

Monoterpenes in the Aromas of Fresh Wild Mushrooms (Basidiomycetes)

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The odorous volatile compounds in the fruiting bodies of 82 fresh wild mushrooms species were investigated for monoterpene compounds by GC/MS using both headspace concentration and solvent extraction techniques. In this study, 34 mushrooms gave positive analyses for monoterpenes and the wide diversity of such molecules extracted from basidiocarps was noted. A total of 27 different monoterpenes was identified in this investigation, for example, limonene, α -pinene, camphene, β -phellandrene, and linalool. Both analysis methods used were well adapted to the identification of monoterpenes in fresh mushrooms.

Keywords: *Aroma; monoterpene; mushroom fruit-body; Basidiomycetes; headspace concentration; solvent extraction*

INTRODUCTION

Many edible or poisonous mushroom species are well-known by mycologists to possess typical odors (Courtecuisse and Duhem, 1994). The fungal odor of fresh mushrooms may be attributed to a series of C₈-aliphatic oxygenated compounds, 1-octen-3-ol being the most important (Maga, 1981; Tressl et al., 1982; Fischer and Grosch, 1987; Jung and Hong, 1991; Mau et al., 1994). Distinct and typical pleasant or unpleasant aromas of mushrooms are also due to aliphatic, aromatic, and heterocyclic volatile compounds, for example, dimethyl sulfide, dimethyl disulfide, benzaldehyde, benzyl alcohol, (*E*)-2-nonenal, lactones, and skatole (Chen and Wu, 1984; Talou et al., 1987; Audouin et al., 1989; Gross and Asther, 1989; Wood et al., 1990, 1994; Laatsch and Matthies, 1992; Buchbauer et al., 1993; Borg-Karlson et al., 1994).

Little data exist concerning the monoterpene hydrocarbon content of basidiocarp aromas. Only small amounts of monoterpene compounds were detected in the volatile constituents of some wild basidiocarps (Chen and Wu, 1984; Vidal et al., 1986; Audouin et al., 1989; Buchbauer et al., 1993; Borg-Karlson et al., 1994; Rapior et al., 1996a,b), when compared with those reported for cultures. Indeed solid and liquid cultures of Basidiomycetes are known to produce high quantities of monoterpene compounds which are often responsible for intensive and pleasant odors (Collins and Halim, 1970; Halim and Collins, 1971; Sastry et al., 1980; Drawert et al., 1983; Berger et al., 1986a,b; Hanssen, 1986; Hanssen and Abraham, 1986; Hanssen et al., 1986; Gallois et al., 1990; Abraham et al., 1993, 1994; Abraham and Berger, 1994; Krings et al., 1995).

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In this study, volatiles of 82 fresh wild and odorous basidiocarps from edible, toxic, or poisonous species were investigated for monoterpene compounds by GC/MS using both headspace concentration and solvent extraction methods.

EXPERIMENTAL PROCEDURES

Materials. A total of 82 fresh wild mushroom species collected in the falls of 1994 and 1995 in France were screened for monoterpenes. The odorous mushrooms were wrapped in waxed paper bags, after morphological identification by one of us (S.R.) according to the classification by Courtecuisse and Duhem (1994). The specimens were brushed clean of forest debris and treated immediately after collection for both techniques. The choice of the mushrooms analyzed and the method used for analysis depended on the wild fungal growth and the quantities of mushroom found for the 1994 and 1995 collection.

Species analyzed by both solvent extraction and dynamic headspace concentration: *Agrocybe aegerita* (Brig.) Fayod, *Amanita citrina* (Sch.: Fr.) S. F. Gray, *Amanita ovoidea* (Bull.: Fr.) Link, *Cantharellus cibarius* (Fr.: Fr.) Fr., *Clitocybe nebularis* (Batsch: Fr.) Kummer, *Clitocybe odora* (Bull.: Fr.) Kummer, *Cystoderma amianthinum* (Scop.) Fayod, *Gomphidius glutinosus* (Sch.: Fr.) Fr., *Hydnum repandum* L.: Fr., *Hygrophoropsis aurantiaca* Wulf.: Fr., *Hygrophorus agathosmus* (Fr.) Fr., *Lepista nuda* (Bull.: Fr.) Cooke, *Marasmius alliaceus* (Jacq.: Fr.) Fr., *Mycena pura* (Pers.: Fr.) Kummer, *Piptoporus betulinus* (Bull.: Fr.) Karst., *Suillus luteus* (L.: Fr.) Roussel, *Tricholoma caligatum* (Viv.) Ricken, *Tricholoma portentosum* (Fr.) Quélet, *Tricholoma sulfureum* (Bull.: Fr.) Kummer.

Species analyzed only by dynamic headspace concentration: *Agaricus silvicola* (Vitt.) Peck, *Boletus aestivalis* (Paulet) Fr., *Cortinarius cinnamomeus* (L.: Fr.) Fr., *Cystoderma carcharias* (Pers.: Fr.) Fayod, *Laccaria amethystina* (Huds.) Cooke, *Lactarius salmonicolor* Heim & Leclair, *Mycena rosea* (Bull.) Gramberg.

Species analyzed only by solvent extraction: *Agaricus campestris* L.: Fr., *Albatrellus ovinus* (Sch.: Fr.) Kotl. & Pouz., *Aleuria aurantia* (Pers.: Fr.) Fuckel, *Amanita caesarea* (Scop.: Fr.) Pers., *Amanita gemmata* (Paulet) Bertillon, *Amanita pantherina* (De Cand.: Fr.) Krombholz, *Amanita phalloides* (Vaill.: Fr.) Link, *Amanita proxima* Dumée, *Amanita rubescens* (Pers.: Fr.) S.F. Gray, *Amanita spissa* (Fr.) Kummer,

Table 1. Monoterpenes Identified by Dynamic Headspace Concentration

monoterpene compounds	Kovats indices	mass spectral data [m/z (%)]	sensory evaluation ^a	mushroom species	relative amount ^{b,c}
α -thujene (I)	928	93 (100); 91 (50); 77 (45); 92 (45); 136 (10)	not described	<i>G. glutinosus</i> <i>A. ovoidea</i> ^d <i>T. caligatum</i>	3 2; 1.8 tr
α -pinene (II)	938	93 (100); 91 (40); 92 (38); 77 (30); 79 (28); 121 (20); 136 (20)	warm, resinous	<i>T. caligatum</i> <i>G. glutinosus</i> <i>A. ovoidea</i> ^d <i>B. aestivalis</i> <i>M. rosea</i> ^d <i>T. portentosum</i> <i>C. carcharias</i> ^d <i>C. cibarius</i> <i>M. pura</i> <i>S. luteus</i> <i>A. aegerita</i> ^d <i>H. agathosmus</i> ^d <i>T. sulfureum</i> <i>H. repandum</i> <i>C. amianthinum</i> ^d <i>C. cinnamomeus</i>	17 16 6; 8 7 2; tr 2 1; 0.5 1 1 0.3; 0 0.4; 0 0.5 0.1 tr; 0 tr
α -fenchene (III)	949	93 (100); 79 (70); 121 (55); 80 (40); 77 (38); 94 (35); 107 (35); 136 (35)	fresh, camphor	<i>G. glutinosus</i> <i>A. ovoidea</i> ^d <i>C. carcharias</i> ^d	2 1.2; tr 1.2; 0.8
camphene (IV)	953	93 (100); 121 (80); 79 (40); 107 (40); 91 (38); 67 (25); 136 (25)	mild camphoraceous	<i>G. glutinosus</i> <i>A. ovoidea</i> ^d <i>C. carcharias</i> ^d <i>C. cibarius</i> <i>M. rosea</i> ^d <i>B. aestivalis</i> <i>S. luteus</i> <i>H. repandum</i> <i>M. pura</i> <i>T. sulfureum</i>	6 2.2; 1.5 1.7; 1.3 1 0.6; 0 0.5 0.1 tr tr tr
sabinene (V)	972	93 (100); 77 (45); 91 (45); 79 (30); 136 (25)	woody, herbaceous	<i>A. ovoidea</i> ^d <i>G. glutinosus</i> <i>S. luteus</i> <i>M. pura</i> <i>T. caligatum</i> <i>T. sulfureum</i>	4; 4.4 2 0.5 tr tr tr
β -pinene (VI)	979	93 (100); 69 (30); 79 (20); 41 (20); 91 (20); 77 (18); 121 (10); 136 (10)	resinous, piney	<i>G. glutinosus</i> <i>A. ovoidea</i> ^d <i>T. caligatum</i> <i>S. luteus</i> <i>M. pura</i> <i>C. carcharias</i> ^d <i>A. ovoidea</i> ^d <i>M. rosea</i> ^d <i>C. carcharias</i> ^d	20 6.3; 4.5 2 0.5 tr 0.2; 0 tr; 0 tr; 0 1.6; 1.5
myrcene (VII)	981	93 (100); 69 (75); 41 (48); 91 (20); 79 (15)	sweet, balsamic resinous	<i>C. carcharias</i> ^d <i>A. ovoidea</i> ^d <i>M. rosea</i> ^d <i>C. carcharias</i> ^d	0.6; 0.8 0.5 tr; 0 0.6; 0
<i>p</i> -mentha-2,4(8)-diene ^e (VIII) <i>M</i> = 136 ^f	988 991	121 (100); 93 (78); 136 (50); 79 (45); 91 (27); 77 (25); 107 (25); 136 (2) 79 (100); 93 (80); 121 (75); 136 (55); 80 (45); 107 (40)	not described	<i>C. carcharias</i> ^d <i>C. odora</i>	0.6; 0.8 0.5
α -phellandrene (IX)	1000	93 (100); 91 (50); 77 (45); 92 (43); 136 (25)	fresh, citrusy	<i>A. ovoidea</i> ^d	0.9; 0.9
α -terpinene (X)	1013	121 (100); 93 (80); 136 (60); 91 (47); 77 (40); 79 (38); 105 (38)	lemony, citrusy	<i>A. ovoidea</i> ^d	0.6; 0
<i>p</i> -cymene (XI)	1016	119 (100); 134 (40); 91 (28); 117 (20); 120 (18)	gassy, kerosene-like	<i>A. ovoidea</i> ^d <i>M. rosea</i> ^d <i>T. caligatum</i>	0.4; tr tr; 0 tr
β -phellandrene (XII)	1028	93 (100); 91 (45); 77 (43); 136 (28)	peppery, minty	<i>A. ovoidea</i> ^d <i>T. caligatum</i> <i>C. cinnamomeus</i> <i>G. glutinosus</i> <i>H. agathosmus</i> ^d <i>S. luteus</i> <i>T. portentosum</i> <i>M. pura</i> <i>T. sulfureum</i> <i>L. amethystina</i>	49.5; 27 7 4 4 1.5; 5.5 2 2 0.5 0.5 tr
limonene (XIII)	1028	68 (100); 93 (90); 67 (85); 79 (40); 121 (30); 136 (20)	fresh, sweet citrusy	<i>A. ovoidea</i> ^d <i>T. caligatum</i> <i>C. carcharias</i> ^d <i>M. rosea</i> ^d <i>C. cinnamomeus</i> <i>M. pura</i> <i>C. cibarius</i> <i>T. sulfureum</i> <i>C. amianthinum</i> ^d <i>C. odora</i>	28; 5.5 26 3; 3.6 1.5; 4.5 1 1 0.5 0.5 0.1; 0 tr
γ -terpinene (XIV)	1053	93 (100); 136 (48); 91 (48); 77 (15); 121 (15)	herbaceous, citrusy	<i>A. ovoidea</i> ^d	tr; 0

Table 1. (Continued)

monoterpene compounds	Kovats indices	mass spectral data [m/z (%)]	sensory evaluation ^a	mushroom species	relative amount ^{b,c}
<i>trans</i> -sabinene hydrate (XV) <i>M</i> = 154 ^f	1060	71 (100); 43 (75); 93 (75); 81 (50); 111 (50); 69 (30); 121 (28)	citrusy-lemon	<i>A. ovoidea</i> ^d	0.1; 0
	1072	83 (100); 111 (75); 55 (55); 70 (50); 93 (30); 121 (20); 136 (5); 139 (2)		<i>C. carcharias</i> ^d <i>C. odora</i> <i>C. carcharias</i> ^d	0.3; 0.4 0.2 2.3; 1.6
fenchone (XVII)	1080	81 (100); 69 (45); 152 (25)	sweet, warm camphoraceous refreshing, floral	<i>L. nuda</i> <i>M. rosea</i> ^d <i>T. sulfureum</i> <i>C. odora</i> <i>H. repandum</i> <i>L. salmonicolor</i>	6 5.2; tr 2 0.5 0.5 0.1
linalool (XVII)	1084	93 (100); 71 (97); 55 (50); 43 (45); 80 (45); 121 (45); 69 (45)		<i>A. ovoidea</i> ^d <i>M. pura</i> <i>A. ovoidea</i> ^d	1.8; 1 0.5; 0.6 tr 0.1; 0.3
terpinolene (XIII)	1085	121 (100); 93 (98); 136 (95); 91 (53); 79 (48)	sweet piney	<i>C. carcharias</i> ^d <i>M. pura</i> <i>A. ovoidea</i> ^d	1.3; 0.5 tr 0.1; 0.3
<i>cis</i> -sabinene hydrate (XIX)	1090	71 (100); 43 (80); 93 (78); 81 (75); 111 (75); 121 (45); 139 (40)	lime-like, camphoraceous mild camphoraceous	<i>C. carcharias</i> ^d	2.5; 0.9
fenchol (XX)	1110	81 (100); 80 (75); 43 (25); 69 (25); 111 (23); 84 (20)		<i>A. ovoidea</i> ^d	0.2; 0.1 tr; 0
camphene hydrate (XXI)	1148	71 (100); 86 (53); 43 (50); 96 (50); 69 (50); 84 (48); 111 (45); 67 (25); 85 (25); 93 (25); 121 (25)	fresh, pungent	<i>A. ovoidea</i> ^d <i>A. ovoidea</i> ^d	
piperitol (XXII)	1197	84 (100); 93 (60); 136 (35); 83 (32)			

^a Sensory evaluation (Fenaroli, 1975; Arctander, 1994). ^b Relative percentage of the identified volatile compounds based on the GC/MS chromatographic area, refers to the total fraction eluted in GC. ^c tr = <0.1%. ^d Tested in duplicate; both values obtained are indicated. ^e Tentatively identified (MS). ^f Monoterpene not identified (*M* = mass of the compound).

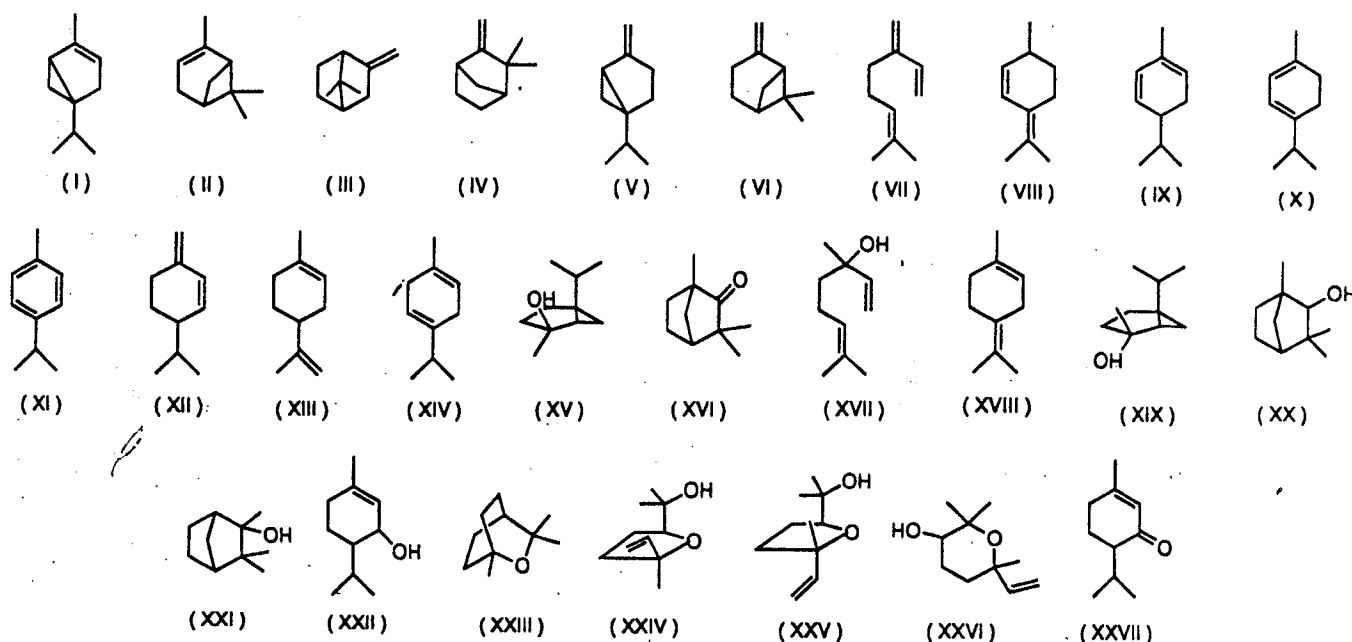


Figure 1. Chemical structures of monoterpenes identified.

Armillaria mellea (Vahl: Fr.) Kummer, *Boletus aereus* Bull.: Fr., *Boletus calopus* Pers.: Fr., *Boletus edulis* Bull.: Fr., *Boletus erythropus* Pers., *Boletus lupinus* Fr., *Boletus luridus* Sch.: Fr., *Boletus radicans* Pers.: Fr., *Cantharellus lutescens* Pers.: Fr., *Cantharellus tubiformis* Fr.: Fr., *Chroogomphus rutilus* (Sch.: Fr.) O. K. Miller, *Clathrus ruber* [Mich.] ex Pers.: Pers., *Clavariadelphus pistillaris* (L.: Fr.) Donk, *Clitocybe geotropa* (Bull.: Fr.) Quélet, *Cortinarius cotoneus* Fr., *Cortinarius orellanus* Fr., *Ganoderma lucidum* (Leyss.: Fr.) Karsten, *Hebeloma sinapizans* (Paulet) Gillet, *Helvella crispa* (Scop.: Fr.) Fr., *Hygrophorus russula* (Sch.: Fr.) Quélet, *Leccinum aurantiacum* (Bull.) S.F. Gray, *Leccinum lepidum* (Bouchet ex Essette) Quadraccia, *Leccinum pulchrum* Lannoy & Estades, *Leccinum quercinum* Pilat & Dermek, *Leccinum versipelle* (Fr.) Snell, *Lentinellus cochleatus* (Hoffin.: Fr.) Karsten, *Clitocybe graminicola* Bon, *Lepista inversa* (Scop.) Patouillard, *Oligoporus caesius* (Schrad.: Fr.) Gilbertson & Ryvardeen, *Paxillus atrotomentosus* (Batsch: Fr.) Fr., *Paxillus*

involutus (Batsch: Fr.) Fr., *Paxillus panuoides* (Fr.: Fr.) Fr., *Pisolithus arrhizus* (Scop.) S. Rauschert, *Russula amoenicolor* Romagnesi, *Suillus bovinus* (L.: Fr.) O. Kuntze, *Suillus collinitus* (Fr.) O. Kuntze, *Suillus granulatus* (L.: Fr.) Roussel, *Suillus grevillei* (Klotzsch) Singer, *Suillus variegatus* (Sw.: Fr.) O. Kuntze, *Suillus viscidus* (L.) Roussel, *Tricholoma columbetta* (Fr.: Fr.) Kummer, *Tricholoma equestre* (L.: Fr.) Kummer, *Tricholoma saponaceum* (Fr.: Fr.) Kummer, *Xerocomus badius* (Fr.: Fr.) Gilbert, *Xerocomus pruvinatus* (Fr.) Quélet, *Xerocomus subtomentosus* (L.: Fr.) Quélet.

Dynamic Headspace Concentration. Fresh mushrooms, ranging from 4 to 88 g according to the availability of each species, were cubed (100–300 mm³) and placed in a glass cell (0.25 L capacity) directly connected to a dynamic headspace concentrator (CHISA device-SGE). Volatiles were concentrated on TENAX trap with a stripping gas (Helium) flow rate of 30 mL min⁻¹ for 20 min at room temperature. Samples were desorbed with a headspace injector (CHISA device-SGE)

Table 2. Monoterpenes Identified by Solvent Extraction

monoterpene compounds	Kovats indices	mass spectral data [<i>m/z</i> (%)]	sensory evaluation ^a	mushroom species	relative amount ^b
α -pinene (II)	927	93 (100); 91 (46); 92 (40); 77 (37); 79 (26); 121 (15); 136 (14)	resinous, piney	<i>G. glutinosus</i> ^c <i>A. citrina</i> <i>A. phalloides</i>	5; 1 1 1
sabinene (V)	965	93 (100); 91 (43); 77 (36); 79 (26); 136 (21)	woody, herbaceous	<i>G. glutinosus</i> ^c <i>A. ovoidea</i>	7; 8 7
β -pinene (VI)	967	93 (100); 41 (45); 69 (39); 91 (33); 79 (32); 77 (30); 121 (14); 136 (12)	resinous, piney	<i>G. glutinosus</i> ^c	6; 2
myrcene (VII)	979	93 (100); 41 (80); 69 (73); 91 (20); 121 (5); 136 (5)	sweet, balsamic, resinous	<i>G. glutinosus</i> ^c	3; 2
<i>p</i> -cymene (XI)	1022	119 (100); 134 (32); 91 (20)	gassy, kerosene-like	<i>B. lupinus</i>	1
1,8-cineole (XXIII)	1025	43 (100); 81 (35); 41 (32); 55 (30); 93 (28); 108 (25); 154 (6)	fresh camphoraceous	<i>B. erythropus</i> <i>P. involutus</i> <i>A. rubescens</i> <i>G. glutinosus</i> ^c <i>A. phalloides</i> <i>G. glutinosus</i> ^c <i>X. subtomentosus</i> <i>B. erythropus</i> <i>A. citrina</i> <i>P. betulinus</i> <i>A. proxima</i> <i>A. rubescens</i> <i>A. spissa</i> <i>H. aurantiaca</i> <i>S. grevillei</i> <i>C. odora</i> ^c <i>L. nuda</i> <i>C. nebularis</i> ^c <i>T. saponaceum</i>	8 6 1 1; 0.2 45 27; 31 7 6 3 2 1 1 1 1 0.2; 0.5 12; 8 2
limonene (XIII)	1026	68 (100); 93 (82); 67 (80); 79 (35); 136 (27); 121 (25)	fresh, sweet citrusy	<i>L. nuda</i> <i>C. odora</i> ^c <i>C. nebularis</i> ^c <i>T. saponaceum</i> <i>L. nuda</i> <i>G. glutinosus</i> ^c <i>A. aegerita</i> <i>C. odora</i> ^c <i>B. erythropus</i> <i>C. nebularis</i> ^c <i>T. saponaceum</i> <i>A. ovoidea</i>	45 27; 31 7 6 3 2 1 1 1 0.2; 0 0; 0.5 3 3; 3 2 2; 1 1 1; 1 1 6
<i>cis</i> -linalool oxide (furanoid) (XXIV)	1057	59 (100); 43 (52); 94 (52); 111 (35); 68 (34); 93 (33); 67 (27); 155 (7)	sweet, woody	<i>A. ovoidea</i>	10
<i>trans</i> -linalool oxide (furanoid) (XXV)	1080	59 (100); 43 (50); 94 (46); 111 (30); 68 (28); 67 (26); 93 (26); 155 (6)	sweet, woody	<i>L. nuda</i>	8
linalool (XVII)	1089	71 (100); 93 (75); 43 (65); 41 (61); 55 (50); 69 (40); 80 (31); 121 (18); 136 (8)	refreshing, floral	<i>B. erythropus</i>	5
<i>trans</i> -sabinene hydrate (XV)	1091	43 (100); 71 (55); 41 (53); 81 (45); 93 (38); 111 (33); 121 (16); 139 (15); 136 (13)	citrusy-lemon		
<i>cis</i> -sabinene hydrate (XIX)	1112	43 (100); 71 (59); 41 (50); 81 (49); 93 (40); 111 (35); 121 (18); 139 (16); 136 (15)	citrusy-lemon		
linalool oxide (pyranoid) (XXVI)	1198	68 (100); 59 (87); 43 (75); 94 (62); 67 (53); 55 (30); 155 (6)	sweet, woody		
piperitone (XXVII)	1242	82 (100); 110 (78); 95 (32); 54 (35); 137 (34); 109 (25); 137 (30); 152 (22)	fresh, minty, camphoraceous		

^a Sensory evaluation (Fenaroli, 1975; Arctander, 1994). ^b Relative percentage of the identified volatile compounds based on the GC/MS chromatographic area, refers to the total fraction eluted in GC. ^c Tested in duplicate, both values obtained are indicated.

directly connected to the analytical column. The temperature for desorption was 210 °C, and volatile compounds were cryofocused at -20 °C in the column's head before being injected directly into this column.

Solvent Extraction. Extraction was performed with fresh mushrooms ranging from 50 to 250 g. The fruit bodies were cubed (approximately 100 mm³) as reported by Rapior et al. (1996b). Volatiles were extracted with dichloromethane in a Soxhlet apparatus for 5 h. The extract was gently concentrated under a nitrogen stream and used directly for analysis.

The reproducibility of both sample preparation techniques has been tested on duplicate extracts of *C. nebularis*, *C. odora*, and *G. glutinosus* for solvent extraction and *A. aegerita*, *A. ovoidea*, *C. amianthinum*, *C. carcharias*, *H. agathosmus*, and *M. rosea* by headspace concentration.

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

Headspace analyses were performed by a 50 m × 0.22 mm × 1 μ m dimethylpolysiloxane BP1 (SGE), fused silica capillary column. The carrier gas was helium and was fixed at 22 psi. The detector temperature was 250 °C. The column was temperature programmed as follows: 50 to 220 °C (3 °C/min).

Solvent extraction analyses were performed by a 25 m × 0.23 mm × 0.13 μ m dimethylpolysiloxane DB1 (J&B), fused

silica capillary column. The carrier gas was helium with a constant flow rate close to 0.9 mL min⁻¹. The injector and detector temperatures were 200 and 220 °C, respectively. The column was temperature programmed as follows: 60 °C (2 min) to 200 °C (4 °C/min).

All monoterpene hydrocarbons were identified by comparison with mass spectral library NBS (McLafferty and Stauffer, 1989), literature spectra (Stenhagen et al., 1976; Jennings et al., 1980; Adams, 1989), Kovats indices data from literature (Jennings et al., 1980; Adams, 1989), and our own data bank. The Kovats indices were calculated using *n*-alkanes (C₅-C₁₈) for the headspace technique, 1 μ L of the mix was deposited in the glass cell and analysis was carried out as is previously described.

RESULTS AND DISCUSSION

The screening of mushrooms for volatile compounds indicated that 20 mushrooms species out of 26 and 19 out of 63 showed the presence of monoterpenes by dynamic headspace concentration (Table 1) and solvent extraction (Table 2), respectively. The chemical structures of the monoterpene compounds identified are shown in Figure 1.

Mass spectral analyses revealed minor and major mushroom volatiles as monoterpene hydrocarbons. This

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study showed the diversity of monoterpenes from basidiocarps such as C₁₀H₁₆ and C₁₀H₁₈O derivatives, and linear, cyclic, and bicyclic compounds.

Chromatogram profiles obtained by both techniques indicated differences in monoterpenes composition. The two extraction techniques used in this study partly explained these differences. The headspace analysis was carried out in order to identify the most volatile components of fresh mushroom aromas such as it could be detected by the human nose, while the solvent extraction method allowed general chemical prints of the volatile compounds.

The most frequently identified monoterpenes were α -pinene, camphene, β -phellandrene, limonene, and linalool by headspace concentration and limonene and linalool by solvent extraction. The investigation of volatiles indicated very high amounts of β -phellandrene (57% in *A. ovoidea*), limonene (28% in *A. ovoidea*), and α -pinene (17% in *T. caligatum*) by headspace concentration, *cis*-linalool oxide (furanoid) (45% in *L. nuda*) and limonene (45% in *A. phalloides*) by solvent extraction. Other compounds commonly described in the plant kingdom, i.e., myrcene, (*Z*)- and (*E*)-ocimene, α and γ -terpinene, α -phellandrene, and *p*-cymene were not, or rarely, detected among the mushrooms analyzed in this study by both techniques (Lawrence, 1993).

A broad spectrum of monoterpenes was described in *A. ovoidea* and *G. glutinosus* by both extraction techniques. The aroma of *A. ovoidea* was characterized by piperitol, α -fenchene, α -thujene, and especially *cis*- and *trans*-sabinene hydrate. It should be noted that *cis*- and *trans*-sabinene hydrate were detected in fresh mushrooms by both extraction techniques and in frozen specimens by solvent extraction (Rapior et al., 1996a). The aroma of *G. glutinosus* contained many monoterpenes which were commonly found in the plant kingdom, i.e., limonene, β -phellandrene, α -pinene, β -pinene, linalool, sabinene, and camphene. *C. carcharias* analyzed by headspace concentration was defined by uncommon monoterpenes in mushroom aromas such as α -fenchene, fenchol, fenchone, camphene hydrate, and the tentatively identified compound *p*-mentha-2,4(8)-diene. The aroma of *L. nuda* was characterized by the presence of linalool and particularly its three related linalool oxides obtained by solvent extraction. *A. rubescens*, *B. erythropus*, *G. glutinosus*, and *P. involutus* showed the presence of 1,8-cineole in solvent extracts. Piperitone, piperitol, α -fenchene, fenchol, fenchone, α -thujene, and camphene hydrate were reported for the first time in fresh mushrooms.

Because of the specificity of some monoterpenes identified in this study, we suggest that these molecules could be used as chemical markers, carrying out a larger number of species and samples, for the identification of mushroom species as it was reported by Audouin et al. (1989).

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