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Drying-induced physico-chemical changes in cranberry products

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ABSTRACT

Sugar-free cranberry juice (XAD) and juice with 15% of maltodextrin were dried by freeze-, vacuum and spray drying methods. Total phenolics (589–6435 mg/kg dry matter) including 5 flavonols, 3 phenolic acids, 2 procyanidins and 5 anthocyanins were stronger affected by juice formulation than by drying methods. Spray drying of juice, regardless of its formulation, was competitive to freeze drying in terms of polyphenols' retention. Increase in temperature up to 100 °C during vacuum drying of XAD extracts resulted in degradation of polyphenolics (down to 4%), except chlorogenic acid. Its content increased with rise in temperature and accelerated hydroxymethylfurfural formation. The stronger the impact of drying, the more chlorogenic acid is present in cranberry products. In all powders analysed, formation of furoylmethyl amino acids was noted. Antioxidant capacity of cranberry products was influenced by juice formulation and was linked to content of polyphenols.

1. Introduction

Cranberry (*Vaccinium* ssp. L.) is an evergreen dwarf shrub that produce edible red fruits, which are rich in vitamins (A, C, B1, B2, B6 and E), minerals, sugars, organic acids and fibre (Borges, Degeneve, Mullen, & Crozier, 2010). Furthermore, this fruit contains significant amounts of phenolic compounds including procyanidins (PACs), phenolic acids, anthocyanins, flavonols and flavan-3-ols with strong antioxidant properties (Borowska, Mazur, Gadzala-Kapciuch, & Buszewski, 2009; Sun, Chu, Wu, & Liu, 2002). Due to the presence of those biologically active constituents cranberries could prevent from i.e. urinary tract infections, reduce the risk of cardiovascular diseases and selected types of cancer, and might have antifungal, antimicrobial, antianemic and detoxifying properties (Blumberg et al., 2013). Taking into account the various beneficial effects of cranberries on human health, consumption of these fruits is recommended. However, the bitter and astringent taste hampers its consumption in a fresh form. Therefore, technological transformations of cranberries are necessary to decrease the inacceptable taste.

Taking into consideration that fruit processing results in significant changes in the profile and the content of biologically active constituents (Horszwald, Andlauer, & Heritier, 2013; Michalska, Wojdyło, Lech, Łysiak, & Figiel, 2016; Nicoli, Anese, & Parpinel, 1999), the processing of the cranberries should be done in a way to get consumer acceptance with a minimum loss of beneficial compounds. Previous studies showed that juicing (Caillet, Côté, Doyon, Sylvain, & Lacroix, 2011; Côté et al., 2011; White, Howard, & Prior, 2011), freeze- (Vvedenskaya et al., 2004) and vacuum microwave drying (Leusink, Kitts, Yaghmaee, & Durance, 2010) of cranberries have strong effects on polyphenolic compounds content and the antioxidant capacity. There is a strong link between processing parameters and alteration in phytochemicals profile and quantity in the products. Interestingly, evaluation of cranberries juice concentrates and freeze-dried powders revealed that some flavonol aglycons were present in the final products only after processing. From this point of view, the production of cranberry juice powders might be a practical tool to prolong the cranberry availability on the market throughout the year and to provide promising bioactive compounds.

The preparation of fruit juices before drying is a key factor for obtaining fine powders, independent from the drying methods applied (Caparino et al., 2012; Fegus, Zigon, Peterman, & Zeljko, 2015; Oberoi & Sogi, 2015). Fruit juices cannot be directly converted to a powder form because of the presence of low molecular weight acids and carbohydrates with a low glass transition temperature (Bhandari, Senoussi, Dumoulin, & Lebert, 1993) and stickiness behaviour. These issues might be overcome by adding a carrier agent i.e. maltodextrin before drying that could affect

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physicochemical properties of the final powders (Oberoi & Sogi, 2015). When preparing the fruit powders, another aspect that should be considered is the formation of the compounds via Maillard reaction/caramelisation (Michalska et al., 2016). Newly–formed constituents after fruit drying were confirmed in pears (Coimbra, Nunes, Cunha, & Guiné, 2011), plum products (Michalska, Honke, Łysiak, & Andlauer, 2016; Michalska et al., 2016), prunes, dried figs (Sanz, del Castillo, Corzo, & Olano, 2001) and selected berries (Megías-Pérez, Gamboa-Santos, Soria, Villamiel, & Montilla, 2014). Thus, Maillard reaction products might serve as a quality indicator for the dry powders. Up to now, powders from cranberry whole fruits, pomace and juice obtained after freeze-drying (Oszmiański, Wojdyło, Lachowicz, Gorzelany, & Matłok, 2016; Vvedenskaya et al., 2004) were analysed for their polyphenolic compounds content. However, no data for cranberry juice formulation and other drying techniques than freeze-drying are available.

Thus, the aim of the study was to evaluate the influence of the cranberry juice formulation and the effect of different drying methods (freeze-drying, vacuum drying and spray drying) on the profile and quantity of polyphenols, Maillard reaction/caramelisation products and the antioxidant capacity of the powders obtained.

2. Materials and methods

2.1. Reagents

Maltodextrin, hydroxymethylfurfural, Trolox®, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, potassium persulfate, 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich (Switzerland). Cyanidin-3-*O*-glucoside, peonidin-3-*O*-glucoside quercetin-3-*O*-glucoside and quercetin-3-*O*-rutinoside were obtained from Extrasynthese (Lyon, France). Chlorogenic acid was obtained from TRANS MIT GmbH (Giessen, Germany). Furosine was purchased from PolyPeptide Group (Strasbourg, France). Acetonitrile for UPLC (Gradient Grade) was from Merck (Darmstadt, Germany). Water for UPLC analysis was prepared using the HLP SMART 1000s system (Hydrolab, Gdansk, Poland) was additionally filtrated through a 0.22 μm membrane filter. The amberlite XAD-16 resin was supplied by Brenntag (Kędzierzyn-Koźle, Poland).

2.2. Material

Five litres of a commercial cranberry juice (100%, pasteurised; Rabenhorst®, Unkel/Rhain, Germany; 8 °Br, pH 2.53 ± 0.1) were centrifuged for 15 min at 5950*g* (HiCen XL, Herolab, GmbH Laborgeraete, Germany). Supernatant obtained was divided into two parts. One part was loaded into a vacuum aspirated column with amberlite XAD-16 resin previously conditioned with water (Kammerer, Kljusuric, Carle, & Schieber, 2005). The absorbed compounds were eluted with ethanol that was removed by scale rotary evaporator Laborota 20 (Heidolph, Schwabach, Germany) at 40 °C down to the final volume of 2 L giving the sugar-free cranberry juice extract (XAD). The second part of the centrifuged juice (supernatant) was mixed with 15% (v/w) of commercial maltodextrin (dextrose equivalent: 19) (15% M). Both formulations of the juice (XAD and juice containing 15% of maltodextrin) were subjected to the drying processes.

2.3. Methods

2.3.1. Drying processes

The two cranberry formulations (XAD and 15% M) (250 mL each, $n = 3$) were subjected to: freeze-drying (FD; LSL Secfroid, Lyolab BII, Aclens-Lausanne, Switzerland) at 0.03 mbar; vacuum drying (VD; Vacuum drying oven, Salvis Lab, Rotkreuz, Switzerland) at 200 mbar at 40 °C, 60 °C, 80 °C and 100 °C and spray drying (SD; Mini spray dryer, B-290, Büchi Labor Technik AG, Flawil, Switzerland) at 50% of pump capacity, aspirator at 100% represented an air flow from 35 m^3/h (Table 1). Powders obtained were pulverised by a mill (Bosch, MKM 6003, Gerlingen, Germany) using a sieve of 1.0 mm diameter (Retsch SM-100, Hann, Germany), vacuum packed and stored at −20 °C until analyses.

2.3.2. Water content

Water content in cranberry powders was determined by Karl-Fisher method using 803 KF Titration Stand (Metrohm, Herisau, Switzerland) in three independent measurements ($n = 3$) and expressed as percentage (%) (±SD).

2.3.3. Identification and quantification of polyphenolic compounds

The identification of polyphenols in cranberry powders was performed by LC-PDA-MS method using the Acquity Ultraperformance LC system (Waters Corp., Milford, USA) coupled with a photodiode detector (PDA; UPLC) connected with a mass detector G2 (QTOf) Micro mass spectrometer (Waters, Manchester, UK) equipped with an electrospray ionization (ESI) source operating in negative mode. The UPLC BEH C_{18} column (2.1 × 50 mm; 1.7 μm; Waters Corp., Milford, USA) set at 30 °C was applied for polyphenols' separation (Wojdyło, Oszmianski, & Bielicki, 2013). The quantification of polyphenolic compounds in powders analysed was performed as described by Wojdyło, Figiel, Lech, Nowicka, and Oszmianski (2014). The runs were monitored at the wavelengths: phenolic acid at 320 nm, flavonols at 360 nm and anthocyanins at 520 nm. Retention times (T_R) and spectra were compared with those of pure standards. Calibration curves (0.05 to 5 mg/mL, $R^2 \leq 0.9998$) were made from chlorogenic acid, peonidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside, quercetin-3-*O*-glucoside and -3-*O*-rutinoside as standards. All determinations were done in triplicates ($n = 3$) and the results were expressed as mg/kg dry matter (dm).

2.3.4. Antioxidant capacity

The antioxidant capacity was measured by Trolox Equivalent Antioxidant Capacity tests against $ABTS^{\cdot+}$ (Re et al., 1999) and $DPPH^{\cdot}$ radicals (Brand-Williams, Cuvelier, & Berset, 1995) adjusted to microplate reader according to Horszwald et al. (2013). Cranberry powders (100 mg) were solubilised in 10 mL of deionised water and left for 24 h. After this time, samples were sonicated (2 × 3 min, ambient temperature) and centrifuged (5000 rpm, 5 min, 21 °C; Eppendorf 5415R, Eppendorf AG, Hamburg, Germany). The results obtained from the two tests were expressed as mmol of Trolox Equivalents (TE)/100 g dm. Results given are average values (±SD) of at least three independent extractions.

Photoluminescence (PCL) assay was applied for evaluation of the antioxidant capacity of the cranberry powders with the Photochem® apparatus (Analytik Jena, Leipzig, Germany). The antioxidant capacity of hydrophilic (ACW) and lipophilic (ACL) extracts was measured against superoxide anion radicals generated from a photosensitiser luminol exposed to UV light using both 'ACW' and 'ACL' kits provided by the manufacturer. Approx. 0.5 g of powder were extracted with 5 mL of deionised water (ACW) or 80% methanol (ACL) by sonication (2 min) and vortexing (1 min). The samples were centrifuged for 5 min (5000*g*, 5 min, 4 °C; Eppendorf 5415R, Eppendorf AG, Hamburg, Germany). The step was repeated 3 times. Supernatants obtained were unified before analyses. The total extraction procedure was carried out in triplicate ($n = 3$), and the antioxidant capacity was expressed as mmol Trolox/100 g dm.