

## CHARACTERIZATION OF CORNELIAN CHERRY (*Cornus mas* L.) GENOTYPES - GENETIC RESOURCES FOR FOOD PRODUCTION IN CZECH REPUBLIC

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The aim of the study was to determine and compare both technological properties and polyphenol content in fruits of eight cornelian cherry (*Cornus mas* L.) cultivars from Czech Republic. The fruits of cultivar 'Vydubeckij' had the highest dry matter (17.4%) and soluble solid (15.8%) content among searched cultivars. The highest crude protein and phosphorus values were determined in the fruits of the 'Titus' cultivar as 10.9 g of crude protein and 435 mg of phosphorus for per kg fresh weight (FW) base. The 'Elegantnyj' and 'Vydubeckij' cultivars are found to be more suitable for canning industry. The fruits of the 'Vydubeckij' cultivar contained 10.8 g of pectin and 22.4 g of citric acid per kg fresh weight base, and could be important for technological use because of their excellent gelling ability. 'Devin', 'Vydubeckij' and 'Titus' cultivars had the most valuable source of chlorogenic acid (135.6, 110.9 and 115.1 mg per 100 g FW, respectively) and quercetin (24.9, 25.2 and 24.2 mg per 100 g FW, respectively).

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This work should contribute to the popularization of this fruit specie as a valuable source of technological parameters for human nutrition and the canning industry.

*Key words:* Cornelian cherry, diversity, fruit properties, industry

#### INTRODUCTION

Many underutilized fruit species are used as ornamentals, but only a few including cornelian cherry are grown for their edible fruits (ERCISLI, 2004). The flowering of cornelian cherry trees begins in early spring but give fruits in late period. The plant is also cultivated for landscaping designs (ROP *et al.*, 2010a).

Cornelian cherry is one of these species with significant antioxidant characteristics (GUNDUZ *et al.*, 2013). The fruits of cornelian cherry are used in different purposes, for example they are eaten fresh, dried, and pickled like olives, or they are used to produce jams, juices, syrups or wines or another traditional products (ROP *et al.*, 2010b; BIJELIC *et al.* 2011a). Cornelian cherry is widely found in the Moravia region of Czech Republic. During the Middle Ages, this specie was one of the most grown fruit in Moravia. Since 18th century, cornelian cherry has been replaced by plums. Today, the growers try to return to this partly forgotten fruit.

The recent studies showed that this unique fruit has high content of mineral elements and antioxidant substances such as carotenoids and polyphenols (GULCIN *et al.*, 2005, YILMAZ *et al.*, 2009; BIJELIC *et al.*, 2011b). MARINOVA *et al.* (2005) clearly outline that the cornelian cherry is richest phenolic sources (432 mg GAE/100 g) among fruits. However the fruits has low anthocyanins (PAULOVICSOVA *et al.*, 2009), which parallels the loss of the fruit's red pigment over time (JU and HSIEH, 2004). Owing to its nutritional, medicinal and industrial applications, cornelian cherry is a good source for dye, oil, tannin and wood industry (GOLOŠIN *et al.*, 2009; BOSNJAKOVIC *et al.*, 2012).

The objective of this study was to determine selected technological parameters – dry matter, soluble solid content (SSC), titrable acidity, the pectin content, the content of crude protein and phosphorus in fruits of eight cornelian cherry (*Cornus mas* L.) cultivars. Moreover, phenolic profile – the content of chlorogenic acid, gallic acid, rutin, resveratrol, quercetin and quercitrin was examined in eight cultivars by HPLC-ED method.

#### MATERIALS AND METHODS

##### *Biological materials*

Cornelian cherry fruits were harvested in experimental orchards of Tomas Bata University Zlin in Czech Republic. These orchards are situated in the south-western part of the White Carpathians near Zlin, the Czech Republic. The average altitude is 340 m above sea level, and the mean annual temperature and precipitation are 7.9 °C and 760 mm, respectively. The soil type was classified as the Mesotrophic Cambisol.

Fruit was harvested in commercial consume ripeness from three trees of each cultivar under study in the course of September 2010 and 2011. 20 randomly chosen fruits from each tree were used for analyses (i. e. altogether 60 fruits each cultivar). The fruit of particular cultivars was processed immediately after the harvest (not later than within two hours). Harvested fruits were pureed in a mixer and the average sample was obtained by dividing into quarters. Each parameter was measured in five replications.

The cultivars used were 'Elegantnyj', 'Jaltsky' and 'Vydubeckij' which are of Russian origin, 'Devin', 'Sokolnický' and 'Titus' with origin in Slovakia, and 'Joliko' and 'Fruchtal' which are Austrian origin.

#### *Chemical analyses*

The dry matter content of fruits was measured after drying off to a constant weight at the standard temperature of  $105\text{ °C} \pm 2\text{ °C}$  on the apparatus VENTICELL 111 (BMT, Brno, the Czech Republic). The soluble solid content was determined by means of polarimetric measurements in juice obtained after squeezing the fruit and the results were expressed as % Brix. For the measurement of SSC, a digital instrument HI 96801 (Hanna Instruments, Woonsocket, RI, the USA) was used. The content of total acids was measured by potentiometric titration of fruit water extract with sodium hydroxide to the pH value of 8.1 by using the apparatus pH 211 (Hanna Instruments, Woonsocket, RI, USA). The obtained result was converted to the content of acids (expressed as citric acid) in g per kg FW.

#### *Crude protein and phosphorus content*

The sample was dried to a constant weight in a drier at  $105\text{ °C} \pm 2\text{ °C}$ ; thereafter, 1 g of homogenised dry matter (with the size of particles 1 mm) was further mineralised in a mixture of concentrated sulphuric acid with 30% hydrogen peroxide. After the mineralization, the obtained samples were quantitatively transferred into a 250 ml volumetric flask and filled to the volume with re-distilled water. The amount of crude protein was determined on the basis of total nitrogen in the Kjeldahl apparatus KJELTEC TM 2300 and the result was multiplied by the coefficient 6.25. The content of phosphorus was measured by vanadate method using the spectrophotometer LIBRA S6 (Biochrom Ltd., Cambridge, UK).

#### *Pectin content*

The content of pectins was measured using the modified method described by Rop *et al.* (2011 a). 10 g of crushed fruit material were extracted with hydrochloric acid in a shaker at  $80\text{ °C}$  for 90 minutes. The hydrolyzate was quantitatively transferred into a 250 ml volumetric flask and filled to the volume with water. Pectins were thereafter measured by photometry as a coloured complex consisting of the product of thermal decomposition of galacturonic acid with *m*-hydroxybiphenyl in a medium containing concentrated  $\text{H}_2\text{SO}_4$ . Thereafter, samples of 5 ml were gradually taken off, put into 50 ml flasks and supplemented always with 6 ml of the solution of sodium tetraborate and 1.5 mg of *m*-hydroxybiphenyl in concentrated sulphuric acid, diluted with distilled water and finally boiled for 5 minutes. After 20 minutes of standing, the samples and the pectin standard were measured in the apparatus LIBRA S6 (Biochrom Ltd., Cambridge, UK) mentioned above at the wavelength of 520 nm and the content of pectins was expressed in g per kg of fresh weight.

#### *HPLC profile of selected antioxidants*

For the determination of the HPLC profiles of the individual cultivars, high performance liquid chromatography (HPLC) with electrochemical and UV-VIS detection was used. The system consisted of two Model 582 ESA chromatographic pumps (ESA Inc., Chelmsford, MA, USA) and a Zorbax SB C18 ( $150 \times 4.6$ ; size of particles  $5\text{ }\mu\text{m}$ , Agilent Technologies, USA) reverse phase chromatographic column. For UV detection, a Model 528

ESA UV detector was used. A twelve-channel CoulArray detector (ESA) was used for electrochemical detection. Samples were injected automatically by an autosampler (Model 542, ESA), which has incorporated a thermostatic space for a column. This method is described in detail in ZITKA *et al* (2011).

#### Statistical analysis

The data obtained were analyzed statistically by the analysis of variance (ANOVA) and Tukey's multiple range test for comparison of means at  $P < 0.05$  (SNEDECOR and COCHRAN, 1967). Correlation functions were calculated using the statistical package Unistat, v. 5.1 and Office Excel® Microsoft 2010.

### RESULTS AND DISCUSSION

The results of chemical analyses of fruit samples in cornelian cherry cultivars are shown in Tables 1 and 2 and content of polyphenolic compounds are given in Figure 1. The results were expressed as an average of a two-year experiment because there was not a statistically significant difference among the years in any parameter investigated.

Table 1. Dry matter content (% w/w), soluble solid content (% Brix), titrable acidity (g per kg FW) and pectin content (g per kg FW) of fruit of particular cornelian cherry cultivars (n = 15).

Cultivar	Dry matter	SSC	Titrable acidity	Pectin
Devin	16.28 ± 0.05 <sup>a</sup>	15.37 ± 0.09 <sup>a</sup>	16.71 ± 1.14 <sup>a</sup>	8.74 ± 0.42 <sup>a</sup>
Elegantnyj	17.42 ± 0.06 <sup>b</sup>	15.81 ± 0.11 <sup>b</sup>	23.02 ± 1.32 <sup>b</sup>	10.71 ± 0.35 <sup>b</sup>
Fruchtal	16.01 ± 0.06 <sup>c</sup>	14.95 ± 0.10 <sup>c</sup>	19.50 ± 1.41 <sup>c</sup>	8.93 ± 0.40 <sup>a</sup>
Jaltsky	23.64 ± 0.65 <sup>a</sup>	16.01 ± 0.10 <sup>c</sup>	19.70 ± 0.15 <sup>a</sup>	9.07 ± 0.29 <sup>a</sup>
Joliko	15.45 ± 0.04 <sup>d</sup>	14.58 ± 0.08 <sup>d</sup>	18.93 ± 1.71 <sup>c</sup>	8.70 ± 0.39 <sup>a</sup>
Sokolnicky	21.30 ± 1.12 <sup>a</sup>	16.34 ± 0.14 <sup>c</sup>	24.00 ± 0.11 <sup>b</sup>	9.89 ± 0.31 <sup>b</sup>
Titus	16.27 ± 0.05 <sup>a</sup>	15.19 ± 0.12 <sup>a</sup>	16.90 ± 1.05 <sup>a</sup>	8.66 ± 0.46 <sup>a</sup>
Vydubeckij	17.12 ± 0.06 <sup>e</sup>	15.46 ± 0.12 <sup>a</sup>	22.37 ± 1.22 <sup>b</sup>	10.80 ± 0.38 <sup>b</sup>

Different superscripts in each column indicate the significant differences in the mean at  $P < 0.05$ .

Table 2. Content of crude protein (g per kg FW) and content of phosphorus (mg per kg FW), (n = 15).

Cultivar	Crude protein	Phosphorus
Devin	10.62 ± 0.32 <sup>a</sup>	431.7 ± 12.7 <sup>a</sup>
Elegantnyj	7.65 ± 0.51 <sup>b</sup>	370.2 ± 14.2 <sup>b</sup>
Fruchtal	8.98 ± 0.32 <sup>c</sup>	321.8 ± 11.1 <sup>c</sup>
Jaltsky	11.45 ± 0.32 <sup>c</sup>	354.6 ± 0.9 <sup>a</sup>
Joliko	7.44 ± 0.30 <sup>b</sup>	363.2 ± 12.8 <sup>b</sup>
Sokolnicky	12.34 ± 0.35 <sup>a</sup>	259.9 ± 8.3 <sup>a</sup>
Titus	10.92 ± 0.40 <sup>a</sup>	435.1 ± 13.7 <sup>a</sup>
Vydubeckij	8.77 ± 0.36 <sup>c</sup>	361.1 ± 12.1 <sup>b</sup>

Different superscripts in each column indicate the significant differences in the mean at  $P < 0.05$ .

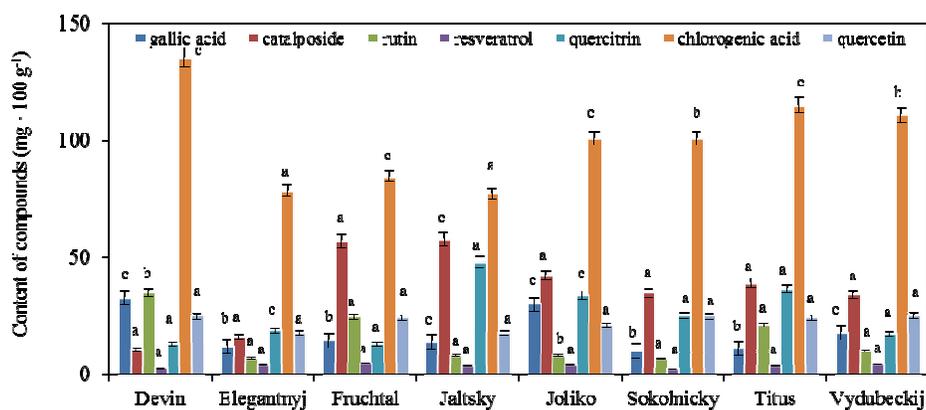


Figure 1. Content of polyphenolic compounds in 8 cultivars of cornelian cherry in mg/100 g FW. Different superscripts in each column indicate the significant differences in the mean at  $P < 0.05$ .

The highest dry matter content was obtained in the fruits of the 'Elegantnyj' cultivar (17.42%). Similarly, the 'Vydubeckij' cultivar contained high (17.12%) of dry matter, while the lowest value was detected in Fruchtal cultivar as 16.01% (Table 1). TURAL and KOCA (2008) reported higher values of dry matter (15.9-28.2%) in cornelian cherry cultivars grown in Turkey. Similarly BIJELIC *et al.* (2011) are also reported higher dry matter content (18.3-33.4%) in Serbia. The differences may have results of growing condition, genotypes used, cultural and technical treatments etc. (ERCISLI *et al.*, 2008; OGNJANOV *et al.*, 2009).

Parallel to dry matter, 'Elegantnyj' and 'Vydubeckij' cultivars had the highest soluble solid content as 15.8% and 15.5%, respectively (Table 1). In the studies of DOKOUPIL and REZNICEK (2012) the soluble solid content (SSC) of cornelian cherry was significantly high in Jolico (17.6%) cultivar compared to Jaltsky (16.0%) and Vydubecky (16.0%) that is in contrast with our results. The SSC in the samples of cornelian cherry grown in Iran was between 5.00 and 12.50% that is indicating lower values than our assayed cultivars (HASSANPOUR *et al.*, 2012). ERCISLI *et al.* (2011) reported SSC content in 13 local cornelian cherry genotypes grown in Turkey between 13.7% and 18.6%. On the other hand, BIJELIC *et al.* (2011) studied cornelian cherry fruits collected over wide areas of Serbia and reported soluble solid contents in a wide range of 17.4% to 32.4%. The soluble solid content indicates there is greater presence of sugars in the cultivars investigated. The sugar content is a major parameter with the influence on not only a direct consumption of fruits, but also on fermentation processes and it helps as one of food preservative aspects when increasing osmotic pressure of canning products. Regarding fermentation processes such as nutrients for yeast plants, nitrogen (in this work presented as crude protein) and phosphorus are the most important. From this point of view, the most valuable fruits are the Slovakian cultivars of 'Devin' and 'Titus' with the crude protein content of 10.6 g per kg FW and 10.9 g per kg FW and in case of phosphorus 431.7 g and 435.1 g per kg FW, respectively. The content of phosphorus in cultivars 'Elegantni', 'Fruchtal', 'Jaltsky', 'Jolico', 'Lukjanovsky', 'Vydubecky' and 'Vyšgorodsky' ranged between 313 and 412 mg per kg that are lower values than report of DOKOUPIL and REZNICEK (2012).

Fresh cornelian cherry fruits are not very rich in protein, a protein content represented of only 0.5 g/100 g of dry weight (BOSNJAKOVIC *et al.*, 2012). In our study, the content of crude proteins represented 7.44 (cv. Joliko)-12.34 (cv. Sokolnický) g per kg FW. On the other hand, ERCISLI *et al.* (2011) reported crude proteins from 7.5 to 21.8 g per kg FW in the samples of 13 local genotypes of cornelian cherry fruits originated from Turkey. While cornelian cherry fruit is not a rich source of proteins in general, it can be stated that the content of phosphorus is abundant. In particular, cornelian cherries are known for their high contents of mineral elements and in relation to phosphorus, on average they contain more of this element than apricots or peaches (ROP *et al.*, 2010a).

The highest pectin content (10.8 g per kg FW) was determined in the fruits of the 'Vydubeckij' cultivar. In addition, in the 'Elegantnyj' cultivar had more than 10 g of pectin per kg FW. The fruits of the 'Elegantnyj' cultivar contained 23 g of citric acid per kg, which higher value in comparison with result of DOKOUPIL and REZNICEK (2012) and it is more than in other stone fruit species. For example, in apricots the value is around 13 g per kg and in plums it is on average 10 g per kg (NUNES *et al.*, 2006; PINA and ERREA, 2006). In comparison with apricots or plums, which have on average 9.7 and 8.6 g per kg FW (ROP *et al.*, 2009), these results are comparable with them. On the other hand, DOKOUPIL and ŘEZNÍČEK (2012) examined higher values of pectin in cultivars Jaltsky (15.5 g per kg), Jolico (14.7 g per kg) and Vyšegorodsky (15.0 g per kg) and organic acids was the highest in variety Fruchtal (27.8 g per kg) and Jolico (22.8 g per kg). On the other hand, in another studies there is a wider range of organic acid content between 12.4-46.9 g per kg (OGNJANOV *et al.*, 2009) and (4.3-18.6 g per kg) (HASSANPOUR *et al.*, 2012) in cornelian cherry fruits.

The utilization of cornelian cherry fruits has a long tradition in Central Europe. Owing to high antioxidant capacity the interest in this fruit is growing nowadays. The technological parameters are also worth noticing since they are important for food processing (SOCHOR *et al.*, 2013).

It can be stated that cornelian cherries are a suitable fruit species for the processing to canning products and this work should also contribute to the repopularization of this fruit species. For food processing antioxidant activity is very important parameter of fruit nutritional value (GAZDIK *et al.*, 2008a). In cornelian cherry fruit, phenolic compounds and flavonoids mostly contributed to antioxidant properties of fruits (ROP *et al.*, 2010b).

Determination of polyphenolic compounds is one of possibilities to express biological and nutritive value of fruits (SOCHOR *et al.*, 2010c; SOCHOR *et al.*, 2011). Phenolic compounds are very suitable for utilization as chemotaxonomic markers (ROP *et al.*, 2011b). Qualitative and quantitative composition of phenolics in fruits is typical and unique for individual species and cultivars (JURIKOVA *et al.*, 2012a; JURIKOVA *et al.*, 2012b). Polyphenolic compounds are mostly associated with antioxidant properties of the fruit (SOCHOR *et al.* 2010a; SOCHOR *et al.*, 2010b; ROP *et al.*, 2013). There is at least 16 phenolic compound in the water extract of *Cornus mas* sp. fruits detected by HPLC method. Several identified compounds were myricetin-3-arabinose, quercetin-3-galactoside, pelargonidin-3-galactopyranoside, and gallic acid (JU and HSIEH, 2004). According to GULCIN *et al.*, (2005), flavonoids and phenolic acids mostly contributed to antioxidant activity of *Cornus mas* fruits.

It is evident that in all assayed samples of cornelian cherry cultivars chlorogenic acid represented the major polyphenolic compounds. In presented study, the content of chlorogenic acid reached from 77 mg (cv. Jaltsky) up to 135 mg/100 g FW (cv. Devin) that are lower than

in another lesser known fruit species-*Lonicera* spp. (86-267 mg/100 g FW), *Morus* and *Amelanchier* (245; 298 mg/100 g FW) (JURIKOVA *et al.*, 2012a). Vydubeckij and Titus cultivars displayed highest content of total polyphenolic and antioxidant activity of fruit (ROP *et al.*, 2010a) and in presented study they represented the the second richest sources of chlorogenic acid content. Moreover, Vydubeckij had the highest content of quercetin. Except for chlorogenic acid, gallic acid was detected between 11 mg (Titus)-32 mg/100 g FW (Devin). Quercitrin was the most presented polyphenols with flavonoid scaffold (12 mg in Fruchtal-36 mg/100 g FW in Titus), followed by rutin (6 mg in Sokolnicky-35 mg/100 g FW in Devin) and quercetin (17 mg in Jaltsky-25 mg/100g FW in Vydubeckij). This results are in contrast to studies provided by PAWLOWSKA *et al* (2010) examined quercetin 3-O- $\beta$ -D-glucuronide as the major flavonoid constituents of *Cornus mas* fruits.

In same way ISSAK *et al* (2013) analysed individual flavonoids in samples of *Cornus stolonifera* revealed the highest levels of rutin and glycoside of quercetin and also higher amount of quercetin reported by GAZDIK *et al* (2008b) in cultivar Vyšegradskij as 47 mg/100 g FW. In generally, quercetin is the predomint flavonol in fruit reach up lesser amount than 15-30 mg/kg FW. The content of quercetin in Vydubeckij and rutin in Elegantnij cultivars are in accordance with results of GAZDIK *et al.* (2008a) analysed the same cultivars by HPLC-ED method.

### CONCLUSIONS

Human health and nutrition are still one of the most studied and also interested topics. One of the current trends of food processing is searching and enriching of raw plant material. One of the possibilities is Cornelian cherry (*Cornus mas* L.), woody plant, originated in Central Europe. The aim of presented paper was to compare 8 cultivars of mentioned specie in term of parameters important for fermentation processes (refractometric dry matter, soluble solids, the total content of pectin etc.). Vydubeckij was the most perspective cultivar with dry matter content 17.4% and soluble solids content 15.8%. For fermentation processes it is also important the content of total proteins and phosphorus that was examined as highest in fruits of cultivar 'Titus' - 10.9 crude proteins per kg FW and 435.1 mg phosphorus per kg FW. Cultivars 'Elegantnyj' or 'Vydubeckij' are perspective in canning industry and for production of fruit jellies. Fruits of cultivar 'Vydubeckij' contained 10.8 g pectines per kg FW and 22.3 g citric acid per kg, that are mostly important for which is ideal for use with excellent gelling abilities. 'Devin', 'Vydubeckij' and 'Titus' represented the perspective cultivars in term of content of chlorogenic acid (135; 110, 115 mg/100 g FW) and quercetin (24.9, 25.2 and 24.2 mg/100 g FW). The results indicating importance of this native specie as valuable source of food for utilization in nutrition and food processing as well.

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### **KARAKTERIZACIJA GENOTIPOVA TREŠNJE (*Cornus mas* L.) KAO GENETIČKIH RESURSA ZA PROIZVODNJU HRANE U ČEŠKOJ REPUBLICI**

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#### Izvod

Cilj istraživanja je bio determinacija i poređenje tehnoloških osobina i sadržaja polifenola u plodovima osam genotipova trešnje (*Cornus mas* L.) u Češkoj republici. Među ispitivanim genotipovima plodovi genotipa „Vydubeckij“ su imali najveći sadržaj suve i rastvorljivih supstanci, plodovi genotipa „Titus“ najviše sirovih proteina i fosfora po kilogramu sveže materije. Za „Elegantnyj“ i „Vydubeckij“ je utvrđeno da su najpogodniji za industriju konzerviranja. Plodovi „Vydubeckij“ sadrže 10.8 g of ptkinai 22.4 g limunske kiseline po kg sveže mase i imaju veliku sposobnost želatizacije. „Devin“, „Vydubeckij“ i „Titus“ su utvrđeni kao najvredniji izvor hlorogene kiseline (135.6, 110.9 i 115.1 mg / 100 gsveže materije) i kvercitunga (24.9, 25.2 and 24.2 mg /100 g sveže materije). Ova ispitivanja doprinose popularizaciji ove voćne vrste kao kvalitetan resurs u industriji proizvodnje hrane.

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