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Thermolysis kinetics and thermal degradation compounds of alliin

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To investigate thermolysis kinetics and identify degradation compounds, alliin solutions were heated at 60, 80, and 89 °C. The degradation compounds of alliin were identified by high performance liquid chromatography–mass spectrometry (HPLC–MS), tandem mass spectrometry (MS/MS) and ultra-pressure liquid chromatography–high resolution mass spectrometry (UPLC–HRMS). The results showed that the thermal degradation kinetic of alliin could be described by a first-order reaction and $k = 4.38 \times 10^{17} \exp(-142494/RT)$, where k is the reaction rate constant, min^{-1}; R is gas constant; T is the absolute temperature, K. Degraded compounds, including S-allyl-L-cysteine and ethers, such as allyl alanine disulfide, allyl alanine trisulfide, allyl alanine tetrasulfide, dialanine disulfide (cysteine), dialanine trisulfide and dialanine tetrasulfide, were identified by HPLC–MS, MS/MS and UPLC–HRMS. Allyl alanine tetrasulfide was identified for the first time in alliin. The results show that alliin is unstable and significant numbers of organosulfur compounds are generated under high temperature treatment.

1. Introduction

Alliin (S-allyl-L-cysteine sulfoxide, SACS, CAS No.556-27-4) is the major sulfur-containing amino acid in garlic (*Allium sativum* L.). The content of alliin in fresh garlic is about 1.29% (Hui, Jian, Lina, & Wenjuan, 2007), which is affected by many factors, such as soil and weather (Bloem, Haneklaus, & Schnug, 2005; Huchette, Kahane, Auger, Arnault, & Bellamy, 2005). Alliin is known to display antioxidant (Helen, Krishnakumar, Vijayammal, & Augusti, 2003), anti-inflammatory (Quintero-Fabian, Ortuno-Sahagun, Vazquez-Carrera, & Lopez-Roa, 2013) and anti-cardiovascular effects (Gunther, 2013). Besides this, it helps to boost the secretion of insulin (Augusti & Sheela, 1996) and regulate cellular immune functions (Salman, Bergman, Bessler, Punsky, & Djaldetti, 1999). When garlic is crushed, alliin can be converted into allicin (diallylthiosulfinate) by alliinase. Allicin is unstable and can decompose to diallyl disulfides and sulfur dioxide under room temperature within 20 h (Rivlin, Budoff, & Amagase, 2006). Allicin and its degraded products have been reported to lower blood pressure (Elkayam, Peleg, Grossman, Shabtay, & Sharabi, 2013), prevent apoptosis and inflammation (Zhang, Li, et al., 2015), inhibit tumor growth (Dipaolo & Carruthers, 1960), and prevent the migration and invasion of colon-cancer cells (Lai et al., 2013). Accordingly, the content of alliin is one of the most important factors that must be considered when evaluating the quality of garlic and its processed products.

Alliin is susceptible to degradation especially upon high temperature (Zhang, Lei, Zhu, & Zhang, 2013) because of its unstable sulfoxide bond. During the processing of black garlic (a processed garlic product produced under controlled high temperature and humidity for several days), the alliin content of garlic significantly decreased (Cui, Zheng, Tian, & Zhang, 2015; Ji et al., 2015; Zhang, Lei, et al., 2015). However, due to the complex composition of garlic, the changes of alliin at different processing stages in the above reports varied. More research, therefore, is needed to focus on the characteristics of the thermolysis of alliin.

The objective of this study was to clarify the ambiguities and investigate the kinetics and products of the degradation of alliin. Alliin instead of garlic was studied in this research in order to eliminate interference from endogenous enzyme, alliin precursors, the species of garlic and other influencing factors (de Queiroz et al., 2014; Yu, Wu, & Ho, 1994).

2. Materials and methods

2.1. Materials

Alliin [Fig. 3A(1)] and S-allyl-L-cysteine [SAC, Fig. 3A(2)] were synthesized according to the method provided by Rabinkov, Zhu, Grafi, Galili, and Mirelman (1994) with purity of 95% and >98% respectively (which were determined by high performance liquid chromatography (HPLC)). Other chemicals and reagents (methanol, acetic acid) were of HPLC grade and were purchased from Ocean-pak (Gothenburg, Sweden). Ultra-pure water was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA).

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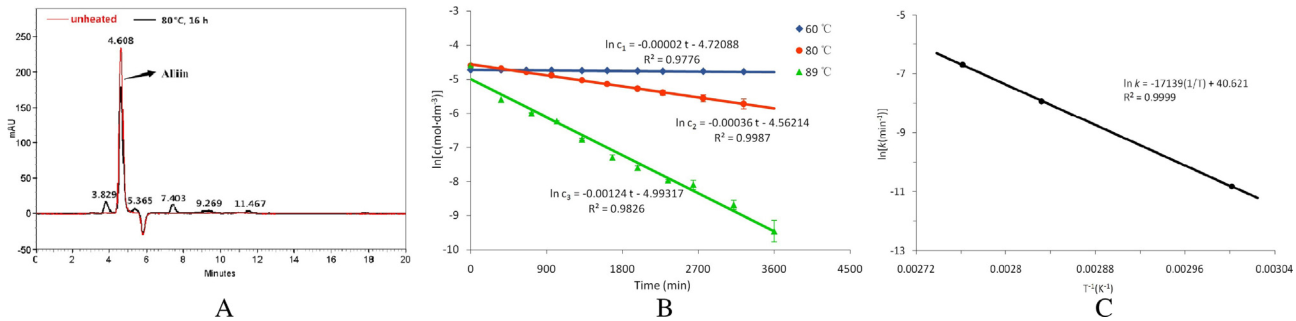

Fig. 1. Thermolysis kinetics of alliin: A. HPLC Chromatogram of unheated alliin and alliin heated at 80 °C for 16 h; B. Relationship between the logarithm of concentration of alliin and time; C. Arrhenius plots for thermal decomposition of alliin.

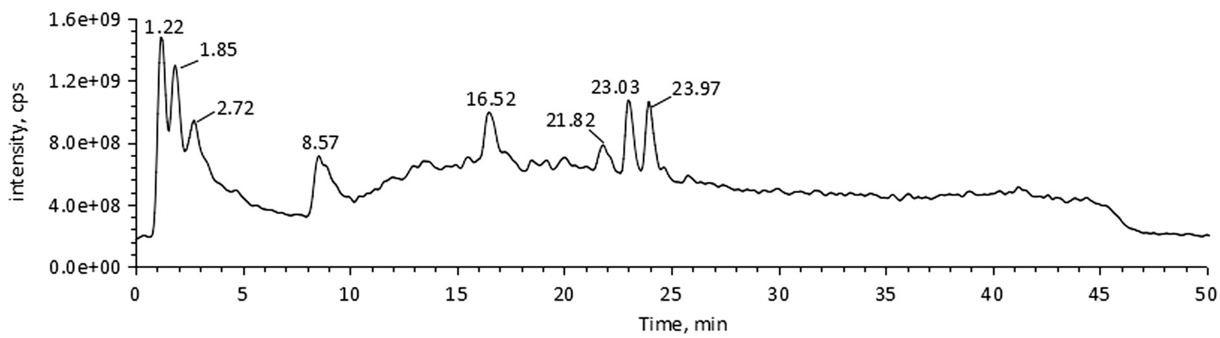

Fig. 2. The total ion chromatogram of alliin degradation compounds as determined by HPLC/MS.

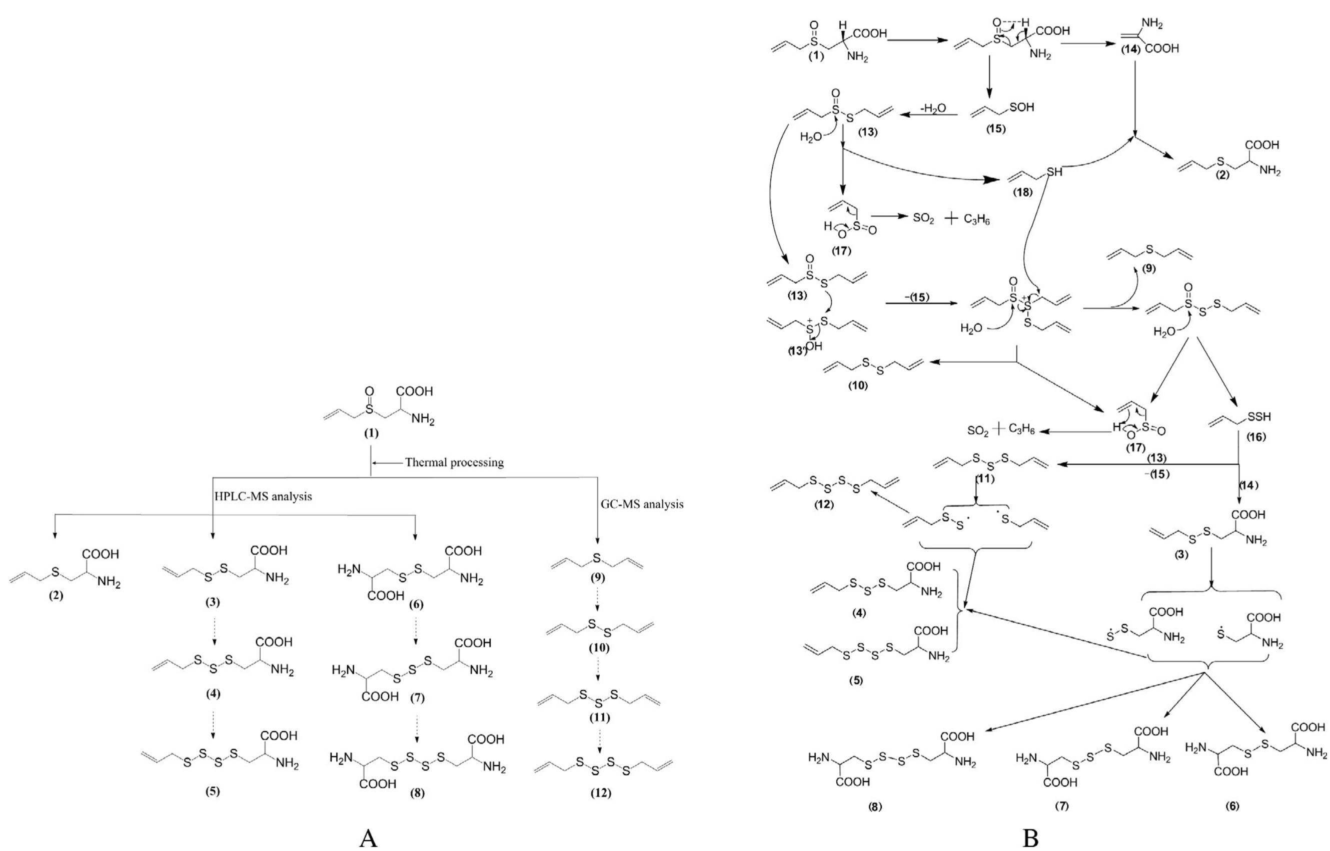

Fig. 3. Possible process (A) and reaction mechanism (B) for the formation of sulfide or polysulfide compounds from thermally degraded alliin: (1) alliin; (2) SAC; (3–5) allyl alanine sulfides; (6–8) dialanine sulfides; (9–12) diallyl sulfides.