

# CHEMICAL COMPOSITION AND NUTRITIONAL Value of European Species of Wild Growing Mushrooms

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Chapter 6

## CHEMICAL COMPOSITION AND NUTRITIONAL VALUE OF EUROPEAN SPECIES OF WILD GROWING MUSHROOMS

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#### ABSTRACT

Tens of wild growing mushroom species are widely consumed as a delicacy in a part of Europe. Knowledge of their nutritional value has so far been fragmentary mainly due to the very limited information on the bioavailability of their constituents. Dry matter content varies usually between 80 and 140 g kg<sup>-1</sup>. Usual medians of crude protein, lipid and ash content are about 25, 3 and 8 g per 100 g of dry matter, respectively. Various carbohydrates form the rest. However, great variations occur. Energy is low, about 150 kJ per 100 g of fresh mushrooms. The proportion of essential amino acids seems to be nutritionally favorable, while the content of n-3 fatty acids is negligible. Chitin, glycogen, mannitol and trehalose are typical carbohydrate constituents. Potassium is the highly prevailing element within minerals. Relatively high proportion of fiber, health-promoting  $\beta$ -glucans, compounds with antioxidation activity and flavor constituents are the topics provoking an increasing interest of both researchers and consumers. Nevertheless, several popular species accumulate high levels of cadmium, mercury and lead if growing on heavily polluted soils.

**Keywords**: edible mushrooms; nutritional value; proximate composition; proteins; lipids; carbohydrates; minerals; vitamins; flavor constituents; detrimental compounds.

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#### **1. INTRODUCTION**

The collection of wild mushrooms can be seen also as a relic drive of bygone hunters and gatherers. In some parts of the world, e.g. in Slavonic countries of central and eastern Europe, it has been a lasting part of cultural heritage. Mushroom picking in forests and grasslands has been a highly evaluated recreational activity<sup>\*</sup> and mushrooms in their natural habitat are regarded for their aesthetic value.

Mushrooms have been mostly collected as a delicacy for pickers own consumption however the collection has been an economic activity for a part of rural population. For instance, the picking is a "national hobby" in the Czech Republic interesting about 70% of the population with a statistical mean of 5.6 kg of fresh mushrooms per household yearly (Šišák, 2007). Nevertheless, some individuals consume over 10 kg yearly.

Specific aroma and texture are appreciated in mushrooms for culinary use. Tens of edible species can be variously preserved and culinary-processed. The knowledge of composition and nutritional value of wild growing mushrooms has been limited as compared with vegetables. This is understandable, because the mushrooms are perceived only as a delicacy. Moreover, their consumption in many developed countries has been marginal and thus off an interest of researchers.

Data on chemical composition and nutritional value of European edible mushroom species were reviewed (Bernaś et al., 2006; Kalač, 2009). Thus, overall knowledge from the reviews supplemented with current information will be given in following sections. Only the weightiest articles until 2007 will be cited, further papers from that period are referred in the reviews.

Medicinal mushrooms, mostly originating from East Asia, will not be referred here. Interesting information on many compounds participating in chemical defense strategies of mushrooms is available from a review of Spitteler (2008).

Various weight units will be used in the following sections according to common convention, e.g. mg per kg of dry matter for trace elements, but mg per 100g of fresh matter for vitamins.

#### **2. MYCOLOGICAL TERMS**

Some mycological terms used in this chapter are given in Figure 1. The term mushroom will be used for a fruit body, mostly aboveground, of higher fungi. A fruit body is formed from spacious underground mycelia by the process of fructification. The lifetime of the bulk of fruit bodies is only 10-14 days.

According to their nutritional strategy, mushrooms can be divided into three groups. Mycorrhizal (symbiotic) species form a close, mutually favorable relationship with their host plant, mostly a tree. Saprotrophic species (or saprophytes) live on and metabolically consume organic matter. Parasitic species live on other species in a non-symbiotic relationship.

Forests are freely accessible with some limitations (nature reserves, military areas, etc.)



Figure 1. A sketch of a typical mushroom.

### **3. DRY MATTER, PROXIMATE COMPOSITION, ENERGY VALUE** AND BIOAVAILABILITY

Dry matter (DM) of mushrooms is very low, usually in the range of 80-140 g kg<sup>-1</sup>. In case that factual DM content is unknown, value 100 g kg<sup>-1</sup> (10%) is commonly used for the calculations. High water content and activity participate in the short shelf life of fruit bodies. Proportion of DM increases during mushroom cooking due to water shrinkage. Dried mushrooms are known for their hygroscopicity.

Proximate composition of dry matter of selected mushroom species is given in Table 1. Carbohydrates content is calculated as [100 - (moisture + crude protein + lipids + ash)]. Considerable differences in the composition are evident not only among species but also within the species among data of different laboratories. Such differences can be partially explained by varied stage of fruit bodies maturity and also by different analytical methods. The data of Table 1 should be thus interpreted as a general information.

As results from Table 1, carbohydrates and crude protein (median 27.5 g 100g<sup>-1</sup> DM) are the two main components of mushroom dry matter. Low dry matter and lipid contents (median only 2.79 g 100g<sup>-1</sup> DM) result in low energy values (median 1,552 kJ 100g<sup>-1</sup> DM). If the median is expressed per "a standard mushroom" containing 100 g DM per kg of fresh matter, 100 g of such fresh mushroom has energy 155.2 kJ or 37.2 kcal. Thus, mushrooms are a delicacy of low energy value.

Information on digestibility and bioavailability of mushroom nutritional constituents has been scarce. A high proportion of indigestible chitin (see section on carbohydrates) apparently limits availability of other components. Nevertheless, credible data for wild growing mushrooms have been lacking.

Moreover, most data deal with fresh mushrooms. Information has been scarce on the changes of the individual constituents during various preservation methods, under storage and during different cooking processes.

Species	n	Dry matter	Crude	Lipids	Ash	Energy	Reference
-		-	protein	-			
Agaricus campestris	3	14.9	38.9	2.70	3.50	1,570	Beluhan and Ranogajec, 2011
Armillariella mellea	15	12.8	17.15	2.10	7.95	-	Ouzuni et al., 2009
	3	11.7	16.4	5.56	6.78	1,670	Vaz et al., 2011b
	1	16.2	14.8	6.08	3.16	1,741	Colak et al., 2009
Boletus aereus	15	12.4	19.05	4.47	6.25	-	Ouzuni et al., 2009
Boletus edulis	3	12.2	36.9	2.92	5.30	1,488	Beluhan and Ranogajec, 2011
Calocybe gambosa	3	13.9	36.65	1.34	7.98	1,398	Beluhan and Ranogajec, 2011
	3	9.1	15.5	0.83	13.9	1,453	Vaz et al., 2011b
Cantharellus cibarius	3	7.6	53.7	2.89	11.5	1,541	Barros et al., 2008c
	15	17.4	15.1	2.88	9.44	-	Ouzuni et al., 2009
	3	14.2	30.9	1.90	8.80	1,488	Beluhan and Ranogajec, 2011
	1	12.1	23.9	1.40	7.78	1,533	Colak et al., 2009
Craterellus cornucopioides	3	10.1	47.2	4.87	10.1	1,730	Beluhan and Ranogajec, 2011
	1	10.4	35.1	5.89	10.3	1,618	Colak et al., 2009
Hydnum repandum	1	6.7	23.9	8.80	11.4	1,810	Colak et al., 2009
Laccaria laccata	3	11.8	62.8	3.76	20.7	1,401	Heleno et al., 2009
Lepista nuda	3	6.2	59.4	1.77	18.5	1,395	Barros et al., 2008c
	15	8.7	24.1	3.23	6.03	-	Ouzuni et al., 2009
Lycoperdon perlatum	3	11.4	17.1	4.41	31.9	1,145	Barros et al., 2008c
	1	30.0	31.5	10.6	2.00	1,854	Colak et al., 2009
Macrolepiota procera	3	13.2	24.2	2.23	5.37	1,630	Beluhan and Ranogajec, 2011
Pleurotus ostreatus	2	-	30.3	1.10	13.2	-	Akyüz and Kirbağ, 2010
	3	11.7	24.9	2.08	7.62	1,552	Beluhan and Ranogajec, 2011
Ramaria botrytis	3	10.2	39.9	1.37	8.80	1,549	Barros et al., 2008c

 Table 1. Dry matter content (g 100g<sup>-1</sup>), proximate composition (g 100g<sup>-1</sup> dry matter) and energy (kJ 100g<sup>-1</sup> dry matter) of mushroom fruit bodies. Content of carbohydrates is calculated: [100 – (moisture + crude protein + lipids + ash)]

n ... number of samples. Contents of crude protein were recalculated for data from papers where factor of 6.25 was used. Factor of 4.38 is thought to be credible for mushrooms.

#### 4. PROTEINS AND AMINO ACIDS

The informative data on crude protein content in fourteen mushroom species are given in Table 1. The values are comparable with those reported by Bauer-Petrovska (2001) in 47 species of Macedonian edible mushrooms. She determined the mean crude protein content of 22.8% with wide variations of 9.8-36.5% in DM. A similar value of 24.9  $\pm$ 1.75 % in DM reported Uzun et al. (2009) for 30 species of Turkish mushrooms. Crude protein variability within a species can be seen from Table 1 (e.g. for *C. cibarius*).

For the calculation of crude protein in mushrooms, if determined by the Kjeldahl method, a specific converting factor has to be used due to the high proportion of non-protein nitrogen, particularly in chitin. The factor of 4.16 was recommended by Bauer-Petrovska (2001), who observed the mean proportion of 33.4% of non-protein nitrogen (from total nitrogen) in numerous samples. The factor of 4.38 has been mostly used in recent publications. This value was used for the correction of data from papers using factor of 6.25 collated in Table 1 and also of both the papers in the previous paragraph.

A unique paper on protein fractions in 24 mushroom species reported mean levels of 24.8, 11.5, 7.4, 11.5, 5.7, 5.3 and 33.8% from total proteins of albumins, globulins, glutelinlike material, glutelins, prolamins, prolamine-like material and residues, respectively (Bauer-Petrovska, 2001).

The information on changes of protein content and digestibility during fruit bodies development and on the distribution within a fruit body remains unclear. Moreover, limited data have been available also on amino acid composition of proteins. It seems from limited data (Kalač, 2009) that the composition of mushroom proteins is of higher nutritional value than that of most plant proteins.

Protein content, expressed as a proportion in DM, remained nearly stable during airdrying of mushrooms at 40 °C or on freezing to -20 °C, while boiling of fresh mushrooms caused a significant decrease (Barros et al., 2007). In cultivated *Pleurotus ostreatus* (oyster mushroom, hiratake), freezing processes followed by 12-month storage resulted in significant decrease of alanine, glutamine, cysteine and tyrosine contents, while arginine, glycine, serine, methionine and threonine contents decreased in the canned mushroom (Jaworska et al., 2011).

The reported contents of total free amino acids vary. While Ribeiro et al. (2008a) determined range between 0.15 and 2.27 % in DM for *Fistulina hepatica* and *Boletus edulis*, respectively, Beluhan and Ranogajec (2011) reported between 4.39 and 7.20 % for *Entoloma clypeatum* and *B. edulis*, respectively. Dembitsky et al. (2010) found arginine, alanine, glutamine and glutamic acid to be the major free amino acids in 15 species of genus *Boletus* and related genera.

The contents of free indispensable (essential) amino acids in various species are given in Table 2. Their nutritional contribution is limited, but some of free amino acids participate in the taste of mushrooms.

Wild mushrooms were formerly called "meat of poverty" in central Europe. However, usual protein content of about 2.5 % in fresh matter, limited knowledge on amino acid composition and lacking information on digestibility challenge the often used characterization of mushrooms as a source of valuable proteins.

#### **5.** LIPIDS

The contents of total lipids (crude fat) ranges mostly from 2% to 6% of dry matter (Tables 1 and 3). Higher values have been reported rarely. Neutral lipids are usually extracted with hexane or another non-polar solvent.

Information on neutral and polar lipid contents in ten species of mushrooms growing in eastern Canada is available (Pedneault et al., 2008). Polar lipids accounted for more than 50% in most species. For instance, the proportions of neutral and polar lipids were 3.3% and 3.1% in DM, respectively, in *Boletus edulis*, while 1.4% and 4.9% in DM, respectively, in *Agaricus arvensis*.

Several tens of fatty acids were identified in mushroom lipids. Nevertheless, only three acids markedly prevail: nutritionally desirable polyunsaturated linoleic acid (C18:2c,n-6), monounsaturated oleic acid (C18:1c,n-9) and undesirable saturated palmitic acid (C16:0) (Table 3). However, low proportion of oleic acid seems to be characteristic for the species of genus *Agaricus* and in a limited extent also for *Cantharellus cibarius* (Table 3). The proportions of nutritionally neutral saturated stearic acid (C18:0) and especially of essential  $\alpha$ -linolenic acid (C18:3,n-3) are low. Only selected species are collated in Table 3. More information is available in the cited references.

Other fatty acids are only minor components of mushroom lipids. The contents of oddand branched-chain fatty acids and hydroxy fatty acids are negligible. Nutritionally undesirable elaidic acid, being *trans* isomer of oleic acid, was firstly reported by Pedneault et al. (2008), however, at low level of <0.1% to 0.3% of total fatty acids.

Barros et al. (2007) observed some changes in fatty acid profiles of dried mushrooms, particularly a decrease of linoleic acid proportion and an increase of monounsaturated acids.

Overall, the nutritional value of lipids of wild growing mushrooms is limited due to low total lipid content and a low proportion of desirable n-3 fatty acids. Linoleic acid is nonetheless an important precursor for the development of attractive smell of dried mushrooms (see section 9).

#### 6. CARBOHYDRATES AND FIBER

Carbohydrates constitute the prevailing component of mushroom dry matter, usually about 50-60%. This group comprises various compounds – monosaccharides, their derivatives and oligosaccharides (commonly called sugars) and both reserve and construction polysaccharides (glycans).

Mannitol and  $\alpha,\alpha$ -trehalose (Table 4) are the main representatives of the polyols and oligosaccharides, respectively. The contents of both the sugars vary widely both among species and probably also within the individual species, as may be supposed from data for *Cantharellus cibarius* determined in the same laboratory. Drying and freezing decreased the contents of mannitol and trehalose in a lower extent than cooking of mushrooms (Table 5). Unfortunately, the contents in fresh mushrooms prior to the preservation or cooking were not reported.

Species	Val	Leu	Ile	Thr	Met	Lys	Phe	Trp	Reference
Agaricus campestris	119	24	41	79	71	53	28	8	Beluhan and Ranogajec, 2011
Amanita rubescens	16	50	25	48	-	16	29	18	Ribeiro et al., 2008a
Boletus edulis	45	43	29	95	-	52	57	72	Ribeiro et al., 2008a
	ND	58	48	19	41	217	104	ND	Tsai et al., 2008
	141	47	12	91	74	55	19	3	Beluhan and Ranogajec, 2011
Calocybe gambosa	127	45	ND	57	101	419	8	9	Beluhan and Ranogajec, 2011
Cantharellus cibarius	ND	14	10	18	-	36	10	15	Ribeiro et al., 2008a
	134	21	ND	90	41	57	6	2	Beluhan and Ranogajec, 2011
Craterellus cornucopioides	172	105	ND	456	16	469	85	12	Beluhan and Ranogajec, 2011
Macrolepiota procera	139	38	19	58	69	411	45	9	Beluhan and Ranogajec, 2011
Pleurotus ostreatus	121	29	ND	70	12	465	9	1	Beluhan and Ranogajec, 2011
Russula cyanoxantha	119	36	45	49	-	20	40	17	Ribeiro et al., 2008a
Suillus granulatus	65	13	50	30	-	12	19	22	Ribeiro et al., 2008a
Suillus luteus	54	7	11	14	-	15	18	13	Ribeiro et al., 2008a
Tricholoma equestre	42	102	71	68	-	252	76	20	Ribeiro et al., 2008a

#### Table 2. Content of free indispensable amino acids (mg per 100g dry matter) in selected mushrooms

Val...valine; Leu...leucine; Ile...isoleucine; Thr...threonine; Met...methionine; Lys...lysine; Phe...phenylalanine; Trp...tryptophan; ND ... not detected

Species	Lipids	Palmitic	Stearic	Oleic	Lino-	α-Lino-	Reference
-	-	acid	acid	acid	leic acid	lenic acid	
Agaricus arvensis	6.2	20.2	5.5	4.5	58.7	0.1	Pedneault et al., 2008 *
Agaricus bisporus	0.92	10.0	4.1	1.3	75.7	0.1	Barros et al., 2008b
Agaricus campestris	13.6	16.5	3.0	4.0	68.8	0.2	Pedneault et al., $2008$ *
Agaricus silvaticus	2.05	11.7	1.4	6.7	74.8	0.1	Barros et al., 2008b
Agaricus silvicola	2.43	10.0	2.6	3.5	76.5	0.1	Barros et al., 2008b
Armillariella mellea	5.56	11.0	3.5	47.7	27.7	Traces	Vaz et al., 2011b
Amanita rubescens	10.6	14.5	4.5	58.0	19.0	0.1	Pedneault et al., 2008 *
	-	22.7	16.1	40.4	21.1	Traces	Ribeiro et al., 2009
Boletus edulis	4.60	10.0	2.8	39.7	44.3	0.1	Barros et al., 2008b
	6.4	10.5	3.2	36.2	42.7	0.2	Pedneault et al., $2008$ *
	-	17.3	10.1	37.9	24.7	Traces	Ribeiro et al., 2009
	-	8.9	3.0	29.4	51.7	1.2	Dembitsky et al., 2010
Calocybe gambosa	1.05	15.2	2.1	18.1	57.8	0.5	Barros et al., 2008b
	0.83	13.6	3.2	32.5	43.9	0.9	Vaz et al., 2011b
Cantharellus cibarius	4.49	13.1	6.5	10.8	53.6	0.1	Barros et al., 2008b
	2.89	7.2	3.3	8.1	50.0	0.1	Barros et al., 2008c
	-	1.9	0.8	17.8	78.8	Traces	Ribeiro et al., 2009
Craterellus cornucopioides	4.88	6.7	7.8	51.9	23.7	0.1	Barros et al., 2008b
Laccaria laccata	3.76	11.6	2.0	60.7	20.5	0.4	Heleno et al., 2009
Leccinum scabrum	-	9.7	3.4	31.7	45.8	3.1	Dembitsky et al., 2010
Lepista nuda	1.77	11.8	2.4	29.5	51.5	0.2	Barros et al., 2008c
Lycoperdon perlatum	4.41	12.9	3.0	4.6	70.7	0.2	Barros et al., 2008c
Marasmius oreades	2.99	13.8	1.7	28.5	50.7	0.1	Barros et al., 2008b
Ramaria botrytis	1.37	9.9	2.4	43.9	38.3	Traces	Barros et al., 2008c

 Table 3. Lipids (crude fat) content (% of dry matter) and proportion of major fatty acids (% of total fatty acids) in selected mushroom species

## Table 3. (Continued)

Suillus granulatus	9.9	13.0	3.0	33.7	44.6	0.3	Pedneault et al., 2008 <sup>*</sup>
	-	3.7	3.6	62.8	35.4	Traces	Ribeiro et al., 2009
Suillus luteus	-	6.3	1.8	61.9	36.7	Traces	Ribeiro et al., 2009
	-	7.6	4.1	37.8	44.1	0.7	Dembitsky et al., 2010
Tricholoma imbricatum	1.88	7.4	4.1	51.5	33.0	0.2	Heleno et al., 2009
Xerocomus badius	-	15.1	2.1	36.5	38.2	1.6	Dembitsky et al., 2010

\*... Data on fatty acid proportion deal with neutral lipids fraction.

Species	Mannitol	Maltose	Trehalose	Total	Reference
				sugars	
Agaricus bisporus	19.6	ND	0.8	20.9	Barros et al., 2008b
Agaricus silvaticus	2.7	0.4	0.3	3.7	Barros et al., 2008b
Agaricus silvicola	6.1	0.6	0.7	7.8	Barros et al., 2008b
Boletus edulis	3.5	ND	9.7	13.5	Barros et al., 2008b
Calocybe gambosa	0.3	ND	8.0	9.1	Barros et al., 2008b
Cantharellus cibarius	8.3	ND	6.1	14.5	Barros et al., 2008b
	1.1	ND	0.8	1.9	Barros et al., 2008c
Craterellus	10.7	ND	0.1	10.8	Barros et al., 2008b
cornucopioides					
Laccaria laccata	0.6	-	5.8	6.5	Heleno et al., 2009
Lepista nuda	Traces	0.1	0.8	0.9	Barros et al., 2008c
Lycoperdon perlatum	Traces	ND	0.3	0.3	Barros et al., 2008c
Marasmius oreades	2.4	ND	10.5	13.5	Barros et al., 2008b
Ramaria botrytis	1.2	ND	0.2	1.4	Barros et al., 2008c
Tricholoma	10.5	-	6.6	17.1	Heleno et al., 2009
imbricatum					

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Table 4	Content of soluble sugars (g 100g	f dr	v matter	) in	selected	mushroom	snecies
	Content of soluble sugars (g 100g	ui.	y matter	,	sciected	musm oom	species

ND...not detected

# Table 5. Soluble sugars content (g 100g<sup>-1</sup> dry matter) in preserved and cooked mushrooms

Species		Mannitol			Trehal	ose	T	Total sugars		
	D	F	С	D	F	С	D	F	С	
Lactarius deliciosus	15.4	13.9	10.2	0.9	3.5	2.2	16.3	17.4	12.4	
Macrolepiota	7.8	4.6	7.5	4.1	5.1	ND	12.0	9.7	7.5	
mastoidea										
Macrolepiota procera	4.7	6.5	2.3	2.9	7.6	1.2	7.7	14.1	3.5	
Sarcodon imbricatus	19.6	25.3	11.8	6.0	5.0	3.4	25.6	30.3	15.2	

D...dried at 40 °C; F...frozen at -20 °C; C...cooked with olive oil, salt and onions; ND...not detected Aadapted from Barros et al., 2007.

Mannitol participates in volume growth and firmness of fruit bodies. Other water-soluble sugars, namely glucose, arabinose, maltose and melezitose, are reported in some papers as minor components.

The reserve polysaccharide of mushrooms is glycogen. The usual content is 5-10% of dry matter. Glycogen is a common component of widely consumed meat and liver and its low intake from mushrooms thus seems to be of low nutritional importance.

Chitin is a water-insoluble structural N-containing polysaccharide, accounting for up to 80-90% of dry matter in mushroom cell walls. Data on its content in both wild growing and cultivated mushrooms have been scarce. The contents about 5-10% of dry matter seem to be taken into consideration. Chitin contents increased with the maturation of several cultivated species and decreased during cooking of fruit bodies (Dikeman et al., 2005). Chitin is

indigestible for humans, and apparently decreases the digestibility of other mushroom components.

It is interesting that mushrooms contain as the main polysaccharides glycogen and chitin, occurring in animals, not starch and cellulose as plants.

Great attention has recently been focused on mushroom  $\beta$ -glucans, due to their healthpositive effects.  $\beta$ -Glucan research and application have been successful, mainly in the east-Asian countries and deal mostly with cultivated mushroom species. Moreover, numerous mushroom polysaccharides are regarded as a potential source of prebiotics. Recent knowledge is auspicious particularly for cultivated *Pleurotus ostreatus* and *P. eryngii* (Aida et al., 2009).

Information on dietary fiber content has also been very limited. Data resulting from several reports (see Kalač, 2009) are about 4-9% and 22-30% for soluble and insoluble fiber, respectively. It is apparent that mushrooms contain other structural polysaccharides in addition to chitin. A single information reported hemicelluloses and pectic substances. Thus, relatively high content of particularly insoluble fiber seems to be a nutritional advantage of mushrooms. Further research into mushroom fiber has been however needed. Moreover, information on changes of polysaccharides during various preservation treatments has been lacking.

#### 7. MINERAL COMPOSITION

Ash content of mushrooms is usually 5-12% of dry matter (Table 1) and its variability seems to be lower than that of crude protein and carbohydrates. Numerous data on the contents of major elements, and particularly on trace elements, have been available.

Information on inorganic anions has been very rare. Isildak (2009) reported contents of eight anions in eight wild growing mushroom species. The decreasing order of medians was sulfate (2.26 % of DM), nitrate (2.04 % of DM) and chlorate (0.36 % of DM). Contents of phosphate, chloride and nitrite were considerably lower and fluorides and bromides were undetectable. The initial data on inorganic iodine were recently published by Vetter (2010). Wild growing mushrooms contained only low level of  $284 \pm 211 \ \mu g \ kg^{-1} DM$ . The highest iodine mean contents of 601, 559, 451 and 449  $\ \mu g \ kg^{-1} DM$  were determined in *Calvatia excipuliformis, Macrolepiota procera, Amanita rubescens* and *Lepista nuda*, respectively. Commonly, mycorrhizal species had higher iodine content than the wood-decaying ones.

#### 7.1. Major Elements

Usual contents of major elements are given in Table 6. The data are collated from original papers cited in a review (Kalač, 2009). Potassium is the prevailing element followed by phosphorus, while calcium and sodium are at the opposite end. However, exceptions do exist. For instance, calcium content was 0.07-0.52 % of DM in seven species of genus *Morchella* (Gursoy et al., 2009).

Element	Content
Sodium	0.01 - 0.04
Potassium	2.0 - 4.0
Calcium	0.01 - 0.05
Magnesium	0.08 - 0.18
Phosphorus	0.5 - 1.0
Sulfur	0.1 - 0.3

 Table 6. Usual contents (% of dry matter) of major elements in wild growing mushrooms

Adapted from Kalač, 2009.

Potassium is not distributed evenly within fruit bodies. Its content decreases in the order cap > stipe > spore-forming part > spores. Potassium is highly accumulated. Its levels are between 20- and 40-fold higher in fruit bodies than in the underlying soils. Similar accumulating abilities were observed for phosphorus. On the contrary, bioaccumulation was not reported for sodium and calcium. Magnesium contents in fruit bodies are even lower than those in surface, mostly organic horizons of soils, from which mycelium uptakes the nutrients.

Overall, ash content of mushrooms is somewhat higher or comparable with most of vegetables. Mushrooms contain elevated levels of phosphorus and potassium. However, the availability of these elements remains unknown.

#### 7.2. Trace Elements

Several hundreds of original papers have been published on many trace element contents in wild growing mushrooms since the 1970s. Overall information is available in a review with numerous references therein (Kalač, 2010). The basic information for 15 trace elements is given in Table 7. The usual contents refer to values reported for non-accumulating species from unpolluted rural areas.

The contents are considerably higher, often by one and sometimes by even two orders of magnitude than those in Table 7, in some accumulating species or in mushrooms growing in heavily contaminated sites, such as in the vicinity of metal smelters, in mining areas or within cities. Such values are markedly higher than those observed in contaminated plant products. Extremely high bioaccumulation from underlying soils is characteristic for cadmium and mercury. However, the relationship between soil contamination with a trace element and its content in fruit body is not tight enough to enable usage of a mushroom species as a reliable bioindicator of local pollution.

Relatively high selenium content in the attractive group of *Boletus* mushrooms, particularly in king bolete (*B. edulis*) and closely related boletes (Costa-Silva et al., 2011), seemed to be promising as a source of this element deficient throughout Europe. However, low availability was reported in the 1980's.

Element	Content	Accumulators
Aluminum	20 - 150	Amanita rubescens, Leccinum scabrum, Xerocomus chrysenteron
Antimony	< 0.1	Suillus spp.
Arsenic	0.5 - 5	Laccaria amethystea, saprotrophic genera
Barium	2 - 4	
Cadmium	1 - 5	Agaricus spp. (group flavescentes)
Cobalt	< 0.5	Ramaria largentii, Hygroporus eburneus, Cantharellus cibarius
Copper	20 - 100	Agaricus macrosporus, A. silvicola, Macrolepiota procera, M.
		rhacodes
Chromium	0.5 - 5	Morchella elata, Armillariella mellea, Macrolepiota procera,
		Marasmius oreades
Iron	50 - 300	Suillus variegatus, S. luteus, Armillariella mellea
Lead	< 1 - 5	some saprotrophic species
Manganese	10 - 60	Boletus edulis, Macrolepiota procera
Mercury	< 0.5 - 5	Boletus edulis, B. pinophilus, Calocybe gambosa
Nickel	< 1 - 15	Laccaria amethystina, Coprinus comatus
Selenium	< 2 - 20	Albatrellus pes-caprae, Boletus edulis, B. pinophilus, B.
		reticulatus (syn. B. aestivalis)
Zinc	25 - 200	Calvatia utriformis, Lycoperdon perlatum

Table 7. Usual content of 15 trace elements (mg kg<sup>-1</sup> dry matter) in fruit bodies of mushrooms from unpolluted areas, and accumulating genera and species

Adapted from Kalač, 2010.

Most of the elements are distributed unevenly within a fruit body. Usually, the highest contents are observed in the spore-forming part of cap (but not in spores), lower in the rest of cap and the lowest in stipe.

A part of detrimental elements can be leached away. Short-term boiling is more efficient than soaking at ambient temperature. The elements are more easily leached from destroyed tissues of frozen mushroom slices than from fresh or dried slices or particularly from intact fruit bodies. Such culinary treatments naturally decrease content of valued taste components.

There exists a consensus that most of edible mushroom species from unpolluted areas do not pose a heath risk. Nevertheless, picking mushrooms from polluted sites should be limited. The most risky elements are cadmium, mercury and lead. Unfortunately, very limited information is available on the chemical forms (species) of the elements and on their bioavailability in humans. Only insufficient data on methylmercury and arsenic and chromium species were published so far.

Contents of risk elements in cultivated mushrooms have been low.

#### 8. VITAMINS AND PROVITAMINS

An initial information on vitamin contents in European wild growing mushrooms is available only since 2008. Therefore, the partial data will be combined with information available for the cultivated species. Ascorbic acid (vitamin C) content of mostly 20-30 mg  $100g^{-1}$  fresh matter (FM) was reported (Barros et al., 2008c; Jaworska and Bernaś, 2009a). Lower values of 3-4 mg  $100g^{-1}$  FM were determined in three *Agaricus* spp., while 40 mg  $100g^{-1}$  FM in *Cantharellus cibarius* (Barros et al., 2008b).

Low contents of 0.29 and 0.33 mg  $100g^{-1}$  FM of thiamin (vitamin B1) and riboflavin (vitamin B2), respectively, were quantified in *B. edulis* (Jaworska and Bernaś, 2009a). These values are considerably higher than data reported by Çağlarirmak (2009) for cultivated *A. bisporus* (brown; portobello).

The contents of all three water-soluble vitamins decreased during *B. edulis* soaking or blanching followed by frozen storage (Jaworska and Bernaś, 2009a). Similar trends were observed also in *Pleurotus ostreatus* (Jaworska and Bernaś, 2009b).

Data for tocopherols (vitamin E) originate from a Portuguese laboratory (Barros et al., 2008a,b,c; Heleno et al., 2010). Usual contents of total tocopherols were 0.05-0.25 mg  $100g^{-1}$  FM. The highest value of 0.80 mg  $100g^{-1}$  FM was reported for *Laccaria laccata*. The prevailing isomer was  $\beta$ -tocopherol, while  $\delta$ -tocopherol, tocotrienols and in some species also  $\gamma$ -tocopherol were not detected.

Earlier data on ergosterol, the provitamin ot ergocalciferol (vitamin D2), were reviewed by Kalač (2009). The contents of tens mg per 100g FM were usual. As was observed in both white and brown cultivated *A. bisporus*, ergosterol contents were higher in early growth stages. It was distributed evenly in caps and stipes during early developmental stages but accumulated more in the caps after maturation (Shao et al., 2010). The irradiation with UV is necessary for the conversion of ergosterol to vitamin D2.

The contents of  $\beta$ -carotene, a provitamin A, were mostly 0.2-1.3 mg 100g<sup>-1</sup> FM (Barros et al., 2008b,c).

The reported vitamin contents are comparable or somewhat lower than those in the bulk of common vegetables. However, much more data are necessary for the credible comparison.

#### 9. FLAVOR AND TASTE COMPONENTS

The characteristic flavor of many mushroom species, mainly dried, is highly valued by many consumers. Until now, hundreds of odorous compounds were identified. According to their chemical structure, they can be classified as derivatives of octane and octenes, lower terpenes, aldehydes, sulfur and heterocyclic compounds and various others.

The very characteristic group of mushroom aroma is formed by the derivatives of octane, 1-octene and 2-octene, particularly alcohols, their esters with volatile fatty acids, and ketones (e.g. 3-octanone). The extraordinary role is ascribed to "mushroom alcohol" 1-octen-3-ol with its "raw mushroom odor". It occurs in fresh mushrooms at level of up to several mg per 100g with elevated content in *B. edulis* and related boletes. Its content increases during mushroom drying because free linoleic acid is oxidized under catalysis of lipoxygenase and hydroperoxide lyase. Such a process is characteristic just for mushroom drying. Moreover, the increase of 1-octen-3-ol was observed also in *B. edulis* preserved in other ways. The contents of 1.41, 1.94 and 6.43 mg per 100g were determined in the fresh, boiled and canned *B. edulis* (Misharina et al., 2009, 2010). As there was proved in cultivated *A. bisporus*, tissue disruption had a major impact on the profile of volatiles, both qualitatively and quantitatively.

Linoleic acid oxidation and the emissions of eight-carbon volatiles decreased with fruit body development and storage (Combet et al., 2009).

The recent state of knowledge of eight-carbon volatiles formation and properties in mushrooms was thoroughly reviewed by Combet et al. (2006).

Among non-volatile taste components, initial data on free 5'-nucleotides of adenosine, guanosine, inosine, uridine and xanthosine are now available. Tsai et al. (2008) determined total content of 2.76 mg g<sup>-1</sup> DM in air-dried *B. edulis*. A wide range between 2.0 and 35.4 mg g<sup>-1</sup> DM was reported for 10 freeze-dried wild mushroom species with *Cantharellus cibarius* and *Craterellus cornucopioides* having the border values (Beluhan and Ranogajec, 2011). The equivalent umami concentrations (EUC), expressed as g of monosodium glutamate (MSG) per 100g of mushroom DM, were calculated from the 5'-nucleotide contents. Values of 10.5, 2.0 and 35.4 g MSG per 100g DM for *B. edulis, C. cibarius* and *C. cornucopioides*, respectively, were given.

#### **10. PIGMENTS**

Mushroom pigments belong to numerous chemical groups. The topic was recently covered with comprehensive reviews (Zhou and Liu, 2010; Velíšek and Cejpek, 2011), particularly from the points of view of biochemists and food chemists, respectively.

As compared with plants, chlorophylls and anthocyanins are not present and carotenoids are not widespread in mushrooms (they are characteristic e.g. for genus *Cantharellus*). Color changes following a mechanical damage of tissues of some mushroom species (e.g. becoming dark or blue) are usually caused by enzymically catalyzed oxidation of various polyphenols to quinones.

#### **11. HEALTH-PROMOTING CONSTITUENTS**

Traditions of folk medicine and the extensive recent research in the east-Asian countries prove various preventive and therapeutic properties of many mushroom species (so-called medicinal mushrooms). Over one hundred of medicinal effects are thought to be produced by such mushrooms (for an overview see Wasser, 2010). Knowledge of European species has so far fallen behind. The overviews of the very wide pharmacological potential of mushrooms were published by Lindequist et al. (2005) and Zhong and Xiao (2009). Recently, reviews dealing with a partial topic are available, namely on mushroom anticarcinogens (Ferreira et al., 2010),  $\beta$ -glucans (Rop et al., 2009) and lectins (Singh et al., 2010).

#### 11.1. Antioxidants

Under the situation of increasing excess of free radicals, mainly of reactive oxygen species (ROS) and reactive nitrogen species (RNS), which may disrupt normal functions of a human organism due to the damage of cellular lipids, proteins and DNA, the interest in antioxidant abilities of various foods has increased for years. This trend includes recently also

wild growing mushrooms. The topic has been the most dynamic within mushroom research during the last years.

A thorough review on the topic with numerous references until mid-2008 is available (Ferreira et al., 2009). Thus, only selected current papers will be given here.

It is not easy to draw a conclusion from the available data on mushroom antioxidants. A number of compounds, particularly various phenolics, tocopherols, ascorbic acid and carotenoids differing in their antioxidant potential (scavenging effect and reducing power), participate in total antioxidation effects. Numerous other compounds can also act as antioxidants. A Quantitative Composition-Activity Relationships (QCAR) model was therefore constructed for the prediction of the reducing power of mushrooms (Froufe et al., 2009). Moreover, several assays have been used for the determination of antioxidation capacity and the results have been expressed in various units, which also complicates the comparability of the published data.

Among widely consumed species, the high antioxidant activity was reported for *Cantharellus cibarius, Lactarius deliciosus* and *Agaricus arvensis* (Barros et al., 2009).

Cooked mushrooms had lower antioxidant activities than their dried or frozen counterparts (Barros et al., 2007). Water-soluble antioxidants of three mushroom species were more resistant to boiling, frying, grilling and microwave heating than methanol-soluble antioxidants (Soler-Rivas et al., 2009).

Wild growing mushrooms have been commonly consumed as mixtures of various species. As reported Queirós et al. (2009) from a study *in vitro*, synergism of species in the inhibition of lipid peroxidation was the effect prevailing over additive and negative synergistic effects. *Marasmius oreades* was present in the mixtures with higher antioxidant properties and synergistic effects, while *Cantharellus cibarius* in the mixtures with the lowest antioxidant properties and negative synergistic effects.

#### 11.1.1. Phenolic Compounds

There exists consensus of various researchers, that phenolics, mainly phenolic acids, are the main antioxidants of mushrooms. Phenolic compounds include various subgroups, particularly phenolic acids, flavonoids, stilbenes, lignans and tannins, distinguishing by a large structural diversity.

Phenolic acids can be divided into two major groups, hydroxybenzoic acids and hydroxycinnamic acids. Among the phenolic acids detected in many mushroom species, *p*-hydroxybenzoic, protocatechuic, gallic, gentisic, vanillic and syringic acids belong to the former group, while *p*-coumaric, caffeic and ferulic acids to the latter one. The acids are mostly bound in various complex structures. Very wide contents were reported in mushrooms, from non-detectable level to several hundreds mg kg<sup>-1</sup> DM (Barros et al., 2009; Vaz et al., 2011a, b). The highest levels of 357 and 284 mg kg<sup>-1</sup> DM were determined in *Ramaria botrytis* and *Agaricus arvensis*, respectively (Barros et al., 2009).

Occurrence of flavonoids in mushrooms was reported only sporadically (Barros et al., 2008b, c; Gursoy et al., 2009). The opinion that this group of nutritionally favorable compounds is lacking has been more frequent.

#### 11.1.2. Other Compounds with Antioxidant Properties

Tocopherols, ascorbic acid and carotenoids, all being mentioned in the section 8, are mushroom components participating in the antioxidant activities. Their contribution has been assessed as limited in comparison with phenolic compounds.

Numerous mushroom species, preferably cultivated ones including mycelium, seem to be a promising source for the isolation of various antioxidants and their use as nutraceuticals. The extensive research has therefore proceeded to find the optimal solvents and conditions for their extraction.

#### **12. DETRIMENTAL COMPONENTS OF EDIBLE MUSHROOMS**

The dangerous constituents of toxic mushrooms have been extensively studied for many decades. Nevertheless, some detrimental compounds occur also in some edible species.

#### **12.1. Natural Components**

Hydrazines with a potential pro-carcinogenic activity occur in *Agaricus* spp. (agaritine) and in *Gyromitra esculenta* (gyromitrin). Abundant literature on agaritine was collated by Andersson and Gry (2004). According to Roupas et al. (2010), the available current evidence suggests that agaritine from consumption of cultivated *A. bisporus* poses no known toxicological risk to healthy humans.

As reported Schulzová et al. (2009), whereas the cultivated *A. bisporus* commonly contains 200-500 mg agaritine per kg FM, 24 of the 53 analyzed wild growing *Agaricus* species contained above 1,000 mg kg<sup>-1</sup> FM. The highest level of up to 10,000 mg kg<sup>-1</sup> FM was found in *A. elvensis.* No correlation was observed between agaritine content and size of the mushroom, season, year or site of the sampling. Agaritine was also detected in some species of genera *Leucoagaricus* and *Macrolepiota*.

*Tricholoma equestre* (syn. *T. flavovirens*) was identified as a cause of several outbreaks of rhabdomyolysis and also as the species with cardio- and hepatotoxic effects (Nieminen et al., 2008).

Consumption of several *Coprinus* spp. has been known to induce ethanol intolerance. The mushrooms contain coprine, a free amino acid, which is converted to toxic cyclopropanone hydrate, blocking oxidation of acetaldehyde, produced from ethanol, to acetic acid.

A significant content of nicotine was detected in some mushrooms, particularly *B. edulis*, imported to the European Union several years ago. As a consequence, temporary maximum residue levels of 0.036, 0.17 and 2.3 mg kg<sup>-1</sup> for fresh, dried mushrooms and dried ceps (boletes) were proposed. In a survey of Italian both wild and cultivated mushrooms, contents of 0.01-0.04 and 0.1-4.5 mg kg<sup>-1</sup> were determined in fresh/frozen and dried samples (Cavalieri et al., 2010). The reasons for surprisingly high level of nicotine in dried mushrooms have not yet been explained.

A short shelf life is characteristic for mushrooms. Biogenic amines thus occur among the products of protein degradation. In 17 species of fresh wild mushrooms, putrescine was the amine with the highest level, sometimes exceeding 150 mg kg<sup>-1</sup> FM, followed by

phenylethylamine. Toxicologically the most significant amines histamine and tyramine were not detected or were present at very low contents (Dadáková et al., 2009).

#### 12.2. Contaminants

Relatively high formaldehyde contents of 119-494 and 110-240 mg kg<sup>-1</sup> FW in cultivated *Lentinus edodes* (shiitake) were reported from China and the UK, respectively (Liu et al., 2004 and Mason et al., 2004). Initially, formaldehyde used for the disinfection and disinfestation of substrate was indicated as a source of the contamination. Nevertheless, in samples of the UK and Chinese shiitake, verified as produced without any formaldehyde treatments, similar formaldehyde levels of 100-320 mg kg<sup>-1</sup> FW were determined. Storage for zip to 10 days had no effect on formaldehyde content, whereas frying significantly reduced the level (Mason et al., 2004). Due to lower formaldehyde content in mushrooms than in many widely consumed foods and the carcinogenity of formaldehyde only through inhalation and not by ingestion, the dietary exposure from mushrooms is not a cause for concern (Claeys et al., 2009).

Negligible contents of dioxins (PCDDs/PCDFs) and polychlorinated biphenyls (PCBs) were determined in cultivated *Flammulina velutipes* (enokitake), *Grifola frondosa* (maitake) and *Lentinus edodes* (Amakura et al., 2003). However, up to 13.1 µg of PCBs per kg of lipids was found in 10 wild species in Poland (Kotlarska et al., 2010). Unfortunately, further data are lacking. A risk of the translocation of PCB congeners from substrate seems to be low. Moeder et al. (2005) found in their study with *Pleurotus ostreatus*, cultivated on straw contaminated with PCBs, only below 0.1% of the applied amount in the fruit bodies.

Radioactivity of mushrooms is described in chapter 10.

#### **13. OTHER COMPOUNDS**

Ribeiro et al. (2008b) determined mean content of carboxylic acids of 10.4, 48.8, 97.3 and 119.5 g per kg DM in *B. edulis, Suillus granulatus, Russula cyanoxantha* and *Amanita rubescens*, respectively. The acids were present preferably in caps. The contents of prevailing acids decreased in order malic > fumaric  $\approx$  citric >oxalic acid.

Polyamines spermidine and spermine are ubiquitous compounds of living organisms. Dietary polyamines participate in numerous physiological processes, e.g. cell growth. Thus, they can participate in tumor growth, and to the contrary, in wound healing or in intestinal mucosa development. Information on their level in foods is therefore needed. The contents of spermidine in 17 wild mushroom species were usually tens mg per kg of FM, sporadically above 100 mg kg<sup>-1</sup>. Mushrooms should be thus included among food items with high spermidine level. The contents of spermine were considerable lower than those of spermine (Dadáková et al., 2009).

Within non-hallucinogenic indole derivatives, 6-7 compounds were detected in cultivated *A. bisporus* and three wild species. Serotonin contents of 52.1, 184, 296 and 317 mg kg<sup>-1</sup> DM were determined in *A. bisporus, Lactarius deliciosus, Cantharellus cibarius* and *Leccinum* 

*rufum*, respectively. The contents of other compounds were considerable lower except for 392 mg kg<sup>-1</sup> DM of kynureine sulfate in *L. deliciosus* (Muszyńska et al., 2011).

The intake of purine compounds needs to be restricted in the individuals afflicted by gout. Total contents of purine bases in seven Japanese cultivated mushroom species varied from 9.5 to 142 mg per 100 g FM with the highest contents in *Pleurotus ostreatus* and *Grifola frondosa*. The values are comparable with vegetables (Kaneko et al., 2008). Unfortunately, information for wild growing species has been lacking.

A steroidal derivative with cytotoxic activity, ergosterol peroxide, seems to be a common compound in mushrooms. After its detection in several cultivated and medicinal species it was found also in dried wild edible mushrooms (Krzyczkowski et al., 2009). The contents of 126, 134, 173 and 293 mg kg<sup>-1</sup> DM were reported in *Xerocomus badius*, *Morchella esculenta*, *Suillus bovinus* and *B. edulis*.

#### **14. CONCLUDING REMARKS**

A part of the European population widely consumes tens of wild growing mushroom species as a delicacy. The credible evaluation of their nutritional value has so far been limited, however, the information increases dynamically during the last years. Unfortunately, very poor knowledge on the bioavailability of the individual constituents remains. Moreover, changes of the constituents during various preservation methods, storage and cooking treatments have been so far poorly understood.

Wild mushrooms have been valued preferably for their characteristic flavor and also for their texture. From the nutritional point of view, low energy, a relatively high fiber and ergosterol contents and antioxidation activity seem to be contributing. Some constituents with propitious effects (e.g.  $\beta$ -glucans) wait for researchers.

In reverse, several widely consumed species (e.g. among wild *Agaricus* spp.) accumulate high levels of several trace elements, mainly cadmium and mercury, if growing on heavily polluted soils. Their consumption should be thus very limited.

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