Original article

Headspace volatiles of Allium subhirsutum L. growing in Turkey

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Abstract

Allium subhirsutum L. (Amaryllidaceae family) is a plant species, widely spread around the Mediterranean region from Spain and the Canary Islands to Turkey and Palestine. The A. subhirsutum is called in the regional name ‘Tüylü körmen, Köremen’ or called ‘Yabani sarýmsak’. A. subhirsutum sample using headspace - SPME procedure the fibres used in this study were coated with polydimethylsiloxane (PDMS, 100 µm) (supplied by Supelco Bellefonte, USA), was used with a sampling time of 30 min. Thermal desorption at 250°C during 10 min for the GC/MS analysis. The GC/MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 m × 0.25 mm, 0.25 mm film thickness) was used with He as carrier gas. GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min, at splitless mode. MS were taken at 70 eV. Mass range was from m/z 35 to 450.

Headspace volatiles of crushed bulbs of A. subhirsutum were analyzed by gas chromatography/mass spectrometry. The volatiles were trapped by SPME in a dynamic headspace set up. Volatiles of crushed bulbs of A. subhirsutum were trapped on an HS-SPME (Red fiber). Main components were found to be allyl methyl disulfide (41.0%), diallyl disulfide (20.7%) and dimethyl sulfide (15.3%).

Key words: Allium subhirtusum L., amaryllidaceae, phytochemistry, GC-MS, SPME

1. Introduction

Allium subhirsutum L. from the Amaryllidaceae family, is a plant species, widely spread around the Mediterranean region from Spain and the Canary Islands to Turkey and Palestine. Family of Amaryllidaceae, Allium genus is represented by 176 species in Turkey. The A. subhirsutum is called the regional name ‘Tüylü körmen, Köremen’ or called ‘Yabani sarýmsak’. A. subhirsutum is represented by a single species in Turkey, is a Mediterranean elements. A. subhirsutum, the species we collected in the region, is used for food and medical purposes (Koyuncu, 2012). Allium species has been used in diuretic diarrhea, antibacterial, wound healing, cardiotonics since the old times. A. subhirsutum is also called ‘körmen böreði’ food, is used in Mugla Turkey (Baytop, 1984).

2. Materials and Methods

2.1 The plant material

A. subhirsutum was collected from Marmaris: Yeýemeler district of Mugla Province on 8 March, 2018. The voucher specimen has been deposited at the herbarium in the Anadolu University (ESSE 15489), Eskiþehir, Turkey.

2.2 Headspace-SPME procedure

SPME fibre precoated with a 100 µm layer of polydimethylsiloxane (PDMS) (supplied by Supelco Bellefonte, USA), was used with a sampling time of 30 min (Room temperature). The fibre was then inserted into the injection port of the GC/MS for the desorption of the adsorbed volatile compounds for analysis. Thermal desorption at 250°C during 10 min.

2.3 GC/MS analysis

The GC/MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 mx0.25 mm, 0.25 mm film thickness) was used with He as carrier gas. GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min, at splitless mode. MS were taken at 70 eV. Mass range was from m/z 35 to 450.

The components of headspace volatiles were characterized by comparison of their mass spectra with those in the Baser Library of essential oil constituents, Wiley GC/MS Library, Adams Library, Mass Finder Library and confirmed by comparison of their retention indices. Alkanes were used as reference points in the calculation of relative retention indices (RRI). The results of analysis are shown in Table 1.
3. Results and Discussion

Headspace volatiles of crushed bulbs of *A. subhirsutum* were analyzed by gas chromatography/mass spectrometry. The volatiles were trapped by SPME in a dynamic headspace set up. Volatiles of crushed bulbs of *A. subhirsutum* were trapped on an HS-SPME (Red fiber). The present work is the first report of the volatile components of *A. subhirsutum*. Six volatile compounds were identified of the crushed bulbs representing 82.3%. Main components were found to be allyl methyl disulfide (41.0%), diallyl disulfide (20.7%) and dimethyl sulfide (15.3%) and other components methyl (methylthio) methyl disulfide (2.0%), methyl trans-propenyl disulfide (1.9%), allyl methyl trisulfide (Table 1).

In the literature, bulbs of *A. cepa* are reported. Solid-phase micro extraction (SPME) was used for the extraction of the volatiles of yellow onions (*Allium cepa* L.). The most important compound found in the headspace of slice onions by SPME-GC-MS after 1 min emission of volatiles was thiopropanal s-oxide. Also, some dipropenyl disulphides and propenylpropyl disulphides were identified. After 30 min, most of the thiopropanal s-oxide disappeared, and other sulphur and non-sulphur compounds appeared in the GC chromatograms. The major constituents were diprop (en) yldisulphides. Similar constituents were also found in the water-slurred onions by headspace and direct SPME (Jarvenpaa, 1998). Treatments of autoclaving, high temperature ageing (aged-black garlic), crushing, and roasting at 100, 150, and 200°C were applied to alter the volatile profiles of garlic (*Allium sativum* L.). Headspace volatiles in samples were analyzed by a SPME-GC/MS. Total peak areas of crushed-raw garlic were the highest and those of aged-black garlic clove were the lowest. Crushing effects were clearly observed in raw garlic, aged-black garlic, and roasted garlic at 200°C for 60 min. Sulfur-containing volatiles including diallyl disulfide and diallyl thio sulfide were major volatiles (Kim et al., 2011).
A volatile profile of ramson (wild garlic, *Allium ursinum* L.), honey was investigated by headspace solid-phase microextraction (HS-SPME) and ultrasonic solvent extraction (USE), followed by gas chromatography and mass spectrometry (GC-FID/GC-MS) analyses. The headspace was dominated by linalool derivatives: cis- and trans-linalool oxides (25.3%; 9.2%), hotrienol (12.7%), and linalool (5.8%). The extracts with diethyl ether contained hydroquinone (25.8-36.8%) and 4-hydroxybenzoic acid (11.6-16.6%) as the major compounds, while (E)-4-(r-10, t-20, c-40-trihydroxy-20, 60, 60 trimethylcyclohexyl) but-3-en-2-one predominated in dichloromethane extracts (18.3-49.1%) (Jerkovic and Kus, 2017).

4. Conclusion

To the best of our knowledge, headspace volatiles of *A. subhirsutum* is the first report on the GC-MS determination of volatile components of *A. subhirsutum*.

Table 1: Chemical composition and relative amounts (% area) of *A. subhirsutum*

<table>
<thead>
<tr>
<th>RRI</th>
<th>Compounds</th>
<th>%</th>
<th>IM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1083</td>
<td>Dimethyl sulfide</td>
<td>15.3</td>
<td>MS</td>
</tr>
<tr>
<td>1292</td>
<td>Allyl methyl disulfide</td>
<td>41.0</td>
<td>MS</td>
</tr>
<tr>
<td>1294</td>
<td>Methyl trans-propenyl disulfide</td>
<td>1.9</td>
<td>MS</td>
</tr>
<tr>
<td>1492</td>
<td>Diallyl disulfide</td>
<td>20.7</td>
<td>MS</td>
</tr>
<tr>
<td>1607</td>
<td>Allyl methyl trisulfide</td>
<td>1.4</td>
<td>MS</td>
</tr>
<tr>
<td>1674</td>
<td>Methyl (methylthio) methyl disulfide</td>
<td>2.0</td>
<td>MS</td>
</tr>
</tbody>
</table>

RRI: Relative retention in dices calculated against n-alkanes. Identification method (IM): MS, identified on the basis of computer matching of the mass spectra with those of the Wiley, Adams and Mass Finder libraries and comparison with literature data.

Conflict of interest

We declare that we have no conflict of interest.

References


