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Thermal processing effects on the chemical constituent and antioxidant activity of s-alk(en)ylcysteine s-oxides (alliin) extract

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To explore the effects of thermal processing on antioxidant activity and the chemical composition of s-alk(en)ylcysteine s-oxides (alliin) extract from garlic, the alliin extract was thermally processed and the chemical constituents were analyzed by HPLC and LC–MS, and antioxidant capacities were investigated by 2,2-Diphenyl-1-picrylhydrazyl (DPPH) assay, hydroxyl free radical assay and ferric reducing/antioxidant power (FRAP) assay. The results showed that thermal treatments resulted in significant changes in the composition and antioxidant activities of alliin extract ($p < 0.05$). The contents of alliin were reduced from 85.7% to 60.8% and new chemicals including s-allylmercaptocysteine (SAMC), s-allylcysteine (SAC) and arginine were found after thermal treatment at 121 °C for 40 min. The IC_{50} value of alliin extract on DPPH assay was decreased from 46.6 mg/mL (untreated) to 7.3 mg/mL (treated). The antioxidant capacity on FRAP assay was increased from 1.45 mmol/L of $FeSO_4$ equivalent (untreated) to 4.36 mmol/L of $FeSO_4$ equivalent (treated) when alliin extracts was at the concentration of 16 mg/mL. These results suggest that thermal treatment is suitable to the antioxidant capacities of alliin extracts and SAC and SAMC might play important roles. These results could be useful for the processing of garlic related products in the food industry.

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1. Introduction

Garlic (*Allium sativum* L.), a perennial plant of *Liliaceae* family, has been used as foods, spices and herbal remedies in many countries for hundreds of years. Today, garlic is a leading herbal remedy among alternative medical practitioners. A wide range of therapeutic effects of garlic such as hypolipidaemic, antiatherosclerotic, anti-diabetic, antimicrobial, anticarcinogen and immunomodulation activities have been reported (Agarwal, Iqbal, & Athar, 2007; Durak et al., 2004; Liu, Hse, Lii, Chen, & Sheen, 2005; Makris, Thornton, Xu, & Hennessy, 2005; Saravanan & Prakash, 2004). Garlic is also used for food safety because of its antioxidant and antimicrobial activity (Ponce, Roura, del Valle, & Moreira, 2008; Sallam, Ishioroshi, & Samejima, 2004; Yin & Cheng, 2003).

Sulfur-containing compounds are responsible for the characteristic smell and health activities of garlic. These substances are formed by the action of alliinase (EC 4.4.1.4) on cysteine derivatives including (+)-*S*-methyl-L-cysteine sulfoxide (methiin), (+)-*S*-(2-propenyl)-L-cysteine sulfoxide (alliin), (+)-*S*-(1-propenyl)-L-cysteine sulfoxide (isoalliin), and (+)-*S*-propyl-L-cysteine sulfoxide (propiin) when plant material is disrupted (Koch & Lawson, 1996; Sendl, 1995).

Many pathological processes including cancer, ischemia, inflammatory diseases, diabetes, and atherosclerosis are mediated by reactive oxygen species (ROS) and free radicals. Although garlic is beneficial to human's health because of its antioxidant activities, the degree of antioxidative efficacy of various garlic preparations differs according to variations in chemical compositions and processing procedures. Some studies have focused on the effects of thermal treatment on the antioxidant activities of garlic. Some reports suggest that thermal treatment does not affect the OH• scavenging capacity, lipid peroxidation inhibition capacity and Cu^{2+}-induced lipoprotein oxidation inhibition capacity (Pedraza-Chaverrí et al., 2004; Pedraza-Chaverrí, Medina-Campos, Ávila-Lombardo, Zúñiga-Bustos, & Orozco-Ibarra, 2006; Prasad, Laxdal, Yu, & Raney, 1996; Shobana & Naidu, 2000), but others showed that heat treatment could reduce garlic's antioxidant capacities to inhibit lipid peroxidation, scavenging effects on $O_2^-\cdot$ and H_2O_2 (Pedraza-Chaverrí et al., 2006; Yin & Cheng, 1998). All these experiments mentioned above were conducted on garlic or crude garlic extracts. It was difficult to illustrate the changes of constituents because of the complexity of the components of garlic.

Various preparation techniques have been applied to isolate garlic's constituents that mainly consist of organosulfur compounds. Raw garlic

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homogenate is the major preparation of garlic that is consumed. Allicin (allyl 2-propenethiosulphinate or diallyl thiosulphinate) is the major thiosulphinate compound found in garlic homogenate and it is considered as the principal bioactive compound in garlic aqueous extract. However, the usage is limited by its unpleasant smell. Therefore many studies focused on alliin, which is the precursor of allicin without the smell of garlic. The process of crushing or cutting of garlic cloves induces the release of the enzyme alliinase, which quickly in seconds catalyzes alliin into allicin (Amagase, 2006). The water extract of heat-treated garlic contains mainly alliin as alliinase is inactivated by heating. Alliin has been proved to have multiple bioactivities including antimicrobial, antioxidant and hypolipidaemic activities (Chung, 2006; Egen-Schwind, Eckard, & Kemper, 1992; Fanelli, Castro, de-Toranzo, & Castro, 1998; Guo, Müller, Pentz, Kress, & Siegers, 1990; Lachmann, Lorenz, Radeck, & Steiper, 1994). Garlic or alliin is usually thermally processed by the manufacturer or consumer for the safety of products. Some studies have focused on the effects of the processing procedure on the bioactivities of garlic (Gorinstein et al., 2006; Moreno, Corzo-Martínez, del Castillo, & Villamiel, 2006; Pedraza-Chaverrí, Medina-Campos, & Segoviano-Murillo, 2007). But the effects of thermal processing on the constituents and bioactivities of alliin extract are unknown till now.

The purpose of this paper was to study the effects of thermal processing on the chemical constituent and antioxidant activity of s-alk(en)ylcysteine s-oxides (alliin) extract. The changes of constituents after the thermal processing were determined by HPLC and LC–MS. The differences of antioxidant activities between untreated and thermal treated alliin extracts were compared. The relationship of antioxidant activities and constituents of alliin extracts was also discussed.

2. Materials and methods

2.1. Materials

Alliin, asparagines, arginine, S-allylcysteine (SAC), S-allylmercaptocysteine (SAMC) standard, 2,2-Diphenyl-1-picrylhydrazyl (DPPH) and 1,3,5-tri(2-pyridyl)-2,4,6-triazine (TPTZ) were purchased from Sigma Chemical Co. (St. Louis, MO, U.S.A.). All other chemicals and reagents were purchased locally and were of analytical grade.

2.2. Sample preparation

Alliin extract was extracted and purified from garlic in our laboratory. Briefly, garlic was peeled and heated at 100 °C for 20 min to kill the enzyme. Then garlic was crushed and the juice was collected by ultrafiltration (Mw = 2000). The ultrafiltrated extract was separated on cation exchange resin 732 column chromatography (Φ2.5 × 50 cm). The main alliin fraction was recrystallized several times and the purified alliin extracts was obtained. The chemical structures were confirmed by UV, IR, ESI-MS, ^{1}H NMR data.

Five grams of alliin extract was dissolved in 40 mL of distilled water in four tubes and thermally treated with water bath or autoclave (YXQ-SG46-280SA, Shanghaiboxun Co., China). Alliin solution (125 mg/mL) was subjected to three different treatments including thermal processing at 100 °C for 20 min, 100 °C for 40 min and 121 °C for 40 min, respectively. The untreated alliin extract was the solution (125 mg/mL) without any thermal treatment. The experiments were conducted in three replicates.

2.3. HPLC analysis

The contents of alliin in the thermally processed and unprocessed samples were determined by HPLC (Chen, Zhang, & Liu, 2009). The contents of S-allylcysteine (SAC), S-allylmercaptocysteine (SAMC), asparagines and arginine were determined according to Bae, Cho, Won, Lee, and Park (2012) and Lanzotti (2006). A model 1090 HPLC (Agilent Technologies, Inc., Palo Alto, CA, U.S.A.) and a YMA-Pack ODS-A C18 (25 cm × 4.6 mm) column (Shimadzu, Japan) were used to conduct the determination. Mobile phase was methanol/water (1/4, v/v) solution. The UV detection wavelength was 214 nm and the whole operation was under room temperature. The flow rate was 0.7 mL/min.

2.4. LC–MS analysis

The HPLC–MS analysis was conducted on a liquid chromatography–mass spectrometer (Surveyor-LCQ Advantage Max 10, Finnigan MAT Ltd., U.S.A.) using a ODS C18 column (100 mm × 2.1 mm, 5 μm, Thermo Electron Corporation, U.S.A.). The column oven was set to a fixed temperature (30 °C). The mobile phase was water/methanol (85/15, v/v) solution. The flow rate was 0.2 mL/min. The ESI was operated in positive mode. Nebulizer gas (N_2) and dry gas (N_2) flow was 30 psi and 5 L/min, respectively. The curve dissolution line (CDL) temperature was 275 °C. The probe voltage and CDL voltage were fixed at 4.5 kV and 10 V, respectively. Mass spectra were recorded in the range of m/z 50–400.

2.5. DPPH radical scavenging capacity

The DPPH radical-scavenging capacity of the thermally treated or untreated alliin extracts was evaluated according to the method reported by Fu, Chen, Dong, Zhang, and Zhang (2010) with slight modification. Briefly, DPPH was dissolved in ethanol at a final concentration of 1.2×10^{-4} M. Then 2.9 mL of DPPH solutions were added to 0.1 mL of sample solutions of different concentration. The mixed solution was allowed to stand for 30 min in the dark at 37 °C for the reaction. UV absorbance was recorded on a spectrometer (model UVmini-1240, Shimadzu Co.) at 517 nm (Ai). The absorbance of the mixture, in which the sample and DPPH methanol solution were replaced by distilled water and ethanol respectively, were Ao and Aj, respectively. The DPPH scavenging activity was calculated.

2.6. Hydroxyl free radical scavenging capacity

Fenton assay was used to assay the scavenging effects of alliin extracts on hydroxyl radical radicals (Wang, Xin, & Hu, 2002). In brief, 1 mL of phosphate buffer solution (10 mmol/L, pH 7.4), 1 mL of safranine T solution (40 μg/mL), 1 mL of hydrogen peroxide (3%), 1 mL of EDTA–Na_2-Fe (II) (0.15 mol/L) and 0.2 mL of samples were mixed in order. The mixture was kept at 37 °C for 30 min. Then sample tubes were centrifuged for 10 min at 3000 × g. The absorbance (A_{sample}) was measured at 520 nm using a spectrophotometer. The absorbance value of the tube without samples was A_{blank}, and the absorbance value of the tube without EDTA–Na_2-Fe (II) solution was $A_{control}$. The percent of antioxidant activity was calculated.

2.7. Ferric reducing/antioxidant power (FRAP) of alliin extracts

The FRAP assay was conducted according to the procedure described by Benzie and Strain (1996). The FRAP solution was warmed to 37 °C in a water bath. Then 0.3 mL of sample solution was mixed with FRAP solution. Ten minutes later, the absorbance of the mixture at 593 nm was determined. A standard curve was obtained using the $FeSO_4$ solution within the concentration from 0.1 mmol/L to 1.0 mmol/L instead of sample solution. Then the FRAP values of alliin extracts were calculated.

2.8. Statistical analysis

The results are presented as means ± standard error (SD). Differences in mean values between groups were analyzed by

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