Volatile Flavor Constituents of Fresh *Marasmius alliaceus* (Garlic *Marasmius*)

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Comparative analyses of volatile flavor constituents of fresh wild *Marasmius alliaceus* (garlic *Marasmius*) were carried out by organic solvent extraction and dynamic headspace concentration using GC/MS and GC/sniffing. Sixteen and 27 volatile components were identified by solvent and headspace methods, respectively. The major linear sulfur-containing compounds identified in *Marasmius* species were 2,4,5,7-tetrathiaoctane and 2,3,5-trithiahexane by solvent extraction and 2,4-dithiapentane, 3,4-dithiahexane, and 2-thiapentanal by headspace concentration. Seven volatile compounds were identified by both methods, i.e., 1,3-dithietane, benzaldehyde, 2,3,5-trithiahexane, 2,3,4,6-tetrathiaheptane, and three dimethyl polysulfide components (dimethyl disulfide, dimethyl trisulfide, dimethyl tetrasulfide). Solvent extraction and headspace concentration analyzed all volatile components present in mushrooms and only exhaled compounds, respectively.

Keywords: *Mushroom; Marasmius alliaceus; flavor; organic solvent extraction; headspace concentration*

INTRODUCTION

Mushrooms are particularly appreciated as food and spices. Several studies investigated their aroma and flavor chemistry (Takama *et al*., 1979; Maga, 1981; Watson *et al*., 1986; Audouin *et al*., 1989; Largent *et al*., 1990; Wood *et al*., 1990, 1994; Buchbauer *et al*., 1993; Mau *et al*., 1994; Breheret *et al*., 1997), considering that the mushrooms are usually consumed for their flavor properties. The typical flavor of mushroom is due to volatile C_8 compounds including 1-octen-3-ol, the most important volatile component associated with fresh mushrooms (Cronin and Ward, 1971; Pyysalo, 1976, 1979; Pyysalo and Suihko, 1976; Tressl *et al*., 1982; Fischer and Grosch, 1987; Rapior *et al*., 1996).

Of them, *Marasmius alliaceus* (Jacq.:Fr.) Fr. (garlic *Marasmius*) can be used as condiment for its special flavor. As expressed by its Latin name, which comes from *allium* (garlic) and *aceous* (like), the striking feature of this little edible species is its strong odor of garlic. Other similar *Marasmius* species have garlicky odor such as *M. scorodonius* (Fr.:Fr.) Fr. [= *M. alliatus* (Schaeff.) Quél., shallot *Marasmius*] and *M. prasiosmus* (Fr.) Fr. (leek *Marasmius*) (McIlvaine and Macadam, 1973; Pomerleau, 1980; Courtecuisse and Duhem, 1994).

Some workers have reported the garlic-like odor of *Marasmius* species culturing *M. alliaceus* mycelium on solid and liquid media (Badcock, 1939; Oddoux and Porte, 1968; Gmelin *et al*., 1976; Maga, 1976; King *et al*., 1977; Lamer-Zarawska *et al*., 1986). A series of metabolites possessing the sesquiterpenoid alliacane skeleton has been isolated from culture fluids of *M. alliaceus* (King *et al*., 1977; Bradshaw *et al*., 1981, 1982; Farrell *et al*., 1981; Hanson, 1981; Avent *et al*., 1985, 1986; La Clair *et al*., 1995). Furthermore, it is shown that γ-glutamylmarasmine, a dipeptide containing a cysteine sulfoxide moiety, was the common natural precursor of the garlic-like odorous secondary products from crushed mycelium and dried fruit bodies of *M. alliaceus*, *M. scorodonius*, and *M. prasiosmus* (Gmelin *et al*., 1976). On the other hand, several strains of *M. alliaceus* were examined for their ability to transform terpene hydrocarbon in agitated submerged culture (Schindler and Schmid, 1982; Busmann and Berger, 1994a–c).

Relatively little is known from the literature about the volatile compounds responsible for the garlic odor of *M. alliaceus*. In the present work, the analyses of these components were undertaken for the first time on fresh carpophores of *M. alliaceus* by organic solvent extraction and dynamic headspace concentration using GC/MS and GC/sniffing to identify the volatile components.

EXPERIMENTAL PROCEDURES

Materials. *M. alliaceus* (Jacq.:Fr.) Fr. (garlic *Marasmius*) is a small mushroom with a brownish cap, whitish gills, and blackish pruinato-velvety stalk. Fresh specimens of *M. alliaceus* were collected in September 1994 and 1995 in France and wrapped in waxed paper bags; the specimens were treated in duplicate immediately after collection.

Solvent Extraction. Within a few hours of collection, the volatile compounds of 35 and 50 g samples of small fresh mushroom cubes from the fall 1994 and 1995 collections were extracted for 5 h in a Soxhlet apparatus with dichloromethane (30 and 60 mL, respectively). After solvent extraction under atmospheric pressure, 63 and 80 mg of extract were obtained, respectively.

Dynamic Headspace Concentration. Fifty grams of small fresh mushroom cubes from the 1995 collection was placed in a glass cell (0.25 L capacity) directly connected to a dynamic headspace injector. Volatile components of the fresh mushroom were concentrated on a Tenax trap with a stripping

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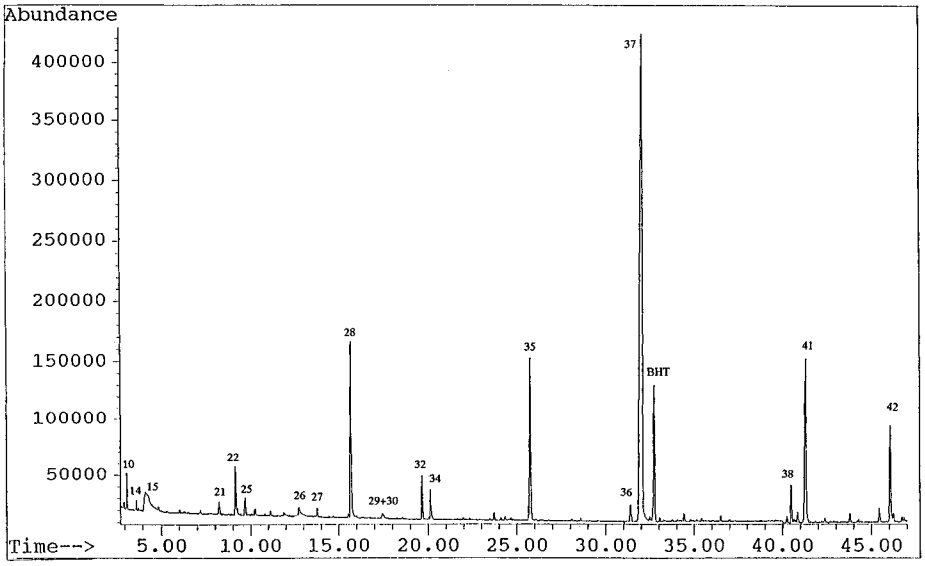

Figure 1. Chromatogram of solvent extract from *M. alliaceus* 1995 collection.

gas (helium) flow rate of 30 mL/min for 20 min at room temperature.

Gas Chromatography/Mass Spectrometry. Analyses were carried out using a gas chromatograph Hewlett-Packard (5890) and a mass selective detector Hewlett-Packard (5971) with a potential of 70 eV for ionization by electron impact.

Solvent extraction analyses were performed with a 30 m × 0.20 mm × 0.25 μm dimethylpolysiloxane DB-1, fused silica capillary column. The carrier gas was helium with a constant flow rate of 0.6 mL/min. The injector and detector temperatures were 200 and 220 °C, respectively. The column was temperature programmed from 50 °C (2 min) to 200 °C at 4 °C/min.

Headspace analyses were carried out by a concentrator/headspace injector (CHISA device, SGE) and performed by a 50 m × 0.22 mm × 1 μm dimethylpolysiloxane BP-1. Pressure of carrier gas (helium) was fixed at 22 psi. The injector and detector temperatures were 210 and 250 °C, respectively. The column was temperature programmed from 50 to 220 °C at 3 °C/min.

Gas Chromatography/Sniffing. Headspace analyses were carried out by a purge and trap injector (DCI device, DELSI Instruments) connected to a gas chromatograph (DELSI 30) and performed with a 50 m × 0.32 mm × 1 μm dimethylpolysiloxane SPB-1 fused silica capillary column. Pressure of carrier gas (helium) was fixed at 14.5 psi. The detector temperature was 230 °C. The column was temperature programmed from 50 to 220 °C at 3 °C/min. Temperatures of the trap system for concentration and desorption were, respectively, −20 and 250 °C. Odor profile description was obtained using a sniffing port (olfactory detector, SGE) with a ratio of FID 30%/sniffing 70%; GC/sniffing was performed by three persons using the olfactory referential "Le champ des odeurs" (Jaubert *et al.*, 1987).

RESULTS AND DISCUSSION

Solvent Extraction. *M. alliaceus* was collected in 1994 and 1995. The collections were separately extracted in a Soxhlet apparatus with dichloromethane; similar yields of extracts were obtained, i.e., 0.18 and 0.16% of fresh mushroom weight, respectively. These extracts with a strong garlic-like odor were directly analyzed by GC/MS on a DB-1 capillary column as described for the 1995 collection (Figure 1); the prior addition of butylhydroxytoluene (BHT) as internal standard (10 mg/L) in both extracts allowed the semiquantitative evaluation of the volatile components.

The results of GC/MS analysis of volatile compounds are shown in Table 1; the compounds are numbered according to their Kovats indices. Identification was accomplished by comparing the Kovats indices and mass spectral data with published data (Stenhagen *et al.*, 1976; Golovnya *et al.*, 1979; The Mass Spectrometry Data Centre, 1986; McLafferty and Stauffer, 1989; Misharina and Golovnya, 1989). The structure assignments of some sulfur compounds were based solely on the interpretation of mass spectral data; these compounds are considered as tentatively identified.

The qualitative composition and the relative proportion of the volatile components were very close in the 1994 and 1995 samples. Figure 1 shows the chromatographic outline of the volatile constituents in *M. alliaceus* organic extract. The estimated volatile proportion corresponds to approximatively 5% of the solvent extract, i.e., 0.008% of fresh mushroom weight.

The main volatile compounds **28**, **35**, **37**, **41**, and **42** (Figure 2) are formed by $-CH_2S-$ unit association as indicated for the identification of their precursors (Gmelin *et al.*, 1976; Yasumoto *et al.*, 1976). 2,3,5-Trithiahexane (**28**) was already described (Stephani and Baltes, 1992; Kubota and Kobayashi, 1994). The mass spectrum of peak **37** presents the same fragments as that of peak **28**, which involves related structures. The respective molecular masses of 186 and 140 suggest the presence of an additional $-SCH_2-$ unit in **37**; this is confirmed by the $M + 2^+/M^+$ ratio, which indicates the presence of four sulfur atoms. Hence, compound **37** is a tetrathiaoctane; the absence of the *m/z* 107 fragment implies that the sulfur atoms are in the 2-, 4-, 5-, and 7-positions. 2,4,5,7-Tetrathiaoctane (**37**) was described by Kubota and Kubayashi (1994). The molecular formula $C_5H_{12}S_5$ and the retention index (1777) of compound **42** showed an additional $-CH_2S-$ unit when compared with compound **37**. Compound **42** with *m/z* 107 fragment was tentatively identified as 2,4,5,7,9-pentathiadecane. Compound **35** has a molecular mass of 172 involving four sulfur atoms. The resulting formula is $C_3H_8S_4$, and the weak intensity of the molecular ion excludes a cyclic structure. Compound **35** is identified as 2,3,4,6-tetrathiaheptane due to the presence of *m/z* 93 and 79 fragments; the value of the chromatographic retention index of **35** is coherent with those of the previous sulfur compounds. Compound **41** with molecular mass 218 and five sulfur atoms should be the superior homologue of **35**; the structure of

Table 1. Gas Chromatographic Analysis of *M. alliaceus* Extract

peak	volatile compound	KI[a]	mass spectral data, *m*/*z* (%)	rel amt[b] 1994	rel amt[b] 1995
10	dimethyl disulfide	740	94 (100); 79 (50); 45 (22)	0.6	1.2
14	1,3-dithietane	783	92 (100); 45 (47); 77 (22); 94 (9); 47 (9)	0.1	0.2
15	not identified	790	94 (100); 45 (80); 61 (80); 47 (50); 96 (8)	3.3	4.0
21	benzaldehyde	937	106 (100); 105 (93); 77 (74); 51 (27)	0.4	0.4
22	dimethyl trisulfide	963	126 (100); 79 (40); 45 (28); 47 (16); 111 (15); 128 (14); 64 (8)	0.8	1.6
25	not identified	979	43 (100); 71 (27); 99 (27); 41 (20)	0.1	0.5
26	1,2,4-trithiapentane	1076	61 (100); 45 (17); 126 (5)	0.2	0.3
27	1,2,4-trithiolane	1106	124 (100); 78 (78); 45 (42); 46 (20); 126 (10)	0.6	0.2
28	2,3,5-trithiahexane	1139	61 (100); 140 (32); 45 (23); 142 (4)	8.4	9.9
29	not identified	1175	61 (100); 140 (63); 92 (54); 45 (51); 47 (45)	0.4	0.1
30[c]	methyl-1,2,4-trithiolane	1177	61 (100); 138 (75); 45 (67); 62 (45); 91 (20)	0.2	0.1
32	dimethyl tetrasulfide	1218	158 (100); 79 (84); 45 (40); 47 (35); 94 (35); 64 (32); 160 (17); 126 (13); 111 (13)	0.2	1.4
34	cyclohexyl isothiocyanate	1231	55 (100); 141 (75); 83 (61); 41 (51); 82 (30); 67 (28)	0.4	1.1
35[c]	2,3,4,6-tetrathiaheptane	1340	61 (100); 45 (63); 93 (48); 46 (29); 79 (25); 172 (16)	12.0	9.3
36[c]	2,3,5,7-tetrathiaoctane	1464	61 (100); 107 (66); 45 (28); 139 (23); 46 (11); 93 (10); 186 (5)	1.2	0.3
37	2,4,5,7-tetrathiaoctane	1476	61 (100); 186 (22); 45 (20); 46 (9); 188 (4)	31.6	51.0
38	not identified	1653	97 (100); 57 (68); 43 (36); 41 (30); 55 (25); 99 (18); 123 (16); 179 (4)	0.1	1.7
39	not identified	1670	61 (100); 139 (96); 45 (31)	0.2	0.1
40	methyl 2,4-dihydroxy-3,6-dimethylbenzoate	1670	164 (100); 136 (91); 196 (53)	0.2	0.1
41[c]	2,3,4,6,8-pentathianonane	1673	61 (100); 139 (49); 93 (26); 45 (24); 154 (14); 46 (12); 141 (7); 218 (4)	33.4	11.1
42[c]	2,4,5,7,9-pentathiadecane	1777	61 (100); 107 (26); 45 (20); 108 (17); 124 (15); 139 (14); 232 (5)	5.0	3.9

[a] Kovats indices on DB-1 column. [b] Relative percentage of the volatile compounds based on the GC/MS chromatographic area. [c] Tentatively identified.

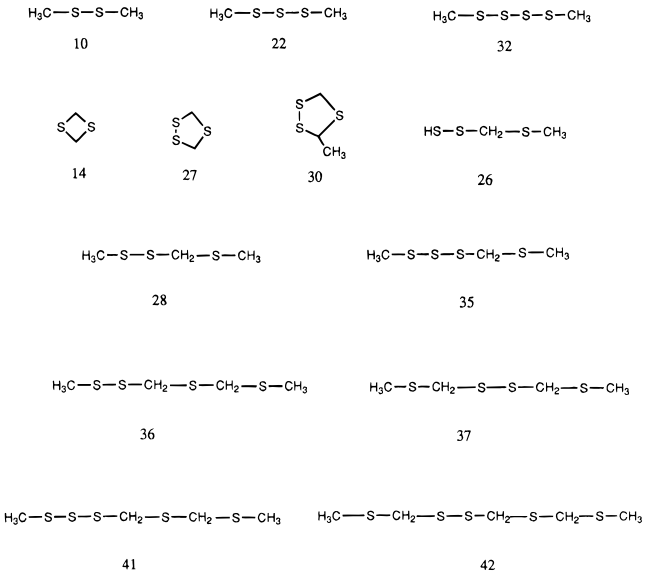

Figure 2. Chemical structures of sulfur-containing molecules.

compound **41** is 2,3,4,6,8-pentathianonane from the presence of *m*/*z* 139 fragment and the retention index as previously explained for compound **35**.

On the other hand, the first three dimethyl polysulfides **10**, **22**, and **32** were identified in *M. alliaceus* as reported in *Lentinus edodes* (Morita and Kobayashi, 1966; Chen and Wu, 1984; Chen and Ho, 1986), cheeses (Cuer *et al.*, 1979), *Allium* species, i.e., onions (Kuo and Ho, 1992) and leeks (Stephani and Baltes, 1992), and brassicaceous vegetables (Maruyama, 1970). 1,2,4-Trithiolane (**27**), which was found in high level in *L. edodes* (Chen and Ho, 1986), was detected in very low amount in *M. alliaceus*; compound **27** was identified by the retention index value and mass spectrum, which were similar to those reported by Chen and Ho (1986).

Other sulfur-containing components found in very low amounts were tentatively identified. Compound **36**, position isomer of **37**, characterized by the presence of an intense *m*/*z* 107 fragment, is probably 2,3,5,7-tetrathiaoctane. Compound **30**, with an intense molecular ion $M^+ = 138$ and three sulfur atoms, is an isomer of 4-methyl-1,2,3-trithiolane reported by Vernin and Metzger (1991). The retention indices of these two compounds were so close (1210 and 1177, respectively) that compound **30** should be methyl-1,2,4-trithiolane. Compound **34** was named cyclohexyl isothiocyanate because of its mass spectrum (McLafferty and Stauffer, 1989).

Among the non-sulfur-containing compounds, benzaldehyde (**21**) was identified in *M. alliaceus* as often reported in the aromas of mushrooms (Dijkstra and Wikén, 1976; Pyysalo, 1976; Takama *et al.*, 1979; Chen and Wu, 1984; Vidal *et al.*, 1986; Watson *et al.*, 1986; Wood *et al.*, 1990; Buchbauer *et al.*, 1993; Rapior *et al.*, 1996). On the other hand, octen-3-ol was not found in the solvent extract of *M. alliaceus* even if it was very often reported in mushrooms (Dijkstra and Wikén, 1976; Pyysalo and Suihko, 1976; Chen and Wu, 1984; Vidal *et al.*, 1986; Mau *et al.*, 1992; Buchbauer *et al.*, 1993).

Dynamic Headspace. Dynamic headspace analysis was carried out by Tenax trapping with fresh specimen of *M. alliaceus* collected in 1995. Volatile compounds were thermally desorbed and analyzed by GC/MS on a BP-1 column (Figure 3); results are gathered in Table 2 and Figure 2. Headspace analysis allowed a semiquantitative evaluation of the concentrated components (relative percentage based on the GC chromatographic area).

The main sulfur-containing constituents of the headspace analysis were dimethyl disulfide (**10**), dimethyl trisulfide (**22**), and 2,3,5-trithiahexane (**28**), which were also described in the solvent extract of *M. alliaceus*. 1,3-Dithietane (**14**), dimethyl tetrasulfide (**32**), and 2,3,4,6-tetrathiaheptane (**35**) were found at low levels.

3,4-Dithiahexane (**20**) and 2,4-dithiapentane (**18**), identified only in low amounts by headspace concentration from *M. alliaceus*, have a significant role in the flavor of dairy products (Cuer *et al.*, 1979); 2,4-dithiapentane was also identified in *Tuber magnatum* by solvent extraction (Fiecchi *et al.*, 1967).

Besides its sulfur-containing compound outline, the headspace extract of *M. alliaceus* is different from the

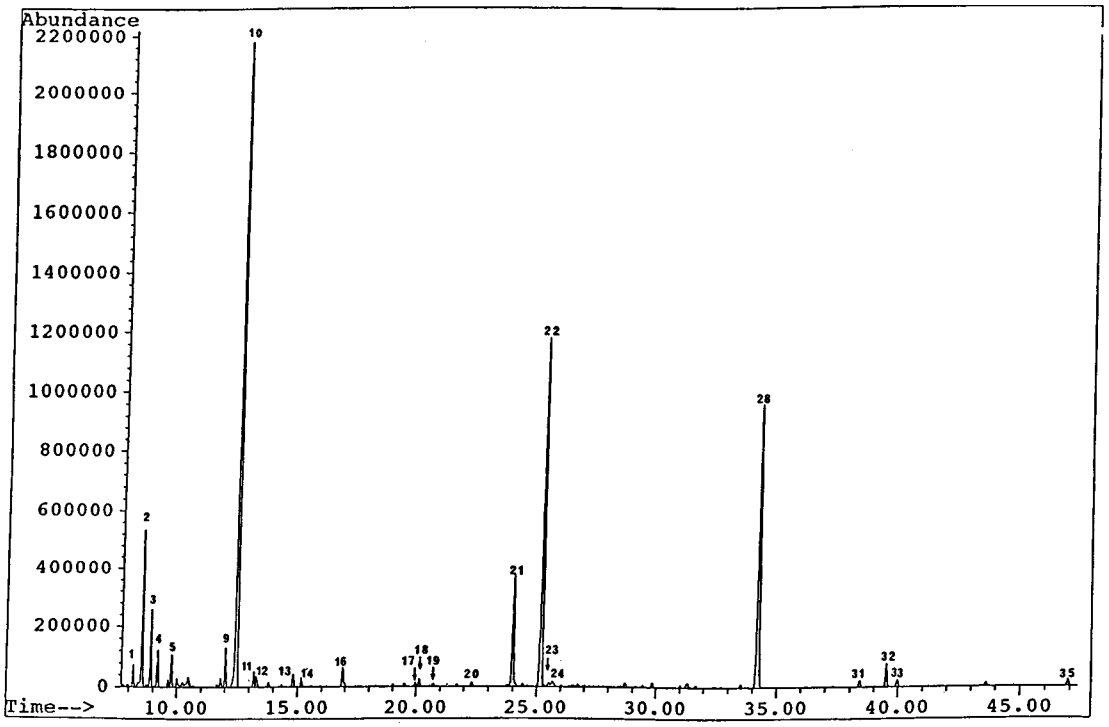

Figure 3. Chromatogram of headspace extract from *M. alliaceus*.

Table 2. Volatile Composition of *M. alliaceus* by Dynamic Headspace Concentration

peak	volatile compound	KI[a]	mass spectral data, *m/z* (%)	sensory eval[b]	rel amt[c]
1	(*E*)-but-2-enal	624	70 (100), 41 (55); 69 (48); 39 (41)		0.8
2	3-methylbutanal	634	44(100); 58 (75); 41 (63); 43 (58); 71 (38); 86 (17)	fruity	9.6
3	(*Z*)-pent-3-en-2-one	652	84 (100); 43 (98); 41 (85); 69 (81); 39 (40)		1.4
4	3-methylbutan-2-ol	664	45 (100); 43 (22); 55 (18); 73 (17); 44 (17); 71 (6)		0.4
5	(*Z*)-pent-3-en-2-ol	667	71 (100); 43 (48); 41 (21) . 86 (15); 58 (12)		1.5
6	pentanal	674	44 (100); 58 (52); 41 (37); 57 (37); 45 (20); 86 (3)		0.4
7	not identified	687	45 (100); 43 (91); 88 (14); 73 (4)		0.4
8	3-methylbutanol	717	55 (100); 70 (88); 42 (60); 43 (50); 41 (45); 57 (27); 45 (20)		0.5
9	2-methylbut-2-enal	720	84 (100); 55 (63); 43 (18); 39 (18); 83 (17); 53 (16)		1.8
10	dimethyl disulfide	732	94 (100); 79 (51); 45 (24); 46 (17); 96 (8); 61 (7)	sulfureous	30.8
11	not identified	745	104 (100); 43 (67); 59 (48); 76 (25); 60 (23); 61 (22); 71 (20); 58 (18); 45 (15); 106 (6)		0.6
12	pentanol	747	55 (100); 42 (95); 70 (90); 41 (58); 57 (30); 43 (25)		0.5
13	hexanal	775	44 (100); 56 (97); 71 (83); 43 (80); 57 (77); 41 (70); 73 (40); 82 (27)		0.7
14	1,3-dithietane	784	92 (100); 45 (48); 77 (25); 47 (13); 76 (13); 94 (10); 64 (8)		0.4
16	not identified	816	45 (100); 73 (71); 120 (25); 75 (20)		1.1
17	2-thiapentanal	870	48 (100); 104 (86); 47 (61); 45 (38); 76 (37); 61 (30)		0.1
18	2,4-dithiapentane	873	108 (100); 61 (90); 45 (23); 110 (11)		0.6
19	(*E,E*)-hexa-2,4-dienal	883	81 (100); 96 (47); 67 (26); 53 (21)		0.1
20	3,4-dithiahexane	910	122 (100); 66 (78); 94 (60); 124 (8)	alliaceous−sulfureous	0.1
21	benzaldehyde	936	106 (100); 105 (95); 77 (81); 51 (17)	mild spicy	6.5
22	dimethyl trisulfide	958	126 (100); 79 (36); 111 (18); 45 (17); 128 (13)	sulfureous	9.3
23	octen-3-ol	964	57 (100); 72 (27); 43 (25): 99 (15); 85 (13); 128 (3)		0.3
24	octan-3-one	965	99 (100); 57 (100); 72 (95); 71 (78); 43 (74)		0.3
28	2,3,5-trithiahexane	1110	61 (100); 140 (33); 45 (20); 142 (4)	alliaceous−sulfureous	18.5
31	not identified	1187	97 (100); 68 (96); 57 (88); 82 (54); 109 (53); 69 (49); 124 (41); 180 (20)		0.3
32	dimethyl tetrasulfide	1207	158 (100); 79 (74); 45 (30); 47 (24); 64 (23); 94 (21); 160 (18)	alliaceous etherous	1.4
33	cyclohexyl isocyanate	1216	141 (100); 55 (90); 83 (71); 82 (33); 41 (31); 67 (24)	sulfureous	0.4
35[d]	2,3,4,6-tetrathiaheptane	1352	61 (100); 45 (68); 93 (46); 46 (28); 79 (25); 47 (25); 94 (18); 172 (16)		0.4

[a] Kovats indices on BP-1 column. [b] Sensory evaluation (Fenaroli, 1975; Arctander, 1994). [c] Relative percentage of volatile compounds based on the GC/MS chromatographic area. [d] Tentatively identified.

solvent extract due to the large amount of aldehydes, ketones, and light alcohols; the major compound of these aliphatic components was 3-methylbutanal (**2**), already observed in other mushrooms (Pyysalo, 1979; Yajima *et al.*, 1981; Bellina-Agostinone *et al.*, 1987; Talou *et al.*, 1987). Benzaldehyde (**21**) was found at a higher level than in the solvent extract. Octen-3-ol (**23**), by far the major component in many mushroom species, was a minor volatile constituent in *M. alliaceus*.

GC/Sniffing. An olfactory analysis by GC/sniffing was performed on fresh mushrooms collected in 1995 using dynamic headspace concentration to give a sensory estimation of the main compounds in the aroma of *M. alliaceus* and to locate the components responsible

for the typical garlic-like odor of this mushroom. The results are gathered in Table 2.

The detected odors were essentially sulfureous and/or garlic-like as to the three major compounds, i.e., dimethyl disulfide (**10**), dimethyl trisulfide (**22**), and 2,3,5-trithiahexane (**28**), together with the minor components, i.e., dimethyl tetrasulfide (**32**), tentatively identified cyclohexyl isocyanate **33**, and 3,4-dithiahexane (**20**). These six compounds are responsible for the significant garlicky odor of *M. alliaceus*. Moreover, the two major aldehydes, benzaldehyde (**21**) and 3-methylbutanal (**2**), with intense fruity odor participate in the general aroma of *M. alliaceus*.

Conclusion. This study shows that both solvent extraction and headspace concentration methods evidence the presence of numerous sulfur-containing compounds in *M. alliaceus*. If the organic solvent extraction allows the obtention of a general chemical print of the volatilizable compounds, the headspace analysis enables an olfactory approach of the mushroom odor comparable to the human sensory perception based on the most volatile compounds.

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