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Volatile composition of *Laetiporus sulphureus*

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Abstract — *Laetiporus sulphureus* was investigated for volatile compounds by GC/MS. Twenty-six components were identified with major constituents being (Z)-3-methylcinnamaldehyde (27.5%), 2-phenylethanol (6.4%), benzaldehyde (4.0%) and N-phenylethylformamide (3.8%). Odorous aromatic derivatives represented 11.5% of the volatile fraction. Observed sulphur derivatives contribute probably to the disagreeable odour of *L. sulphureus* developed in maturation process. © 2000 Adac / Éditions scientifiques et médicales Elsevier SAS

mushroom / *Basidiomycotina* / *Laetiporus (Polyporus) sulphureus (sulfureus)* / volatile components / solvent extraction

Résumé — Les composés volatils de *Laetiporus sulphureus* ont été étudiés par chromatographie en phase gazeuse couplée à la spectrométrie de masse. Le champignon frais présente 26 composés volatils avec comme principaux composés le (Z)-3-méthylcinnamaldéhyde (27,5 %), le 2-phényléthanol (6,4 %), le benzaldéhyde (4,0 %) et le N-phényléthylformamide (3,8 %). Les dérivés aréniques représentent 11,5 % de la fraction volatile. Des composés soufrés furent également détectés dont le 3-méthylthiopropanal qui contribue très probablement à l'odeur désagréable se développant lors de la maturation du champignon. © 2000 Adac / Éditions scientifiques et médicales Elsevier SAS

champignon / *Basidiomycotina* / *Laetiporus (Polyporus) sulphureus (sulfureus)* / composés volatils / extraction solvant

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INTRODUCTION

The beautiful yellow-orange *Laetiporus sulphureus* (sulphur shelf) produces very large fruit-bodies in overlapping clusters of 5 to 50. According to the authors, the odour of *L. sulphureus* was described as being either more or less pleasant (Laskibar Urkiola & Palacios Quintano, 1974), fungal (Marchand, 1974) or often strongly musky to strongly fungoid (Ammirati *et al.*, 1985) while according to Romagnesi (1971) and Læessøe *et al.* (1996) the mushroom develops a disagreeable odour with age.

Benjamin (1995) recently suggested that the fungus' common name 'chicken-of-the-woods' suggests a culinary treat. Excellent in stews when young, *L. sulphureus* becomes somewhat indigestible as it ages. Appleton *et al.* (1988) reported a case of severe intoxication of a child in Canada accompanied by visual hallucinations and ataxia.

According to List (1958) and Lee *et al.* (1975), *L. sulphureus* contains *N*-methylated tyramine derivatives. The presence of polysaccharides, i.e., an α-D-glucan derivative and chitin was also established by Jelsma & Kreger (1978). The present authors investigated the presence of other chemical constituents in the fruit-bodies. A lectin has been isolated and its characterization showed a specificity for *N*-acetyllactosamine residues (Konska *et al.*, 1994). This lectin was found to be very useful to demonstrate the glycoconjugate modifications of breast cells associated with the cancer process (Konska *et al.*, 1998). On the other hand, triterpene acids and fat were biosynthetized in submerged culture of *Polyporus sulfureus* (Nour El Dein & Abdallah, 1967; Villanueva *et al.*, 1967); phospholipids were also detected in mycelium of *L. sulphureus* (Kapich & Shishkina, 1993).

The present work is the first approach to the volatile composition of *Laetiporus sulphureus*. The mushroom was investigated for volatile components by solvent extraction using gas chromatography/mass spectrometry.

MATERIALS AND METHODS

Mushroom material and solvent extraction

Specimens of *Laetiporus sulphureus* (Bull.: Fr.) Murr., representing a combination of young and old basidiocarps, were collected on *Salix alba* in summer 1998. Solvent extraction of the volatile constituents was performed from fresh mushrooms (240 g) with dichloromethane (750 ml).

Gas Chromatography – Mass Spectrometry

Analyses were carried out using a gas chromatograph (5892-Hewlett-Packard) and a mass selective detector (5971-Hewlett-Packard) with a potential of 70 eV for ionization by electron impact. Solvent extract analyses were performed by a 25 m × 0.25 µm × 0.13 µm dimethylpolysiloxane DB1, fused silica capillary column. The injector and detector temperatures were 200 °C and 220 °C, respectively. The column was temperature-programmed as follows: 60 °C (2 min) to 200 °C (4 °C/min). The carrier gas was helium with a constant flow rate set close to 0.6 ml/min (Rapior *et al.*, 1996).

The volatile components were identified using mass spectra and retention indices in our own data bank and reference libraries (Stenhagen *et al.*, 1976; Jennings & Shibamoto, 1980; Adams, 1989; MacLafferty & Stauffer, 1989).

RESULTS AND DISCUSSION

Twenty-six volatile components were identified by GC/MS in *L. sulphureus* (Tab. 1). The major compound was found to be (Z)-3-methylcinnamaldehyde (27.5%) determined by its retention indice and the experimental mass spectrum. 2-Phenylethanol (6.4%), benzaldehyde (4.0%) and N-phenylethylformamide (3.8%) were detected in lower amounts.

Sulphur compounds, i.e. 3-methylthiopropanal (0.6%) and 2,2'-bithiophene (0.1%) were also detected from the sulphur shelf. 3-Methylthiopropanal probably contributes to the disagreeable odour of *L. sulphureus* which develops when it ages.

Benzoic acid, octen-3-ol, 2-phenylethanol and 2-phenylethanal were identified in the volatile composition of *L. sulphureus* (Tab. 1). The presence of these compounds and of benzaldehyde is widespread and well documented in Basidiomycetes (Maga, 1981; Audouin *et al.*, 1989; Gross & Asthier, 1989; Wood *et al.*, 1990; Breheret *et al.*, 1997, 1999; Rapior *et al.*, 1996, 1997, 1998).

Among the volatile flavour components, the arenic derivatives (benzaldehyde, phenylethanal, 2-phenylethanol, 2-phenylpropenal, benzoic acid, phenethyl acetate, N-phenylethylformamide, phenethyl valerate) represented 17.6% of the volatile fraction. Thus, within the aromatic components, (Z) and (*E*)-3-methylcinnamaldehyde (27.5 and 0.6%, respectively), and 2,3-diphenylbut-2-enal (1.8%) have related benzoyl structures. Rapior *et al.* (1998) already reported many benzenic derivatives from the mushroom *Tricholoma sulfureum* as an endogenous source.

Tab. 1 also lists several volatile aliphatic C2-esters (ethyl hexanoate, ethyl octanoate, ethyl phenylacetate, ethyl laurate, ethyl 9-decenoate, ethyl myristate, ethyl pentadecanoate, ethyl palmitoleate) apparently being uncommon compounds in the mushroom kingdom.

Finally, C16-derivatives compounds such as ethyl palmitoleate (7.8%) previously mentioned and palmitic acid (5.8%) were also described in *L. sulphureus*. A large amount of ethyl palmitate was also found in the fresh mushroom.

On the other hand, a low percentage of methyl orsellinate was detected (0.1%) in the wood-decaying *L. sulphureus*. This component was particularly reported rather in lichens (Hylands & Ingolfsdottir, 1985) and mosses (Schulz & Albroscheit, 1989).

The present work stresses for the first time the broad spectrum of volatile compounds from *L. sulphureus*. The phenyl derivatives, i.e. 2-phenylethanal (floral-green odour), 2-phenylethanol (rose odour), benzaldehyde and benzoic acid (bitter almond odour) apparently contribute to the pleasant smell of the mushroom. Sulphur-containing constituents with a disagreeable odour such as 3-methylthiopropanal were also reported for *L. sulphureus*. These findings could bear a biotechnological interest for 'natural' flavour compound production.

Tab. 1. Volatile composition (percentage) of fresh *Laetiporus sulphureus*

Volatile compounds	*Retention Indices*	*Relative amounts*[a]
3-Methylthiopropanal	900	0.6
Benzaldehyde	953	4.0
Octen-3-ol	965	2.0
Ethyl hexanoate	990	0.8
Non identified	1027	0.7
2-Phenylethanal	1035	0.9
Non identified	1052	0.5
2-Phenylethanol	1112	6.4
2-Phenylpropenal	1150	1.0
Benzoic acid	1197	0.2
Ethyl octanoate	1215	0.4
Ethyl phenylacetate	1246	1.2
(*Z*)-3-Methylcinnamaldehyde	1265	27.5
(*E*)-3-Methylcinnamaldehyde	1290	0.6
2,2'-Bithiophene	1438	0.1
N-Phenylethylformamide	1488	3.8
Phenethyl valerate	1539	0.1
Ethyl laurate	1590	0.4
Ethyl 9-decenoate	1595	2.8
Methyl orsellinate	1760	0.1
Myristic acid	1783	0.3
Ethyl myristate	1790	0.6
Pentadecanoic acid	1890	1.2
4(3-indoyl)butanoic acid	1885	1.8
Ethyl pentadecanoate	1890	18.0
2,3-diphenylbut-2-enal	1930	1.8
Non identified	1943	2.5
Ethyl palmitoleate	1970	7.8
Palmitic acid	1983	5.8

[a] Relative percentage of the identified volatile constituents based on the GC/MS chromatographic area.

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