RESEARCH ARTICLE



Chemical composition and nutritional value of Argentine commercial edible mushrooms

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Abstract The chemical composition and nutritional value of four edible mushroom varieties (Cham-Portobellos, Girgolas and Shiitakes) commonly cultivated and consumed in Argentina was determined. The analysis of the chemical composition included the analysis of water content, crude protein, lipids, ash, carbohydrates, mineral composition and bioactive components (dietary fiber, chitin content and phenolic compounds). Results show that edible mushrooms are rich sources of water and carbohydrates and have low amounts of lipids. Also, they are rich in potassium and phosphorus whereas they have a low content of sodium. The composition of bioactive components reveals that mushrooms are rich in fiber and have an interesting amount of total phenolic compounds that imply an antioxidant capacity. Chitin content is an important part of total fiber and in this work a new method for chitin isolation is proposed. Multivariate analysis (principal component analysis) was applied to discriminate among the different mushrooms varieties and to establish relationships among samples and nutritional parameters.

Keywords Argentine mushrooms · Nutritional value · Food composition · Chitin extraction · Multivariate analysis

1 Introduction

Edible mushrooms are becoming more and more important in human diet for their nutritional (Barros et al. 2007), organoleptic (Mau 2005) and medicinal (Lee et al. 2009) characteristics. Mushrooms are valuable healthy foods, low in calories and high in proteins of non-animal origin, vitamins, iron, zinc and potassium (Ouzouni et al. 2009). They are a potential source of dietary fiber because fungal cell walls contain chitin, hemicelluloses, mannans and interesting bioactive components like beta glucans (Manzi and Pizzoferrato 2000). Also mushrooms contain phenolic compounds that have been found to be excellent antioxidants (Cheung et al. 2003). Production and consumption of higher fungi have increased dramatically worldwide over the past two decades and show a changing attitude toward edible higher fungi (Albertó and Gasconi 2003). Mushrooms represent a special place in human food and this can be held by mushrooms and truffles world production that reached a volume of 3,414,392 metric tones in 2007 (USDA 2009). In Argentina mushroom production began in 1940 and in the last few years both new technologies and varieties were incorporated. The main cultivated areas in the country are defined by the provinces of Buenos Aires, Neuquén, Río Negro, Mendoza, Santa Fe and Córdoba (Albertó et al. 2010).

A lot of studies have been carried out on the chemical composition and nutritional value of European edible mushrooms (Kalač 2009) in different countries like Finland (Mattila et al. 2002), Poland (Jaworska and Bernaś 2009), Spain (Diéz and Alvarez 2001), Portugal (Barros et al. 2007, 2008a, b; Heleno et al. 2009), Italy (Manzi et al. 2001, 2004), Greece (Ouzouni

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et al. 2009; Ouzouni and Riganakos 2007) and Turkey (Colak et al. 2009). Whereas all the nutritional properties are already available in the literature, there are no reports about the chemical composition and nutritional value of the most consumed edible mushrooms in Argentina: *Agaricus bisporus* (white mushrooms/Champignons), *Agaricus bisporus* (brown mushrooms/Portobellos), *Lentinula edodes* (Shiitakes) and *Pleurotus ostreatus* (Girgolas/Oyster mushrooms). It is known that the growth substrate can influence the nutritional value of cultivated mushrooms, so as a consequence, there is variability within the same species of mushrooms depending on the geographic origin (Manzi et al. 1999).

The objective of this study is to evaluate the nutritional quality of the four mushrooms consumed most often in Argentina by means of classical chemical analysis and multivariate tools. The following parameters were analyzed in fruiting bodies, pileus and stipes: water content, ash, crude protein, lipids, carbohydrates, minerals (sodium, magnesium, phosphorous, potassium, calcium, iron and zinc) and bioactive components such as total, soluble and insoluble dietary fiber, total phenolic and chitin content. An analysis of variance (ANOVA) with a Tukey-HSD test was done to evaluate if there was a significant difference among the three parts of mushrooms. Finally, a well known multivariate technique such as principal component analysis (PCA) was used as exploratory analysis to visualize the natural grouping of the mushroom varieties (samples) and to evaluate the relation among the nutritional parameters (variables) and among samples and variables.

2 Materials and methods

2.1 Samples

Samples of Champignons, Portobellos, Girgolas and Shiitakes were obtained from local supermarkets. The mushrooms were stored at $-30\,^{\circ}\text{C}$ and lyophilized upon arrival at the laboratory. Prior to the analysis, the mushrooms were ground in a mill Brawn household mill, sieved through a # 70 mesh and then stored in desiccators until further analyses.

2.2 Standards and reagents

For all chemical analysis analytical grade reagents were used. Hexane, ethanol (95 % v/v), acetic acid and N,N-dimethylacetamide were obtained from Merck

(Buenos Aires, Argentina), lithium chloride and NaOH were provided by Cicarelli (Santa Fe, Argentina) and Folin–Ciocalteau phenol reagent and gallic acid by Sigma-Aldrich (St. Louis, MO, USA).

2.3 Chemical composition

Chemical composition including water content, ash, carbohydrates, lipids and crude protein were determined according to the Association of Official Analytical Chemists Methods (AOAC 1995). Water content was determined by drying samples overnight at 105 °C in an oven until constant weight. Ash content was determined by incineration at 550 °C for 24 h. Crude protein (N \times 4.38) was estimated by the macro-Kjeldhal method (Manzi et al. 1999). Lipids were determined by extracting a powdered mushroom sample using a Soxhlet apparatus with hexane as solvent. Total carbohydrates were calculated by difference as follows: total carbohydrates (% fresh weight) = 100 - (q water content + q protein + q)lipids + g ash) (Beluhan and Ranogajec 2011). Total energy was calculated according to the following equation: energy (kcal) = $4 \times (g \text{ protein} + g \text{ carbo-}$ hydrate) $+ 9 \times (g \text{ lipid})$ (Manzi et al. 2001).

Mineral composition was determined employing an Atomic Absorption Spectrometer (AAS) with airacetylene burner for flame and Inductively Coupler Plasma Atomic Emission Spectrometer (ICP-AES) with argon plasma (Shimadzu sequential 1000 Model III).

2.4 Dietary fiber, chitin and phenolic compounds contents

Dietary fiber (insoluble and soluble fraction) was determined according to the AOAC Method 991.43 (AOAC 2007).

Chitin content was obtained according to a modified Wu et al. method (2005). Freeze-dried mushroom powder (1.0 g) was stirred with 30 mL of 2.5 % HCl and heated at 100 °C with reflux for 1 h. The slurry was centrifuged (2500 rpm, 15 min, room temperature) and washed with deionized water to reach a neutral pH. Then 20 mL of ethanol 50 % was added and heated in a boiling water bath for 5 min and separated by centrifugation. The obtained slurry was stirred at room temperature with 35 mL of NaOH 1 M during 24 h. The extracted chitin was washed, centrifuged and freeze-dried.

Chitin was also extracted using a second extraction method which uses lithium chloride—N,N-dimethylacetamide (LiCl/DMAc) as solvent (Teng et al. 2001, method 2). Mushroom powder was placed in 5 % LiCl



in DMAc at a ratio of 1 g/150 mL with constant stirring at room temperature overnight. Suspension was centrifuged at 2500 rpm for 20 min. Distilled water was added to the supernatant (1:1) over 24 h to precipitate chitin. The obtained chitin was centrifuged, washed with distilled water to remove the remaining *N*,*N*-dimethylacetamide, freeze-dried and finally weighted.

Chitin was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) analysis and X-ray diffraction analysis (XRD). SEM was equipped with a LEO EVO 40 XVP microscope with a secondary electron detector. Samples were assembled in a SEM sample holder and then metalized with gold in a PELCO 91000 sputter coater. FTIR spectra were recorded on a Nicolet-Nexus 470 FTIR spectrometer on translucent disk obtained by pressing the ground material with KBr (1 % w/w). Finally X-ray diffraction data were collected using a Rigaku X-ray diffractometer D-Max. III-C, 35 kV and 15 mA, with Cu K α radiation and a monochromator of curved single crystal (graphite).

The content of phenolic compounds was estimated in both ethanolic and aqueous extracts according to the method proposed by Tsai et al. (2009). For ethanolic extraction, 1.0 g of dried samples were stirred with 100 mL of ethanol 95 % at 25 °C during 24 h and filtered on Watman paper no. 1. The residues were then extracted with two additional 100 mL portions of ethanol as described above. Ethanolic extracts were concentrated under reduced pressure to dryness. For water extraction, 1.0 g of dried samples were extracted by stirring with 100 mL of distilled water at 100 °C during 10 min, centrifugation (5000 rpm) during 15 min and filtration on Watman paper no. 1. The residues were extracted two additional times as described above and were then freeze-dried. The total phenol content was determined by the Follin-Ciocalteu assay (Dubost et al. 2007). Total phenolics were determined based on a standard curve of gallic acid (25-250 µg/mL). Results were expressed as µg of gallic acid equivalent (GAE) per mg.

2.5 Statistical analysis

All chemical assays were carried out in triplicate. A one factor analysis of variance (ANOVA, p < 0.05) was employed to evaluate if the different mushroom parts (fruiting body, pileus and stipe) differed significantly. Tukey-HSD multiple comparisons were

carried out to test for any significant differences between the means (p < 0.05 %).

PCA is a useful tool that searches for relationships between objects, between variables and between objects and variables (Massart et al. 1997). In PCA, the relationship between samples and variables can be simultaneously seen on a biplot. A study of the biplots shows that the scores represent the relationship between samples as distance, while the loadings represent the relationship between variables as angles between vectors. Statistical analysis was implemented with Matlab software (Version 7.0, The Math Works Inc., Natick, USA) and PLS Toolbox 3.5 (Eigenvector Research Incorporated).

3 Results and discussion

3.1 Chemical composition

Table 1 shows the chemical composition of the studied mushrooms. The studied parameters are discussed taking into account the results obtained either from the complete fruiting body or the pileus or stipe, respectively. When the nutritional value of mushrooms is evaluated, water content is the most important factor. Water content in mushrooms is dependent on the mushroom variety and other parameters related to harvest, growth and storage conditions (Reis et al. 2012). It can be observed that water content values range from 88.3 to 92.8 % so mushrooms are a highly rich source of water being Portobellos the richest variety.

Mushroom proteins seem to be of higher nutritional value than most proteins of plant origin (Bauer-Petrovska 2001). These proteins present levels of essential amino acids comparable to proteins of animal origin in relation to their good biological value (Mattila et al. 2002). Crude protein values are similar in the four mushroom varieties ranging from 1.7 to 2.1 % (Table 1) being Portobellos the richest variety.

Lipids are around 0.25 % for all mushrooms varieties (Table 1). The low fat content makes mushrooms ideal for low-energy diets. There are all types of lipids in edible mushrooms such as free fatty acid, tri-, di-, and monoglycerides, sterols and phospholipids (Breene 1990; Hanuš et al. 2008).

Carbohydrates are the most abundant macronutrients in mushrooms. It can be observed from Table 1 that Champignons and Portobellos have similar values while Girgolas and Shiitakes have the



	Champignons			Portobellos			Girgolas			Shiitakes		
	Fruiting body Pileus		Stipe	Fruiting body Pileus	Pileus	Stipe	Fruiting body Pileus		Stipe	Fruiting body Pileus	Pileus	Stipe
Water content 91.69 \pm 1.17	91.69 ± 1.17	92.2 ± 0.74	92.2 ± 0.74 92.3 ± 0.07 92.77	92.77 ± 0.64	92 ± 0.20	92 ± 0.20 92.82 ± 0.07	$89.19 \pm 0.45 89.75 \pm 1.14$	89.75 ± 1.14	88.13 ± 0.98	88.13 ± 0.98 88.28 ± 1.34	87.24 ± 1.24	83.25 ± 1.52
Proteins	$\textbf{1.99} \pm \textbf{0.15}$	$\textbf{1.95} \pm \textbf{0.15}$	$\textbf{1.81} \pm \textbf{0.25}$	$\textbf{2.15} \pm \textbf{0.04}$	$\textbf{2.14} \pm \textbf{0.06}$	$\textbf{2.07} \pm \textbf{0.12}$	1.71 ± 0.06	$\textbf{1.72} \pm \textbf{0.04}$	$\textbf{1.95} \pm \textbf{0.08}$	$\textbf{2.04} \pm \textbf{0.09}$	$\textbf{2.04} \pm \textbf{0.09}$	$\textbf{2.11} \pm \textbf{0.09}$
Lipids	$\textbf{0.24} \pm \textbf{0.01}$	$\textbf{0.26} \pm \textbf{0.01}$	$\textbf{0.24} \pm \textbf{0.01}$	$\textbf{0.27} \pm \textbf{0.01}$	$\textbf{0.27} \pm \textbf{0.01}$	$\textbf{0.27} \pm \textbf{0.02}$	$\textbf{0.24} \pm \textbf{0.03}$	$\textbf{0.24} \pm \textbf{0.01}$	$\textbf{0.24} \pm \textbf{0.01}$	$\textbf{0.26} \pm \textbf{0.01}$	$\textbf{0.23} \pm \textbf{0.02}$	$\textbf{0.23} \pm \textbf{0.01}$
Carbohydrates	$\textbf{5.17} \pm \textbf{0.06}$	$\textbf{4.54} \pm \textbf{0.08}$	$\textbf{4.73} \pm \textbf{0.05}$	$\boldsymbol{3.94 \pm 0.06}$	$\textbf{3.76} \pm \textbf{0.08}$	$\textbf{3.98} \pm \textbf{0.05}$	$\textbf{7.99} \pm \textbf{0.06}$	$\textbf{7.26} \pm \textbf{0.08}$	$\textbf{8.82} \pm \textbf{0.05}$	$\textbf{8.54} \pm \textbf{0.06}$	9.66 ± 0.08	$\textbf{12.81} \pm \textbf{0.05}$
Ash	$\textbf{0.89} \pm \textbf{0.07}$	$0.89 \pm 0.07 1.05 \pm 0.12$	$\textbf{0.91} \pm \textbf{0.10}$	$\textbf{0.87} \pm \textbf{0.06}$	1.10 ± 0.08	$\textbf{0.86} \pm \textbf{0.05}$	$\textbf{0.87} \pm \textbf{0.06}$	$\textbf{1.10} \pm \textbf{0.08}$	$\textbf{0.86} \pm \textbf{0.05}$	$\textbf{0.88} \pm \textbf{0.09}$	$\textbf{0.83} \pm \textbf{0.10}$	0.60 ± 0.09
Energy (kcal)	30.88 ± 0.06	Energy (kcal) 30.88 ± 0.06 28.30 ± 0.08 28.32 ± 0.08	28.32 ± 0.08	26.79 ± 0.06	26.03 ± 0.08	26.63 ± 0.05	40.96 ± 0.06	37.8 ± 0.08	$37.8 \pm 0.08 \ 45.20 \pm 0.05$	44.66 ± 0.07	48.87 ± 0.09	61.71 ± 0.07

are means of the six samples (n=3), g/100 g edible weight

highest values. These values correspond to bioavailable and non-bioavailable carbohydrates like fiber.

Mushrooms have low energy because of the low values of dry matter and lipids. It can be observed from Table 1 that all varieties have very low-energy values ranging from 26.8 (Portobellos) to 44.70 (Shiitakes) kcal/100 g. These results suggest that mushrooms are ideal for hypo-caloric diets.

Following the analysis of the chemical parameters, ash content values are around 0.88 % on wet weight. Regarding mineral composition (Table 2) the most abundant mineral is potassium in agreement with literature data (Mallikarjuna et al. 2013) ranging from 12,271 to 24,155 mg/100 g on dry weight, followed by phosphorus content. However, mushrooms have relatively low levels of sodium and calcium. Iron and zinc have the lowest levels. Overall, minerals present the highest variability among all the studied nutritional parameters.

According to the recommended daily intake (RDI) 100 g of fresh mushrooms cover around 10 % of potassium and phosphorus requirements (FAO/WHO 2004). On the other hand the low level of sodium and the high amount of potassium suggest the utilisation of mushrooms in anti-hypertensive diets. It has to be mentioned that the highest zinc content are present in Shiitakes (100 g) and represents 11 % of the RDI.

As general trend, the studied nutritional parameters do not have significant differences (ANOVA, p < 0.05) among fruiting body, pileus and stipe for all mushroom varieties. These results were corroborated with Tukey-HSD. Therefore, bioactive components (dietary fiber, chitin and phenolic compounds contents) are reported considering the whole mushroom (fruiting body). Besides, the Tukey test shows that water content and energy level of Champignons and Portobellos differs significantly from water content and energy level in Shiitakes, whereas ash, protein and lipid contents do not differ significantly for all the varieties mushrooms.

3.2 Dietary fiber, chitin and phenolic compounds contents

3.2.1 Dietary fiber

The American Association of Cereal Chemistry (AACC) defines the dietary fiber as edible parts of plants or analogous carbohydrates that are resistant to the digestive processes and is not absorbed by the human intestine. Fiber has beneficial physiological effects such as laxation, blood glucose attenuation and reduction of plasma cholesterol, among others



 Table 2
 Mineral composition

Name Fruiting body Flieux Stipe Fruiting body Flieux Fruiting body Flieux Stipe <		Champignons			Portobellos			Girgolas			Shiitakes		
858 ± 25 801 ± 97 827 ± 106 677 ± 76 710 ± 56 871 ± 94 1313 ± 124 1323 ± 170 1800 ± 120 404 ± 14 403 ± 15 891 ± 104 846 ± 107 904 ± 106 989 ± 113 1106 ± 101 818 ± 30 1079 ± 151 1051 ± 174 777 ± 27 1114 ± 161 1218 ± 187 8221 ± 941 8239 ± 785 7819 ± 798 8789 ± 880 10,649 ± 530 6849 ± 339 5267 ± 172 5767 ± 132 2312 ± 193 5562 ± 148 6173 ± 85 24,155 ± 2248 24,159 ± 241 23,839 ± 1691 23,247 ± 2184 31,155 ± 3163 20,832 ± 2061 13,802 ± 2781 12,984 ± 1510 13,024 ± 1518 12,241 ± 1977 13,264 ± 1640 281 ± 96 303 ± 73 291 ± 100 598 ± 82 632 ± 106 664 ± 158 76 ± 19 75 ± 19 73 ± 18 204 ± 94 250 ± 63 77 ± 12 99 ± 26 79 ± 9 127 ± 29 112 ± 30 98 ± 23 112 ± 41 104 ± 20 109 ± 7 75 ± 14 85 ± 12 41 ± 3 37 ± 8 36 ± 4 36 ± 9 36 ± 9<		Fruiting body	Pileus	Stipe									
891±104 846±107 904±106 989±113 1106±101 818±30 1079±151 777±27 1114±161 1218±187 8221±941 8239±785 7819±798 8789±880 10,649±530 6849±339 5267±172 5767±132 2312±193 5562±148 6173±85 24,155±2248 24,139±241 23,839±1691 23,247±2184 31,155±3163 20,832±2061 13,802±2781 12,984±1510 13,024±1518 12,271±1977 13,264±1640 281±96 303±73 291±100 598±82 632±106 664±158 76±15 75±19 73±18 204±94 250±63 77±12 99±26 79±9 127±29 112±30 98±23 112±41 104±20 109±7 50.6±8 55±4 41±3 37±8 36±4 38±4 40±8 36±9 49±6 47±8 36±4 75±14 85±12	Ra	858 ± 25	801 ± 97	827 ± 106	9Z = Z29	710 ± 56	871 ± 94	1313 ± 124	1323 ± 170	1800 ± 120	404 ± 14	403 ± 15	289 ± 32
8221 ± 941 8239 ± 785 7819 ± 795 8789 ± 880 10,649 ± 530 6849 ± 339 5267 ± 172 5767 ± 132 2312 ± 193 5562 ± 148 6173 ± 85 24,155 ± 2248 24,155 ± 2248 24,139 ± 241 23,839 ± 1691 23,247 ± 2184 31,155 ± 3163 20,832 ± 2061 13,802 ± 2781 12,984 ± 1510 13,024 ± 1518 12,271 ± 1977 13,264 ± 1640	Mg	891 ± 104	846 ± 107	904 ± 106	989 ± 113	1106 \pm 101	818 ± 30	1079 ± 151	1051 ± 174	777 ± 27	1114 \pm 161	1218 ± 187	808 ± 23
24,155 ± 2248 24,139 ± 241 23,839 ± 1691 23,247 ± 2184 31,155 ± 3163 20,832 ± 2061 13,802 ± 2781 12,984 ± 1510 13,024 ± 1518 12,271 ± 1977 13,264 ± 1640 281 ± 96 303 ± 73 291 ± 100 598 ± 82 632 ± 106 664 ± 158 76 ± 15 75 ± 19 73 ± 18 204 ± 94 250 ± 63 77 ± 12 99 ± 26 79 ± 9 127 ± 29 112 ± 30 98 ± 23 112 ± 41 104 ± 20 109 ± 7 50.6 ± 8 55 ± 4 41 ± 3 37 ± 8 36 ± 4 38 ± 4 40 ± 8 36 ± 9 49 ± 6 47 ± 8 36 ± 4 75 ± 14 85 ± 12	۵	8221 ± 941	8239 ± 785	7819 ± 798	8789 ± 880	$10,649 \pm 530$	6849 ± 339	5267 ± 172	5767 ± 132	2312 ± 193	5562 ± 148	6173 ± 85	5302 ± 112
281 ± 96 303 ± 73 291 ± 100 598 ± 82 632 ± 106 664 ± 158 76 ± 15 75 ± 19 73 ± 18 204 ± 94 250 ± 63 77 ± 12 99 ± 26 79 ± 9 127 ± 29 112 ± 30 98 ± 23 112 ± 41 104 ± 20 109 ± 7 50.6 ± 8 55 ± 4 6 41 ± 3 37 ± 8 36 ± 4 38 ± 4 40 ± 8 36 ± 9 49 ± 6 47 ± 8 36 ± 4 75 ± 14 85 ± 12	×	$24,155 \pm 2248$	$24,139 \pm 2411$	$23,839 \pm 1691$	23,247 \pm 2184	$31,155 \pm 3163$	$20,832 \pm 2061$	$13,802 \pm 2781$	$12,984 \pm 1510$	$13,024 \pm 1518$	$12,271 \pm 1977$	$13,264 \pm 1640$	$10,529 \pm 1171$
77 ± 12 99 ± 26 79 ± 9 127 ± 29 112 ± 30 98 ± 23 112 ± 41 104 ± 20 109 ± 7 50.6 ± 8 55 ± 4 41 ± 3 37 ± 8 36 ± 4 38 ± 4 40 ± 8 36 ± 9 49 ± 6 47 ± 8 36 ± 4 75 ± 14 85 ± 12	S	281 ± 96	303 ± 73	291 ± 100	598 ± 82	632 ± 106	664 ± 158	76 ± 15	75 ± 19	73 ± 18	204 ± 94	250 ± 63	170 ± 49
41 ± 3 37 ± 8 36 ± 4 38 ± 4 40 ± 8 36 ± 9 49 ± 6 47 ± 8 36 ± 4 75 ± 14 85 ± 12	Fe	77 ± 12	99 ± 26	6 ± 62	127 ± 29	112 ± 30	98 ± 23	112 ± 41	104 ± 20	109 ± 7	50.6 ± 8	55 ± 4	62.2 ± 4
	Zu	41 ± 3	37 ± 8	36 ± 4	38 ± 4	40 ± 8	36 ± 9	49 ± 6	47 ± 8	36 ± 4	75 ± 14	85 ± 12	69 ± 11

are means of the six samples (n=3), mg/kg dry weight

(AACC Report 2000). Compared to other conventional sources of dietary fiber such as cereals, fruits, legumes and vegetables, mushrooms are underutilized. In fact edible mushrooms are a novel source rich in dietary fibers that have various beneficial health effects to humans (Cheung 2013). Table 3 shows the total, insoluble and soluble dietary fiber contents of the studied mushrooms. Total fiber values are similar in the species Agaricus bisporus (Champignons/Portobellos) with values around 22.2 %, Girgolas have an intermediate value of 27.2 % and Shiitakes have the highest content with 37.4 %. The recommended daily intake of fiber is between 25 and 30 g, so by consuming 100 g of fresh mushrooms from the species Agaricus bisporus about 7 % of this recommendation is covered, 10 % considering Girgolas and 15.0 % in case of Shiitakes. Therefore, it can be stated that mushrooms are important in achieving the fiber daily intake.

3.2.2 Chitin, extraction and characterization

All fungal walls contain a mixture of fibrillar components and amorphous or matrix components. Chitin is the main fibrillar component which is a straight-chain β -(1–4)-linked polymer of N-acetylglucosamine and the most abundant mushroom polysaccharides are hemicelluloses, α - and β -glucans, mannans, xylans and galactans. These cell wall components are resistant to human enzymes and can be considered as dietary fiber (Nitschke et al. 2011). Chitin contents obtained with two different extraction methods are summarized in Table 3. It can be seen that the first method gives higher chitin values than the second one for all mushroom varieties. This can be explained by the fact that the first method extracts chitin that would be associated with other components like β -D-glucans, whereas the second method uses a solvent that only dissolves chitin which implies that this extraction is more selective. Table 3 shows that Girgolas and Shiitake mushrooms have the highest chitin content, which is in agreement with the total fiber values.

Chitin obtained with the two extraction methods was characterized with XRD, FTIR and SEM. As an example, the results obtained from a Champignon sample were used in all cases. The X-ray spectrum exhibits two main crystalline peaks at 2θ from chitin extracted using a specific solvent (method 2): the first between $8^{\circ}58'-10^{\circ}26'$ and the second between $19^{\circ}58'-20^{\circ}00'$ as it can be seen in Fig. 1b. These characteristic peaks are also found in the spectrum from chitin extracted with the first method (Fig. 1a).



 Table 3 Dietary fiber, chitin and phenolic compounds contents

	Champignons	Portobellos	Girgolas	Shiitake
Total diet fiber ^a	23.6 ± 1.0	20.9 ± 0.3	27.2 ± 1.8	37.4 ± 1.1
Insoluble diet fiber ^a	18.0 \pm 1.1	16.4 ± 0.6	25.0 ± 1.6	29.3 \pm 1.2
Soluble diet fiber ^a	5.6 ± 0.2	4.5 ± 0.1	2.7 ± 0.4	8.1 ± 0.8
Chitin (method 1) ^a	14.07 ± 0.95	19.00 \pm 1.06	21.53 ± 1.02	21.91 ± 0.98
Chitin (method 2) ^a	11.50 ± 0.10	9.89 ± 0.60	11.87 \pm 0.20	15.73 \pm 0.70
Phenolic compounds				
Ethanolic extract ^b	4.42 ± 0.40	3.03 ± 0.11	$\textbf{3.32} \pm \textbf{0.30}$	$\textbf{2.87} \pm \textbf{0.30}$
Aqueous extract ^b	11.25 \pm 1.90	11.63 ± 3.10	$\textbf{11.44} \pm \textbf{2.30}$	8.42 ± 1.60
Total phenolic compounds ^b	15.67 \pm 1.20	14.66 ± 1.10	14.76 \pm 1.30	$\textbf{11.29} \pm \textbf{0.96}$

Data are means of the six samples (n = 3)

^b mg eq Gallic acid/g dry sample

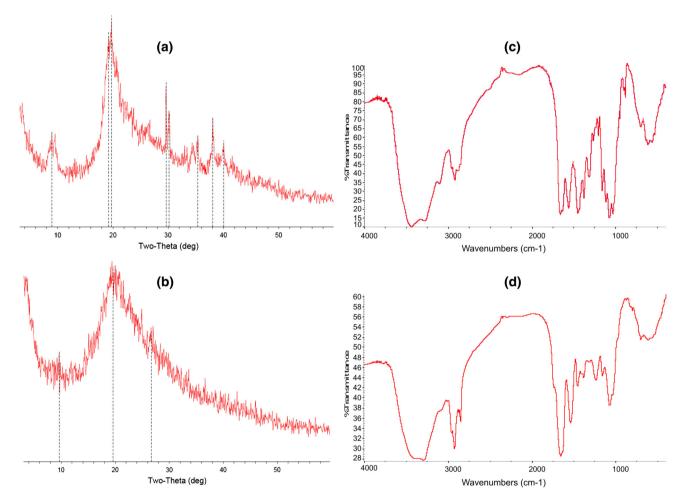


Fig. 1 XRD patterns of chitin obtained with method 1 (a) and method 2 (b). FTIR spectra of chitin obtained with method 1 (c) and method 2 (d)

The obtained spectra are in concordance with chitin spectra obtained from other sources (Yen et al. 2009). Moreover, FTIR spectra for chitin obtained with the first and second method are shown in Fig. 1c, d,

respectively. Wide bands between 3400 and $3050~\rm cm^{-1}$ associated with the O–H and N–H stretching can be observed, some bands around $2900~\rm cm^{-1}$ corresponding to C–H stretching and the



^a % dry weight

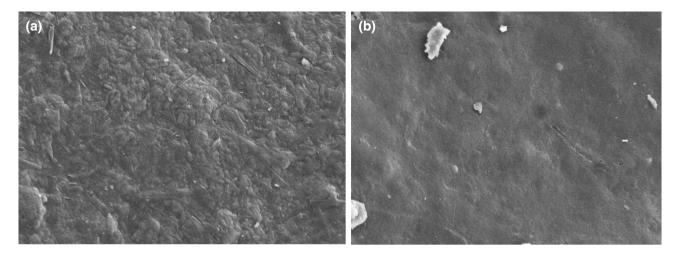


Fig. 2 SEM micrograph (×6000 magnification) of chitin obtained with method 1 (a) and method 2 (b)

bands associated with amide group between 1600 and 1700 cm⁻¹ (amide I) and around 1550 cm⁻¹ (amide II). Also the C=O stretching can be found between 1000 and 1200 cm⁻¹ (Rinaudo 2006). It can be concluded that both spectra show the IR characteristics bands of chitin. Finally, chitin morphology was characterized by SEM. Chitin obtained with the first method presents a tough surface with irregular and fibrillar morphology (Fig. 2a) whereas extracted chitin with method 2 shows a smooth and uniform surface (Fig. 2b). It is clear that SEM chitin morphology depends on the type of extraction method used, and it is interesting to note that there is no porosity in both extracted chitins.

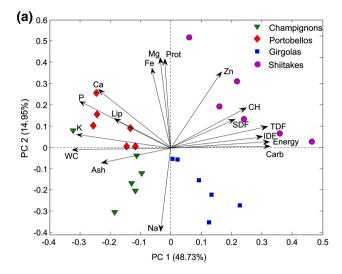
3.2.3 Phenolic compounds

There is a direct positive correlation between the antioxidant activity and phenolic compounds of mushrooms. Mushrooms accumulate a variety of secondary metabolites including phenolic compounds, polyketides, terpenes and steroids, so their consumption is recommended because phenolics have been associated with the prevention of diseases like cancer and coronary heart disease (Cheung et al. 2003; Kozarski et al. 2012). Total phenols were determined using the Folin-Ciocalteu reagent, which despite the fact that it can be reduced by various nonphenolic compounds as summarised by Prior et al. (2005), it is still widely used in quantification of phenols in food analysis. Table 3 shows the phenolic content in both ethanolic and aqueous extracts. The yields of phenols were higher for water extracts than ethanolic extracts for all studied varieties. This is in agreement with results found by Tsai et al. (2009). It can be seen that Champignons, Portobellos and Girgolas have similar total phenolic contents (around 15 %) while it slightly decreases in Shiitakes (11.3 %).

3.3 Multivariate analysis

Up to now, mushroom's nutritional quality has been discussed based on chemical parameters. This information can also be shown with PCA biplots. A PCA model was built considering the information provided by the first three PCs, which explain a 73.7 % of the total information. Figure 3a shows the biplot for PC1 vs. PC2 and four defined groups corresponding to Champignon, Portobello, Girgolas and Shiitake samples can be observed. PC1 clearly separates Shiitakes and Girgolas (PC1 positive values) from Champignons and Portobellos (PC1 negative values). Indeed, Champignons and Portobellos are close to each other in the multivariate space, and this is somehow expected as they belong to the same mushroom species (Agaricus bisporus). On the other hand, Shiitakes and Portobellos have positive PC2 values while Girgolas and Champignons have negative PC2 values. Regarding the relationships among samples and variables, samples positioned close to an arrow of a variable show strong relationship. Shiitakes are richer in carbohydrates, bioactive components and zinc and are also related with a higher energetic value in concordance with the lowest water content. Otherwise Portobellos are related with higher water content, phosphorous, potassium, calcium and lipids. Lipid content seem to be the least relevant variable because of its shortest vector, followed by ash and soluble dietary fiber. On the other hand, by inspecting the relationship among nutritional parameters,





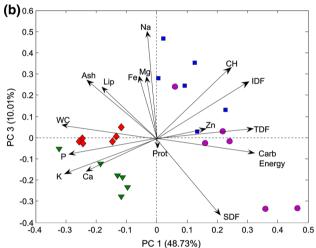


Fig. 3 PCA biplots of samples (mushrooms varieties) and variables (nutritional parameters). **a** PC1 vs. PC2 biplot and **b** PC1 vs. PC3 biplot. *WC* water content, *Carb* carbohydrates, *Lip* lipids, *Prot* proteins, *CH* chitin, *TDF* total dietary fiber, *IDF* insoluble dietary fiber, *SDF* soluble dietary fiber

variables with the same direction show positive correlation. Figure 3a shows four highly correlated groups: carbohydrates, energy and bioactive compounds (total, insoluble and soluble dietary fiber and chitin); lipids, phosphorous and calcium; water content, ash and potassium; proteins, magnesium, and iron. On the other side, sodium is negatively correlated with the last mentioned group (the angle between them is almost 180°) and it is complementary to the other variables (with angles near to 90°).

Concerning the PC1 vs. PC3 biplot (Fig. 3b), it can be observed that the discrimination within the species *Agaricus bisporus* is slightly improved while the global relationships among variables are unchanged in respect to the first biplot. When PC3 is considered,

sodium is positively correlated with iron and magnesium whereas soluble dietary fiber is less correlated with most of variables and the importance of proteins considerably decreased. In this case, Champignons are also related with potassium, calcium, and phosphorus like Portobellos do in the PCI/PC2 biplot. Finally, Girgolas is the mushroom variety that is more related with sodium content as it can be observed in both biplots.

4 Conclusions

The chemical composition and nutritional value of the four mushrooms consumed most often that are cultivated in Argentina (Champignons, Portobellos, Girgolas and Shiitakes) have been evaluated. These mushrooms are highly rich in water, poor in lipids and the most abundant macronutrients are carbohydrates that include dietary fiber. Also, they can be considered a rich source of potassium and phosphorus with low sodium levels. Such characteristics make mushrooms ideal for both low-caloric and anti-hypertensive diets.

Considering mushroom bioactive components, a method for extracting chitin was proposed. The extracted biopolymer was compared with chitin directly isolated from mushrooms with a specific solvent (LiCl/DMAc). The comparison of chitin extraction methods shows that both extracted chitins are similar. Therefore it can be concluded that the proposed method is suitable for chitin extraction. Also chitin can be considered as a part of not bioavailable carbohydrates (fiber) which means that mushrooms can be considered a potential source of fiber. Moreover, the amount of antioxidants found in aqueous extracts is noticeable. Antioxidants can provide various health benefits to humans.

Multivariate analysis enabled us to discriminate among the four mushroom varieties studied. This is very advantageous considering that most of the nutritional parameters have similar chemical values. PCA biplots are useful for simultaneously obtaining information about the relationships among the groups and chemical parameters. This study can be applied to discriminate among other mushrooms varieties with similar nutrient composition with classical chemical data and multivariate tools.

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Conflict of interest The authors declare that they have no conflict of interest.

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