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Stability of polyphenols in chokeberry juice treated with gas phase plasma

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ABSTRACT

Chokeberry juice was subjected to cold atmospheric gas phase plasma and changes in hydroxycinnamic acids, flavonols and anthocyanins were monitored. Plasma treatments were carried out under different treatment times and juice volumes under constant gas flow (0.75 $dm^3\ min^{-1}$). The results were compared against control (untreated) and pasteurized chokeberry juice (80 °C/2 min). During pasteurization, the most unstable were hydroxycinnamic acids with losses of up to 59%, while flavonols and anthocyanins increased by 5% and 9%, respectively. On the contrary, plasma treated chokeberry juice showed higher concentrations of hydroxycinnamic acids and 23% loss of anthocyanins in comparison to untreated juice. In order to obtain the optimal cold plasma treatment parameters principal component and sensitivity analysis were used. Such parameters can be potentially used for pasteurization in terms of phenolic stability of chokeberry juice. Optimal treatment was at 4.1 min and sample volume of 3 cm^3.

1. Introduction

Chokeberries (*Aronia melanocarpa*) have attracted considerable attention as a functional food due to high levels of phenolic phytochemicals (Bolling et al., 2015; Lee et al., 2014). The potential health benefits of phenolics from chokeberries received high interest as a result of their significant antioxidant properties (Denev, Kratchanov, Ciz, Lojek, & Kratchanova, 2012). The major class of chokeberry phenolic compounds are flavonoids, mainly anthocyanins, the most quantitatively important polyphenolics present in form of a cyanidin derivatives (Jakobek, Seruga, & Krivak, 2011). High levels of hydroxycinnamic acids and proanthocyanidins were also reported, while flavonols (quercetin glycosides), and flavan-3-ols were present, but in lower amounts (Taheri, Connolly, Brand, & Bolling, 2013). These polyphenols contribute to the high *in vitro* antioxidant activity of chokeberry extracts (Jakobek et al., 2011). Likewise, they contribute to antioxidant and anti-proliferative activity, show positive impact on inflammatory status and hepatoprotective, antiatherogenic, and cardioprotective effects (Daskalova et al., 2015; Stanisavljevic et al., 2015).

Chokeberries are not only consumed fresh but also processed into various products including juices, nectars, wines and liqueurs. Moreover, chokeberry by-products can be valuable ingredients used for the preparation of extracts with high content of bioactive compounds (Ramic et al., 2015). Today, many juice manufacturers produce chokeberry juice (CJ) due to increased consumers' demand for this foods and increased number of reported nutritional and health benefits. The stability of polyphenolic compounds in berries during processing seems to be highly correlated with the processing technology (Barba, Galanakis, Esteve, Frigola, & Vorobiev, 2015).

Previous reports indicated that non-conventional technologies represent a promising tool to recover high-added value compounds from winery wastes and by-products. Further, it was observed that processing and storage of chokeberry nectars and purees resulted with substantial decrease of anthocyanins (Trost, Golc-Wondra, Prosek, & Milivojevic, 2008). Furthermore, some reports indicated that flavonols, total proanthocyanidins, and hydroxycinnamic acids were retained in the chokeberry juice to a greater extent than anthocyanins, which were extensively degraded by thermal processing (Wilkes, Howard, Brownmiller, & Prior, 2014). Thermal processing is the most widely used technology for pasteurization of fruit juices, even though the applied heat can cause complex physical and chemical reactions, affecting the phenolic composition and stability.

Presently, non-thermal technologies are regarded with special interest as an alternative to conventional thermal methods, such as pasteurization, since they preserve original nutritional and sensory characteristics of fresh foods. Conventional thermal methods

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are based on heating process that facilitate the mass transfer between the different phases of the system, consume lots of energy and may promote the degradation of thermolabile compounds, such as polyphenols (Barba, Parniakov et al., 2015; Barba, Terefe, Buckow, Knorr, & Orlien, 2015; Barba, Zhu, Koubaa, Sant'Ana, & Orlien, 2016; Zinoviadou et al., 2015). Cold atmospheric gas phase plasma as non-thermal technology has been investigated intensively for providing both, microbial safety and polyphenols stability in fruit juices (Bursać Kovačević et al., 2016; Herceg et al., 2015; Režek Jambrak et al., 2014). Plasma is a neutral ionized gas characterized by active particles in permanent interactions such as: photons, electrons, positive and negative ions, atoms, free radicals, and excited or non-excited molecules. This treatment can be categorized by its thermodynamic properties into thermal and non-thermal plasmas (Schluter et al., 2013). Contrary to thermal plasma, non-thermal plasma (with temperatures below 70 °C) is obtained at lower pressures and with drastically different electron and gas temperatures. In particular, the electron temperature in non-thermal plasmas can reach up to 10,000 K, whereas the entire gas temperature can be close to the room level, hence the term "cold plasma" (Schluter et al., 2013). Due to low operating temperatures and simultaneous high antimicrobial effects, cold plasma may be regarded as a future alternative for thermal pasteurization. The impact of cold plasma on the chemical composition of plant foods has been studied with lamb's lettuce, pomegranate and apple juices, where positive influences of this treatment on phenolic stability and color were observed (Bursać Kovačević et al., 2016; Grzegorzewski, Rohn, Kroh, Geyer, & Schluter, 2010; Surowsky, Frohling, Gottschalk, Schluter, & Knorr, 2014). Herceg et al. (2016) found that phenolic stability of pomegranate juice treated with the cold plasma may be a good match to pasteurization (Herceg et al., 2016).

Near infrared spectroscopy (NIRS) is a useful analytical technique for measuring quality parameters in foods. It is applicable to multiproduct and multicomponent analysis, especially because it allows non-destructive analysis, and requires little or no sample preparation. Also, NIRS calibration models have been used for fruit and related products, particularly for the analysis and prediction of various chemical compositions (Wang, Peng, Xie, Bao, & He, 2015). Our previous research demonstrated the potential of NIRS for the prediction of phenolics in pomegranate juice, before and after the thermal and plasma treatment (Herceg et al., 2016). Hence, this study also intended to assess the suitability of NIRS technology for predicting phenolic compounds in fresh, pasteurized, and cold plasma treated CJ.

The objective of this study was to evaluate the influence of the non-thermal and thermal treatments on the stability of anthocyanins, hydroxycinnamic acids, and flavonols in CJ. Stability of polyphenols after the treatments was evaluated and predicted by the NIR spectroscopy. Cold atmospheric gas phase plasma treatment represented non-thermal treatment, and pasteurization was thermal alternative. The previously reported gas flow of 0.75 $dm^3\ min^{-1}$ was used as constant for plasma treatments due to the best observed phenolic retention and stability (Bursać Kovačević et al., 2016; Herceg et al., 2016).

2. Materials and methods

2.1. Chemicals and standards

Methanol, acetonitrile and formic acid were used for extraction and analysis were HPLC grade, purchased from Gram-mol (Zagreb, Croatia). Phenolic standards cyanidin-3-glucoside, cyanidin-3-O-arabinoside chloride, cyanidin-3-O-galactoside chloride, quercetin-3-O-rutinoside, quercetin-3-O-galactoside were purchased form Extrasynthese (Lyon, France), while quercetin 3-β-D-glucoside, quercetin-3-D-xyloside, caffeic acid and chlorogenic acid were obtained from Sigma (Steinheim, Germany).

2.2. Juice preparation

Chokeberry fruits (*Aronia melanocarpa* cv. Viking) were harvested manually in Zagreb, Croatia surroundings, at the commercial maturity stage. After harvesting, berries were transported to the laboratory where the CJ was obtained by cold press juicer (Vervita Hurom HU-100). Immediately after pressing the cloudy juice was treated with cold plasma and analyzed. Thermal pasteurization was done in a small scale laboratory tubular pasteurizator (Euclid d.o.o., Croatia) at 80 °C for 2 min. All juices were done in duplicates. Pasteurization p-value for chokeberry juice was 10.4, as estimated for berry juice from the literature for our pasteurization conditions (Marques, da Silva, & Gibbs, 2009).

2.3. Plasma treatment of chokeberry juice

The cold atmospheric gas phase plasma jet was generated in argon (purity 99.99%; Messer, Sulzbach, Germany) by applying 25 kHz electric field trough the electrode. Used plasma source was a single-electrode atmospheric jet (End-field Jet type), designed at the Institute of Physics in Zagreb, Croatia with previously published schematics (Bursać Kovačević et al., 2016). This plasma source produced plasma jet extending out of the capillary tube to the proximal length of 2.2 cm with argon gas flow. Further increase of gas flow decreased plasma jet length.

Samples were treated by plasma running at a constant power of 4 W, while the gas flow was set to 0.75 $dm^3\ min^{-1}$. Treatment volume was 3, 5 and 7 cm^3, and time 3 and 5 min. Discharge gap between the plasma nozzle tip and samples was fixed to 1.5 cm. Juice samples were placed in a tissue culture test plate that consisted of 16 sample positions (TPP Techno Plastic Products AG, Trasadingen, Switzerland). After completion of the plasma treatment, extraction of polyphenols followed.

Temperature measurement were done before and immediately after the cold plasma treatment by non-contact infrared thermometer with laser pointer (Maplin Electronics, UK). All samples before and after the cold plasma exposure had ambient temperatures of 24 ± 1 °C. Plasma treatment pasteurization p-value for chokeberry juice was 3.1, as estimated for berry juice from the literature for our pasteurization conditions. That corresponds to the thermal pasteurization conducted at 91 °C (Vinagre Marques da Silva & Gibbs, 2009).

2.4. HPLC-DAD analysis of phenolic compounds (hydroxycinnamic acids, flavonols and anthocyanins)

2.4.1. Extraction

Chokeberry polyphenols were extracted from 1.5 mL of CJ with 3 mL of 1% formic acid in 80% methanol. The mixture was vortexed for a minute and extracted at 50 °C in ultrasonic bath with frequency of 40 kHz for 15 min (Bandelin Sonorex, Germany). The extracts were filtered through Whatman filter paper No. 40 (Whatman International Ltd., Kent, UK), and made up to 5 mL in volumetric flask with extraction solvent, and then centrifuged at 5000×*g* (Hettich, Rotofix 32). The supernatant was filtered through an Acrodisc syringe filter (with 0.45 μm nylon membrane; Sigma-Aldrich Co., St. Louis, MO, USA), and the filtrate was stored at −18 °C in an inert gas atmosphere for a maximum of 2 days prior to analysis.