Variability of Characteristic Components of Aronia

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Abstract

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The variability of characteristic components of aronia (*Aronia melanocarpa*, black chokeberry) and to evaluate the chemical composition and quality of aronia products in order to complete the already available data and to facilitate authentication of fruit products were estimated. The mean values obtained for the set of aronia fruits were: soluble solids 19.9 °Brix, titratable acidity 9.8 g malic acid/kg, formol number 11.9 ml 0.1M NaOH/100 g, ash 6.7 g/kg, phosphorus 0.34 g/kg, potassium 2.90 g/kg, calcium 0.27 g/kg, magnesium 0.16 g/kg, sucrose 0.10 g/kg, glucose 47.1 g/kg, fructose 37.8 g/kg, sorbitol 66.1 g/kg, malic acid 9.6 g/kg, citric acid 1.0 g/kg, quinic acid 5.0 g/kg, isocitric acid 0.02 g/kg. These values can potentially be a useful tool to determine aronia content in foodstuffs or to determine adulteration of other fruit-based products with aronia. The most promising markers appeared to be the content of sorbitol, quinic acid and characteristic profile of anthocyanins measured by HPLC.

Keywords: *Aronia melanocarpa* L.; chokeberry; chemical composition; authenticity

Aronia, also known under the name chokeberry, has origins in North America before spreading all over the world. The genus of this fruit includes three species: *Aronia arbutifolia* [L.] Elliot (red chokeberry), *Aronia melanocarpa* [Michx.] Elliot (black chokeberry), and *Aronia prunifolia* (Marsh.) Rehd. (purple chokeberry). Aronia is cultivated as an ornamental plant and also for its high nutritional value, antioxidant properties and characteristic taste. The name chokeberry comes from the astringency of the fruits. A lot of aronia genotypes are known and the most important in Europe are: Aron (Denmark), Nero (Czech Republic), Viking (Finland), Rubin (Russia through Finland), Kurkumäcki (Finland), Hugin (Sweden), Fertödi (Hungary) (Jeppsson 1999; Janick & Paull 2008).

Originally, the extended cultivation was developed due to a deep purple pigment resulting from their high content of anthocyanins and consequently it was used as a natural colourant in food and pharmaceutical industries. The food industry mainly produces aronia juices and syrups. But the fruits can also be eaten raw, dried or used to make compotes, jams, wines, and liqueurs. Because of the aronia sour and astringent taste, juice consumers prefer mixture products with other kinds of fruits, such as apple, pear, and black currant (Lehmann 1990; Ara 2002).

The chemical composition of aronia is highly variable and depends on many factors, especially on genotype (or hybrid), degree of ripeness, climate, date of harvesting and on the use of fertilisers (Jeppsson 2000; Skupień & Oszmiański 2007).

Aronia fruits are characterised by a high biological and nutritional value. They contain vitamins B (B_1, B_2, B_6, niacin, pantothenic acid), vitamin C (13–270 mg/kg), β-carotene (7.7–16.7 mg/kg), a significant amount of dietary fibre (approx. 55 g/kg according to Kulling and Rawel 2008), minerals

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(4.4–5.8 g/kg as ash value), approx. 16–18% of carbohydrates (glucose, fructose, sorbitol) and 1–1.5% of organic acids (malic, quinic, citric). The specific almond smell is imparted by cyanogenic glycosides – amygdalin (20 mg/100 g fresh weight – FW) (Lehmann 1990; Kulling & Rawel 2008).

Phenolic compounds are the most important constituents present in aronia, which are also responsible for many of its medicinal properties. Aronia berries have a high content of procyanidins, anthocyanins and phenolic acids. Procyanidins, oligomeric and polymeric (epi)catechins (1578–8191 mg/100 g dry weight – DW), were identified as the major class of polyphenolic compounds in chokeberries (Oszmiański & Wojdylo 2005).

The berries contain 460 mg anthocyanins/100 g FW, mainly cyanidin-3-galactoside and cyanidin-3-arabinoside, which are reported to constitute 64% and 29% of the total amount of anthocyanins, respectively, and are found in the peels as well as throughout the fruit flesh. Aronia was found to be also a very rich source of phenolic acids (chlorogenic and neochlorogenic, approx. 96 mg/100 g FW) (Jeppsson 2000; Benvenuti *et al.* 2004; Oszmiański & Wojdylo 2005).

The intention of this paper is to contribute to a better understanding of the composition, potential of the nutritional contribution and authenticity proof of aronia (*Aronia melanocarpa*) berries and derived products. The emphasis is laid thereby upon the variability and stability of selected nutritive parameters to assess potential adulteration or incorrect labelling of fruit based products.

MATERIAL AND METHODS

Material. We obtained ten samples of aronia fruit from nine different geographic locations in the Czech Republic, and one sample from Poland. These samples were collected between 2010 and 2012, homogenised and stored frozen at –18°C. Two of these samples were dried, reconstituted by demineralised water (Milli Q quality), homogenised and stored frozen at –18°C. From the market, we acquired three samples of juices, one syrup sample, one compote sample and two samples of jams. Samples were homogenised and stored frozen at –18°C. Country of origin, composition and declared fruit content are summarised in Table 1.

Chemicals. Chemical standards used in this study were purchased from Sigma-Aldrich (St. Louis, USA): sucrose (99.5%), glucose (D(+), 99%), fructose (D(–), 99%), sorbitol (D, 98%), quinic acid (D(–), ≥ 98%), shikimic acid (> 99%), gallic acid monohydrate (≥ 98%) and cyanidin-3-glycoside (≥ 95%). Malic acid (DL, ≥ 99%) was purchased from Carl Roth (Karlsruhe, Germany) and citric acid (monohydrate, 100.4% p.a.) from Lachner (Neratovice, Czech Republic).

Methods. Soluble solids content was determined according to the standard ČSN EN 12143:1998. Titratable acidity was determined by titration according to ČSN EN 12147:1998. Formol number was determined by titration under pH 8.1 according to ČSN EN 1133:1996. Ash was determined by gravimetry according to ČSN EN 1135:1996. Phosphorous was determined according to ČSN EN 1136:1996. Cations (potassium, magnesium and calcium) were determined by isotachophoresis according to Kvasnicka *et al.* (1993).

Major sugars (sucrose, glucose, fructose) and sorbitol were determined by HPLC/RI according to Opatová *et al.* (1992) with one modification: the column temperature was kept at 80°C and the flow rate was 1 ml/minute. Major acids (malic, quinic, and citric acid) were determined by HPLC/DAD according to Scherer *et al.* (2012) with some modifications: the temperature of the column was kept at 30°C; the mobile phase consisted of 0.02 mol/l potassium phosphate monobasic (KH_2PO_4) in water, pH 2.5 was equilibrated with phosphoric acid. The extract for determination of total phenolic content and total anthocyanins was prepared according to Jakobek *et al.* (2007). Total phenolics content was determined by the Folin-Ciocalteu method according to Velioglu *et al*. (1998). Total anthocyanin content was determined by the pH differential method according to Jakobek *et al.* (2007). Anthocyanin profile was examined by the reverse phase HPLC method according to IFU (1998).

Table 1. Country of origin, fruit content and composition of single fruit products

Sample	Country	Fruit content (%)	Composition
Juice 1	Germany	100	aronia fruit
Juice 2	Germany	100	aronia fruit
Juice 3	Germany	100	aronia fruit
Compote	Czech Republic	70	aronia fruit, water, sucrose, citric acid
Jam 1	Czech Republic	50	aronia fruit, sucrose, pectin
Jam 2	Czech Republic	70	aronia fruit, sucrose, rum
Syrup	Germany	53	aronia fruit, sucrose

Table 2. Variability in the chemical composition data on 8 native fruits and 2 dried fruits of aronia (after reconstitution), comparison with literature data

Marker	From	To	Mean	Median	Literature data	Reference	Proposed mean value[1]	Comments
Soluble solids (°Brix)	15.2	22.9	19.9	20.7	11.3–24.3	Hukkanen *et al.* (2006); Skupień and Oszmiański (2007)	19.9	Soluble solids are directly related to the fruit content, but are influenced by the ripeness stage or by the addition of ingredients such as sugars and acids.
Titratable acidity (g malic acid/kg)	6.7	11.9	9.8	9.7	7.0–14.1	Jeppsson (1999); Hukkanen *et al.* (2006)	9.8	The acidity is influenced by the ripeness stage or by the addition of acids as additives.
Formol number (ml 0.1M NaOH/100 g)	10.0	19.9	12.7	11.3	6.5–14.0	Ara (2002)	11.9[2]	Formol number is directly related to the fruit content.
Ash (g/kg)	4.2	11.8	7.6	7.2	3.6–7.0	Lehmann (1990); Kopec (1998)	6.7[2]	–
Phosphorus (mg/kg)	257.0	417.5	340.6	319.8	260.0–830.0	VÚP SK (2009); Kopec (1998)	340.6	Phosphorus value is influenced by technological processing.
Potassium (mg/kg)	1356.3	3659.7	2748.5	2794.2	1969.0–2850.0	Kulling and Rawel (2008); Ara (2002)	2903.2[2]	A lower potassium value can be caused by fruit substitution (such as strawberries, raspberries, apples).
Calcium (mg/kg)	119	552.3	271.9	218.0	80.0–322.0	Ara (2002); VÚP SK (2009)	271.9	Calcium value is influenced by technological processing.
Magnesium (mg/kg)	83.3	314.2	155.4	120.0	90.0–280.0	Ara (2002)	155.4	Magnesium value is influenced by technological processing.
Sucrose (g/kg)	0.0	0.7	0.1	0.0	0.0–15.0	Ara (2002); Skupień and Oszmiański (2007)	0.10	Sucrose is not present in the fruit. Its detection indicates the addition of sugar or other type of fruit.
Glucose (g/kg)	36.3	57.0	47.1	47.4	30.0–60.0	Ara (2002)	47.1	Higher glucose values indicate sugar addition and/or fruit substitution.
Fructose (g/kg)	26.0	47.1	37.8	38.7	28.0–58.0	Ara (2002)	37.8	Higher fructose values indicate sugar addition and/or fruit substitution.
Sorbitol (g/kg)	46.3	85.6	66.1	70.0	42.0–100.0	Hofsommer and Koswig (2005); Ara (2002)	66.1	Lower sorbitol values indicate potential dilution or fruit substitution.
Glucose:fructose	1.1	1.4	1.3	1.3	1.0–1.1	Ara (2002)	1.3	Different ratio may indicate microbial contamination or fruit substitution or sugar addition.
Malic acid (g/kg)	4.5	12.8	9.1	9.2	5.0–19.0	Ara (2002)	9.6[2]	L-Malic acid is the major one. D-malic acid is not present in aronia and its detection indicates its addition as an additive.
Citric acid (g/kg)	0.7	1.3	1.0	0.9	0.2–2.1	Ara (2002); Kulling and Rawel (2008)	1.0	If the value is higher, it may be supposed that citric acid has been added as an additive.
Quinic acid (g/kg)	4.1	6.8	5.0	4.5	1.5–5.0	Ara (2002)	5.0	A lower concentration of quinic acid indicates dilution or fruit substitution.
Isocitric acid (mg/kg)	17.2	37.3	24.0	21.9	30–100	Ara (2002)	24.0[3]	A lower concentration of isocitric acid indicates dilution or addition of extraneous fruit.
Total polyphenols (mg GAE/kg)	6872	8223	9724	8156	6902–25 560	Benvenuti *et al.* (2004); Zheng and Wang (2003)	–	The value of total polyphenols is influenced by technological processing.
Total anthocyanins (mg cya-3-glu/kg)	2055	6231	5006	5386	4280–4605	Zheng and Wang (2003); Benvenuti *et al.* (2004)	–	Unstable; pH, temperature, light, oxygen, metal ions are generally known to affect the colour and stability of anthocyanins.

[1]In most cases proposed mean values are the same as mean values obtained for the analysed set of authentic aronia fruits; [2]In some cases (formol number, ash, potassium, malic acid) calculated mean values were proposed as mean values for the analysed set of authentic aronia fruits, but some outliers were removed in accordance with the literature (e.g. for the calculation of malic acid the lowest value 4.5 g/kg was removed, because it was found only in one case of dried fruit and the other values of fresh aronia were higher than 8.1 g/kg); [3]The robustness of the parameter of isocitric acid cannot be verified due to the lack of literature references

Statistical analysis. The tests were done in triplicate for each sample and the mean values are reported. All statistical analyses were performed using Excel 2007 (Microsoft, Redmond, USA).

RESULTS AND DISCUSSION

Most of the recent works that evaluated the quality of fruit juices, purées or fruit products, come out with the confirmation that declared composition and real composition are different and identify an undeclared sugar content, the addition of other fruits and organic acids (Fügel *et al.* 2005). For the evaluation of fruit content, the traditional approach, based on the assessment of the range of components that appear in the fruit over a relatively narrow range, is used. In European conditions, the A.I.J.N. Code of Practice (COP) (Anonymous 2011) is used as a source for the chemical composition (and its variability and stability) of authentic fruits. Because the COP database is limited to the 22 most common species, it remains a problem to prove the quality and authenticity of products contained in other fruits. Aronia berries are among them.

In this work, at first the set of parameters of authentic raw materials (aronia berries) was measured in order to design the variability and mean values of characteristic components, according to which the authenticity of products could be subsequently evaluated. In conformity with the recommendation of COP, it is necessary, apart from analytical determination, to assess the results (i.e. removal of outliers) from the aspect of the influence of maturity, addition of ingredients (especially sugars and acids) or analytical error. Chemical composition data of authentic samples, data found in the literature, proposed mean values and comments for each marker are shown in Table 2. Aronia berries differ from other fruit species in their high content of anthocyanins, sorbitol, and quinic acid and in a very low concentration of sucrose.

The real fruit content of aronia products (commercial samples) is calculated proportionally to the proposed mean values of measured raw materials, according to formol number and concentration of sucrose, glucose, fructose, sorbitol, ash, phosphorus, potassium, titratable acidity, citric acid, malic acid and quinic acid, the outlier values are removed. Fruit estimation is loaded with relatively high error caused by considerable variability of selected markers in the raw material. Estimated fruit contents of products which were declared as pure single fruit are shown in Figure 1. The differences between the

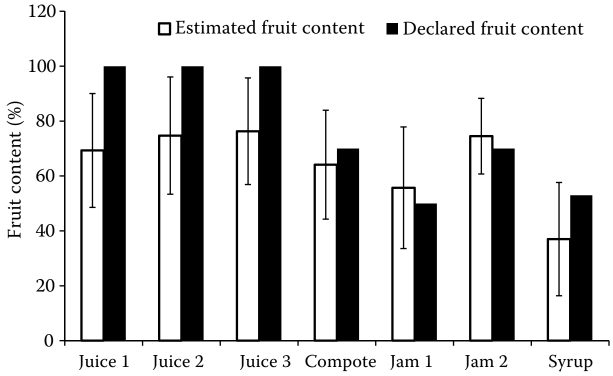

Figure 1. Estimated fruit content of products which were declared as single fruit

estimated and declared values varied usually within the relative high error of calculation (RSD 19.7%), but almost half of the analysed samples failed to confirm the fruit content declared on the label. This can be caused either by the insufficient sensitivity of the calculation approach to the variation in recipes and composition of the aronia products or by the low or altered quality of raw materials or by the intentional reduction of the fruit (aronia) content by producers.

The nutritive value of aronia products closely correlates with the fruit content, while the highest total polyphenols and total anthocyanin content was found in the samples with higher fruit content (Figure 2). The concentration of total polyphenols in the samples varied from 2550 to 12 000 mg (gallic cid equivalent (GAE)/kg and the content of anthocyanins ranged from 104 to 651 mg cyanidin-3-glucoside (cya-3-glu)/kg. However, phenolic compounds are unstable and degrade during the tech-

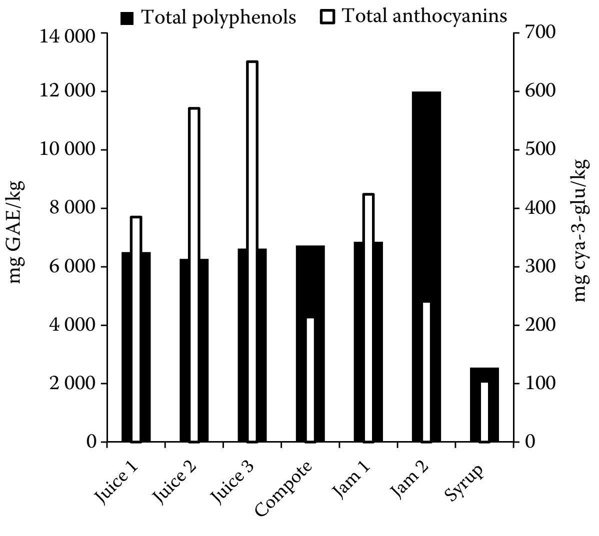

Figure 2. Total phenolic content and total anthocyanin content in aronia products (GAE – gallic acid equivalent)

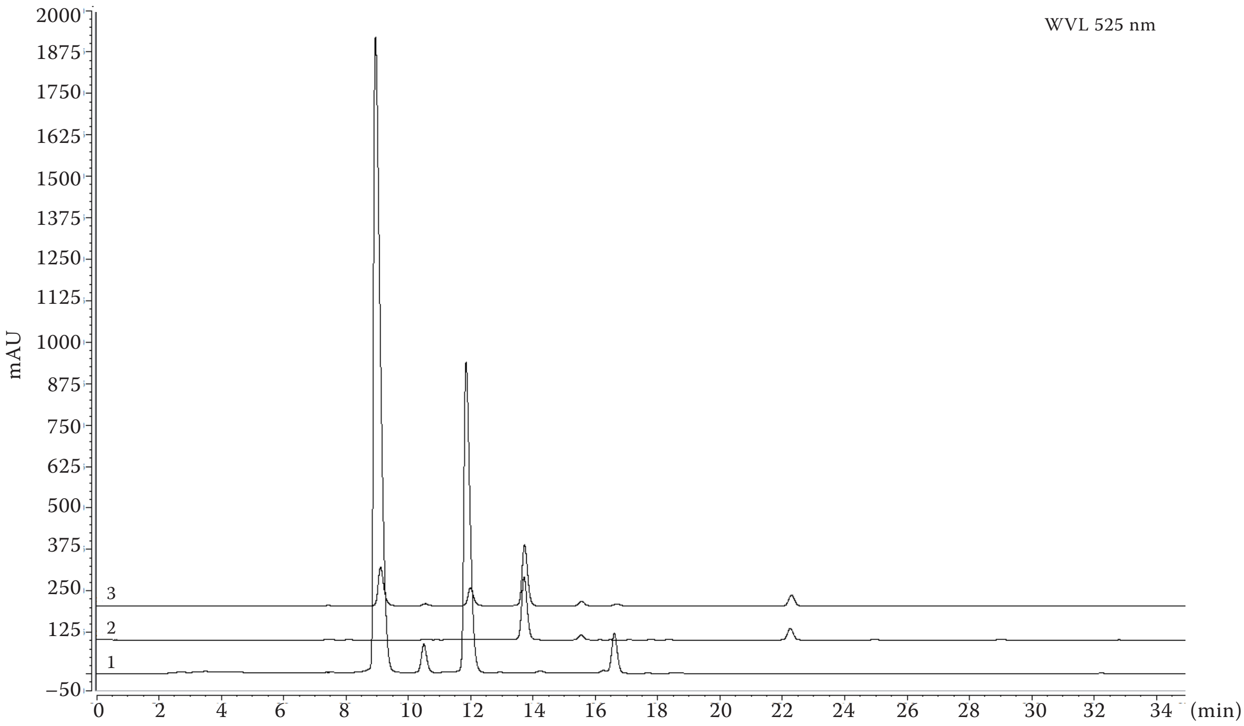

Figure 3. HPLC chromatographic profiles of anthocyanins in aronia [cyanidin-3-galactoside (t = 8.8 min); cyanidin-3-glucoside (t = 10.3 min); cyanidin-3-arabinoside (t = 11.7 min); cyanidin-3-xyloside (t = 16.4 min)] and strawberry [pelargonidin-3-glucoside (t = 13.7 min); pelargonidin-3-rutinoside (t = 22.3 min)]

1 – aronia, 2 – strawberry, 3 – 5% addition of aronia to strawberries

nological processing and storage. In the case of our samples, an approx. 90% decline of anthocyanins was observed after conversion to the real fruit content. Therefore, these parameters cannot be used for the calculation of fruit content of aronia products but they are powerful tools as qualitative markers. The characteristic profile of anthocyanins measured by HPLC can be used for the detection of undeclared colouring of juices and jams (such as strawberry, raspberry, black currants) by aronia fruits or extracts of aronia fruits. As an example, Figure 3 shows overlaid chromatograms of aronia, strawberry and 5% addition of aronia to strawberries. It is evident in this figure that the authentic strawberries have a different anthocyanin profile from aronia, so a 5% addition of aronia would be detected very easily.

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