Chemical Composition and Bioactive Compounds of Some Wild Edible Mushrooms

Melinda NAGY, Sonia SOCACI*, Maria TOFANĂ, Elena-Suzana BIRIS-DORHOI, Dorin ȚIBULCĂ, Liana SALANȚĂ, Georgiana PETRUȚ

Faculty of Food Science and Technology, University of Agriculture Science and Veterinary Medicine, Cluj-Napoca, Calea Mănăştur 3-5, 400372, Cluj-Napoca, Romania;
*Corresponding author, e-mail: sonia.socaci@usamvcluj.ro

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ABSTRACT

Recently, mushrooms consumption has risen notably thanks to the proof of their capacity to improve the organism efficiency in the combat and prevention of several diseases. The particular nutritional properties of fruiting bodies of mushrooms are one of the reasons for their consumption, besides their texture and flavour for which they are considered a delicacy. In this paper data were collected from several scientific studies with the aim to characterize the chemical composition and content of bioactive compounds (moisture, ash, total carbohydrates, total sugars, crude fat, crude protein and energy) of five edible mushrooms species: *Agaricus bisporus, Boletus edulis, Cantharellus cibarius, Pleurotus ostreatus, Lactarius piperatus*.

Keywords: *bioactive compounds, chemical composition, mushrooms.*

INTRODUCTION

The term ''mushroom'' describes the reproductive structure of fruiting body of a fungus (Berch *et al.,* 2007). Mushrooms belong to the kingdom of fungi, a group very distinct from plants, animals and bacteria. Mushrooms often live in symbiosis with other plants, mostly the roots of certain trees, both profiting from this relationship (Olumide, 2007). Commercial mushrooms are either produced in cultivation or harvested from the wild, including forests. The species produced in cultivation are all decomposers (or saprobes) capable of completing their life cycles on dead organic matter. Most of the forest harvested mushrooms are ectomycorrhizal and can form fruiting bodies only when growing with living host trees fungus (Berch *et al.*, 2007).

Generally, mushrooms posses four functionalities, including nutritional values, tasty properties, physiological effects, and cultural characteristics (Beluhan and Ranogajec, 2011). Wild growing mushrooms are known as a delicacy in many countries, due to the high proteins and trace minerals content (Kalac 2012, Murugkar and Subbulakshmi*,* 2005). On the other hand wild mushrooms are reported to have a high nutritional value and be a rich source of vitamins B and D (Diez and Alvarez*,* 2001), which lead to the increase of their contribution to our diet (Olumide, 2007). They are used in the treatment and prevention of diseases and they exhibit varied biological properties such as antibacterial, antimutagenic, antitumoral and antiviral activities (Colak *et al*., 2009). The most widely distributed molecules with antitumor properties in mushrooms are sesquiterpenes, triterpenoids, glucans and glycoproteins (Reis *et al*., 2011). Traditionally, people consume mushrooms also for medicinal reasons such as reducing obesity and lowering

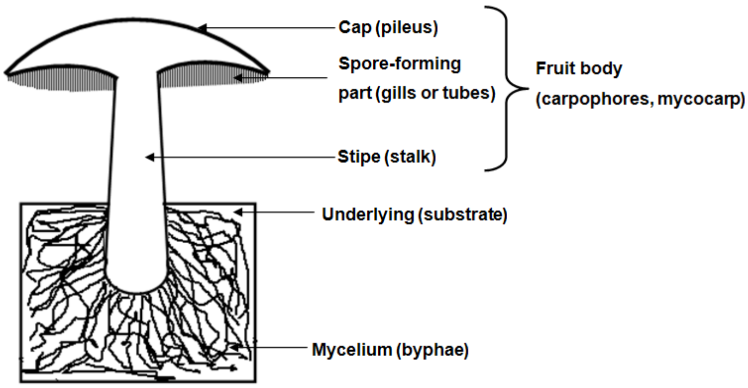

Fig. 1. General presentation of mushrooms

blood pressure in hypertensive patients (Obodai *et al*., 2014, Armao *et al.,* 2001).

Different functional compounds have been found in mushrooms, including phenolic compounds, sterols, terpenes, ceramides, etc. (Vamanu and Nita, 2014).

Besides macronutrients with a well-balanced proportion, the studied wild mushrooms have also important micronutrients (vitamins) and non-nutrients (phenolics) with bioactive properties such as antioxidant potential (Obodai *et al*., 2014). Among the antioxidant compounds, polyphenols and tocopherols have gained importance due to their large array of biological actions that include free radical scavenging, metal chelation enzyme modulation activities and inhibition of LDL oxidation (Keleş *et al*., 2011, Heleno *et al*., 2015). The high proteins and trace minerals concentration is the main reason for the significant increase of wild edible mushrooms consumption (Ogundana and Fagade, 1982, Senatore, 1990, Thimmel and Kluthe,1998). Many researches revealed that the amino acid intake through the compositions of mushrooms are comparable to animal proteins (Fink and Hoppenhause, 1958; Gruen and Wong, 1982), which has great importance due to the fact that human nutrition has become more complex since the appearance of several diseases affecting animal meat production. However, it is evident that the step by step substitution of meat with mushroom will involve a very detailed assessment of chemical and biological properties.

Moreover, many authors have been noticed that mushrooms were used as food flavouring materials because of their unique and subtle flavor. Particularly, oct-1-en-3-ol, octan-3-ol, octan-3-on and oct-1-en-3-on are well-known as the cause of characteristic mushroom odor (Chang and Miles, 2004; Fernandes *et al.,* 2013).

Many mushroom species and varieties are known, but the most important of these are *Agaricus spp., Boletus spp., Pleurotus spp., Cantharellus spp.,* and *Lactarius spp.*

CHEMICAL COMPOSITION OF MUSHROOM SPECIES

Research on fungi composition assessment revealed surprising results in terms of variety of classes of compounds identified in their quantity. It is known that the chemical composition of the fungi, and thus the nutritional value depends on various factors: the variety of fungi, the soil in which the plant is growing, soil and climate maturation stage (Mattila *et al*., 2002, Stojkovici *et al*., 2014).

The higher fungi and the parts above ground such as the fruiting body are called mushrooms (carpophore, mycocarp). A fruiting body is formed from spacious underground mycelia (hyphae) by the process of fructification and has a lifespan generally between 10 and 14 days. The main description of the fruiting body is shown in Fig. 1. Mycelia of ectomycorrhizal species live in symbiosis with roots of a plant, mostly a tree. Terrestrial saprobic species gain nutrients mostly from organic compounds of the plant and animal debris.

Overall considerations

Several authors have reported significant specific variations in the nutritive compounds in different species of mushrooms, origin from Portugal, Croatian, Serbia (Beluhan and Ranogajec,

Tab. 1. Proximate chemical composition of wild edible mushroom species in a dry weight basis.

Species	*Crude protein*	*Lipids*	*Ash*	*Carbohydrates*	*Reference*
Agaricus bisporus	38.90	2.70	3.50	37.50	Beluhan and Ranogajec, 2011
	56.30	2.70	3.50	37.50	Barros . *et al*., 2007
	10.00	3.12	15.00	71.86	Glamoclija . *et al*., 2015
	34.68	2.41	7.24	50.32	Nagy ., 2016
Boletus edulis	36.90	2.92	5.30	1.488	Beluhan and Ranogajec, 2011
	10.65	2.23	5.26	81.86	Heleno. *et al*., 2015
	36.24	1.92	8.38	46.23	Nagy., 2016
	29.70	3.10	5.30	51.70	Cheung Peter *et al*., 2013
Cantharellus cibarius	53.70	2.89	11.50	31.90	Barros *et al*., 2008
	21.03	2.17	9.57	57.96	Nagy, 2016
	30.91	1.90	8.80	52.50	Beluhan and Ranogajec, 2011
	21.50	5.00	8.60	64.90	Cheung *et al*., 2003
Pleurotus ostreatus	30.30	1.10	13.20	-	Akyüz and Kirbağ, 2010
	17.92	1.26	11.11	62.45	Nagy, 2016
	30.40	2.20	9.80	57.60	Cheung *et al.,* 2003
Lactarius piperatus	29.80	2.20	5.10	62.90	Barros *et al*., 2007
	31.81	2.69	8.30	43.00	Nagy, 2016
	13.06	2.00	7.21	77.68	Vieira *et al*., 2014

2011, Glamoclija *et al.,* 2015, Kalac, 2009). The Romanian researchers also analyzed the chemical composition of edible mushrooms from five species: fresh material and air-dried sample, harvested in Transylvania (Nagy, 2016, Vamanu and Nita, 2013). Proximate chemical composition collected of the most important mushroom species (*Agaricus bisporus Pleurotus osteoratus, Cantharellus cibarius, Boletus edulis* and *Lactarius piperatus*) are given in (Tab. 1).

The chemical composition of 5 wild edible mushrooms, including moisture, ash, total carbohydrates, crude fat and crude protein were determined according to AOAC procedures. Carbohydrates content is calculated as [100 – (moisture + crude protein + lipids + ash)] (Fernandes *et al*., 2015).

Considerable differences in the composition are evident not only among species but also within the species. Such differences can be partially explained by varied stage of fruit bodies maturity and also by the geographical origin. The data of Table 1 should be thus interpreted as a general information.

Carbohydrates and crude proteins are the two main components. Considerable differences are apparent for three species (*Agaricus bisporus, Boletus edulis* and *Cantharellus cibarius*) reported by different authors. Low fat content (media only 2.79 g 100g-1 DM) results in a reduced amount of energy (1552 kJ median 100g-1 DM). If the median is expressed in a "standard mushroom" containing 100 g DM / kg, then 100 g of fresh mushrooms has an energy content of 155.2 kJ or 37.2 kcal. Thus, we can express that mushrooms are a delicacy due to low energy value (Stojkovi *et al.,* 2014).

Among other particularities the digestibility and bioavailability of mushroom parts have not been highlighted in the description of mushroom nutritional value. It is well known that the availability of mushroom constituents is limited by the high concentration of indigestible chitin (Grangeia *et al.*, 2011). Still in the case of wild growing mushrooms there is a deficiency of credible data considering that most of the literature data is focused on fresh mushrooms. This is also true for the impact of preservation methods, under storage and during different cooking processes, on the modification of the individual constituents of mushrooms.

Proteins and amino acids in mushrooms

Regarding the structure of proteins, essential amino acids, compared to the structure of the

Tab. 2. Content of free indispensable amino acids (mg / 100g DW) in five mushroom species

Species	*Val*	*Leu*	*Ile*	*Thr*	*Met*	*Lys*	*Phe*	*Trp*	*Reference*
Boletus edulis	45	43	29	95	-	52	57	72	Ribeiro *et al*., 2008
Cantharellus cibarius	ND	14	10	18	-	36	10	15	Ribeiro *et al*., 2006
Pleurotus ostreatus	121	29	ND	70	12	465	9	1	Beluhan and Ranogajec, 2011
Amanita rubescens	16	50	25	48	-	16	29	18	Ribeiro *et al*., 2008
Agaricus bisporus	119	24	41	79	71	53	28	8	Beluhan and Ranogajec, 2011
Lactarius piperatus	42	37	24	89	-	48	53	68	Beluhan and Ranogajec, 2011

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

Tab. 3. Proportion of major fatty acids (% of total fatty acids) in mushrooms

Species	*Palmitic acid*	*Stearic acid*	*Oleic acid*	*Linoleic acid*	*Linolenic acid*	*Reference*
Agaricus bisporus	10.0	4.1	1.3	75.7	0.1	Barros *et al*., 2008
Boletus edulis	10.0	2.8	39.7	44.3	0.1	Barros *et al*., 2008
Cantharellus cibarius	13.1	6.5	10.8	53.6	0.1	Barros *et al*., 2008
Pleurotus ostreatus	8.3	2.1	35.9	41.3	0.1	Barros *et al*., 2008
Lactarius piperatus	1.10	81.46	6.58	6.66	0.04	Barros *et al*., 2007

contents of albumin, casein, gliadin are similar. Consistent with meat protein daily consumption of 200 g dried mushrooms have the effect of replacing the meat, ensuring a balance of protein. An amount of 1 kg dried mushrooms comes with an intake of two times greater than the contents of albumin beef, three times than pork and eleven times than milk. This super food, acceptance resulting in significant value bioactive compounds, stands out in a balanced diet given the absence of fats and low calorific value (Nagy, 2016). Free indispensable amino acids content (mg/100g DW) in five mushroom species are given in (Tab. 2).

The composition of mushroom proteins seems to be of a higher nutritional value than that of most plant proteins (Belitz *et al.,* 2009).The highest contents of proteins 53.7, 38.9 and 36.9 were observed in *Cantharellus cibarius Agaricus bisporus* and *Boletus edulis*, respectively, while the lowest value of only 17.92% was in the *Pleurotus ostreatus*. Beluhan and Ranogajec (2011) and Barros *et al.* (2008) reported this data about the selected mushrooms. Beluhan and Ranogajec, (2011) have found that the main constituents of the amino acid were valine and lysine represented by the species, *Agaricus bisporus* and *Pleurotus ostreatus.*

Lipids in mushrooms

The content of total lipids ranges mostly from 1 g/100 DW to 4 g/100 DW (Tab. 1 and Tab. 3). Within fatty acid composition (Tab. 3), polyunsaturated linoleic acid ($C_{18:2n-6}$), monounsaturated oleic acid ($C_{18:1n-9}$) and nutritionally undesirable saturated palmitic acid ($C_{16:0}$) prevail. However, low proportion of linoleic acid seems to be characteristic for the all species of mushrooms and in a limited extent. Barros et al. (2011) in several researches has reported a high concentration of stearic acid represented by *Lactarius piperatus*. The occurrence of trans fatty acids in mushrooms has not been reported and it is not expected. It is evident that the low total lipid content and a low proportion of desirable n3 fatty acids limit the nutritional value of wild growing mushroom.

Major minerals in mushrooms

Many studies can be found in the literature, since the 1970s, which quantify the element contents in wild growing mushrooms. Several papers and reviews with numerous references give important information about mineral content of mushrooms (Kalacˇ, 2012, Akyuz and Kirbag, 2010). Based on the literature, the general compo-

Tab. 4. Content of mineral element in mushroom species (% of dry matter)

Element	*Content*
Sodium	0.01 – 0.04
Potassium	2.0 – 4.0
Calcium	0.01 – 0.05
Magnesium	0.08 – 0.18
Phosphor	0.5 – 1.0
Sulfur	0.1 – 0.3

Tab. 5. Total phenolics (TP) and antioxidant activity (ABTS) of mushroom extracts (Keles *et al*. 2011, Robaszkiewicz *et al.,* 2010, Yim *et al.,* 2010)

Mushroom species	TP mg GAE/100 g DW)	ABTS uM Trolox/g DW
Agaricus bisporus	402.00	8.00
Pleurotus ostreatus	545.52	9.75
Cantharellus cibarius	120.30	23.93
Boletus edulis	1277.5	12.41
Lactarius piperatus	334.22	70.10

sitions regarding the content of mineral elements are given in (Tab. 4).

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 Agaricus (Gursoy *et al.,* 2009). According to researchers the potassium content is not distributed evenly within fruit bodies and descends in the following order Cap-stipe-spore-forming part-spores. It was also found that potassium content in the fruit bodies are more than 20 to 40 times higher than in the parts found in the soil (Zeng *et.al.,* 2012) The same tendency can be noticed in the case of phosphorus while the bioaccumulation of sodium and calcium was not been detected. Magnesium contents in fruit bodies are even lower than those in surface, mostly organic horizons of soils, from which mycelium uptakes the nutrients (Smolskaitė *et al*., 2015).

Overall, ash content of mushrooms is somewhat higher or comparable with most of vegetables.

Antioxidant properties and phenolic profile of the wild edible mushrooms

Numerous studies report that the antioxidant activity of fungi is closely related to their polyphenol content (Reis *et al.,* 2012, Smolskaite *et al.,* 2015).

Several authors evaluated the antioxidant activity of mushroom extracts sequentially isolated by cyclohexane, dichloromethane, ethanol, methanol, and water from *Agaricus bisporus, Pleurotus ostreatus, Boletus edulis, Cantharella cibarius* and *Lactarius piperatus* (Barros L, et al., 2008, Keles A. et al., 2011) and were assessed by DPPH, ABTS, ferric reducing antioxidant power (FRAP), oxygen radical absorbance capacity (ORAC) methods. To evaluate the total phenolic content (TPC) of the selected species were performed Folin–Ciocalteu (Arnao *et al*., 2001).

Recent published data (Tab. 5) revealed that total polyphenols for methanolic extract of Pleurotus ostreatus contain 545.52 ± 3.92 mg GAE/100g, DW (Robaszkiewicz *et al.,* 2010, Yim *et al.,* 2010). Keles *et al*. (2011) also found that the methanolic extract of Agaricus bisporus contains 402 mg/100 g, but they found higher value for Boletus edulis and Lactarius piperatus (1277.5 mg/100 g, 334.22 mg/100 g, respectively).

The ability to scavenge the ABTS cathion radical depends on the harvesting stage and climate soil (Heleno *et al*., 2012, Smolskaite *et al*., 2015).

Tab. 6. Main eight-carbon volatile compounds present in mushrooms (Combet *et al*., 2006)

Compound	Relative concentration (%)	Threshold value (ppm)	Aroma
1-Octen-3-ol	33	0.010	Mushroom like, sweet
1-Octen-3-one	0.02	0.004	Boiled mushroom
3-Octanol	1	0.018	Cod liver oil, nutty, sweet
3-Octanone	4	0.050	Sweet, fruity, musty, lavender
Octanol	0.3	0.48	Detergent, soap, orange like

Natural flavor and aroma compounds in mushrooms

Mushrooms have long been used as food or food flavouring materials because of their unique and subtle flavour which has been studied by many authors (Zawirska-Wojtasiak, 2004). Recently many papers have focused on the assessment of volatile compounds content of mushrooms, using combined gas chromatography and mass spectrometry. Thomas (1973) reported more than 60 compounds in dried fruit bodies of *Boletus edulis* among which nine pyrazines, seven 2-formyl-pyrroles, six fatty acids (C_5 to C_{10}), five furan derivatives, four lactones and four aliphatic ketones. However it is believed that some of the compounds may have been the product of the drying process. In fresh *Boletus edulis* Dudareva (1975) found benzaldehyde, 3-heptanone, isovaleric aldehyde, acetaldehyde, methyl cyclohexanone and four unknown compounds. Ethylene together with low boiling volatiles (acetaldehyde, acetone, ethanol and ethyl acetate) and short-chain fatty acids (acetic, isobutyric, isovaleric and n-butyric acids) was also identified in *Agaricus bisporus.*

As a complementary study to the composition evaluation of Agaricus bisporus, we intended to perform a quantitative analysis and an assessment using a taste panel which showed the impact on the flavour of the known constituents of Agaricus bisporus.

As a result, the parts of the mushrooms were submitted to chemical analysis, followed by an organoleptic evaluation. Also, we used as reference some flavour compounds found in other edible mushrooms. The main odorants of the mushroom (Tab. 6.) aroma are eight carbon atom (C8) compounds including 1-octanol, 3-octanol, 3-octanone, 1-octen-3-ol, 2-octen-1-ol, and 1-octen-3-one. 1-octen-3-ol is the key contributor to mushroom flavor and have been described by many in Agaricus bisporus and other fungi (Dudareva 1975,Chambers *et. al.,* 1998, Combet *et al.,* 2006).

As it is well know the volatile compound are characterized by a particular odor or aroma, such as 1-octen-3-ol for sweet and ketone 3-octanone responsible for fruity. It was also found that benzyl alcohol leads to an almond-like aroma while cyclo-octanol gives a leafy odor and can result from the cyclization of 1-octen-3-ol. In addition, studies revealed that 1-octen-3-ol concentration can determine the resulting odor sensation (Jong and Birmingham*,* 2005, Venkateshwarlu *et al.*, 1999). There are also studies which do not always show accurate flavor profile of volatile species emitted from fruit bodies or mycelium due to the fact that they involve analytical methods, like solvent extraction, which can led to degradation of the sample in parallel with the production of the volatile compounds concentrate.

CONCLUSIONS

Mushrooms can be used as source of alternative food in addition to fortification or supplementation of diet for enhanced nutrition, thanks to their high content of bioactive compounds. The most studied mushrooms were *Agaricus bisporus* and *Boletus edulis* in terms of chemical composition and bioactive compounds.

Studied mushrooms proved to be rich sources of proteins, carbohydrates and ash containing also different bioactive compounds such as flavonoid compounds, phenolic compounds and antioxidant activity. Polyunsaturated fatty acids predominated over mono and unsaturated fatty acids. The studied mushroom species are poor in fat content, making them low caloric foods. Furthermore, all these samples revealed antioxidant activity, being *B. edulis* more effective in ABTS and reducing power assays.

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