Journal of Food Composition and Analysis 61 (2017) 4–19

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Study review

# Analytical methods for bioactive sulfur compounds in *Allium*: An integrated review and future directions

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ARTICLE INFO

*Article history:*
Received 31 May 2016
Received in revised form 7 September 2016
Accepted 28 September 2016
Available online 29 September 2016

*Keywords:*
Food composition
Food analysis
*Allium*
Organosulfur compounds
Analytical methodologies
Bioactive compounds
Alk(en)yl cysteine sulfoxides
Allicin
Sulfides
Vinyldithiins
Ajoene

*Chemical compounds:*
Allyl sulfide (PubChem CID: 11617)
Diallyl disulfide (PubChem CID: 16590)
Diallyl trisulfide (PubChem CID: 16315)
Allicin (PubChem CID: 65036)
E-Ajoene (PubChem CID: 5386591)
Z-Ajoene (PubChem CID: 9881148)
Vinyldithiin (Pub Chem CID: 54113692)
Methiin (PubChem CID: 90659041)
Propiin (PubChem CID: 91819955)
Alliin (PubChem CID: 25200619)
Isoalliin (PubChem CID: 90657185)
Ethiin (PubChem CID: 91820395)
Pyruvate (PubChem CID: 107735)

ABSTRACT

Plant organosulfur compounds represent one of the main groups of phytochemicals that evidence an ample spectrum of biological activities. There are two major sources of sulfur-containing compounds in plant foods; *Allium* vegetables, such as garlic, onion, and leek; and cruciferous vegetables, such as broccoli, cabbage, and cauliflower. Among them, garlic is the most studied species, mainly due to the multiple health-enhancing effects attributed to its consumption. Most of these properties have been attributed to organosulfur compounds. Thus, knowledge on the analytical determinations available for the main bioactive sulfur compounds in *Allium* is of interest. In the present review, an extensive bibliographic survey was performed to compile information regarding the different methodologies that can be used for the determination of alk(en)yl cysteine sulfoxides (ACSOs), S-allyl cysteine (SAC), thiosulfinates (mainly allicin), diallyl, mono- di-, and tri-sulfides, vinyldithiins and (E)- and (Z)-ajoene, as influenced by plant matrices and other factors. The gathered information was analyzed and presented in a systemic and comparative way, describing advantages and disadvantages of the methodologies, considering both extractive and separative techniques, the type of matrices, columns and analytical performance data. In addition, new trends and future prospects for the analysis of sulfur compounds in plants were critically discussed.



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http://dx.doi.org/10.1016/j.jfca.2016.09.012
0889-1575/

## 1. Introduction

The concept of functional food was first introduced in Japan three decades ago. It refers to foods that contain components (whether or not a nutrient) that benefit one or more functions in the body in a targeted way that are relevant to either the state of well-being and health, or the reduction of the risk of a disease (Roberfroid, 2000). Plant-derived compounds that when consumed are responsible for various health-enhancing effects are defined as phytochemicals. Currently, a major goal among researchers in food science is finding objective evidence that demonstrates food functionality. Consequently, studies regarding both the biological properties of putative phytochemicals and the chemical composition of plant foods are of interest. *Allium* vegetables, such as garlic (*A. sativum*), onion (*A. cepa*), and leek (*A. ampeloprasum* var. *porrum*) are widely consumed for their characteristic flavor (as spices) and their health-promoting effects (Block, 2010). Garlic is one of the most extensively studied functional species, not only among *Alliums*, but among all vegetables, and it has been considered a medicinal food for centuries, being used as a traditional remedy for common disorders (Rivlin, 2001). Garlic consumption is associated with decreased risk of some types of cancer, particularly those of the gastrointestinal tract (Guercio et al., 2014; Nicastro et al., 2015; Omar and Al-Wabel, 2010). Preclinical and clinical evidence demonstrated that garlic consumption can reduce risks associated with cardiovascular diseases (CVD), by lowering cholesterol level, inhibiting platelet aggregation, and lowering blood pressure (Bradley et al., 2016; Camargo and Manucha, 2016; Cavagnaro et al., 2007; Sikand et al., 2015). In addition to these cancer- and cardio-protective effects, various other biological activities have been reported for garlic, including antimicrobial, antioxidant, and anti-inflammatory properties (Block, 2010; Borlinghaus et al., 2014; Charu et al., 2014; Suvarna and Rajagopalan, 2015). Because of all these health-promoting effects associated with garlic consumption, these species have been considered as one of the most important herbs for promoting good health and longevity (Jainarinesingh, 2014). This broad spectrum of health-benefits is mainly attributed to the presence of organosulfur compounds, characteristic of garlic and other *Allium* species. It must be noted that different *Allium* species contain different profile of organosulfur compounds (Block, 2010).

A scheme of OSCs production and subsequent transformations, and their biochemical and physicochemical pathways, is presented in Fig. 1. Intact garlic bulbs contain S-amino acids, including cysteine and methionine (traces), as well as γ-glutamyl peptides and the alk(en)yl cysteine sulfoxides (ACSOs). Thiosulfinates (TSs), are formed upon enzymatic hydrolysis of the ACSOs, located in the cytoplasm, by the vacuolar enzyme alliinase, when garlic tissues are disrupted (Lancaster and Collin, 1981). Allicin is the predominant garlic TS, and represents 70–80% of the total TSs. TSs are reactive molecules that can undergo a number of transformations depending on temperature, pH and solvent of the medium. These reactions can lead to different OSCs, including diallyl, methyl, allyl, and diethyl mono-, di-, tri-, tetra-, penta-, and hexasulfides, vinyldithiins and (E)- and (Z)-ajoene (Box et al., 1989; Iberl et al., 1990; Lawson et al., 1991).

In addition to TSs biosynthesis *via* the ACSOs-alliinase interaction, γ-glutamyl peptides are converted to S-allylcysteine (SAC) through a different pathway (Amagase et al., 2001).

The functional properties attributed to this vegetable have encouraged the manufacturing and marketing of various garlic

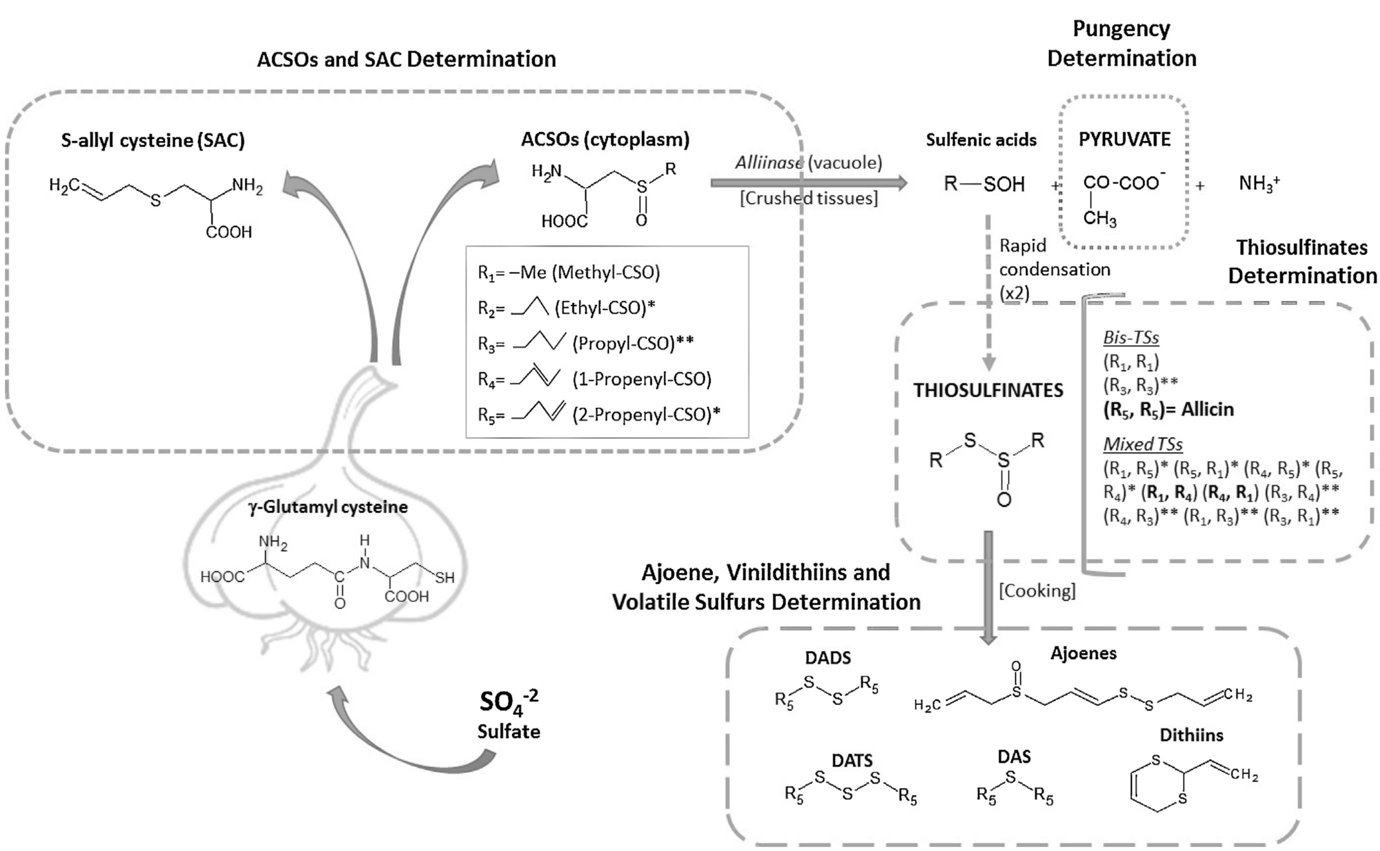


**Fig. 1.** Scheme of OSCs biochemical pathways, including synthesis and subsequent transformations upon different processing stages. Major OSCs groups sharing common structures and physicochemical characteristics are differentiated from each other by closed dashed lines. (ACSOs: Alk(en)ylcysteine sulfoxides; SAC: S-allylcysteine; DAS: diallyl sulfide; DADS: diallyl disulfide; DATS: diallyl trisulfide).