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Chemical constituents of *Allium stipitatum* regel (persian shallot) essential oil

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ABSTRACT

A. stipitatum (Synonym: A. hirtifolium) or Persian shallot from Amaryllidaceae family with indigenous name of ''Mooseer'' is one of the important edible Alliums in Iran. It is native and endemic from northwestern to southern of Iran and grows as a wild plant in the Zagross Mountains at high elevations of different provinces with the climate of very cold to moderate cold. In this study, essential oil constituents of A. stipitatum were investigated through gas chromatography/mass spectrometry (GC-MS) technique. After obtaining the chromatograms and mass spectra, the essential compounds of the essential oil were determined. As shown 1-Butene,1-(methylthio)-(Z) (18.21%), Methyl methylthiomethyl disulfide (8.41%), Dimethyl tetrasulfide (6.47%), Piperitenone oxide (4.55%) were the most abundant components and comprised 37.64% of the essential oil (Figure 1). While 2,5-Diethylthiophene (0.07%) and n-Nonanal (0.06%) were detected in lower amounts. The presence of compounds showed mono-sulfur (22.42%), disulfide (1.81%), tri-sulfur (13.57%) and tetra-sulfur compounds (6.47%). The results indicated that the highest amount of sulfur compounds is related to mono-sulfur compounds.

Keywords: Allium *stipitatum*, *Amaryllidaceae*, essential oil, chemical composition, GC/MS.

INTRODUCTION

Allium is the largest and most important representative genus of *Amaryllidaceae* family [1]. *Allium* is a very variable and taxonomically difficult genus [2]. The most recent taxonomy proposal for this genus, based on morphological characters and as also molecular data, accepted about 780 species belonging to fifteen subgenera and 56 sections. Recently, more taxa were newly described raising this number to more than 800 species. Currently, about 115 species (including more than 40 endemic ones) are known in the territory of Iran. These numbers indicate that Iran belongs to main center of *Allium* diversity in southwest and central Asia [1].

Persian Shallot, scientifically called *Allium stipitatum* Regel., belongs to *Allium* genus and Amaryllidaceae family. Garlic, onion, shallot and leek are the most important species in this genus and have been long used as spices and also medicine. Saponins, sapogenins, sulphuric compounds (thiosulfinates) and flavonoids, including quercetin and kaempferol, are found in different species of *Allium* genus. Research has shown that both the bulb and the flower of shallot contain a high density of glycosidic flavonols. Disulphide and trisulphide compounds are amongst the most important compounds existing in *Allium* genus species [3]. There have been reports about shallot having pharmacological effects, e.g. antioxidant [4-6]. immune system regulating [7, 8], anticancer [9], anti-platelet aggregation [10], antihyperlipidemic [11], antifungal effects [12] and protective effect in improving liver function [13, 14].

A. stipitatum (Synonym: *A. hirtifolium*) or Persian shallot from *Amaryllidaceae* family with indigenous name of ''Mooseer'' is one of the important edible *Alliums* in Iran. It is native and endemic from northwestern to southern of Iran and grows as a wild plant in the Zagross Mountains at high elevations of different provinces with the climate of very cold to moderate cold. It is different from common shallot (*Allium cepa*) for many characteristics [15].

It is one of the valuable members of *Allium* with its bulbs commonly used as a traditional remedy [7, 16]. Besides, the dried bulb slices are used as additives to yogurt as well as pickling mixtures. For instance, the bulbs of common shallot are pear shaped with the skin reddish brown in color and its cluster may contain as many as 15 bulbs, while for the Persian shallot its bulbs are oval shaped and have white color of skin and normally consists of single or sometimes two bulbs [17].

Several studies have been reported the pharmaceutical activity of Persian shallot including anti-microtubule activities [9], *in vitro* anti-trichomonas activity [18], immunomodulatory effects [7], nematocidal activity [19], anti-proliferative activity on tumor cell lines [9, 20] and antioxidant activity [21]. Other study exhibited that *A. hirtifolium* did not show valuable inhibitory activity on α- amylase enzyme [22]. The effectiveness of *A. hirtifolium* alcoholic extract on reduction of ALP, AST, and ALT is also reported more than Glibenclamide [13].

Studies carried out on the chemical composition of the plant show that sulfur compounds such as Allicin are important constituents of the plant [23]. Although allicin (diallyl-dithiosulfinate) is the most important organosulfur compound that is generally claimed to be responsible for their beneficial effects and numerous studies have been conducted so far [24], it is pointed out that other sulfur compounds such as diallyl disulphide (DDS), S-allylcysteine (SAC) and diallyl trisulfide (DTS) also have some roles in the effects of the plant [2]. In addition to *A. sativum*, allicin, ajoene and other organosulfides are present in A. *hirtifolium* and play important pharmacological roles for example: Antibacterial activities [25], Antiparasitic activities [26], Antiviral effect [27], Antifungal activities [28]. The aim of this study was to analyze and clarify the chemical constituents of this spice essential oils.

MATERIALS AND METHODS

Plant Material

The bulbs of *Allium stipitatum* Regel were collected from Mount Sabz-e-koh, Chaharmahal-e-bakhtiari Province of Iran during fall 2014 at 2510 m above sea level. The plant specimen (Number: HMPRC-423) was deposited in the Herbarium of Medicinal Plants Research Center, Shahr-e-kord University of medical sciences, Shahr-e-kord, Iran.

Essential oils extraction

After collecting and cleaning up, the fresh bulbs of *A. stipitatum*, were kept in nitrogen tanks in order to preserve the volatile compounds left to dry in freeze dryer. They were chopped and then passed through sieve size 60 (25/0mm). The powdered bulbous onions of plant were subjected to Clevenger-type apparatus for hydrodistillation about4 hours at 120°C. The obtained light yellow-color essential oils was dehydrated with anhydrous sodium sulphate weighed and stored in a refrigerator at -20°C until use.

Analysis of Essential oil

Gas chromatography-Mass spectrometry

For identifying the essential oil constituents, the GC and GC/MS devices were used. GC analysis was done using a Thermoquest gas chromatograph with a flame ionization detector (FID). The analysis was carried out using a fused silica capillary DB-5 column (60 m × 0.25 mm i.d.; film thickness 0.25μm). The injector and detector temperatures were kept at 250°C and 300°C, respectively. Nitrogen was used as carrier gas a flow rate of 1 mL/min; oven temperature program was 60–250°C at the rate of 5°C/min, and finally held isothermally for 10 min; split ratio was 1:50. GC-MS analysis was performed using a Thermoquest-Finnigan gas chromatograph equipped with the same column, coupled with a TRACE mass ion trap detector (Manchester, UK). Helium was used as carrier gas with an ionization voltage of 70 eV. Ion source and interface temperatures were 200°C and 250°C, respectively. Mass range was from 40 to 460 *m/z*. Oven temperature program was the same as mentioned above for the GC.

Identification of Compounds.

The constituents of the essential oils were identified by calculation of their retention indices under temperature-programmed conditions for *n*-alkanes (C6–C24) and the oil on a DB-5 column under the same chromatographic conditions. Identification of individual compounds was made by comparison of their mass spectra with those of the internal reference mass spectra library (Adams and Wiley 7.0) or with authentic compounds and confirmed by comparison of their retention indices with authentic compounds or with those reported in the literature [29]. For quantification purpose, relative area percentages obtained by FID were used without the use of correction factors.

RESULTS

Chemical Composition

The essential oil yield of powdered bulb of *A. stipitatum* using hydro distillation method was 0.06 % (v/w). GC and GC/MS analysis of essential oil led to the identification and quantification of forty nine components which accounted for 73.8% of the total essential oil. Table 1 shows the results of the qualitative and quantitative essential oil analyses listed in order of retention indices (RI). As shown 1-Butene,1-(methylthio)-(Z) (18.21%), Methyl methylthiomethyl disulfide (8.41%), Dimethyl tetrasulfide (6.47%), Piperitenone oxide (4.55%) were the most abundant components and comprised 37.64% of the essential oil (Figure 1). While 2,5-Diethylthiophene (0.07%) and n-Nonanal (0.06%) were detected in lower amounts. The presence of compounds showed mono-sulfur (22.42%), disulfide (1.81%), tri-sulfur (13.57%) and tetra-sulfur compounds (6.47%). The results indicated that the highest amount of sulfur compounds is related to mono-sulfur compounds. Differences were observed in the sulfur content of the constituents of this plant with other *Allium* species [30].

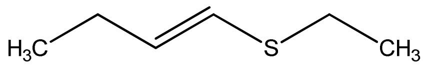
Table 1. Chemical composition of the essential oil of the bulb of *A. stipitatum*

No	[a]RI	Area% GCMS	Compounds
1	971.023	2.39	2,3,4-Trithiapentane
2	1030.22	0.13	Methyl n-butyl disulfide
3	1033.33	0.62	Butane(dithioic) acid, methyl ester
4	1091.56	0.06	2,5-Diethylthiophene
5	1102.22	0.04	n-Nonanal
6	1130.99	8.41	Methyl methylthiomethyl disulfide
7	1200.41	0.12	n-Dodecane
8	1222.76	6.47	Dimethyl tetrasulfide
9	1248.13	2.16	1-Butene, 1-(methylthio)-, (E)
10	1256.72	18.21	1-Butene, 1-(methylthio)-(Z)
11	1288.06	0.28	1,5-Dithionan-3-one
12	1302.76	1.4	5,6-Dithiadecane
13	1304.33	2.2	3,5-heptandione
14	1307.48	0.29	1,2,3-benzenetrithiol
15	1343.7	0.58	Piperitenone
16	1361.81	0.45	Methane, tris(methylthio)
17	1369.29	4.55	Piperitenone oxide
18	1381.5	0.24	2,6-dimethyl-3-formyl-1-thia-3-cyclohexene
19	1396.46	0.47	n-Tetradecane
20	1421.22	1.25	trans-Caryophyllene
21	1434.29	0.27	Gurjunene<beta->
22	1451.43	0.17	Geranyl acetone
23	1460.82	0.46	2,3,4-Trithiapentane
24	1484.9	0.75	2,3-dihydro-α-ionone
25	1487.76	0.93	trans-β-Ionone
26	1508.51	0.18	Cuparene
27	1514.89	0.46	1-(2,4-dimethylphenyl)-2-phenylethne
28	1531.91	1.57	3,5-Diisopropyl-1,2,4-trithiolane
29	1558.3	0.7	Dimethyl 3-sulfinopropionate
30	1581.28	0.51	Spathulenol
31	1585.96	0.43	Caryophyllene oxide
32	1594.89	1.48	1,1,3,3-Tetrakis(methylthio)propene
33	1629.46	0.48	1,1,3,3-Tetrakis(methylthio)propene
34	1674.11	0.24	2-(2,2-dimethylpropanoyl)thiazole
35	1694.64	0.46	Pentadecan-2-one
36	1722.89	0.14	Methyl myristate
37	1771.14	0.28	Benzyl benzoate
38	1789.55	0.78	6-(Carbomethoxy)-1,6-dimethoxy-1,4-cyclohexadiene
39	1800.49	0.28	n-Octadecane
40	1817.73	0.81	2-Butyltetrahydrothiophene
41	1847.29	2.86	Hexahydrofarnesyl acetone
42	1928.35	2.25	Methyl palmitate
43	1995.88	0.2	Ethyl hexadecanoate
44	2000.27	0.19	n-Docosane
45	2049.59	1.14	Methyl linoliate
46	2053.15	2.86	Methyl linolenate
47	2100	0.13	n-Heneicosane
48	2300	1.98	n-Tricosane
49	2399.39	0.49	n-Tetracosane

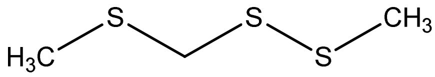
[a] Compounds listed in order of retention indices (RI)

Figure 1. Molecular structure of important organosulfur compounds from *Allium stipitatum* oil

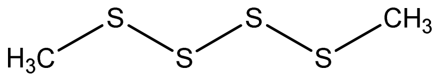
1-Butene, 1-(methylthio)-(Z)



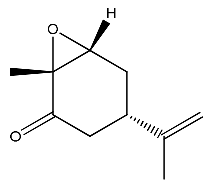
Methyl methylthiomethyl disulfide



Dimethyl tetrasulfide



Piperitenone oxide



DISCUSSION

Medicinal plants have been used for various conditions since ancient times [31-33]. The effects of these plants have substantially been confirmed by scientific investigations [34-36]. Hence, medicinal plants are considered as a valuable source for preparation of new drugs [37, 38]. Therefore, researchers try to identify the chemical constituents of medicinal plants and the most effective component for preparation of new drugs [39-42]. In this regard, medicinal plants with high level of antioxidant activity are very important, due to effective on a wide variety of diseases such as diabetes [43], atherosclerosis [44], infections [45, 46], inflammatory disorders [47, 48] Parkinson's disease [49, 50], Alzheimer [51, 52] and other oxidative induced diseases [53, 54]. *Allium* species is one of these plants. *Allium* a genus belongs to *Amaryllidaceae* family, including important food plants such as onion, garlic, shallot, chive, leek and rakkyo [55]. Moreover *Allium* species are reported to have several effects on immune functions and antibacterial, antifungal, antivirus, anticancer and practically effect on cardiovascular diseases. They have been used for hundreds of years and have been recognized as significant sources of photochemical especially organosulfur compounds with healthful effect. Although, there are many scientific studies on different genus of *Allium*, little work has been reported about chemical composition and pharmacological effects of Persian shallot essential oil. It is widely consumed as flavor enhancers. Chemical composition analysis showed 1-Butene,1-(methylthio)-(Z), Methyl methylthiomethyl disulfide, Dimethyl tetrasulfide, Piperitenone oxide were the most abundant components in *A. stipitatum* oil.

Mahboubi *et al*. (2014) presented 5-chloroorcylaldehyde, methyl methylthiomethyl disulfide, tricosan, pentylthiophene, and dimethyl trisulfide were the main components, and the major sulfides in *A. hirtifolium* oil were 27.7% while in our study the major sulfides are 33.09%. It seems that some differences in the volatile composition arise and which could be attributed to the geographic origin of the plant [56].

Generally, the present study showed sharp organosulfur content. In the other hand, it seems that *A. stipitatum* growing in Chaharmahl-e-bakhtiari may be remarkable source of sulfides compounds. Also it should be noted that presence Ethyl hexadecanoate (0.2%) is another component of *A. stipitatum* oil that the similar reported in other study [15]. It is normally used for flavoring in food field and also used as intermediate for organic synthesis [57-64].

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