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PHENOLIC ACIDS IN SELECTED EDIBLE BASIDIOMYCOTA SPECIES: *Armillaria mellea, Boletus badius, Boletus edulis, Cantharellus cibarius, Lactarius deliciosus* AND *Pleurotus ostreatus*

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Abstract. Phenolic acids, both derivatives of benzoic and cinnamic acids, possess valuable biologically properties: anti-inflammatory, antioxidant, anticarcinogenic and others. Studies of the accumulation of these compounds focused mostly on plant material, but the Basidiomycota taxon are also the rich sources of these compounds. The aim of the study was qualitative and quantitative HPLC analysis of phenolic acids and cinnamic acid in fruiting bodies of selected edible mushroom species belonging to the phylum Basidiomycota: *Armillaria mellea*, *Boletus badius*, *Boletus edulis*, *Cantharellus cibarius*, *Lactarius deliciosus* and *Pleurotus ostreatus*. The investigations revealed the presence of the following acids: protocatechuic, *p*-hydroxybenzoic, *p*-coumaric, ferulic, sinapic, vanillic and cinnamic. Both the composition and the amount of phenolic acids in these species were diverse. The total amount ranged from 6.00 mg · kg^{-1} DW in A. mellea to 48.25 mg · kg^{-1} DW in *Boletus badius*. Protocatechuic acid amounts fluctuated in the range of 1.37–21.38 mg · kg^{-1} DW, with its maximum in *Boletus badius*. *p*-Hydroxybenzoic and sinapic acid dominated in *Pleurotus ostreatus*. Cinnamic acid levels amounted from 1.09 to 8.73 mg · kg^{-1} mg DW and *Boletus badius* contained its highest content. The results show that edible mushrooms are a good dietary source of phenolic acids with antioxidant activity.

Key words: Basidiomycota, edible mushroom, phenolic acids

INTRODUCTION

Edible mushrooms possess remarkable dietetic and medicinal values, including anticancer, immunostimulating (glucans, glycoproteins, sesquiterpens, triterpenoids), antiatherosclerotic properties (chitin, chitosans, statins), antibacterial and antifungal actions (antibiotics) and antioxidant potential (sterols, tocopherols, flavonoids, carotenoids, indole compounds and phenolic compounds) [Barros et al. 2007a, b, Muszyńska et al.

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2010, Wasser and Weis 1999]. Phenolic acids constitute the major part of phenolic compounds present in mushrooms [Ferreira et al. 2009, Karaman et al. 2010]. They exhibit a wide spectrum of biological activities which have been attributed to their strong antioxidant activity and ability to protect vital cellular structures, like cell membranes, and also structural proteins, enzymes, membrane lipids or nucleic acids [Ferreira et al. 2007, Froufe et al. 2009]. The strongest antioxidant properties and capability of cell protection against hydrogen peroxide was evidenced for vanillic acid, and among cinnamic acid derivatives, for caffeic acid. *p*-Hydroxybenzoic, gallic and protocatechuic acids found in mushrooms are characterized by antioxidant, antibacterial, antiviral, antifungal, anti-inflammatory and gastric secretion-stimulatory actions, documented by *in vitro* and *in vivo* studies [Rodriguez Vaquero et al. 2007, Karaman et al. 2010]. In addition, protocatechuic acid was shown to possess immunomodulating, spasmolytic, cardioprotectant, anticoagulant and chemopreventive properties [Wee 2010]. Phenolic acids from *Inonotus hispidus* were proved to be protective against influenza virus type A and B [Cheung 2010].

A strong positive correlation was observed between antioxidant activity of edible mushrooms and the amount of phenolic compounds [Dubost et al. 2007]. This relationship has also been noted in plants [Kim et al. 2008]. Phenolic compounds are the most abundant antioxidants in human diet. The antioxidants daily intake approximates 1 g while phenolic acids is about one third of this amount and they are considered to be the most valuable antioxidants. For comparison, daily dietary intake of vitamin C is 10-fold lower and vitamin E and carotenoid intake even up to 100-fold lower [Scalbert et al. 2005, Singh et al. 2008, Terpinc and Abramovič 2010].

The aim of the present studies was qualitative and quantitative HPLC analysis of phenolic acids in extracts after acidic hydrolysis. Moreover, the studies aimed to isolate and confirm the identity one of the phenolic acids: protocatechuic acid, the main metabolite from fruiting bodies of *Boletus badius*. Material for the study were edible fungi of the class Basidiomycota: *Armillaria mellea* (Vahl.) P. Kumm. – Honey mushroom, *Boletus badius* Pers. – Bay Bolete, *Boletus edulis* (Bull. ex Fr.) – King Bolete, *Cantharellus cibarius* Fr. – Chantarelle, *Lactarius deliciosus*, (L. Fr.) S. F. Gray – Saffron milk-cap and *Pleurotus ostreatus* (Jacq. ex Fr.) Kumm. – Oyster mushroom. These species were chosen because they are widespread in Europe and Asia and popular among consumers. Literature reports mostly contain data on total contents of phenolic compounds in mushrooms and their antioxidant activity [Santoyo et al. 2009, Sarikurkcu et al. 2008]. In addition, all these species contain numerous primary and secondary metabolites exhibiting significant biological activity (for example: polysaccharides, unsaturated fatty acids, water- and fat-soluble vitamins, wide spectrum of proteins, flavonoids, terpenoids, sterols, carotenoids, indole compounds and elements, e.g. selenium) [Muszyńska et al. 2010, 2011b]. Moreover, they have unique therapeutic potential. For instance, one of earlier studies on therapeutic properties of *B. edulis* mycelium conducted in 1957 demonstrated that extracts from this species increased survival of mice bearing Sarcoma 180 [Wasser and Weis 1999]. Furthermore, its fruiting bodies had high antioxidant power due to the combination of different organic acids: oxalic, citric, fumaric, succinic and malic acid [Ribeiro et al. 2006], ergosterol and ergothionein. As was shown by Ey et al [2007], this species contained the highest amount

of the latter compound in comparison with other food products. According to Turkish studies, *B. badius* was evidenced to possess excellent antioxidant properties. The inhibition ability of methanolic extracts of dried *B. badius* at 100 μg · ml^{-1} concentration on peroxidation in linoleic acid system was 99.2% [Elmastas et al. 2007].

Comparison of the present results on the accumulation of individual phenolic acids and cinnamic acid in mushrooms with those of other authors revealed that *B. badius* was tested for the amounts of these compounds for the first time. Interestingly, this species was shown in our studies that contain the largest number of phenolic compounds.

A. mellea was found to contain ergosterol and its superoxide possessing antioxidant and anticancer properties and prosomtostatin with the same potential. The latter peptide was efficient in pancreatic cancer therapy [Muszyńska et al. 2011a, Muszyńska et al. 2011c]. *L. deliciosus* contains azulens (lactarioviolin and lactarazulen) with antibacterial actions [Stamets 2002]. *P. ostreatus* is a source of the statin, lovastatin used in the treatment of hypercholesterolemia and cancer [Gunde-Cimerman and Cimerman 1995, Seeger et al. 2003, Sleijfer et al. 2005], while *C. cibarius* is an example of a "champion" among *Basidiomycota* in the amount of vitamin B (B_1, B_2, B_6 – comparable with its content in *Saccharomyces cerevisiae* and vitamin C (7.2 mg · 100 g^{-1} DW (dry weight), which constitutes almost one-tenth of daily requirement). These vitamins are accompanied by flavonoids (0.67 mg · g^{-1} DW), which increase the antioxidant activity, ergocalciferol (vitamin D_2 the mean amount of which approximates 1.43 μg · g^{-1}), β-carotene (13.56 μg · g^{-1} DW) and tocopherols [Muszyńska et al. 2012, Rangel-Castro et al. 2002]. This is the first report about mycochemical analysis of phenolic acids in edible mushroom originating from natural state in Poland.

MATERIALS AND METHODS

Reagents and standard. Methanol and acetic acid both of HPLC-grade were from Merck (Darmstad, Germany), ethyl acetate; chloroform and methanol both of analytical grade were from POCh (Polish Chemicals Company, Gliwice, Poland). Standards: caffeic acid, chlorogenic acid, protocatechuic acid, syryngic acid were from Sigma-Aldrich (St Louis, Mo, USA), cinnamic acid, ferulic acid, *p*-coumaric acid, *p*-hydroxybenzoic acid, sinapic acid and vanillic acid were from Fluka (Chemie, AG). All standards were of HPLC – grade. Standard solutions were prepared in methanol HPLC grade (1 mg·ml^{-1}). Water was purified by redistillation and filtered through Milipore Millex-GP, 0.22 μm (Merck, Darmstad, Germany).

Materials. Study material comprised fresh fruiting bodies of *Armillaria mellea, Boletus badius, Boletus edulis, Cantharellus cibarius, Lactarius deliciosus* collected from natural habitats (mixed forests of southern Poland surrounding the village Brodła near Kraków) in autumn 2010–2011 and fruiting bodies of *Pleurotus ostreatus* of commercial origin. Fresh material (50 g of each species) after taxonomic identification according to Knudsen and Vesterholt [2008] and online keys (http://www.mycokey.com/) was frozen and lyophilized (Freezone 4.5, Labconco; Kansas City, MO, USA), in temperature: -40°C. Samples of sporocarps were deposited in the Department of Pharmaceutical Botany, Jagiellonian University, Collegium Medicum, Kraków, Poland.

Sample preparation. The lyophilized materials were weighed (5 g of each species) and ground in a mortar, then they were subjected to acid hydrolysis (2 mol · dm^{-3} HCl) at 100ºC for 4 h. The obtained hydrolysates were filtered through paper filters (Munktell, Germany) and shaken in a percolator with a 5-fold excess of ethyl acetate. The organic fractions obtained after shaking were combined. The extracts were concentrated by distillation in a vacuum evaporator (Rotavapor R-114, Büchi, Germany) under reduced pressure at 40ºC. The residues were quantitatively dissolved in methanol (1.5 ml), filtered through Milipore Millex–GP, 0.22 μm and subjected to HPLC analysis.

HPLC analyses. The obtained extracts were analyzed for amount of: caffeic acid, cinnamic acid, chlorogenic acid, ferulic acid, *p*-coumaric acid, *p*-hydroxybenzoic acid, protocatechuic acid, sinapic acid, syringic acid and vanillic acid. These analyses were carried out according to the procedure developed by Ellnain-Wojtaszek [1997] with some modifications. HPLC analyses were performed using a Merck-Hitachi apparatus with an L-7100 pump; Purospher® RP-18e (4 × 200 mm, 5 μm) column; thermostated at 25°C (thermostat L-2305). Detection was carried out using a UV detector, using λ = 254 nm. The mobile phase consisted of solvent A: methanol/ 0.5% acetic acid 1:4 (v/v), and solvent B: methanol; flow rate: 1ml/min. The gradient elution scheme was used (A : B ratio): 100% : 0% t = 0–25 min.; 70% : 30% t = 35 min.; 50% : 50% t = 45 min.; 0% : 100% t = 50–55 min.; 100% : 0% t = 57–67 min. The comparison of UV spectra and retention times with standard compounds enabled the identification of phenolic acids presented in analyzed samples. Identified phenolic acids were quantified against

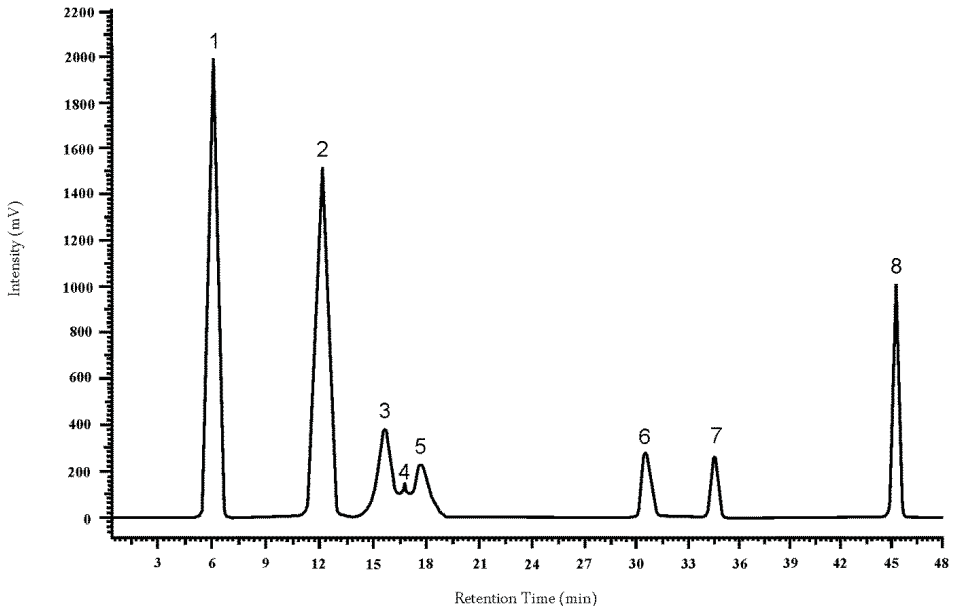

Fig. 1. HPLC chromatogram of standards of selected phenolic acids: (1) protocatechuic acid, (2) *p*-hydroxybenzoic acid, (3) vanillic acid, (4) caffeic acid, (5) syryngic acid, (6) *p*-coumaric acid, (7) ferulic acid (8) cinnamic acid

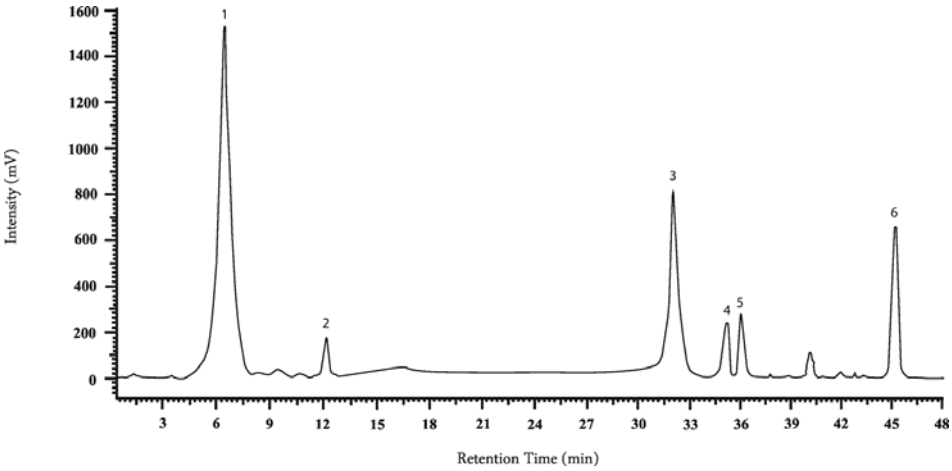

Fig. 2. HPLC chromatogram of extract from fruiting bodies of *Boletus badius*: (1) protocatechuic acid, (2) *p*-hydroxybenzoic acid, (3) *p*-coumaric acid, (4) ferulic acid, (5) sinapic acid, (6) cinnamic acid

their external standards (the calibration curve method). The results were expressed in mg·100 g^{-1} of DW (dry weight). Data are presented as the mean ±SD of 3 series (SD-standard deviation). A representative HPLC chromatogram of standards of selected phenolic acids is presented on Fig. 1, and representative HPLC chromatogram of extract from fruiting bodies of *Boletus badius* is presented on Fig. 2.

Isolation and identification of protocatechuic acids. The isolation and purification one of the phenolic acid from the extract of *Boletus badius* was performed using preparative TLC. For the purification of the extract we used aluminum-backed silica gel 60 (Merck, Art. No 1.055540001), on to which 5 ml of the extract was applied as bands. Chromatograms were developed to a distance 19 cm with chloroform/acetic acid/methanol 30 : 1 : 10 (v/v/v) as a mobile phase. Spot corresponding to the protocatechuic acid was identified under UV lamp at $\lambda = 254$ nm and eluted from silica gel with methanol. Dried sample was subjected to NMR analysis. The ^{1}H-NMR spectra were recorded using a Mercury 300-Brucker (1H, 300.08; MHz) apparatus in the NMR Spectroscopy Laboratory of the Organic Chemistry Department, Jagiellonian University Collegium Medicum. Identity of protocatechuic acid in the extract of *Boletus badius* was confirmed and an example of their spectral details are shown below ^{1}H-NMR (300 MHz, DMSO-d) 6.565 (1 H, d, J = 8.1 Hz, H5-Ph), 7.155 (1 H, dd, J = 2.0, J = 2.6 Hz, H-6-Ph), 7.273 (1 H, d, J = 8.0 Hz, H-5).

RESULTS AND DISCUSSION

Studies have shown the usefulness of chromatographic methods (TLC, HPLC) for separation and quantification of phenolic acids after hydrolysis process in extracts of

fruiting bodies of the analysed species: *Armillaria mellea, Boletus badius, Boletus edulis, Cantharellus cibarius, Lactarius deliciosus, Pleurotus ostreatus*. Of the ten analyzed phenolic acids the fruiting bodies of the above mentioned species contained seven compounds: protocatechuic, *p*-hydroxybenzoic, *p*-coumaric, ferulic, sinapic, vanillic acid and cinnamic acids. The identity of protocatechic acids from the extracts of *Boletus badius* was confirmed by spectral analysis (^{1}H-NMR) and by comparison with reported data [Hatzipanayioti and Petropouleas 2006].

B. badius, C. cibarius and *P. ostreatus* were the species containing the greatest diversity of phenolic acids (their fruiting bodies were shown to contain five or six phenolic compounds). Amounts of individual phenolic acids are presented in Table 1.

Table 1. The amount of phenolic acids in the extracts from fruiting bodies of *Armillaria mellea, Boletus badius, Boletus edulis, Cantharellus cibarius, Lactarius deliciosus, Pleurotus ostreatus* (mg kg^{-1} DW)

Species	*A. mellea*	*B. badius*	*B. edulis*	*C. cibarius*	*L. deliciosus*	*P. ostreatus*
Phenolic acid	mg kg^{-1} DW					
Protocatechuic acid	2.23 ±0.05	21.38 ±0.40	7.50 ±0.20	1.54 ±0.03	1.37 ±0.02	2.52 ±0.03
p-Hydroxybenzoic acid	–	1.28 ±0.20	1.94 ±0.04	2.30 ±0.05	–	3.60 ±0.05
Vanilic acid	–	–	–	3.32 ±0.04	–	–
p-Coumaric acid	–	13.91 ±0.20	–	–	–	–
Sinapic acid	3.77 ±0.04	1.50 ±0.20	–	3.04 ±0.03	14.29 ±0.40	2.11 ±0.03
Cinnamic acid	–	8.73 ±0.10	–	1.29 ±0.03	4.06 ±0.20	1.09 ±0.01
Ferulic acid	–	1.45 ±0.02	–	–	–	0.46 ±0.01
Total amount	6.00 ±0.07	48.25 ±0.30	9.44 ±0.14	11.49 ±0.08	19.72 ±0.09	9.78 ±0.016

- – not detected

Protocatechuic acid was identified in all species under study (1.37–7.50 mg · kg^{-1} DW) and its largest amount of 21.38 mg · kg^{-1} DW was determined in *B. badius*. p-hydroxybenzoic acid was found in *B. badius* (1.28 mg · kg^{-1} DW), *B. edulis* (1.94) and *C. cibarius* (2.30) while its highest amount was observed in *P. ostreatus* (3.60). Sinapic acid, the amount of which ranged from 1.50 to 14.29 mg · kg^{-1} DW, was also detected in four species: *A. mellea, C. cibarius, L. deliciosus* and *P. ostreatus*. Cinnamic acid occurred in the concentration range from 1.09–4.06 mg · kg^{-1} DW in *C. cibarius*, *L. deliciosus* and *P. ostreatus*, whereas its highest content was noted in *B. badius* (8.73 mg · kg^{-1} DW). Ferulic acid was determined in *B. badius* (1.45 mg · kg^{-1} DW) and in *P. ostreatus* (0.46 mg · kg^{-1} DW). *p*-Coumaric acid and vanillic acid were detected only in single species (in *B. badius* at 13.91 mg · kg^{-1} DW and in *C. cibarius* at 3.32 mg · kg^{-1} DW, respectively).

Interesting results were received in the case of *Boletus badius*. Studies have shown the presence of numerous phenolic acids: protocatechuic acid, *p*-hydroxybenzoic acid,

p-coumaric acid, ferulic acid, sinapic acid and cinnamic acid. The total amount was the highest in this species – 48.25 mg · kg^{-1} DW. The above described data can explain high total antioxidant capacity of extracts from this species (99.2%) reported by Elmastas [2007]. It may be noteworthy, because it is one of the most popular edible species. Amounts of phenolic acids and cinnamic acid in the remaining species did not differ from quantities obtained by other authors, though there were differences in their qualitative composition.

According to the studies of Barros [2008, 2009], phenolic acid amount ranged from 2.26 mg·kg^{-1} DW in *L. deliciosus* fruiting bodies to 35.67 mg · kg^{-1} in *Ramaria botrytis*. *p*-hydroxybenzoic acid dominated in 50% of the species under analysis (contents up to 23.87 mg·kg^{-1} DW). Protocatechuic acid was the dominating phenolic acid in two species, vanillic acid was detected in two species and *p*-coumaric acid in three species. *C. cibarius, Lycoperdon perlatum* and *Macrolepiota procera* were demonstrated to contain only cinnamic acid at amount up to 14.97 mg · kg^{-1} DW [Barros et al. 2008, Barros et al. 2009]. On the other hand, Valanteo [2005] examined *C. cibarius* and identified 3-,4- and 5-O-caffeoylquinic acids, caffeic acid and *p*-coumaric acid at amount up to 20 mg · kg^{-1} DW 3-O-caffeoylquinic acid accounted for 64% of all investigated compounds. The level of phenolic acid in *A. mellea* estimated by Vaz et al. [2011a] amounted to 4.00 mg · kg^{-1} DW for *p*-hydroxybenzoic acid and 8.67 mg · kg^{-1} DW for cinnamic acid. In *L. delicious*, Barros [2009] quantified only *p*-hydroxybenzoic acid occurring at 22.66 mg · kg^{-1} DW.

Other edible mushroom species: *Agaricus bisporus* and *Lentinus edodes* were demonstrated to contain relatively low amounts of *p*-hydroxybenzoic acid, even lower quantities of trans-cinnamic acid and protocatechuic acid, and trace amounts of cinnamic acid [Mattila et al. 2001]. *Fistulina hepatica* proved to be one of the richest sources of phenolic acids described so far. Protocatechuic acid and *p*-hydroxybenzoic acid contents in this species were very high: 67.62 mg · kg^{-1} DW and 41.92 mg · kg^{-1} DW, respectively [Vaz et al. 2011b]. Ribeiro [2007] determined comparable contents of phenolic acids in this species, namely about 54.90 mg · kg^{-1} DW, of which elagic acid accounted for 50%, *p*-coumaric acid for 26% and caffeic acid for 24%. Kim [2008] estimated the amount of phenolic compounds in ten edible and medicinal mushroom species and showed their higher levels. Like in the present study, only protocatechuic acid was occurred in all analyzed species. The same authors identified gallic, homogentistic, chlorogenic and protocatechuic acids in *P. ostreatus* [Kim et al. 2008].

CONCLUSIONS

It can be suggested that the differences in qualitative and quantitative composition of phenolic compounds can be caused by genetic differences between species, different natural habitats, diverse environmental conditions during growth and maturation of mushrooms, extent of damage or air pollution [Puttaraju et al. 2006, Karaman et al. 2010]. Other authors underline importance of storage conditions, sample preparation for analysis, temperature, UV irradiation or phenyloxidase present in mushrooms which is responsible for breakdown of phenolic compounds. For this reason, lyophilization was

recommended as a drying method since it changed the level of these compounds the least [Alvarez-Parilla et al. 2007]. Based on the obtained results confirming the presence of phenolic compounds in edible mushrooms, it can be concluded that they can be a valuable dietary source of antioxidants. Consumption of dishes prepared from edible mushrooms is safe and beneficial due to good assimilability of their nutrients that are protective against civilization diseases and have vitalizing potential for human organism. In addition, the present analysis indicates that *B. badius, C. cibarius* and *P. ostreatus* are the richest species in phenolic compounds both in terms of their contents and composition.

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KWASY FENOLOWE W WYBRANYCH JADALNYCH GATUNKACH BASIDIOMYCOTA: *Armillaria mellea, Boletus badius, Boletus edulis, Cantharellus cibarius, Lactarius deliciosus* I *Pleurotus ostreatus*

Streszczenie. Kwasy fenolowe, zarówno pochodne kwasu benzoesowego jak i cynamonowego, posiadają liczne, cenne właściwości biologicznie: przeciwzapalne, przeciwutleniające czy przeciwnowotworowe. Badania akumulacji tych związków koncentrują się głównie na materiale pochodzenia roślinnego. Bogatym źródłem tych związków są również przedstawiciele grzybów wyższych z taksonu Basidiomycota. Celem pracy była jakościowa i ilościowa analiza HPLC związków fenolowych w owocnikach wybranych jadalnych gatunków grzybów należących do taksonu Basidiomycota: opieńki miodowej – *Armillaria mellea*, podgrzybka brunatnego – *Boletus badius*, borowika szlachetnego – *Boletus edulis*, pieprznika jadalnego – *Cantharellus cibarius*, mleczaja rydza – *Lactarius deliciosus* i boczniaka ostrygowatego – *Pleurotus ostreatus*. Badania wykazały obecność następujących kwasów: protokatechowego, *p*-hydroksybenzoesowego, ferulowego, *p*-kumarowego, synapinowego, wanilinowego i cynamonowego. Całkowita zawartość kwasów fenolowych i kwasu cynamonowego w tych gatunkach była zróżnicowana jakościowo i ilościowo i wynosiła od 6,00 mg · kg^{-1} DW w Armillaria mellea do 48,25 mg · kg^{-1} DW w *Boletus badius*. Kwas protokatechowy występował w największej ilości w gatunku *Boletus badius*. Kwas *p*-hydroksybenzoesowy dominował w gatunku *Pleurotus ostreatus*, podobnie jak kwas synapinowy. Z kolei kwas cynamonowy występował w ilościach od 1,09 do 8,73 mg · kg^{-1}DW, a największą jego zawartość stwierdzono w gatunku *Boletus badius*. Rezultaty analiz wykazały, że owocniki grzybów jadalnych są dobrym źródłem kwasów fenolowych o właściwościach antyoksydacyjnych.

Słowa kluczowe: Basidiomycota, grzyby jadalne, kwasy fenolowe

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