



CAN BE BLUEBERRIES THE RISK FOOD AND RAW MATERIAL?

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ABSTRACT

Fruits of the highbush blueberries are popular for their beneficial effects on human health and for their excellent sweet-vine taste. Our work is focused on risk assessment of selected elements in relation to the content of bioactive compounds in wild and cultivated of highbush blueberries (*Vaccinium corymbosum* L.). Anthocyanins are polyphenols that are widely distributed in plants, and contribute to the brilliant blue, red or purple colour in leaves, flowers or fruits. In the samples the antioxidant capacity by the method of Brand – Williams using DPPH (2,2-difeny-1-pikrylhydrazyl) and the content of anthocyanins by the modified method Lapornik in two samples of wild blueberries from different areas of Slovakia (Čertovica and Oravské Veselé) and in 6 cultivated varieties highbush blueberry (Bluejay, Bluecrop, Patriot, Berkeley, Brigitta, Nelson) were determined. The contents of risky elements - Cd, Pb were assessed by AAS method. The contents of Pb were in all observed samples higher than the maximum limit given by the legislation (cultivated: 0.5612 – 0.9912 mg.kg⁻¹, wild: 0.792 – 0.874 mg.kg⁻¹). The measured content values of Cd were in all samples of blueberries lower than hygienic limit. The highest content of anthocyanins from analysed samples was in wild blueberries from surrounding Čertovica 4870.125 ± 22.803 mg.dm⁻³, but in this sample was simultaneously the lowest antioxidant capacity of 61.15 ± 1.002 %. The highest antioxidant capacity was measured in sample of cultivated variety Bluejay 87.175 ±

0.45 %. It is important to carry out monitoring of heavy metals to consumption of safe food raw materials and foodstuffs.

Keywords: blueberries, antioxidant capacity, DPPH, anthocyanins, heavy metals, AAS

INTRODUCTION

Blueberry is the fruit of the genus *Vaccinium*, which belongs to the *Ericaceae* family. It is recognized for its anthocyanin and flavonoid content, antioxidant activity (Prior et al., 1998), and for its potential health benefits (Smith et al., 2000). Anthocyanins are flavonoids (Rui et al., 2011), and colorant candidates (Maier et al., 2009), because they are representative pigments widely distributed in nature, and are responsible for the attractive red, purple and blue color in many fruits and flowers (Xiong et al., 2006). Anthocyanins also exhibit antioxidant activity (Malien-Aubert et al., 2001) and they possess characteristics known to be effective against cancer, heart and inflammatory diseases (Estupinan et al., 2011). Heavy metals are among the contaminants, which are characterized by different sources of origin, properties and action on living organisms (Tóth et al., 2005). Heavy metals are irreplaceable biological micronutrients (Cu, Zn, Fe) as well as numerous non-essential chemical elements (Cd, Pb, Cr, etc.). Toxic can be also biological irreplaceable microelements, if they exceed a certain concentration (Tomáš et al., 2001; Tóth et al., 2000). In terms of content of risk elements is especially high demands on the productive parts of plants that are used in human nutrition.

The aim of this study was on risk assessment of selected elements in relation to the content of bioactive compounds in wild and cultivated of highbush blueberries (*Vaccinium corymbosum* L.).

MATERIAL AND METHODS

The observation group were two samples of wild blueberries from two different areas of Slovakia (Čertovica and Oravské Veselé) and 6 cultivated varieties highbush blueberry (Bluejay, Bluecrop, Patriot, Berkeley, Brigitta, Nelson) from Regional Research Station at Krivá on Orava which is a remote branch of the Grassland and Mountain Agriculture Research Institute in Banská Bystrica.

We were performed analysis of lyophilized samples to determinate the concentrations of risk elements after "wet" mineralization by microwave digestion on *MARS X-press* equipment. Analytical extension was atomic absorption spectrometry on the *VARIAN AA 240 FS* equipment.

Antioxidant capacity was determined by the Brand - Williams method (1995), using a compound DPPH (2,2-diphenyl-1-pikrylhydrazyl) (Merck). 2,2-diphenyl-1-pikrylhydrazyl (DPPH) was pipetted to cuvettes (3.9 cm³), then was wrote the value of absorbance, which corresponded to the initial concentration of DPPH solution in time A₀. Then 0.1 cm³ of the followed solution was added and then was immediately started to measure the dependence A = f(t). The solution in the cuvette was mixed and measured the absorbance of 1, 5 and 10 minutes at 515.6 nm in the spectrophotometer *Shimadzu UV/VIS - 1240*. The percentage of inhibition reflects how is the followed compound able to remove DPPH radical at the given time.

$$\text{Inhibition (\%)} = \frac{A_0 - A_{10}}{A_0} \times 100$$

The content of anthocyanins was determined in fresh samples by the modified method of Lapornik (2005). From blueberries samples 25 g were homogenised and extracted by 50 cm³ 80 % ethanol during 16 hours. Into two tubes 1 cm³ of extract was pipetted and 1 cm³ 0,01 % HCl in 80 % ethanol was added. Then 10 cm³ 14 % HCl into the first tube and 10 cm³ McIlvain agens (pH 3,5) into another tube were added. Absorbance was measured at 520 nm against blank sample in the spectrophotometer *Shimadzu UV/VIS -1240*.

RESULTS AND DISCUSSION

Figures 1 and 2 show the content of risk metals Cd and Pb in selected berries cultivated varieties of highbush blueberry and wild blueberries in relation to the maximum limit given by the legislation Codex Alimentarius SR.

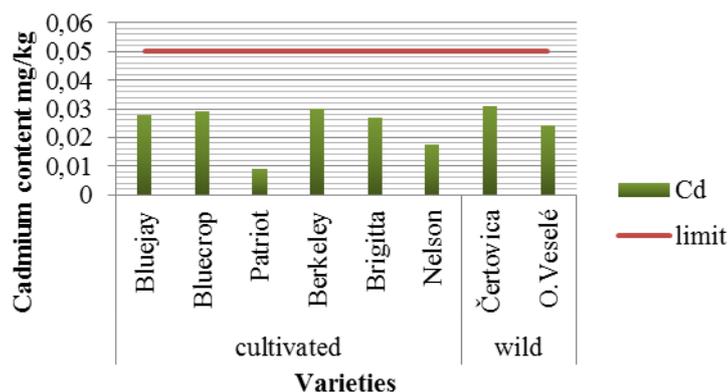


Figure 1 Cd content ($\text{mg}\cdot\text{kg}^{-1}$) in selected samples of cultivated and wild blueberries in relation to the hygienic limit

The measured values for the content Cd in observed blueberry fruits did not exceed in either variety the maximum amount of Cd which is defined in the Codex Alimentarius SR (PK SR: Cd $0.05 \text{ mg}\cdot\text{kg}^{-1}$). The average content of Cd in observed varieties of blueberries was $0.0244 \text{ mg}\cdot\text{kg}^{-1}$. Reimann et al. (2001) in their results indicate even lower values for the content Cd in the fruits of blueberries ($0.009 \text{ mg}\cdot\text{kg}^{-1}$).

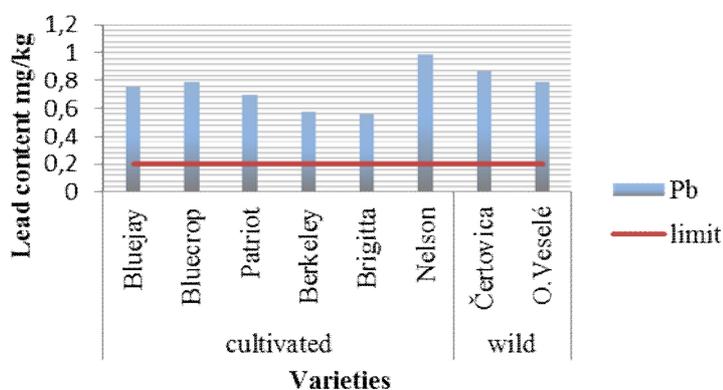


Figure 2 Pb content ($\text{mg}\cdot\text{kg}^{-1}$) in selected samples of cultivated and wild blueberries in relation to the hygienic limit

Contents of Pb were in all observed samples higher than the maximum limit given by the legislation (PK SR: Pb $0.2 \text{ mg}\cdot\text{kg}^{-1}$) from the 2.5-fold increase in the cultivated variety Brigitta to almost 5-fold increase in the cultivated variety Nelson. Reimann et al. (2001) indicate a significantly lower average content of Pb ($0.13 \text{ mg}\cdot\text{kg}^{-1}$) than the average content of Pb in our studied varieties of blueberries ($0.7538 \text{ mg}\cdot\text{kg}^{-1}$).

Figures 3 and 4 present the average contents of anthocyanins and antioxidant capacity in six cultivated varieties of highbush blueberries (*Vaccinium corymbosum* L.) and in two wild blueberries from different areas of Slovakia (Čertovica, Oravské Veselé).

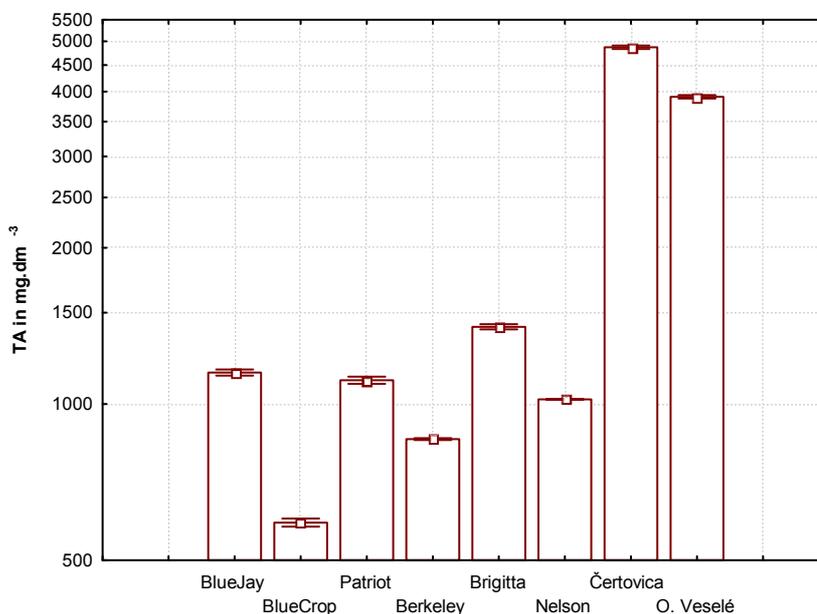


Figure 3 The content of anthocyanins (TA - total anthocyanins) in selected samples of cultivated and wild blueberries (mg.dm⁻³)

Figure 3 shows that the highest content of anthocyanins is in a sample of wild blueberries from the site Čertovica 4870.125 ± 22.803 mg.dm⁻³. Berries wild blueberries are small, dark violet to black, deep a wine sour taste. On the other side the lowest content of anthocyanins in studied samples blueberry variety Bluecrop (591.089 mg.dm⁻³) was determined. Berries of this variety are large to very large, light blue with waxy and full taste. Our results (cultivated varieties: $591.089 \pm 6.702 - 1408.94 \pm 10.065$ mg.dm⁻³) correspond with the findings of the authors Ścibisz a Mitek (2007), to determine the average content of anthocyanins in different varieties of blueberries in the range $450 - 1205$ mg.dm⁻³. The contents of anthocyanins in wild blueberries samples 4-fold excess of the upper limit fixed by the interval of the authors.

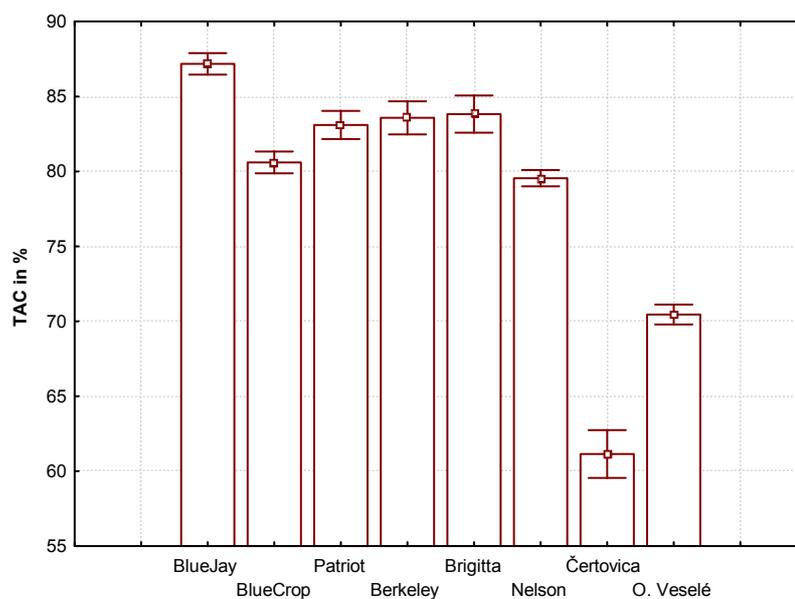


Figure 4 Antioxidant capacity (TAC – total antioxidant capacity) in selected samples of cultivated and wild blueberries, reported as % inhibition

Figure 4 shows the antioxidant capacity in 6 cultivated varieties, and 2 samples of wild blueberries from different areas of Slovakia. The highest antioxidant capacity was measured in the sample of the medium late variety Bluejay 87.175 ± 0.45 %. The lowest antioxidant capacity was measured in the sample of wild blueberries from the area Čertovica 61.15 ± 1.002 %. Su and Chien (2007) in his work determined the antioxidant capacity (60.6%), which corresponds to our findings that blueberries have high antioxidant capacity. Confirming the arguments the authors Smith et al. (2000), the bioactive extracts of wild blueberries, rich in anthocyanins and proanthocyanidins, exhibit antioxidant activity.

CONCLUSION

Blueberries contain bioactive compounds with potential health benefits. They are a rich source of macro and microelements, vitamins and other positive effective phytochemicals. They are also an important source of polyphenolic substances, flavonoids, especially anthocyanins and are characterized by high antioxidant capacity.

On the other side our results confirmed that blueberry fruit can accumulate relatively high content of some risk elements as Pb. In our samples the Pb content exceeded the hygienic limit given by Codex Alimentarius SR (2,5 – 5 fold). This fact can be connected not only with high Pb content in the soil, but also with contaminated atmosphere from industrial

sources, because wet and dry atmosphere deposition of Pb is one of the most important sources of Pb input into the plant raw materials. The summ of Pb in the plant is significantly influenced by the remote transport.

So, it is necessary to monitor heavy metal content in blueberry fruits to ensure the food safety and to support the significant benefit of this fruit to the human health.

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REFERENCES

- BRAND – WILLIAMS, W. – CUVELIER, M. E. – BERSET, C. 1995. Use of a free radical method to evaluate antioxidant activity. In *Lebensmittel-Wissenschaft und Technologie*, vol. 28, (1), 1995, p. 25 – 30.
- ESTUPINAN, D. C. - SCHWARTZ, S. J. - GARZÓN, G. A. 2011. Antioxidant activity, total phenolics content, anthocyanin, and color stability of isotonic model beverages colored with andes berry (*Rubus glaucus* Benth) anthocyanin powder. In *Journal of Food Science*, vol. 76, 2011, p. 26 – 34.
- LAPORNIK, B. - PROŠEK, M. - WONDRA, A. G. 2005. Comparison of extracts prepared from plant by-products using different solvents and extraction time. In *Journal of Food Engineering*, vol. 71, 2005, p. 214 - 222.
- MAIER, T. - FROMM, M. - SCHIEBER, A. - KAMMERER, D. R. - CARLE, R. 2009. Process and storage stability of anthocyanins and non-anthocyanin phenolics in pectin and gelatin gels enriched with grape pomace extracts. In *European Food Research and Technology*, vol. 229, 2009, p. 949 – 960.
- MALIEN - AUBERT, C. - DANGLES, O. - AMIOT, M. J. 2001. Color stability of commercial anthocyanin-based extracts in relation to the phenolic composition. Protective effects by intra and intermolecular copigmentation. In *Journal of Agricultural and Food Chemistry*, vol. 49, 2001, p.170 – 176.
- PRIOR, R. L. - CAO, G. - MARTIN, A. - SOFIC, E. - MCEWEN, J. - O'BRIEN, C. - LISCHNER, N. - EHLENFELDT, M., KALT, W. - KREWER, G. - MAINLAND, C. M. 1998. Antioxidant capacity as influenced by total phenolic and anthocyanin content, maturity,

and variety of *Vaccinium* species. In *Journal of Agricultural and Food Chemistry*, vol. 46, 1998, p. 2686 – 2693.

REIMANN, C. - KOLLER, F. - KASHULINA, G. - NISKAVAARA, H. - ENGLMAIER, P. 2001. Influence of extreme pollution on the inorganic chemical composition of some plants. In *Environmental Pollution*, vol. 115, 2001, p. 239 - 252.

RUI, L. - PING, W. - QING-QI, G. - ZHEN-YU, W. 2011. Anthocyanin composition and content of the *Vaccinium uliginosum* berry. In *Food Chemistry*, vol. 125, 2011, p. 116 - 120.

ŚCIBISZ, I. - MITEK, M. 2007. Antioxidant properties of highbush blueberry fruit cultivars. In *Food Science and Technology*, vol. 10, (4), 2007.

SMITH, M. A. L. - MARLEY, K. A. - SEIGLER, D. - SINGLETARY, K. W. - MELINE, B. 2000. Bioactive properties of wild blueberry fruits. In *Journal of Food Science*, vol. 65, 2000, p. 352 – 356.

SU, M. S. - CHIEN, P. J. 2007. Antioxidant activity, anthocyanins, and phenolics of rabbiteye blueberry (*Vaccinium ashei*) fluid products as affected by fermentation. In *Food Chemistry*, vol. 104, 2007, p. 182 - 187.

TOMÁŠ, J. - TÓTH, J. - LAZOR, P. 2001. Heavy metals content and distribution in soils in relation to soil hygiene. In *Polnohospodárstvo*, vol. 47, (1), 2001, p. 11 – 26.

TÓTH, J. - TOMÁŠ, J. - LAZOR, P. 2000. Hodnotenie bioprístupnosti kadmia, olova, medi, zinku a chrómu v silne kontaminovanej fluvizemi. In *Acta Fytotechnica et Zootechnica*, vol. 3, (1), 2000, p. 25 – 28.

TÓTH, T. - POSPÍŠIL, R. - PARILÁKOVÁ, K. - MUSILOVÁ, J. - BYSTRICKÁ, J. 2005. Distribúcia ťažkých kovov v pôdach aplikáciou substrátu po výrobe biokalu. In *ChemZi*, vol. 1, (1), 2005, p. 108 – 109.

XIONG, S. - MELTON, L. D. - EASTEAL, A. J. - SIEW, D. 2006. Stability and antioxidant activity of black currant anthocyanins in solution and encapsulated in glucan gel. In *Journal of Agricultural and Food Chemistry*, vol. 54, 2006, p. 6201 – 6208.