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Volatile aroma constituents of Agarics and Boletes

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ABSTRACT

This article reviews papers relative to the volatile constituents of mushrooms from *Agaricus* genus and five Boletes genera, i.e., *Boletus*, *Boletinus*, *Leccinum*, *Suillus* and *Xerocomus*. Headspace samples, solvent extracts, vacuum and steam distillates of fresh, frozen, dried and processed sporophores are treated considering the specificity of this topic.

1. INTRODUCTION

The consumption of cultivated and particularly wild mushrooms is increasing considerably today. Despite the fact that mushrooms have been used for their nutritive (1-5) and medicinal values (6-9), fruit-bodies are usually consumed for their unique flavour properties.

The isolation and characterization of volatile constituents from fungi belonging to the Macromycetes have been previously reviewed by authors (10,11). Since the general literature concerning volatiles of mushrooms is very extensive, and considering the specificity of the topic in our own research programme, this review will focus on the highly esteemed Agarics and Boletes species used commercially as foodstuffs as well as the toadstools within the related inedible and poisonous species (12-14).

In this review, papers relative to the volatile constituents of gilled *Agaricus* and tubulate *Boletinus*, *Boletus*, *Leccinum*, *Suillus* and *Xerocomus* species are reported. We treated the articles on volatilisable and volatile aroma components from fresh, frozen, dried and processed sporophores investigated by headspace analysis, solvent extraction, vacuum and steam distillation. Identified volatiles are listed in alphabetical order. Tentatively identified volatile constituents have been removed, but not unlikely compounds.

The purpose of this report is to obtain objective evidence whether the volatile composition of mushrooms is influenced by the material state and the extraction method. Due to the great diversity of the results described in the literature, i.e., qualitative and quantitative data expressed with various units, only qualitative differences in volatiles are reported in Agarics and Boletes species.

2. STORAGE, EXTRACTION AND ANALYSIS CONDITIONS

It is currently conceded that a series of C_8-containing compounds, i.e., octan-1-ol, octan-3-ol, 3-octanone, oct-2-en-1-ol, oct-1-en-3-ol and oct-1-en-3-one, are the primary volatiles of mushroom flavour (11). From their investigation, Pyysalo and Suihko (15) note that oct-1-en-3-ol and oct-1-en-3-one are the most important aroma components associated with fresh mushrooms and that oct-1-en-3-ol can serve as the precursor of oct-1-en-3-one through oxidation.

Because fresh mushrooms contain 90% water, their delicious and attractive flavour is easily spoilt and lost due to enzyme action if not processed and consumed within 4 or 5 days of picking (15,16). In addition, the aroma of mushrooms changes during storage and processing (15,16). Mushrooms can be processed in different ways by drying, freezing, canning and packaging. Various methods are performed to dry mushrooms such as hot-air drying (17-19), infra-red drying (19), drum drying (20), fluidized bed drying and spray drying (21), and microwave drying (22). Obviously, the best flavour retention is reported in freeze-dried mushrooms (18,21,23). Recently, Mau and Hwang (24) have studied the effect of γ-irradiation on flavour compounds of *Agaricus bisporus* and showed that the amount of total volatiles is affected by the doses applied.

Sophisticated techniques for the separation and identification of volatile flavour compounds from mushrooms are currently used. The main extractive methods to isolate and concentrate the fraction responsible for the aroma are headspace technique, solvent extraction, distillation and

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supercritical fluid extraction (10,11,25). Comparison of the extraction methods reveals large qualitative and quantitative differences in volatiles (26,27).

The headspace technique (28-30) has the advantage of not introducing solvent peaks into the chromatograms and enables an olfactory approach of the mushroom odour comparable to human sensory perception based on the most volatile compounds (25,26,31-33). Therefore, solid adsorbents may retain compounds or cause artifacts (34). Combined headspace/multi-odour gas sensor devices are used for on-line differentiation of mushroom aromas (35).

Solvent extraction is the most simple method for the isolation of flavour components from mushrooms. It is an easy, reliable and suitable technique for routine analysis of flavour compounds (11). The disadvantages of liquid-solid extraction are the formation of an emulsion in the separatory funnel and the loss of flavour when the solvent is separated off. Steam distillation leads to a pronounced "cooked-mushroom" flavour (27). Thus, distillation can be carried out under reduced pressure and temperature to lower the thermal degradation.

The most recent technique, i.e., the extraction by liquid or supercritical carbon dioxide minimizes thermal degradation of volatile components (26,27,36-39). Nevertheless, condensation of volatiles seems to be difficult by supercritical fluid extraction; this technology has limited selectivity and represents a considerable investment for the users (40-42). The pervaporation technique using a propylene tubular membrane permits the extraction of selective aroma compounds such as oct-1-en-3-ol (43,44).

After concentration of extracts, the volatile compounds are then separated by gas chromatography (GC) and identified either by comparing their retention times or Kovats indices data to those of pure products (45), or by the coupling of GC to a mass spectrometer (46) with comparison to mass spectral library (47-50), and literature spectra (45,51-55). Combining Solid Phase Microextraction with chiral GC analysis (SPME-GC) can provide a simple and inexpensive quality-control method for mushroom flavour compounds as (+) and (-)-oct-1-en-3-ol (56). GC/Sniffing (57) using the olfactory referential « Le champ des odeurs » (58) gives a sensory and semi-quantitative estimation of the main compounds in the aroma of mushrooms (30,32,33) based on the sensory evaluation reported in literature (59,60). The volatiles are also investigated by GC/FID, GC/FTIR and GC/FTIR/MS (26,33).

Sensory panels may be performed and allow aroma, colour, appearance and texture of mushroom foodstuffs to be appreciated by experienced panels of tasters (15,61,62).

3. VOLATILES OF *AGARICUS* SPECIES

Most of the *Agaricus* species are edible and range from excellent to fair in food value (14,63). Some have grown commercially, i.e., *Agaricus bisporus*, *A. bitorquis* and *A. subrufecens*. Aside from the cultivated species, other wild species, i.e., *A. augustus* and *A. campestris*, are often collected from various countries.

Wurzenberger and Grosch (64) note that a brown strain of *A. bisporus* (var. *avellanea*) produces more oct-1-en-3-ol than a white strain of *A. bisporus* (var. *alba*). The volatile oct-1-en-3-ol also known as "mushroom alcohol" or "matsutake mushroom alcohol" has been first isolated and identified originally from *Armillaria matsutake* (65,66). Later, (-)-oct-1-en-3-ol is first identified from fresh wild *A. campestris* steam distillate by Freytag and Ney (67).

Because volatile constituents of mushrooms occur in complex mixtures, various effective extraction methods, i.e., headspace analysis, solvent extraction and distillation are used to isolate volatile flavour compounds from fresh, frozen, dried and processed *Agaricus* materials.

3.1. Volatiles of *A. bisporus*

Considering that the most common cultivated mushroom is usually consumed for its flavour properties, the volatile constituents of *A. bisporus* (Lange) Imbach (Cultivated Mushroom) have been well studied.

3.1.1. VOLATILES FROM FRESH AND FROZEN MUSHROOMS

Fresh and frozen mushrooms and mushroom extracts are investigated for volatile components using non-destructive methods, i.e., headspace analysis, solvent extraction and vacuum distillation.

• Headspace analysis means that only the most volatile components are detected and is representative of the true aroma of the mushroom sample. Headspace extract of cubed fresh mushroom yields an aroma extract obtained using the closed-loop stripping apparatus of Grob and Zürcher (68) modified and concentrated by microdistillation according to Bemelmans (69) in which octan-3-one, oct-1-en-3-one and ethylhexanoate are the major components and oct-1-en-3-ol belongs to the minor fraction (70). The authors conclude that oct-1-en-3-one is the most important volatile flavour compound in fresh *A. bisporus*. Nevertheless, Belmelmans (69) reports that high recoveries are obtained from all compounds except the most volatile ones when ether solution obtained by desorption of Tenax-CS is reduced to a small final volume (50 µl). Furthermore, thirteen volatile flavour components are described from the headspace concentrate of mushroom aqueous extract obtained from fresh cultivated *A. bisporus* sporophores (Table 1[a]). Later, forty-four constituents are identified from the headspace samples of cultivated fresh *A. bisporus* obtained at room temperature (Table 1[b]).

Table 1. Composition of volatiles identified from fresh and frozen *Agaricus bisporus* headspace concentrates, solvent extracts and vacuum distillates.

	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]
Anisaldehyde		+	+					
Benzaldehyde	+	+	+	+	+	+	+	+
Benzothiazole							+	
Benzyl acetate							+	
Benzyl alcohol	+	+	+	+	+	+	+	+
Butanal		+	+					
Butan-2,3-diol		+						
Butanoic acid		+	+					
Butan-1-ol							+	
Butan-2-ol							+	
Butyl acetate		+	+	+				
Butyrolactone		+	+					
(2E,4Z)-Decadienal				+				
(2E,4E)-Decadienal				+				
Decane		+						
Decan-4-one			+					
Diethylether							+	
Dimethylformamide			+					
1,4-Dioxane		+	+					
Dodecane			+					
Ethyl acetate							+	
5-Ethylbutyrolactone			+					
Ethyl formate							+	
Ethyl hexanoate	+							
4-Ethyltoluene			+					
Furfural					+			
Heptanoic acid			+					
Heptan-1-ol							+	
Heptan-2-ol		+	+					
(E)-2-Heptenal	+							
Hept-1-en-3-ol								+
Hept-2-yl acetate		+						
Hexanal	+	+	+	+			+	
Hexanoic acid		+	+					
Hexanol		+	+				+	
(Z)-Hex-3-en-1-ol		+	+					
Hexyl acetate		+	+					
4-Hydroxydecan-5-one		+	+					
3-Methylbutanal							+	
3-Methylbutanoic acid		+	+					
3-Methylbutanol		+	+		+	+	+	
3-Methylbutyl acetate		+	+					
Methylene chloride							+	
Methyl 3-methylbutanoate		+	+					
Methyl propanoate		+	+					
Nonanal		+	+					
Nonane			+					

Nonan-1-ol		+	+					
Nonan-3-ol		+						
(*Z*)-Non-2-en-1-ol		+	+					
Octanal	+							
Octane			+					
Octanoic acid		+	+					
Octan-1-ol	+	+	+				+	+
Octan-3-ol	+	+	+		+	+	+	+
Octan-3-one	+	+	+		+	+	+	+
(*E*)-2-Octenal	+	+					+	
Oct-1-en-3-ol	+	+	+	+	+	+	+	+
(*E*)-Oct-2-en-1-ol	+	+	+				+	+
(*Z*)-Oct-2-en-1-ol					+			
Oct-1-en-3-one	+	+					+	+
Oct-1-en-3-yl acetate		+	+				+	
Oct-1-en-3-yl propanoate		+					+	
Pentane							+	
Pentan-1-ol							+	
Pentanoic acid			+					
1-Phenylethanol							+	
2-Phenylethanol		+	+				+	
2-Phenylethyl acetate		+	+					
Tetradecane			+					
Toluene		+	+					
Tetradecanoic acid		+	+					
Tridecanoic acid		+	+					
Undecan-2-one		+	+					
o-Xylene		+						

[a] Headspace concentrate of fresh mushroom aqueous extract (70); [b] Headspace concentrate of fresh mushroom (33); Solvent extract of [c] fresh mushroom (33) and [d] frozen mushroom (71); Vacuum concentrated distillate (72) from fresh mushroom, [e] Ref. (31) and [f] Ref. (21); Vacuum distillate from fresh mushroom extract, [g] Ref. (16) and [h] Ref. (70).

• Forty-seven volatile substances are identified from dichloromethane extracts of fresh cultivated *A. bisporus* by GC/FID (Table 1[c]) and six from frozen cultivated *A. bisporus* by GC/MS (Table 1[d]). The apparent discrepancy between these two results is only due to the threshold limit: 0.1% for Buchbauer *et al.* (33) and 3% for Rapior *et al.* (71).

• The volatiles of fresh *A. bisporus* sporophores and mushroom extracts are investigated by vacuum distillation under reduced pressure and temperature to minimize the risks of thermal degradation.

Eight volatile components are reported from fresh cultivated fruit-bodies of *A. bisporus* vacuum distillate by Wasowicz (31) and listed in Table 1[e]. Three years later, the results from Sulkowska and Kaminski (21) confirm that the fresh *A. bisporus* aroma is based on the presence of six volatiles (Table 1[f]).

Vacuum distillation method is also suitable for fresh *A. bisporus* mushroom extracts at low temperatures. The fresh mushrooms are pressed into juice at room temperature. The extract is then distilled under vacuum at approximately 35°C. The main volatiles are benzyl alcohol and benzaldehyde in cultivated fresh *A. bisporus* and oct-1-en-3-ol in wild fresh *A. bisporus* (Table 1[g]). In 1987, aqueous extract from cold slurry (4°C) of fresh cultivated mushroom was distilled at 35°C and concentrated by microdistillation (69). The distillate revealed nine volatiles (Table 1[h]). The quantitative data indicated that oct-1-en-3-ol was present at the largest amount in the supernatant of a mushroom homogenate isolated by vacuum distillation while oct-1-en-3-one appeared only in traces.

3.1.2. VOLATILES FROM DRIED MUSHROOMS

Since fresh mushrooms are high in moisture, drying and dehydration were the most used ways of mushroom preservation in the past. Moreover, because dried and freeze-dried mushrooms develop a stronger flavour than fresh mushrooms, the quality of *A. bisporus* dried by different processes has been studied and compared to vacuum distillates by Sulkowska and Kaminski (21).

The results reveal that substantial losses of volatile compounds occur during drying steps (Table 2). Losses of the main volatile aroma compound, oct-1-en-3-ol, reach ca. 90% when contents from dried and fresh mushroom vacuum distillates are compared (Tables 1[f] and 2). The best flavour properties of mushroom, particularly the oct-1-en-3-ol content, are preserved by vacuum-freeze-drying and vacuum-roller drying. Benzyl alcohol is found in all vacuum distillates of dried mushrooms obtained according to Kaminski *et al.*

Table 2. Volatile composition of dried cultivated *A. bisporus* distillates.

	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]
2-Acetylfuran								+
Butan-1-ol			+		+		+	
Benzaldehyde	+	+	+	+	+	+	+	+
Benzyl alcohol	+	+	+	+	+	+	+	+
Benzyl isothiocyanate								+
Chloroform								+
Ethylbenzene								+
Ethyldimethylpyrazine								+
2-Ethyl-5-methylpyrazine								+
2-Ethyl-6-methylpyrazine								+
Ethylpyrazine								+
2-Ethyl-3,5,6-trimethylpyrazine								+
Furfural		+		+	+	+		+
Hexanal								+
Hexane								+
Hexan-1-ol					+			
Indole								+
3-Methylbutanal								+
3-Methylbutanol	+					+	+	
Methylphenol								+
Methylpyrazine								+
Octan-3-ol	+	+	+	+	+	+	+	
Octan-3-one		+	+			+		
Oct-1-en-3-ol	+	+	+	+	+	+	+	
Oct-1-en-3-one								+
Pentan-1-ol	+	+		+			+	
2-Pentylfuran								+
Phenylacetonitrile								+
Pyridine								+
Toluene								+
Undecan-2-one								+
Xylenes								+

Vacuum distillate of *A. bisporus* (21) dried by [a] Traditional method; [b] Freeze drying method; [c] Fluidization drying method; [d] Lower pressure roller-drying method (LPRD); [e] Slurry dried by the LPRD method; [f] Spray drying method; [g] Slurry dried by the spray drying method; [h] Steam distillate of dried *A. bisporus* (23).

(72). The highest level of benzaldehyde is linked to traditional (blow-air drying) and fluidization methods. Sulkowska and Kaminski (21) state that benzyl alcohol and benzaldehyde are the fundamental constituents of volatiles in dried mushrooms (Table 2[a]-[g]). When volatiles of dried mushrooms are steam distilled, many thermally-produced volatiles are detected (Table 2[h]) (23).

3.1.3. VOLATILES FROM COOKED MUSHROOMS

Volatiles are studied from cooked, fresh, and dried mushrooms, and mushroom extracts by headspace analysis and distillation methods.

• Headspace samples are prepared from cultivated fresh *A. bisporus* basidiocarps placed in a water bath at 90°C. The headspace analysis shows that six volatiles have an effect on the odour impression of *A. bisporus* and makes it possible to observe that one of the basic volatiles is oct-1-en-3-ol (Table 3[a]).

• Dijkstra and Wikén (73) distilled extract from boiled slurry of fresh cultivated *A. bisporus* at 50°C under reduced pressure. Five volatiles were identified as oct-1-en-3-ol, benzyl alcohol, benzaldehyde, butanoic acid and 3-methylbutanoic acid while oct-1-en-3-one was not detected (Table 3[b]). The authors reported that the distillation of *A. bisporus* mushroom extract shows a significant loss in flavour intensity.

• Because mushrooms are normally eaten cooked, the volatile isolation by steam distillation apparatus is a satisfactory method for obtaining mushroom concentrate. Fresh cultivated fruit-bodies of *A. bisporus* are investigated for volatiles by extraction-distillation using Likens-Nickerson apparatus (74). According to Cronin and Ward (75), the mushroom extract is dominated by nine volatile components identified as C_8 derivatives (octan-3-one, oct-1-en-3-one, octan-3-ol, oct-1-en-3-ol), aromatic compounds (benzaldehyde, benzyl alcohol, phenylacetaldehyde), 3-methylbutanol and furfural (Table 3[c]). Seven of the most important volatile compounds of fresh *A. bisporus* steam distillate are also reported by Le Loch-Bonazzi *et al.* (76) and listed in Table 3[d].

Recently, forty-three volatile substances were identified by GC/FID from steam distillate of fresh cultivated *A. bisporus* fruit-bodies (Table 3[e]). Benzyl alcohol is described like thermal artifact as already reported in literature (75,76) in steam distillate. 3-Methylbutanol and 3-methylbutanoic acid (isovaleric acid) were also identified in steam distillates of *A. bisporus* by Stäuble and Rast (77).

• The volatile flavour constituents of fresh *A. bisporus* are also investigated from fruit-bodies by distillation methods at various temperatures.

The aroma concentrates characteristic of both raw and cooked flavours from fresh *A. bisporus* are obtained at low (40°C) and boiled temperatures by Card and Avisse (78)(Table 3[h] and 3[i]) using a long-tube evaporator (79) and at medium (from 60°C to 80°C) and boiled temperatures by Picardi and Issenberg (80) (Table 3[f] and 3[g]) using a Likens-Lickerson apparatus (74) connected or not to a vacuum pump. So, the term of « raw flavour » has not the same meaning according to the authors due to the various temperatures used for distillation.

The major volatiles of raw *A. bisporus* are octan-1-ol, octan-3-one, benzaldehyde, oct-1-en-3-ol, octan-3-ol and oct-2-en-1-ol according to Picardi and Issenberg (80). The three latter volatiles are also the determinative constituents of raw mushroom aroma according to Card and Avisse (78); the authors establish the *(E)*-structure of oct-2-en-1-ol, a volatile component previously reported by Pyysalo (16) in the vacuum distillate of the fresh cultivated mushroom extract (Table 1[g]).

Card and Avisse (78) report higher levels of carbonylated compounds, i.e., benzaldehyde, octan-3-one and oct-1-en-3-one in cooked *A. bisporus* than in raw material and also notice the emergence of furfural and methylfurfural in cooked fresh *A. bisporus* mushroom (Table 3[h] and 3[i]). Picardi and Issenberg (80) observe a higher level of only oct-1-en-3-one, by increasing the temperature of cooking from 60-80°C to 105°C (Table 3[f] and 3[g]).

3.1.4. COMPARATIVE VOLATILE COMPOSITION OF COOKED FRESH AND DRIED MUSHROOM STEAM DISTILLATES

The volatiles of cooked dried mushrooms (Table 2[h]) are qualitatively very different from those of cooked fresh mushrooms (Table 3[j]) obtained by simultaneous distillation-extraction in a Likens and Nickerson apparatus modified by MacLeod and Cave (81). Only one of the seven C_8 compounds, oct-1-en-3-one, survives processing; phenylacetonitrile and benzyl isothiocyanate are identified, and a number of pyrazines and other thermally-produced artifacts of processing are recognized (Table 3[j]). The authors also detect cyclooctanol, apparently formed by cyclisation of oct-1-en-3-ol during cooking of dried *A. bisporus* mushroom (23). Thermal decomposition of volatile constituents is the major problem of mushroom drying preparation, and distillation techniques with extraction carried out at atmospheric pressure.

Working on seven major volatiles of *A. bisporus*, Le Loch-Bonazzi *et al.* (76) show that a drastic reduction of the concentration of C_8 compounds (octan-3-ol, octan-3-one, oct-1-en-3-ol, *(E)*-oct-2-en-1-ol) occurs in steam distillates (74) during dessication process as already observed in dried *A. bisporus* vacuum distillates by Sulkowska and Kaminski (21), and in dried fairy ring mushroom (*Marasmius oreades*)

Table 3. Composition of volatiles identified from cooked fresh cultivated *A. bisporus* headspace concentrate and distillates

	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]	[i]	[j]
Acetophenone									+	
Anisaldehyde					+					
Benzaldehyde	+	+	+	+	+	+	+	+	+	+
Benzyl alcohol	+	+	+	+	+			+	+	+
Benzyl isothiocyanate										+
Butanal					+					
Butanoic acid		+			+					
Butan-1-ol			+							
Butyl acetate					+					
Chloroform										+
Cyclooctanol										+
Dichlorobenzenes										+
Dichloromethane										+
Dimethylformamide					+					+
1,4-Dioxane					+					
Dodecane					+					
5-Ethyl-butyrolactone					+					
4-Ethyltoluene					+					
Furfural			+						+	+
Guaiacol								+	+	
Heptanoic acid					+					
Heptan-2-ol					+					
Hexadecane					+					
Hexanal					+					+
Hexane										+
Hexanoic acid					+					
Hexan-1-ol			+		+			+	+	
Hex-1-en-3-ol										+
(Z)-Hex-3-en-1-ol					+					
4-Hydroxydecan-5-one					+					
3-Methylbutanal			+							
Methyl-3-methylbutanoate					+					
3-Methylbutanoic acid		+			+					
3-Methylbutanol	+		+		+			+	+	+
Methylfurfural									+	
Methyl propanoate					+					
Nonanal					+					
Nonane					+					
(Z)-Non-2-en-1-ol					+					
Octane					+					
Octanoic acid					+					
Octan-1-ol					+	+	+	+	+	+
Octan-3-ol	+		+	+	+	+	+	+	+	+
Octan-3-one	+		+	+	+	+	+	+	+	+
Oct-1-en-3-ol	+	+	+	+	+	+	+	+	+	+
(E)-Oct-2-en-1-ol				+	+	+	+	+	+	+
Oct-1-en-3-one			+				+	+	+	+

Pentanoic acid					+					
Pentan-1-ol			+							
Phenylacetaldehyde			+	+				+	+	+
2-Phenylethanol					+			+	+	
2-Phenylethyl acetate					+					
N-Phenylpyrrole										+
Pyridine										+
Terpineol			+					+	+	
Tetradecane					+					
Tetradecanoic acid					+					
Toluene					+					+
Tridecanoic acid					+					
3,5,5-Trimethylcyclohex-2-en-1-one										+
Undecan-2-ol					+					
Undecan-2-one					+					
Xylenes										+

[a] Headspace concentrate of cooked mushroom from fresh material (21); [b] Vacuum distillate of boiled slurry from fresh mushroom (73); Steam distillate from fresh mushrooms [c] Ref. (75), [d] Ref. (76), [e] Ref. (33); Simultaneous distillation-extraction of fresh material (80) with a heating tape (74) maintained at 60 to 80°C [f] and approximately 105°C [g]; Simultaneous distillation-extraction (79) of fresh mushrooms (78) at 40°C [h] and 100°C [i]; [j] Simultaneous distillation-extraction (81) of fresh material (23).

steam distillates by Vidal *et al.* (27). Results by Le Loch-Bonazzi *et al.* (76) confirm the superiority of vacuum freeze-dried products: oct-1-en-3-ol predominates in vacuum freeze-dried mushroom as in fresh, while the major compound becomes benzyl alcohol by freeze-drying on a fluidized bed of adsorbent. The authors demonstrate that the majority of C_8 compounds lost during the freeze-drying are released during the freezing stage and that, the aromatic compounds found in the vacuum freeze-dried mushroom are generated during sublimation or rehydration of material before extraction. Then, Kompany and René (82,83) describe the optimal freeze-drying conditions based on chamber pressure and heating plate temperature in order to improve aroma retention in *A. bisporus* using Likens-Nickerson distillation-extraction.

3.1.5. AROMA CHANGES IN POSTHARVEST STORAGE AND PROCESSING

Results show that whatever the strain and the developmental stage of *A. bisporus*, oct-1-en-3-ol is the major effluent compared with octan-3-one and oct-1-en-3-one (84,85). Cruz *et al.* (85) also demonstrate that the released amounts of the three volatile components from fresh material are found to be greater at the medium stage of development, and are smaller at button and flat stages.

Wurzenberger and Grosch (64) report that oct-1-en-3-ol level decreases relatively fast during storage of white and black strain of *A. bisporus*. This finding is in contrast with a previous study by Maga (61) which shows that oct-1-en-3-ol and oct-1-en-3-one increase with maturity, storage and cooking and that high levels of both volatiles are found in the caps as compared to the stems of *A. bisporus*. Furthermore, the oct-1-en-3-ol content obtained from the organic extract of freeze-dried sporophores increases in each flush up to the third out of sixth and decreases rapidly during postharvest storage at 12°C for the first three days (86); the latter results are consistent with those reported by Wurzenberger and Grosch (64).

Few investigations are also undertaken to study the effects of blanching, chemical treatments and freezing methods on quality of *A. bisporus* mushroom (87,88) and liquid extract of this species (28). During the processing of canned mushrooms, blanching step stops all life processes and inactivates enzymes that would cause changes in flavour and aroma (20). The concentrations of oct-1-en-3-ol in canned and dried *A. bisporus* are much lower than in fresh cultivated mushroom; the concentration of glutamic acid is increased moderately by sterilization and is lowered on drying (89). Benzaldehyde, oct-1-en-3-ol and octan-3-one are identified as major constituents of raw, extracted and concentrated juices of *A. bisporus* (90).

In general terms, freeze-drying is the process that gives the best quality of *A. bisporus* dehydrated mushrooms (21,76), Therefore, combination of microwave and hot air drying allows a partially complete preservation of the original ratio between oct-1-en-3-ol and oct-1-en-3-one responsible for the *A. bisporus* mushroom aroma, because of the limited oxidation of oct-1-en-3-ol (22).

3.2. Volatiles from other *Agaricus* species

The volatiles of *A. campestris*, *A. subrufecens* and *A. augustus* are studied from headspace sample, steam distillates and organic extract.

Headspace sample of fresh edible *A. campestris* L.:Fr. (Meadow Mushroom) are investigated for volatiles by Buchbauer *et al.* (33). The headspace sample of *A. campestris* shows that thirty-two constituents have an effect on the odour impression of this species (Table 4[a]). Eleven C_8 components are detected from the steam distillate of *A. campestris*, and also eight oxo- and hydroxy acids previously characterized as enzymic products from linoleic acid by Tressl *et al.* (91) (Table 4[b]).

Aromatic compounds such as benzaldehyde, benzyl alcohol, methyl benzoate and benzonitrile identified from the steam distillate of fresh *A. subrufecens* (Peck) Moll. could be responsible for the "almond-like" aroma of the mushroom (Table 4[c]). In addition, benzaldehyde, benzyl alcohol and 4-hydroxybenzaldehyde are identified from the diethyl ether extract of fresh *A. augustus* Fr. (Prince), a mushroom described as having a bitter almond- or anise-like aroma; since the odour panel experiments judge the mixture of benzaldehyde and benzyl alcohol at different concentrations, both odour desciptions can be considered accurate for *A. augustus* (93).

3.3. Sensory tests on *Agaricus* species

As previously reported for *A. augustus*, the aroma

Table 4. Composition of volatiles identified from *A. campestris* and *A. subrufecens*

	[a]	[b]	[c]
Anisaldehyde	+		
Benzaldehyde	+	+	+
Benzonitrile			+
Benzyl acetate			+
Benzyl alcohol	+		+
Benzyl formate			+
Butanal	+		
Butanoic acid	+		
Butyrolactone	+		
1,2-Dimethylbenzene	+		
1,4-Dioxane	+		
Hexanal		+	+
Hexanoic acid	+		
Hexan-1-ol			+
(Z)-Hex-3-en-1-ol	+		
4-Hydroxydecan-5-one	+		
Limonene			+
Menthol			+
Methyl benzoate			+
3-Methylbutanoic acid	+		
3-Methylbutan-1-ol	+		
2-Methylcyclohexanone			+
Methyl 3-methylbutanoate	+		
5-Methyl-2-phenyl-2-hexenal			+
Methyl propanoate	+		
Neryl hexanoate			+
Nonanal	+		

	[a]	[b]	[c]
(Z)-Non-2-en-1-ol	+		
(Z,Z)-Octa-2,5-dienal		+	
(Z)-Octa-1,5-dien-3-ol		+	
(Z,Z)-Octa-2,5-dien-1-ol		+	
(Z)-Octa-1,5-dien-3-one		+	
Octanal			+
Octanoic acid	+		
Octan-1-ol	+	+	
Octan-3-ol	+	+	
Octan-3-one	+	+	+
(Z)-Oct-2-enal	+	+	
Oct-1-en-3-ol	+	+	+
(Z)-Oct-2-en-1-ol	+	+	+
Oct-1-en-3-one	+	+	+
Oct-1-en-3-yl acetate	+		
Oct-1-en-3-yl propanoate	+		
Pentadecan-2-one			+
Pentanal			+
Pentan-1-ol			+
5-Pentylbutyrolactone			+
2-Pentylfurane			+
Phenol			+
2-Phenylethyl acetate	+		
Tetradecanoic acid	+		
Toluene	+		
Tridecanoic acid	+		
Undecan-2-one	+		+

[a] Headspace analysis from fresh *A. campestris* (33); [b] Steam distillation according to Teranishi (94) from fresh *A. campestris* (91); [c] Steam distillation according to Römer & Renner (95) from fresh *A. subrufecens* (92).

research work involves both the identification of volatiles and organoleptic characterization of the aromas with sensory evaluation made by panellists (96).

Anticipating the general introduction of naturally occurring *A. bitorquis* (Quélet) Sacc. (Spring *Agaricus*) as a new cultivated species, a laboratory scale sensory evaluation favors *A. bisporus* (97). Several tasters find *A. bitorquis* too strongly flavoured as confirmed by Dijkstra (89). The author report, that *A. bitorquis* contains 5-7 times as much oct-1-en-3-ol as *A. bisporus* and indicates that the high level of the volatile is less pleasant. Another sensory experiment concludes that the major locus of aroma in *A. campestris* are the central portions of both pileus and stipe exclusive of the cuticle (98).

In contrast with the work by Bernhard and Simone (98) who find no significant difference in aroma intensity between the raw and steamed states of *A. campestris*, sensory data by Maga (61) indicate that raw caps (containing the gills) of *A. bisporus* have a higher degree of desirable mushroom aroma than raw stems.

According to Wurzenberger and Grosch (64), more oct-1-en-3-ol is produced in the cap and the gills than in the stipe of raw *A. bisporus*. However, cooked caps and stems are judged to be the same in aroma (61). The authors also note that medium sized mushrooms are generally found to have a more desirable cooked aroma than smaller or larger mushrooms. In his sensory test on the cooked mushroom aroma of *A. bisporus*, Tape (99) reports that a gradual increase of aroma intensity occurs from young "buttons" to old "flats".

4. VOLATILES OF BOLETES SPECIES

Boletes are fleshy, stalked tubulate mushrooms that grow on the ground in woods. Most of Boletes are edible (*Boletus edulis*, *B. aereus*, *Leccinum aurantiacum*, *L. scabrum*, *Xerocomus badius*, *X. subtomentosus*) (5,100,101); some are toxic (*B. satanas*) or poisonous unless well prepared (*Suillus collinitus*, *S. granulatus*, *S. luteus*) (14,63).

The volatile composition of many Boletes species belonging to five genera, i.e., *Boletinus*, *Boletus*, *Leccinum*, *Suillus* and *Xerocomus*, are studied from headspace samples, solvent extracts and distillates.

4.1. Volatiles of *Boletus edulis*

King Bolete and Cep are names given to the best-known Bolete (*Boletus edulis* Bull.:Fr.), a mushroom that is sold all the year round as fresh, frozen and dried food.

4.1.1. VOLATILES FROM FRESH AND FROZEN MUSHROOMS

Volatiles from the King, the most edible prized Bolete, are investigated by headspace analysis and distillation methods.

- The headspace analysis of fresh wild *B. edulis* shows thirty-eight volatiles with more than 50% of components at trace level (Table 5[a]). The major flavour constituent is oct-1-en-3-ol (ca. 87 % of the volatile fraction).

- Distillation performed at low pressure is carried out on both frozen *B. edulis* fruit-bodies and mushroom extract.

Wasowicz and Kaminski (102) identified six aliphatic volatile components from frozen wild fruit-bodies of *B. edulis* using vacuum distillation method (Table 5[b]). The most predominant constituent is oct-1-en-3-ol (82% of the volatile fraction).

The juice from pressed frozen *B. edulis* is distilled in vacuum at approximately 35°C. The main volatile of the juice distillate is also oct-1-en-3-ol (Table 5[c]). The fresh mushroom-like aroma of *B. edulis* is attributed mainly to oct-1-en-3-ol, *(E)*-oct-2-en-1-ol, oct-1-en-3-one and octan-3-one (16). The compound oct-1-en-3-ol can be expected to oxidize to oct-1-en-3-one, a volatile constituent described as "boiled mushroom" and at certain levels of concentration as "metallic" in fresh *B. edulis* according to Pyysalo and Suihko (15). 2-Phenyl-2-butenal found for the first time in *B. edulis* juice distillate by Pyysalo (16) has been previously reported in *Phallus impudicus* mushroom distillates by List and Freund (103).

4.1.2. VOLATILES FROM DRIED MUSHROOMS

As well as fresh and frozen materials, the commercially dried *B. edulis* is also investigated for volatiles by vacuum distillation.

A dried *B. edulis* sample is submitted to vacuum distillation by Craske and Reuter (104) using the apparatus of Guadagni and Dimick (105). The distillate shows a rubber and/or town gas flavour and carries no aroma that may be classified as typical of mushrooms. The true mushroom flavour is found to be non-volatile and due to nitrogenous constituents from the residue after distillation.

4.1.3. VOLATILES FROM COOKED MUSHROOMS

The volatiles from dried *B. edulis* mushroom and mushroom extract are investigated by steam distillation and vacuum distillation, respectively.

Volatile aroma compounds from a steam distillate of dehydrated *B. edulis* are then investigated by Ney and Feytag (106). Many acids, alcohols, amines and sulfur components are identifed (Table 5[d]). Some of these volatiles are probably artifacts due to the drying process and extract preparation.

On the other hand, the pentane extract from a boiled

Table 5. Composition of volatiles identified from *Boletus edulis*.

	[a]	[b]	[c]	[d]	[e]
2-Acetylfuran					+
2-Acetyl-5-methylfuran					+
2-Acetylpyrrole					+
Anisaldehyde	+				
Anthracene/Phenanthrene					+
Benzaldehyde	+		+		+
Benzothiazole			+		
Benzyl alcohol	+		+		
Biphenyl					+
Butanal	+				
Butanoic acid	+			+	
Butan-1-ol			+		
Butan-2-ol			+	+	
Butyl acetate	+				
Butyrolactone					+
Cyclohepta-1,3,5-triene	+				
Decane	+				
Decanoic acid				+	+
Decan-2-one					+
Decan-4-one	+				
Dec-3-en-2-one					+
Dibutylphthalate					+
Diethylether			+		
Diethylphthalate					+
Dimethylsulfide				+	
Dimethylphthalate					+
2,3-Dimethylpyrazine					+
2,5-Dimethylpyrazine					+
2,6-Dimethylpyrazine					+
Dimethyltrisulfide					+
2,6-Ditertiobutyl-4-methylphenol			+		
Dodecane	+				
Ethanoic acid				+	
Ethyl acetate			+		
Ethylamine				+	
3-Ethyl-2,5-dimethyl-pyrazine					+
Ethyl formate			+		
1-Ethyl-2-formylpyrrole					+
2-Ethyl-5-methylpyrazine					+
2-Ethyl-3,5,6-trimethyl-pyrazine					+
Eugenol				+	+
2-Formyldimethyl-thiophene					+
2-Formyl-1-heptylpyrrole					+

	[a]	[b]	[c]	[d]	[e]
2-Formyl-1-(3-methyl-butyl)pyrrole					+
2-Formyl-5-methyl-1-(2-phenylethyl)pyrrole					+
2-Formyl-5-methylpyrrole					+
2-Formyl-1-(2-phenyl-ethyl)pyrrole					+
2-Formylpyrrole					+
2-Formylthiophene					+
Furfural					+
Heptan-2-ol	+				
Heptanoic acid				+	+
Heptan-2-one					+
Hexadecane	+				
Hexanal	+				+
Hexan-1-ol	+		+	+	+
Hexan-2-ol					+
Hexan-3-ol					+
Hexanoic acid	+			+	
Hexyl acetate	+				
Hydrogen sulfide				+	
2-Hydroxymethylfuran					+
Methylamine				+	
3-Methylbutanal			+		
3-Methylbutanoic acid				+	+
3-Methylbutan-1-ol		+	+		
3-Methylbutan-2-ol				+	
Methylbutylacetamide					+
3-Methylbutylamine				+	
2-Methylbutyrolactone					+
5-Methylbutyrolactone	+				+
Methylchlorophenol					+
Methylene chloride			+		
5-Methylfurfural					+
Methylmercaptan				+	
Methyl 3-methylbutanoate	+				
2-Methylphenol				+	+
3-Methylphenol				+	
Methyl propanoate	+				
2-Methylpropanoic acid				+	
2-Methylpropyl acetate	+				
1-Methylpropylamine				+	
Methylpyrazine					+
Methylquinazoline					+
2-Methyltetrahydrofuran-3-one					+
Nonane	+				

Nonanoic acid				+	+
Nonan-1-ol			+	+	
Nonan-2-ol				+	
Nonan-3-ol	+				
Octanoic acid	+				+
Octan-1-ol	+	+	+	+	
Octan-3-ol	+	+	+		
Octan-3-one	+	+	+		
(E)-2-Octenal			+		
Oct-1-en-3-ol	+	+	+	+	+
(E)-Oct-2-en-1-ol	+	+	+		
Oct-1-en-3-one	+		+	+	
Oct-3-en-2-one					+
Oct-1-en-3-yl propanoate			+		
Octylamine	+				
Pentane			+		
Pentanoic acid	+			+	+
Pentan-1-ol			+	+	
2-Pentylfurane	+				
Phenol				+	+
Phenylacetaldehyde			+		
Phenylacetic acid					+
2-Phenyl-2-butenal			+		
1-Phenylethanol			+		
2-Phenylethanol	+		+		

2-Phenylethyl acetate	+				
3-Phenylpropanoic acid					+
3-Phenyl-2-propenoic acid					+
Propanoic acid				+	
Propan-1-ol				+	
Propylamine				+	
2-Propylpyrrole					+
Putrescine				+	
Pyridine				+	
α-Terpineol					+
Tetradecane	+				
Tetradecanoic acid	+				
Tetramethylpyrazine					+
Thiobutyrolactone					+
Toluene	+				
Tridecanoic acid	+				
Trimethylamine				+	
2,3,6-Trimethylpyrazine					+
Trithiolan					+
Undecanoic acid				+	
Undecan-2-one					+
Vanillin					+
4-Vinylphenol					+

[a] Headspace concentrate of fresh mushroom (33); [b] Vacuum distillate of frozen mushroom (102); [c] Vacuum distillate of frozen mushroom extract (16); [d] Steam distillate of dried mushroom (106); [e] Vacuum distillate of boiled extract from dried mushroom (129).

aqueous extract of dried mushroom is vacuum distilled. The distillate reveals 64 constituents, including nine pyrazines and seven formyl pyrroles (Table 5[e]). Oct-1-en-3-one and *(E)*-oct-2-en-1-ol are not found in the distillate from the extract of dried wild *B. edulis* mushroom as reported for the distillate from the extract of frozen mushroom (16).

4.2. Volatiles of other Boletes species

Lots of species from *Boletinus, Boletus, Leccinum, Suillus* and *Xerocomus* genera are screened for volatiles by headspace analysis, solvent extraction and distillation from fresh and frozen materials.

4.2.1. HEADSPACE ANALYSIS OF FRESH MUSHROOMS

Vanhaelen *et al.* (107) identify oct-1-en-3-ol, and *(E)*- and *(Z)*-octa-1,5-dien-3-ol from fresh *B. carpini* headspace sample based on the methodology by Vanhaelen *et al.* (108).

Furthermore, the monoterpene profile from the aroma of fresh *Boletus aestivalis* and *Suillus luteus* is characterized by α-pinene and camphene. *S. luteus* aroma also contains sabinene, β-phellandrene and β-pinene (30).

4.2.2. SOLVENT EXTRACTION OF FRESH AND FROZEN MUSHROOMS

In these studies, volatiles of fresh and frozen wild basidiocarps of edible, toxic and poisonous species are studied by GC/MS.

- The dichloromethane extracts of eleven fresh Boletes from *Boletus, Leccinum, Suillus* and *Xerocomus* genera are investigated for volatiles by Rapior *et al.* (109,110) (Table 6[a]-[k]). The major volatiles belong to the C_8 derivatives, aromatic compounds, monoterpenes and sesquiterpenes. The sesquiterpene *(E,E)*-farnesol is also isolated from the methanolic extract of *Boletinus cavipes* (111).

Subsequently, twenty-one fresh Boletes are

investigated for monoterpene compounds by GC/MS using solvent extraction (30). The extracts of *S. grevillei*, *X. subtomentosus* and *B. erythropus* contain limonene. *B. erythropus* also shows the presence of cineole, linalool and piperitone; the latter is reported for the first time in solvent extract. *B. lupinus* extract is characterized by *p*-cymene

Table 6. Composition of volatiles identified from fresh wild Boletes organic extracts (109,110).

	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]	[i]	[j]	[k]
Benzaldehyde		+	+	+							
Benzothiazole		+	+								
Benzyl alcohol				+							
Butyrolactone				+	+						
Cyclohexyl isothiocyanate			+								
Eugenol			+								
(E,E)-Farnesol					+						
Farnesylacetone					+		+		+		
Geranylacetone							+	+	+		
Heptadec-8-ene			+								
Hex-4-en-3-one			+								
5-(2-Hydroxyethyl)-4-methylthiazole				+							
4-Hydroxy-4-methylpentan-2-one											+
2-Hydroxyoctan-4-one		+									
Indole		+									
Limonene		+	+					+			+
5-Methylbutyrolactone					+						
Methyl 2,4-dihydroxy-3,6-dimethylbenzoate								+	+		
6-Methylheptan-3-one									+		
2-Methylthiobenzothiazole			+								
(2E,4E)-Octadienal								+			
Octan-1-ol					+	+	+			+	
Octan-3-ol		+		+				+	+	+	
Octan-2-one							+				
Octan-3-one		+		+				+	+	+	+
Oct-1-en-3-ol	+	+	+	+	+	+	+	+	+	+	
Oct-1-en-3-one		+	+	+							+
(E)-Oct-2-en-1-ol	+	+	+	+	+	+	+	+	+		+
Oxacyclohexan-2-one				+							
Oxa-3,5,5-trimethylcyclohex-3-en-2-one		+	+	+							
2-Phenoxyethanol				+							
2-Phenylethanol				+							
N-(2-Phenylethyl)acetamide		+	+							+	+
1-Phenyloctene			+								
4-Thiomethylphenol			+								
3,5,5-Trimethylcyclohex-2-en-1-one			+					+			
(E,E)-7,11,15-Trimethyl-3-methylene-hexadeca-1,6,10,14-tetraene									+		

[a] *Boletus aereus*; [b] *Boletus calopus*; [c] *Leccinum aurantiacum*; [d] *Leccinum quercinum*; [e] *Suillus bovinus*; [f] *Suillus collinitus*; [g] *Suillus granulatus*; [h] *Suillus grevillei*; [i] *Suillus luteus*; [j] *Suillus variegatus*; [k] *Xerocomus subtomentosus*.

which is not commonly identified within mushrooms. No monoterpene compound is detected from organic extract of the fresh following mushrooms: *B. aereus, B. calopus, B. edulis, B. luridus, B. radicans, L. lepidum, L. pulchrum, L. quercinum, L. versipelle, S. bovinus, S. collinitus, S. granulatus, S. luteus, S. variegatus, S. viscidus, X. badius* and *X. pruinatus*. These results confirm that the extracts of most of the *Leccinum* species have no volatiles (110).

• Five volatile components are identified from the extract of frozen *B. satanas* Lenz (Satan's Bolete). The major constituents are oct-1-en-3-ol and 2-methylbutan-2-ol and the minor volatiles are oct-1-en-3-ol, 3-methylbutan-2-one, octan-3-ol and 2-phenylethanol (71).

4.2.3. VOLATILES OF COOKED FRESH AND FROZEN MUSHROOM DISTILLATES

Wozniak *et al.* (112) investigate the volatile aroma constituents of fresh and frozen *Xerocomus badius* (Fr. : Fr) Gilbert (Bay Bolete) by distillation-extraction technique (Table 7[a] and 7[b]). 3-Methylbutanol and benzyl alcohol were the two additionnal appearing volatiles in the frozen mushroom distillate. The authors stated that freezing preserves the general character of typical aroma for long time (over 1 year). Then, Rapior *et al.* (113) report eight volatiles from steam distillate of fresh *X. subtomentosus* (Table 7[c]).

Table 7. Volatile composition of fresh and frozen *Xerocomus badius* and *X. subtomentosus* mushroom distillates.

	[a]	[b]	[c]
Benzaldehyde	+	+	
Benzyl alcohol		+	
Hexadecane	+	+	
3-Methylbutan-1-ol		+	
2-Methylheptan-1-ol	+	+	
2-Methylheptan-3-ol	+	+	
Heptan-2-one	+	+	
Methyl tridecanoate	+	+	
Nonanol	+	+	
Nonen	+	+	
Octan-1-ol			+
Octan-3-ol			+
Octan-3-one			+
Oct-1-en-3-ol	+	+	+
(E)-Oct-2-en-1-ol	+	+	+
Oct-1-en-3-one			+
2-Phenylacetaldehyde			+
Thujone			+

Steam distillates of *Xerocomus badius* (112), [a] fresh mushroom, [b] frozen mushroom; [c] Steam distillate of fresh *Xerocomus subtomentosus* (113).

5. DISCUSSION AND CONCLUSION

Current opinion is that a series of compounds containing eight carbon atoms constitutes the primary volatiles contributing to fresh mushroom flavour, i.e., octan-1-ol, oct-2-en-1-ol, octan-3-ol, octan-3-one, oct-1-en-3-ol and oct-1-en-3-one (10,23). Oct-1-en-3-ol and oct-1-en-3-one are of basic importance for the top note of the investigated mushrooms (15,78). Freytag and Ney (67) demonstrate a levorotatory form for oct-1-en-3-ol in *A. campestris*.

Different proposals exist concerning the formation of *(R)*-(-)-oct-1-en-3-ol such as non-enzymatic and enzymatic pathways (11). According to Wasowicz (31), oct-1-en-3-ol is formed by non-enzymatic autooxidation process of fatty acids as previously reported in dairy products (114) and in oxidized soybean oil (115). Therefore, the optical activity indicates a biosynthetic formation of (-)-oct-1-en-3-ol in mushrooms. Various mechanisms based on enzymic action are reported (116).

Linoleic acid, the major fatty acid from *A. bisporus* (117), is now recognized to be the precursor of the oct-1-en-3-ol which is identified in many vegetables and mushroom species (84,91,118-120). Oct-1-en-3-ol and *(E)*-10-oxo-8-decenoic acid have been identified as enzymic breakdown products of linoleic and linolenic acids in *A. campestris* and *A. bisporus* basidiocarps (121-123). A reduction product of the second compound, 10-hydroxydecanoic acid, has also been isolated (91). By using ^{18}O-labelled gaseous dioxygen and [^{18}O]-OH_2, Wurzenberger and Grosch (124) demonstrate that the oxygen in the oct-1-en-3-ol originates from the vapour phase and discussed the incorporation of ^{18}O in the 10-oxo-8-decenoic acid. *A. bisporus* also contains enzymes which oxidatively cleave linolenic acid into *(5Z,3R)*-octa-1,5-dien-3-ol, *(Z,Z)*-octa-2,5-dien-1-ol (in a 3:2 ratio) and *(E)*-10-oxo-6-decenoic acid (125). The *(5Z,3R)*-octa-1,5-dien-3-ol has the same *R*-configuration at the chiral centre as the oct-1-en-3-ol produced by mushrooms (123).

The existence of an alcohol reductase for the reduction of oct-1-en-3-one into oct-1-en-3-ol is reported in *A. campestris* (116) and *A. bisporus* (126). The reductase system of mushrooms may also reduce the double bond of oct-1-en-3-one to form octan-3-one. This phenomenon can possibly be explained by two separate enzymes of *A. bisporus* sporophore responsible for the formation of oct-1-en-3-ol and octan-3-one or by only one enzyme the activity of which is affected by the pH (126). According to Mau *et al.* (84), two enzymes lipoxygenase and hydroperoxide lyase are also involved in the formation of oct-1-en-3-ol from *A.*

bisporus. The authors indicate that the optimal activity of lipoxygenase-hydroperoxide lyase enzymes for the formation of oct-1-en-3-ol is in the range of pH 5.0 to 7.0. The reactions take place in mushrooms particularly when the tissue of the basidiocarps is damaged (120).

According to Pyysalo and Suihko (15), oct-1-en-3-ol is the major aroma compound in fresh mushrooms and can be expected to oxidize to oct-1-en-3-one, a mushroom volatile which is thought to be a major contributor to cooked mushroom aroma (80). This finding is in contrast with the study by Fischer and Grosch (70) which report that oct-1-en-3-one is the most important volatile component in fresh mushrooms.

Whatever the hypothesis of the authors, the aroma research work involves the identification of volatiles and then the organoleptic characterization of the aromas by sensory evaluation made by panellists. Undoubtedly, the most extensive investigation on odour descriptions from the primary volatiles isolated from mushrooms was conducted by Pyysalo and Suikho (15) as summarized by Maga (10). Sensory tests carried out with (*R*)-(-)-oct-1-en-3-ol and (*S*)-(+)-oct-1-en-3-ol showed that the characteristic fruity, mushroom-like flavour is exclusively caused by the (*R*)-(-)-oct-1-en-3-ol while the (*S*)-(+) enantiomer exhibits a moldy grassy note (73,127,128). Oct-1-en-3-one was described as boiled-mushroom aroma and possesses a metallic flavour at certain levels of concentration, specially of *B. edulis* (15). Cronin and Ward (75) demonstrated that concentration may significantly influence the odour sensation as reported for oct-1-en-3-one.

Aroma changes appear in processing methods. All drying methods result in substantial losses of about 90% of oct-1-en-3-ol and presence of benzyl alcohol from 27% to 67% of the volatile fraction from *A. bisporus* (21). In drying, the aroma of mushrooms, i.e., *B. edulis* is changed, and pyrazines, pyrroles and lactones are formed (129).

Cooking can also result in major volatile changes such as an increase of oct-1-en-3-one (80), and benzaldehyde and octan-3-one (78). Furfural and methylfurfural (78), cyclooctanol, pyrazines and pyrroles derivatives (23) are newly formed compounds. In the literature dealing with the occurrence of pyrazines and pyrroles in foodstuffs, there is some evidence that they are particularly associated with roasted and dried materials (130-134). In general, thermally-produced artifacts of drying and cooking contribute to undesirable flavour characteristics.

More and more industries are turning to a search for novel sources for natural aroma components. Considering the unique and subtle flavour of mushrooms, studies relative to the flavour chemistry of Agarics and Boletes have been compiled here. Thus, many mushrooms species having specific odours are attractive natural ressources for research programmes and also for aroma applications in food industry.

In conclusion, we would like to claim that the volatile composition is less dependent on the mushroom state (fresh, frozen, or dried) than on the extraction process (dynamic headspace concentration, solvent extraction, vacuum and steam distillation).

6. LITERATURE

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