

HS-SPME-GC-MS Analysis of onion (*Allium cepa* L.) and shallot (*Allium ascalonicum* L.)

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Abstract

The volatile organic compounds of onion and shallot were determined via HS-SPME-GC-MS. The main components were dipropylidysulphide and allylpropylidysulphide. Thiopropanal S-oxide were detected only in onion volatiles. In shallot is interesting the presence of 2-methyl-2-pentenal, a compound with an intense fruity aroma, that can characterize the different aroma between onion and shallot. The SPME-GC-MS analysis of shallot after absorption on the SPME fiber at 50°C showed the presence of new compounds, whose structures have been discussed.

1. Introduction

Solid Phase MicroExtraction (SPME) has been widely used to determine volatile organic compounds. In our experience in this field, we used this method to determine fire accelerant in fire debris (D'Auria, 2006), volatile organic compounds in crude oil (D'Auria *et al.*, 2009), olive oil (Bentivenga, D'Auria, Fedeli *et al.*, 2004), wine (Acquaviva *et al.*, 2014), saffron (D'Auria *et al.*, 2006), truffles (D'Auria *et al.*, 2014), honey (Bentivenga, D'Auria, Mauriello *et al.*, 2004), horseradish (D'Auria *et al.*, 2004) thymus, rosemary, laurel, sage (D'Auria and Racioppi, 2015), lavender and oregano (D'Auria *et al.*, 2005), kiwi (Celano *et al.*, 2006), *Monilinia* species (Mang *et al.*, 2015) and in the scent of an orchid (D'Auria *et al.*, 2017).

The analysis of the volatile organic compounds of onions has been the object of several works (Mondy *et al.*, 2001; Auger *et al.*, 2005; Lanzotti 2013). SPME has been used in the analysis of onion (Järvenpää *et al.*, 1998; Mondy *et al.*, 2002; Soto *et al.*, 2015). However, SPME has not been used in the determination of volatile organic compounds of shallot (*Allium ascalonicum* L.).

In this article, we want to report the SPME

analysis of both onion and shallot in order to understand the origin of possible differences in the volatile organic compounds composition.

2. Materials and methods

Onion and shallot have been cleaned of the outermost layers and finely cut with a knife. The analysis was carried out immediately after cutting, using approximately two grams for each species.

A 50/30- μ m DVB/CAR/PDMS module (57328-U, Supelco, Milan, Italy) was employed to determine VOCs. SPME fiber was maintained over the sample in a 20 ml vial at 20°C and at 40°C for 20 min. Analyses were accomplished with an HP 6890 Plus gas chromatograph equipped with a Phenomenex Zebron ZB-5 MS capillary column (30-m x 0.25-mm i.d. x 0.25 μ m FT) (Agilent, Milan, Italy). An HP 5973 mass selective detector (Agilent) was utilized with helium at 0.8 ml/min as the carrier gas. A splitless injector was maintained at 250°C and the detector at 230°C. The oven was held at 40°C for 2 min, then gradually warmed, 8°C/min, up to 250°C and held for 10 min. Tentatively identification of aroma

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components was based on mass spectra and Wiley 6 and NITS 98 library comparison. Single VOC peak was considered as identified when its experimental spectrum matched with a score over 90% that present in the library. The Kovats Retention Index was used to identify the aroma components (Kovats, 1958). All the analyses were performed in triplicate.

3. Results and discussion

The origin of sulfur-containing compounds in onions has been extensively studied in the past (Block, 1992). They originate from *S*-alkyl or *S*-alkenyl-L-cysteine-*S*-oxide (**1**), present in the cytoplasm, when they react with alliinase, located in the vacuoles. The reaction allowed the formation of the corresponding sulfenic acids **2**, that was converted into the corresponding thiosulfinates **3** (Figure 1). This type of compounds are not stable and was converted in several derivatives, some of them are reported in Figure 1). In onions, a relative importance was attributed to the propanethial *S*-oxide, a lachrymatory factor found in onions.

We performed the analysis of both onion (*Allium cepa* L.) and shallot (*Allium ascalonicum* L.) by absorption of volatiles in sliced samples at 20 °C. The use of this temperature has been due to the need to avoid rapid decomposition of the lachrymatory agent emitted by onion. The results are reported in Table 1.

The analysis of onion allowed the identification of ten components. The main components were dipropyldisulphide and allylpropyldisulphide. It is noteworthy that, by using this type of analysis, thiopropanal *S*-oxide, the lachrymatory agent emitted by onions, can be detected. This compound cannot be detected in the analysis of shallot. Also in shallot the main components were dipropyldisulphide and allylpropyldisulphide. It is interesting the presence of 2-methyl-2-pentenal, an intense fruity aroma, that can characterize the different aroma between onion and shallot.

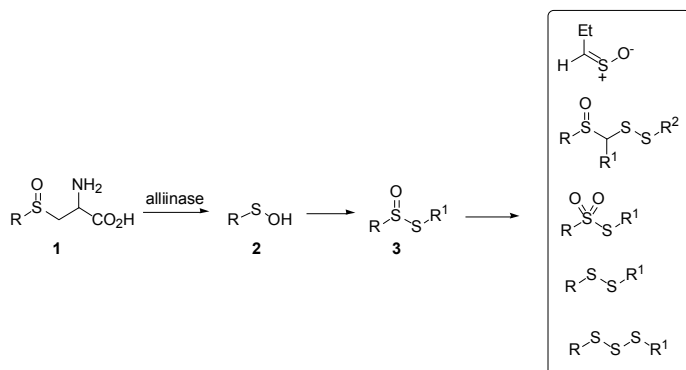


Figure 1. The origin of sulphur compounds in onion.

Table 1. Volatile organic compounds in onion and shallot with absorption on SPME fiber at 20°C.

Compound	r.t. [min]	KI	Area %	
			Onion	Shallot
Methanethiol	1.61	500	3.25 ± 0.02	0.46 ± 0.01
Propanethiol	2.30	600	2.30 ± 0.01	4.20 ± 0.02
Thiopropanal <i>S</i> -oxide	4.37	740	0.36 ± 0.03	
2-Methyl-2-pentenal	5.66	804		0.13 ± 0.01
2,5-Dimethylthiophene	7.18	865	2.33 ± 0.01	1.06 ± 0.01
Methylisopropyldisulphide	7.78	880	3.53 ± 0.03	2.74 ± 0.02
Dipropyldisulphide	11.64	1094	51.41 ± 0.05	58.57 ± 0.05
Allylpropyldisulphide	11.82	1098	20.69 ± 0.05	13.27 ± 0.05
Methyl propylthiosulfonate	12.35	1154	0.59 ± 0.01	0.46 ± 0.02
Dipropyltrisulphide	15.52	1294	4.66 ± 0.02	6.99 ± 0.03
Allylpropyltrisulfide	15.74	1309	1.31 ± 0.01	0.83 ± 0.01

It is noteworthy that in previously published paper on *Allium cepa* L. and *Allium porrum* L. 2-methyl-2-pentenal was one of the main components found in the analyzed oil (Schulz *et al.*, 1998). Probably, this observed difference depends on the extraction methodology used in the article where an aqueous blend was extracted with pentane for three hours.

Furthermore, it is noteworthy that most of the compounds we found in both onion and shallot did not compare in the list of the compound found in previous SPME study on onion samples (Mondy *et al.*, 2002).

When the absorption of volatile organic compounds was performed at 50°C the nature of the compounds found in onion and shallot considerably changed. The results are collected in Table 2. We collected the results only for shallot, in order to see if the increased temperature can change the volatile profile of the species. We observed a neat reduction of the amounts of dipropyl- and allylpropyldisulphide, while the amount of dipropyl and allyldipropyltrisulphide increased. Furthermore, we observed the formation of new compounds, in our knowledge never observed before.

Table 2. Volatile organic compounds in shallot with absorption on SPME fiber at 50°C.

Compound	r.t. [min]	Area %
Propanethiol	2.31	2.57 ± 0.01
2-Methyl-2-pentenal	5.65	0.20 ± 0.01
2,5-Dimethylthiophene	7.18	0.51 ± 0.01
Methylpropyldisulphide	7.77	1.42 ± 0.03
Dipropyldisulphide	11.62	34.80 ± 0.05
Allylpropyldisulphide	11.79	7.14 ± 0.03
Methylpropylthiosulfonate	12.36	1.72 ± 0.02
Dipropyltrisulphide	15.66	21.70 ± 0.05
Allylpropyltrisulphide	15.82	9.18 ± 0.03
Compound 4	19.41	4.35 ± 0.03
Compound 5	19.64	2.00 ± 0.02
Compound 6	19.80	3.72 ± 0.02
Compound 7	22.51	2.02 ± 0.02

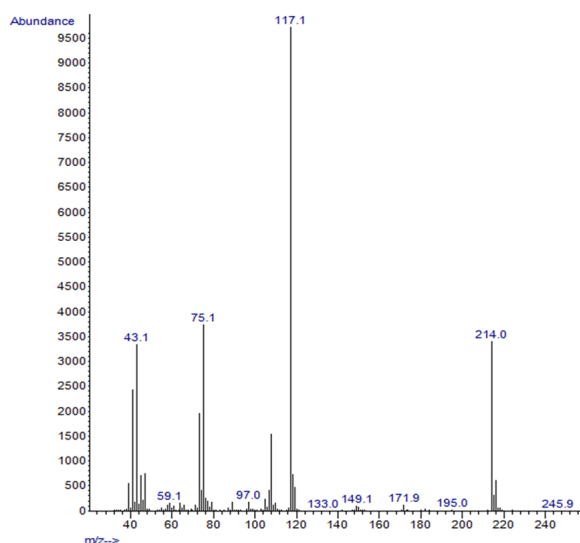


Figure 2. Mass spectrum of compound 4.

Figure 2 showed the mass spectrum registered for the compound **4** found at 19.41 min. The molecular peak showed a very small abundance and can be found at m/z 214. The analysis of the relative abundance of the isotopic peak at m/z 216 showed that this molecule contained four sulfur atoms. The peak at m/z 117 can be in agreement with $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2^+$ ion. The assignment is in agreement also with the fragment at m/z 43 ($\text{CH}_3\text{CH}_2\text{CH}_2^+$) and that at m/z 75 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{S}^+$). On the basis of this assignment, the fragment at m/z 214 can be identified as $(\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SSSH})^+$. The compound **4** can be tentatively identified as described in Figure 3 as 3-(propanethiyl)propanetrithiol.

The compound **5**, found after 19.64 min in our gas-chromatographic analysis, shown the mass spectrum reported in Figure 4. The spectrum did not show the molecular peak. The fragment at m/z 115 is in agreement with the presence of the structure $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}=\text{CH}-\text{CH}_2^+$. The presence of a stabilized allylic carbocation can account for the absence due to the loss of sulfur. The proposed structure is shown in the Figure 3 as 3-(propanethiyl)-2-propenetrithiol. The compound found at 19.80 min in the gas-chromatogram showed a molecular peak at m/z 212 (Figure 5). The fragment at m/z 147 is due to the loss of SSH, while the fragment at m/z 115, can be due to the loss of SSSH from the molecular peak. The mass is in agreement with the structure $\text{CH}_2=\text{CHCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2^+$. The proposed structure for the compound **6** is shown in Figure 3 as 3-(2-propenethiyl)-propanetrithiol.

The compound **7**, found at 22.51 min, showed the mass spectrum reported in Figure 6. The molecular peak was not present in the spectrum. The main fragmentation

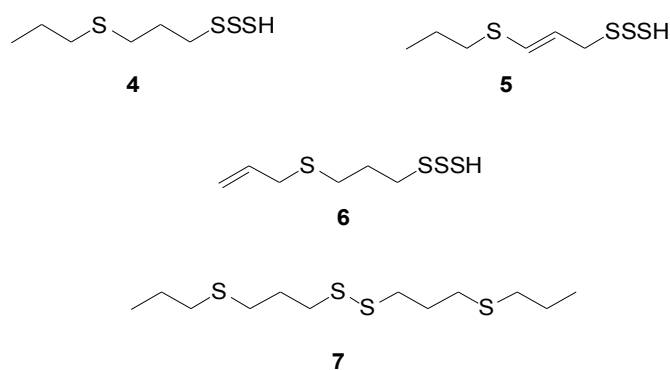


Figure 3. Proposed structures for compounds 4-7

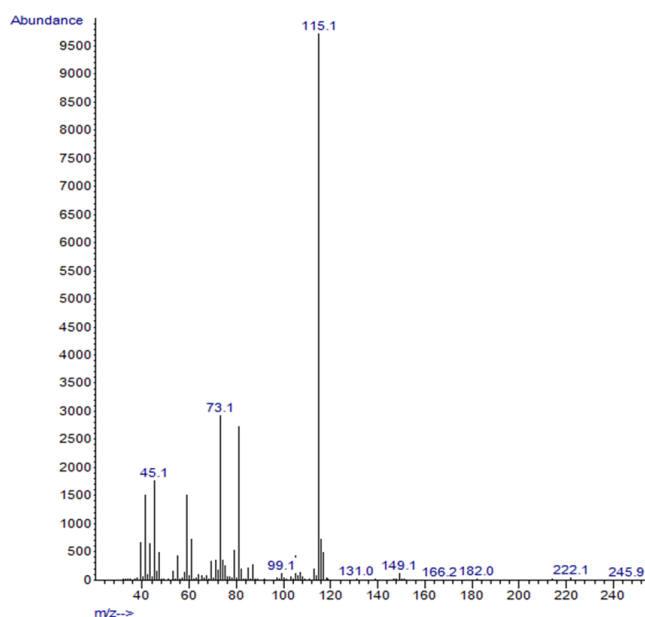


Figure 4. Mass spectrum of compound 5

at m/z 149 is in agreement with a dimeric structure 7 (Figure 3) as 3,3'-di(propanethiyl)dipropyldisulphide.

In conclusion, we have shown that SPME can be used in order to characterize the volatile organic compounds emitted by sliced onions and shallots. We observed some differences between these two species attributable to the organoleptic differences between the species. In fact, it is well known that shallot has less intense, more aromatic and slightly garlicky smell.

Furthermore, the analysis obtained through absorption on the SPME fiber at higher temperature allowed to isolate new compounds.

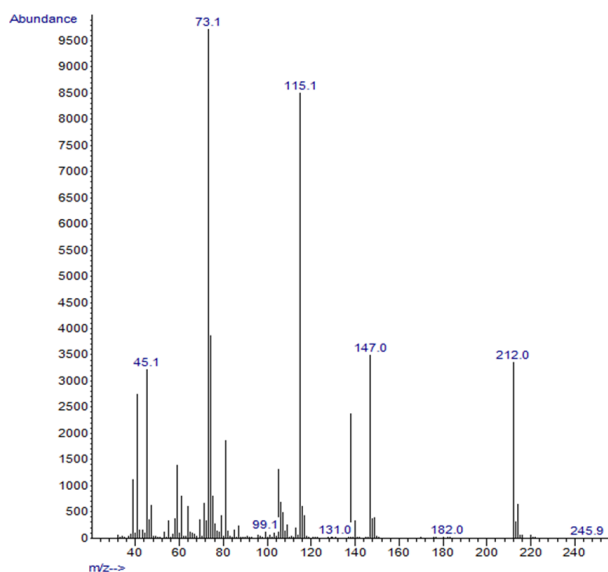


Figure 5. Mass spectrum of compound 6

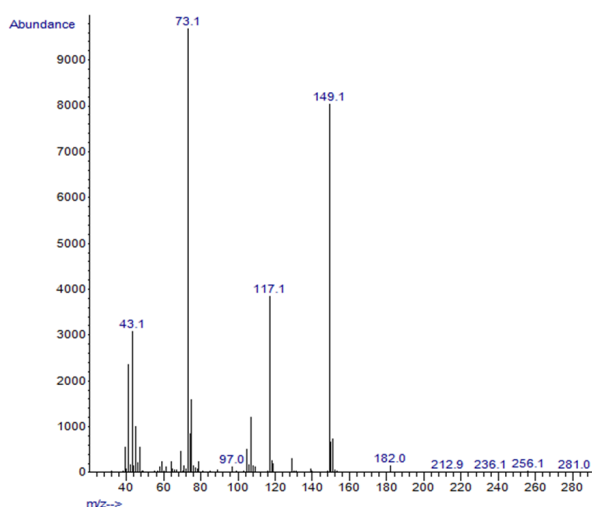


Figure 6. Mass spectrum of compound 7

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