability may also be adversely affected by the food matrix and other food ingredients/additives because of the interactions between the flavor components and food ingredients or interactions among different flavor components. And the flavor generation mechanisms may be remarkably altered under different conditions, such as processing temperature, pH, and water activity (Yu, Wu, and Ho 1993). As such, a better understanding of flavor generation mechanisms under different conditions is required.

Based on the research status, the future research interests should be carried out from the following aspects: (1) new methods for accurate, rapid, and precise characterization of flavor precursors and flavors are needed because of their instability and mutability, (2) the investigation of biochemical

properties of the flavor components, along with their correlation with sensory properties, are another area that needs more investigation in order to develop palatable and healthy flavor products, (3) food-safe techniques should be explored to stabilize the flavor precursor or flavor components to extend the shelf life and quality, (4) the compatibility of plant-based flavor precursors or flavors with food matrices should be evaluated to determine when and where they can be best applied in the respective food manufacturing processes. This information would shed light on the possible ways of incorporating plant-based flavors into different food matrices, pave the route for the food industries to take initiatives to replace their synthetic flavors and adopt clean label formulation, and subsequently enhance the consumer's eating experience.

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## Author contributions

Jieying Li and Younas Dadmohammadi searched, collected, compiled, and wrote the manuscript. Alireza Abbaspourrad supervised and guided the work. All authors were responsible for the idealization and read and approved the manuscript.

## Disclosure statement

The authors declare that there is no conflict of interest.

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