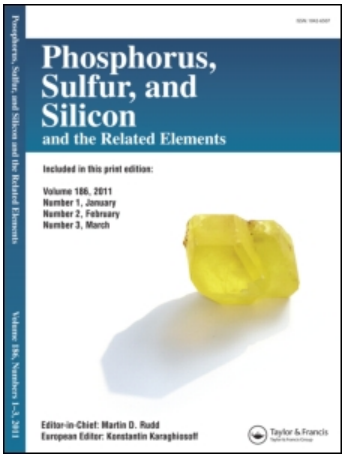

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GC and Mass-Spectrometric Comparison of Organo Sulfur Compounds in Two Varieties of Iranian Garlic

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Garlic antibiotic action is well known; it is reputed to offer protection against coronary thrombosis and atherosclerosis exhibiting antioxidant and anticancer effects.[1,2] *In this work* ^{1}*H NMR and gas chromatography in conjunction with mass spectrometry have been used for the identification and determination of these compounds in two varieties of Iranian garlic [*Allium sativum var. sativum ***(I)*** *and* Allium sativum var. holmense ***(II)****]. The organosulfur compounds in (****I****) exhibiting a concentration higher than 1% are diallyl sulfide (1.3%), diallyl disulfide (8%), methyl allyl disulfide (19%), methyl allyl trisulfide (3.2%), diallyl trisulfide (5.5%), diallyl tetrasulfide (2%), 2,3-dimethyl thiophen (1.8%), 5-methyl-1,2,3-thiadiazol (5%), and 1,2-ditiolan-3-carboxilic acid (1.5%). The amount of organosulfur compounds in (****II****) are diallyl disulfide (2%), methyl allyl trisulfide (6.3%), diallyl tetrasulfide (5%), and cyclopentanthiol (2.5%).*

Keywords Garlic; GC-mass; holmens; organosulfur

INTRODUCTION

Garlic is a member of the lily family that has been cultivated by humans as a food plant for over 10,000 years. It has been the bane of fictional vampires and a folk remedy for thousands of years. Garlic antibiotic action is well known. It is reported to offer protection against coronary thrombosis and atherosclerosis; antioxidant, anticancer, and antihepatotoxic effects had been related to it.[1–6] Lawson reported that intact garlic cloves contain alliin and isoalliin, cycloalliin, and methin.[7] The enzyme allinase acts upon these organosulfur compounds to form sulfenic acid intermediates. The intermediates rapidly self-condense, resulting in the dialkyl thiosulfinates in crushed garlic [cysteine sulfoxide + allinase → sulfenic acid) intermediate → thiosulfinate]. Depending on their chemical environment, the thiosulfinates are transformed into other organosulfur compounds. To the best of our knowledge, there

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has been no data available about the sulfur components in garlic of variety *Holmense* in Iran. The aim of this study was to specify the kind of organosulfur compounds and to compare them with the same compounds in the variety of *sativum*.

MATERIALS AND METHODS

The two *Allium* varieties were obtained directly from the growers in Astaneh (north of Iran). Solvent-grade dichloromethane, pentane, hexane, and isopropanol were obtained from Merck Chemical Company without further purification. Anhydrous sodium sulfate was used as drying agent.

Gas Chromatography/Mass Spectrometry

GC analysis was performed on a 30-m capillary column of silicon 5, CB. The programmed temperature was 40°C (held for two min), rising up to 250°C. The carrier gas was helium with 10 psi pressure and the amount of sample injection was 1 μL. GC-MS was performed with a Fisons Instruments GC 8000/Trio 1000. Quantification was achieved using peak area calculation, and compound identification was partially carried out using correlation between retention times. Mass spectra correlations were done using Wiley, NBS, NIST, and our own online library, as well as using published offline mass spectral data.[8–13]

Extraction and Separation of Garlic Components

Chopped garlic pieces (1000 g) were soaked in methanol (1000 mL) at 18°C. The methanol was replaced 3 times for 3 days, using a total of 3 L methanol.[14] The methanol extract was concentrated *in vacuo* to about 100 mL, diluted with water, and extracted with ether (4 × 300 mL). The combined ether extracts were dried by magnesium sulfate, and concentrated in *vacuo*, affording 3.5 g for the variety *sativum* and 4.2 g for the variety *holmens*, which were kept in methanol (15 mL) for 4 days at room temperature. The methanol solution was filtered to remove any solid material, and the filtrate was concentrated *in vacuo*, giving a yellow oil that was suspended in 50% aqueous methanol (200 mL) and repeatedly extracted with pentane (75 × 4 mL) to separate the less polar compounds from the more polar ones. The aqueous methanolic layer was then extracted with methylene chloride. The pentane and methylene chloride extracts were dried over magnesium sulfate and concentrated separately *in vacuo*, giving an oily residue (0.8 g and 1.0 g, respectively) for var. *sativum* and 0.75 g and 0.65 g for var. *holmens*,

respectively. Repeated preparative TLC (silica gel/hexane) of the pentane extract gave several divalent sulfur compounds and analysis of the methylene chloride extract by TLC (silica gel/92:8 hexane-isopropanol) gave different components, which were characterized by direct comparison of their spectral data and GC retention times with data on authentic material.

RESULTS AND DISCUSSION

Repeated TLC (silica gel/hexane) gave several divalent sulfur compounds, which were characterized by direct comparison of GC retention times and mass spectra (Tables I–III). The IR spectrum of samples displayed a strong =CH absorption at 3025–2900 cm^{-1} and sulfoxide (S=O)

TABLE I Compounds of *Allium sativum* var. *sativum*

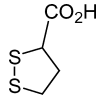
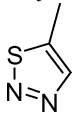
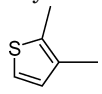
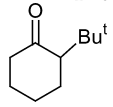
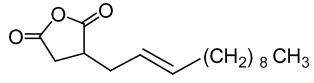
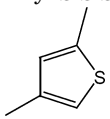
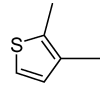
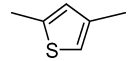
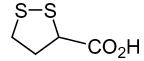
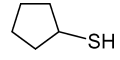
Compound	GC RT min	MW	(%)
Me-S-S-Me	3.413	94	0.98
Allyl-S-Allyl	6.254	114	1.272
Allyl-S-S-Me	8.094	150	18.8
i-Pe-S-S-Me	8.228	120	5.9
	9.255	150	1.5
Allyl-S-S-Allyl	15.070	146	7.9
	15.336	100	4.7
Allyl-S-S-S-Me	17.390	152	3.3
	19.391	112	1.75
n-Pe-SO-Me	23.363	120	2.5
Allyl-S-S-S-Allyl	24.513	178	5.5
Allyl-S-S-S-S-Allyl	33.835	210	2.2
$Me(CH_2)_{10}$-CO_2Me	47.305	186	1.032
	50.266	154	2.9
	40.597	266	1.3

TABLE II Compounds of *Allium sativum* var. *holmens*

Compound	GC RT, min	MW	(%)
Allyl-S-S-Allyl	15.490	146	1.8
Allyl-S-S-S-Me	17.880	152	6.3
	8.276	112	0.8
Allyl-S-S-S-Allyl	24.95	178	1.417
Allyl-S-S-S-S-Allyl	34	210	5.0

stretching at 1020 cm^{-1}. Absorption at 1600–1500 cm^{-1} indicates the presence of double bonds. The ^1H NMR spectrum was quite complex, suggesting the presence of several CH=CH hydrogens. The major nonpolar components for var. *sativum* were identified as dimethyl disulfide

TABLE III Comparison of Organosulfur Compounds of *Allium sativum* var. *sativum*(I) and *Allium ampeloprasum* var. *holmense*(II)

Compound	% **I**	% **II**
Me-S-S-Me	0.98	—
Allyl-S-Allyl	7.9	1.8
Allyl-S-S-Me	18.8	—
i-Pe-S-S-Me	5.9	—
Allyl-S-S-S-Me	3.3	6.3
Allyl-S-S-S-Allyl	5.5	1.4
Allyl-S-S-S-S-Allyl	2.2	5.0
n-Pe-SO-Me	2.5	—
	1.75	—
	—	0.8
	4.7	—
	1.4	—
	—	2.5

(1%), diallyl sulfide (1.2%), methyl isopentyl disulfide (19%), methyl allyl disulfide (6%), diallyl disulfide (8%), and diallyl trisulfide (3.2%); 2,3-dimethyl thiophene, 5-methyl, 1,2,3-thiadiazole, and 1,2-dithiolan-3 carboxylic acid were also identified (Table I). The major organosulfur components for var. *holmens* are diallyl trisulfide (6%) and diallyl tetrasulfide (5%) (Table I). Analysis of methylene chloride extract of var. *sativum* and var. *holmens* did not show any traces of allicin or ajoene. It seems that all allicin and ajoene had been transformed into other organo sulfur compounds because of their high unstability.

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