



Research Note

Comparison of mineral and hazardous heavy metal contents in *Lentinula edodes* produced from Korea and China

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한국과 중국에서 생산된 표고버섯의 다량, 미량 미네랄 및 유해 중금속 함량 비교

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Abstract

Lentinula edodes, an edible mushroom, is mainly produced in Korea, China, and Southeast Asia. Thus, very few studies have reported the identification of the country origin of *L. edodes* samples. Herein, the macro mineral, trace mineral, and hazardous heavy metal contents of domestic and Chinese *L. edodes* samples were analyzed and their production countries were compared. The mineral contents of 13 domestic and 17 Chinese *L. edodes* samples were analyzed using atomic absorption spectrophotometer and inductively coupled plasma mass spectrometer. The Na, Mg, K, and Ca contents in domestic *L. edodes* were determined to be 161.33, 746.22, 17,676.84, and 50.50 mg/kg, respectively, whereas those in Chinese *L. edodes* were 310.69, 318.49, 11,182.01, and 33.36 mg/kg, respectively. The Cr and Cu contents in domestic and Chinese *L. edodes* were 2.82 and 77.13 mg/kg (Cr) and 12.955 and 101.19 mg/kg (Cu), respectively. The hazardous heavy metal contents in domestic and Chinese *L. edodes* were determined to be within the levels recommended by the Korean Food Code. Taken together, our results reveal significant differences between Na, Mg, and K contents ($p < 0.001$) and Cr content ($p < 0.01$) in domestic and Chinese *L. edodes* samples. Thus, Na, Mg, K, and Cr contents may serve as basic data to determine the origin of domestic and Chinese *L. edodes* samples; further studies on the Na, Mg, K, and Cr contents in domestic and Chinese *L. edodes* samples are needed for identifying the country origin of this mushroom.

Key words : *Lentinula edodes*, macro mineral, trace mineral, hazardous heavy metal, production country

Introduction

Lentinula edodes belongs to the family omphalotaceae. It is an edible mushroom, similar to *Sarcodon aspratus* and *Tricholoma matsutake* (Jiang et al., 2013; Han et al., 2015).

L. edodes is mainly produced in Korea, China, and southeast Asia, where it is reported to grow on pieces of wood and stubble, such as those of oak (Kim et al., 2003). *L. edodes* contains numerous nutrients, including proteins, vitamins, and minerals, as well as β -glucan, eritadenine, ergosterin,

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and lentinan (Hong et al., 1988).

The domestic production of *L. edodes* in Korea in 2016, 2017, and 2018 was 23,470 tons, 23,984 tons, and 22,255 tons, respectively. Developments in mushroom- cultivation technologies have resulted in increased mushroom production (Korean Forest Service, 2020; RDA, 2011). However, since the domestic production of this mushroom is unable to meet consumer demand in Korea, Chinese *L. edodes* are imported in large quantities (Bak et al., 2013; Kim et al., 2017), and these low-priced Chinese *L. edodes* samples are falsely sold as domestic products. *L. edodes* is reported as a product vulnerable to fraudulent sale, along with pork and red pepper powder (KREI, 2011). The origin of *L. edodes* is judged by the visual identification of several features, such as a hat-like shape and the condition of wrinkles (Lee et al., 2006); because such methods are not reliable, an accurate and objective method of identifying the country of origin of *L. edodes* is needed. However, thus far, studies have only performed the volatile fragrance component analysis and residual pesticide survey of *L. edodes*; very few studies have reported the identification of the country of origin of *L. edodes* (Hong et al., 1988; Kim et al., 2020).

Therefore, this study analyzed the contents of macro minerals, trace minerals, and hazardous heavy metals in domestic and Chinese *L. edodes* samples and compared the contents of these components to ascertain the differences observed according to the production country.

Material and methods

Lentinula edodes

In total, 13 domestic and 17 Chinese *L. edodes* samples were used in this study. *L. edodes* samples were randomly purchased from Jangheung in Korea (domestic *L. edodes*) and Korea Songi Trading Co. Ltd., Chilgok, Korea (Chinese *L. edodes*).

Sample treatment

The *L. edodes* samples were decomposed according to the microwave method recommended by the Korean Food Code (MFDS, 2020). Briefly, approximately 0.5 g of the dried mushroom sample was placed in the microwave digestion system, followed by decomposition using nitric acid and hydrogen peroxide (Dong Woo Fine Chem. Co., Ltd., Iksan,

Korea); finally, the samples were added with distilled water. The nitric acid and hydrogen peroxide solutions used for the treatment were of extra pure grade.

Verification of method

To verify the analytical method, a calibration curve was prepared using a standard solution, and the correlation coefficient (R^2) of the calibration curve was calculated. The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to the International Conference on Harmonization for Registration of Pharmaceutical for Human Use (ICH) (Kim, 2020; ICH Steering Committee, 2014).

$$\text{LOD} = 3.3 \times (\delta / S)$$

$$\text{LOQ} = 10 \times (\delta / S)$$

δ : Standard deviation of the response

S: Slope of the calibration curve

The standard solution prepared at each concentration was added to the sample, and the accuracy and precision were measured three times. According to the ICH criteria, the accuracy range should lie within 80-120%, and the precision range should be within 20% (ICH Steering Committee, 2014).

$$\text{Recovery (\%)} = (\alpha / \beta) \times 100$$

α : Spiked concentration

β : Measuring concentration

Analysis of macro minerals

The contents of macro minerals such as Na, Mg, K, and Ca were analyzed in accordance with the atomic absorption spectrophotometric method specified by the Korean Food Code (MFDS, 2020). The conditions set for the analysis using an atomic absorption spectrophotometer (AAAnalyst 400, Perkin Elmer, Norwalk, CT, USA) were fuel and oxidant flow at 2.0 L/min for C_2H_2 and 10.0 L/min for air. The analytical wavelengths for Na, Mg, K, and Ca were determined to be 589.00, 285.51, 766.49, and 422.67 nm, respectively.

Analysis of trace minerals and hazardous heavy metals

Trace minerals (Cr and Cu) and hazardous heavy metals

(Cd and Pb) were analyzed in accordance with the inductively coupled plasma mass spectrometer method specified by the Korea Food Code (MFDS, 2020). The conditions set for the analysis using an inductively coupled plasma mass spectrometer (NexION 300 D, Perkin Elmer, Norwalk, CT, USA) were as follows: RF power, 1,600 W and pulse stage voltage, 900 V. The flows of the Aux. and Neb. gases were 1.2 L/min and 1.02 L/min of argon, respectively. The mass spectra for Cr, Cu, Pb, and Cd were determined to be 51.941, 62.930, 207.977, and 110.904 m/z, respectively.

Statistical analysis

Statistical analysis was performed using the SPSS statistics program (Statistical Package for the Social Science, Version 26.0, SPSS Inc., Chicago, IL, USA) to calculate the means and standard deviations. Significant differences were analyzed using independent sample t-tests or one-way ANOVA and Duncan's multiple range test.

Results and discussion

Verification of analytical methods

The accuracy, precision, correlation coefficient, LOD, and LOQ of the analyses of the contents of minerals and hazardous heavy metals by atomic absorption spectrophotometry (AAS) and inductively coupled plasma mass spectrometry (ICP/MS) are presented in Table 1. For the AAS analysis, the accuracy obtained was 94- 109%, the precision was within 20%, and the correlation coefficient was over 0.995. For the ICP/MS analysis, the accuracy was 98-101%, the precision was within 20%, and the correlation coefficient was over 0.999. These results satisfied the ICH criteria, which require an accuracy of 80-120% and precision of <20% (ICH Steering Committee, 2014).

Macro mineral contents

The macro mineral contents of domestic and Chinese *L. edodes*, as analyzed using AAS, are presented in Table 2.

Table 1. Accuracy, precision, correlation coefficient, limit of detection (LOD), and limit of quantification (LOQ) of mineral and hazardous heavy metal analysis by atomic absorption spectrophotometer (AAS) and inductively coupled plasma mass spectrometer (ICP/MS)

Instrument	Mineral	Accuracy (%)	Precision (RSD%)	Correlation coefficient (R ²)	LOD (mg/kg)	LOQ (mg/kg)
AAS	Na	97.40	0.03	0.9954	0.1945	0.5894
	Mg	95.40	0.01	0.9984	0.1586	0.4807
	K	109.40	0.02	1.0000	0.2394	0.7255
	Ca	94.60	0.03	0.9990	0.7920	2.4000
ICP/MS	Cr	98.46	2.30	0.9999	0.0098	0.0296
	Cu	98.34	1.40	1.0000	0.0090	0.0274
	Cd*	101.20	2.00	1.0000	0.0004	0.0014
	Pb*	99.90	0.60	0.9993	0.5000	1.6000

*The unit of LOD and LOQ is µg/kg.

Table 2. Comparison of mineral contents in *Lentinula edodes* produced in Korea and China

Collected site	Macro mineral (mg/kg)				Trace mineral (mg/kg)	
	Na	Mg	K	Ca	Cr	Cu
Korea (n=17)	161.33±44.34 ¹⁾	746.22±197.55	17,676.84±3,279.58	50.50±26.98	2.82±2.61	77.13±45.88
China (n=13)	310.69±84.80	318.49±45.06	11,182.01±2,446.44	33.36±6.08	12.95±10.05	101.19±43.78
p-value	0.000 ^{***2)}	0.000 ^{***}	0.000 ^{***}	0.021 [*]	0.004 ^{**}	0.158

¹⁾All values are mean±SD.

²⁾*p<0.05, **p<0.01, ***p<0.001.

The contents of Na, Mg, K, and Ca in domestic *L. edodes* were determined to be 161.33±44.34 mg/kg, 746.22±197.55 mg/kg, 17,676.84±3,279.58 mg/kg, and 50.50±26.98 mg/kg, respectively, whereas those in Chinese *L. edodes* were 310.69±84.80 mg/kg, 318.49±45.06 mg/kg, 11,182.01±2,446.44 mg/kg, and 33.36±6.08 mg/kg, respectively. Upon comparing the macro mineral contents of domestic and Chinese *L. edodes*, it was found that the Na content was significantly higher in the Chinese *L. edodes* samples ($p<0.001$), whereas significantly higher levels of Mg and K were present in the domestic *L. edodes* samples ($p<0.001$).

L. edodes is a cultivable mushroom that grows on broad-leaf trees, such as oak trees. The mineral content of *L. edodes* is reported to be mainly affected by the acidity and organic content of the soil, as well as the growing environment (Gast et al., 1988; Kim et al., 2003). Our results revealed significant differences between the Na, Mg, and K contents in domestic and Chinese *L. edodes* ($p<0.001$). We believe that examining the Na, Mg, and K contents in many samples of *L. edodes*, whose exact cultivation conditions have been investigated, will help determine the country of origin of the mushroom samples.

Trace minerals and hazardous metal contents

The contents of trace minerals and hazardous heavy metals in domestic and Chinese *L. edodes* were analyzed using ICP/MS (Tables 2 and 3). The Cr and Cu contents in domestic *L. edodes* samples were determined to be 2.82±2.61 mg/kg and 77.13±45.88 mg/kg, respectively, while those in Chinese *L. edodes* samples were 12.95±10.05 mg/kg and 101.19±43.78 mg/kg, respectively. Upon comparing the contents of trace minerals in *L. edodes* according to the production country, no significant difference

was observed for the Cu contents, but the Cr contents were significantly higher in the Chinese *L. edodes* samples ($p<0.01$). The mineral content of *L. edodes* is reportedly influenced by the cultivation environment (Gast et al., 1988; Kim et al., 2003). Our results showed significant differences between the Cr contents of domestic and Chinese *L. edodes* ($p<0.01$). Thus, we propose that the Cr content can be used to distinguish between domestic and Chinese *L. edodes* samples.

The hazardous heavy metal contents of domestic and Chinese *L. edodes* were as follows: 1.80±0.84 µg/kg and 5.44±4.43 µg/kg for Cd, respectively, and 1.94±4.52 µg/kg and 2.41±3.44 µg/kg for Pb, respectively. Only a few studies have reported the hazardous heavy metal contents in *L. edodes*; hence, comparisons of such results with those of the current study are not possible. According to the Korea Food Code (MFDS, 2020a), the hazardous heavy metal content of mushrooms is defined as less than 300 µg/kg for Cd and Pb. Thus, the results of the current study demonstrate that the heavy metal contents in the *L. edodes* samples analyzed herein are within the safety limits specified by the Ministry of Food and Drug Safety standards in Korea. In conclusion, our results revealed significant differences between the Na, Mg, and K contents ($p<0.001$) and Cr contents ($p<0.01$) of domestic and Chinese *L. edodes* samples. These results showed that the Na, Mg, K, and Cr contents can be used as basic data to determine the origin of domestic and Chinese *L. edodes*. Therefore, there is a requirement for further studies that analyze the Na, Mg, K, and Cr contents in many samples of domestic and Chinese *L. edodes*, the cultivation conditions for which have been investigated, for the accurate identification of the country origin of *L. edodes* mushrooms.

Table 3. Comparison of hazardous heavy metal contents in *Lentinula edodes* produced in Korea and China

Collected site	Hazardous heavy metal (µg/kg)			
	Cd		Pb	
	Mean±SD	Range	Mean±SD	Range
Korea (n=17)	1.80±0.84 ¹⁾	0.48-3.21	1.94±4.52	0.04-19.30
China (n=13)	5.44±4.43	1.43-16.71	2.41±3.44	0.43-13.63
p-value	0.012 ²⁾		0.755	

¹⁾All values are mean±SD.

²⁾* $p<0.05$, ** $p<0.01$, *** $p<0.001$.

요 약

표고는 한국, 중국, 남아시아 등에서 재배되고 있으나 원산지 판별에 관한 연구가 미약한 실정이다. 따라서 본 연구에서 표고의 다량무기질, 미량무기질 및 중금속 함량을 분석하여 원산지와 비교 분석하였다. 13종의 국내산 표고버섯과 17종의 중국산 표고버섯의 무기질 함량은 원자흡광도계와 유도 결합플라즈마 질량분석기로 분석하였다. 국내산 표고의 Na, Mg, K 및 Ca 함량은 161.33 mg/kg, 746.22 mg/kg, 17,676.84 mg/kg, 50.50 mg/kg으로 분석되었으며, 중국산의 경우 310.69 mg/kg, 318.49 mg/kg, 11,182.01 mg/kg, 33.36 mg/kg으로 분석되었다. 국내산 표고의 Cr과 Cu 함량은 2.82 mg/kg, 12.955 mg/kg으로 분석되었으며, 중국산의 경우 77.13 mg/kg, 101.19 mg/kg로 분석되었다. 국내산과 중국산 표고 모두 유해 중금속 함량은 식품공전 기준규격 이내로 검출되었다. 연구 결과 국내산과 중국산 표고의 Na, Mg, K, Cr 함량이 유의적인 차이를 나타내었다. 따라서 표고의 원산지 판별을 위해 Na, Mg, K, Cr 함량에 대한 추가적인 연구가 필요한 것으로 판단되었다.

Conflict of interests

The authors declare no potential conflict of interest.

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