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Phenolic content and antioxidant activities of selected potato varieties and their processing by-products

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ABSTRACT

The total content of free, esterified and bound phenolics of the peel and flesh of four potato varieties (Purple, Innovator, Russet and Yellow) were determined using the Folin–Ciocalteu method. The respective antioxidant activities of these potatoes and/or their skins were evaluated using several *in vitro* assays. The phenolic profiles of potato peel and flesh samples were determined using high-performance liquid chromatography with photodiode array detection (HPLC-DAD). Bound and esterified phenolics contributed as much or even more than the free phenolics to the antioxidant activity of the peels; extracts from Purple variety showing the highest activity. The peels of all varieties showed significantly ($p < 0.05$) higher phenolic content and antioxidant activities than their respective flesh. Chromatographic data showed differences in the amounts, but not in types, of phenolic compounds in the potato peel samples. Thus, potato processing discard may be used in food formulations and their extracts could potentially be employed as an effective source of antioxidants in food systems.

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1. Introduction

Vegetables are rich sources of phytochemicals, in addition to other components, that may act synergistically with phytochemicals that contribute to the nutritional quality and health benefits of such food commodities. Potato (*Solanum tuberosum*) is a major staple food for humans and the fourth largest crop that is grown worldwide after rice, wheat, and maize (Singh & Saldana, 2011). Though there is increasing interest, relatively little is known about the important phytochemicals contained in this most-consumed vegetable and its processing by-products. Potato peels are a good source of phenolic compounds which may potentially be used in food formulations or when extracted can be used as natural antioxidants to prevent oxidation of selected foods (Schieber & Saldana, 2009). Potato peels are by-products of the potato processing industry and are an excellent source for the recovery of phenolic compounds because almost 50% of phenolics are located in the peel and adjoining tissues and their concentration decreases towards the centre of the tuber (Al-Weshahy & Rao, 2009; Friedman, 1997). Thus, value-added use of this by-product is of interest to the potato industry (Habeebullah, Nielson, & Jacobsen, 2010). Polyphenols are recognised as the most abundant antioxidants in the human diet (Manach, Scalbert, Morand, & Jimenez, 2004). As antioxidants, phenolic compounds prevent or control the formation of free radicals with deleterious health effects and are therefore important in disease risk reduction (Shahidi, 2000). They have also been shown to render positive effects on certain types of cancer (Birt, 2006), including cancer of the stomach, colon, prostate, and breast as well as cardiovascular diseases (CVD) (Hertog et al., 1995) and various inflammatory disorders (Andriantsitohaina, Andriambeloson, & Stoclet, 1999).

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Phenolic compounds in potatoes can be present in both the soluble (free and soluble esters and soluble glycosides) and insoluble-bound forms. They are mostly substituted derivatives of hydroxycinnamic acid in the free form and hydroxybenzoic acid in the bound form (Shahidi & Naczk, 1995). The most common hydroxycinnamic acid derivatives in potato and potato peels were reported to be chlorogenic acid (CGA), caffeic acid (CFA), and ferulic acid (FA), while the hydroxybenzoic acids present were gallic acid (GA), protocatechuic acid (PCA), and their derivatives (Al-Weshahy & Rao, 2009; Kanatt, Chander, Radhakrishna, & Sharma, 2005; Nara, Miyoshi, Honma, & Koga, 2006). Anthocyanins, a subgroup within the flavonoids, are present in substantial amounts in pigmented potatoes (Brown, Durst, Wrolstad, & De Jong, 2008). The purple flesh has a higher concentration of flavonoids than white flesh, while their peel showed higher contents and antioxidant activities than the corresponding flesh (Lewis, Walker, Lancaster, & Sutton, 1998; Rodriguez de Sotillo, Hadley, & Holm, 1994; Velioglu, Mazza, Gao, & Oomah, 1998).

Though there have been studies on the free phenolics and their antioxidant activities in potatoes (Al-Weshahy & Rao, 2009; Kanatt, Chander, & Sharma, 2004; Mansour & Khalil, 2000), there appears to be very little information available on their esterified and bound phenolics, thus reported values and corresponding antioxidant activities in the literature are often underestimated due to their exclusion in the determinations. Insoluble-bound phenolics are linked to the cell wall polysaccharides in plant materials (Fry, 1986). Ferulic acid esters have a functional role in cell adhesion, thermal stability and the texture of plant foods (Ishis, 1997) and also have high antioxidative potential (Ohta, Semboku, Kuchii, Egashira, & Sanada, 1997). In the present study, the phenolic constituents of potato peel and flesh were fractionated into their respective free, esterified (soluble), and insoluble-bound forms by alkali hydrolysis and the relative proportions of various phenolic acids determined both chemically and by using high-performance liquid chromatography (HPLC). To the best of our knowledge, this is the first study that extensively examines all three forms of phenolics in potatoes along with their contribution to antioxidative activities. The study sheds light on potential use of potato peels and their extracts in food and model systems. It also compares the phenolic content of the peel and flesh of different potato varieties (Russet, Innovator, Purple and Yellow potatoes) and their corresponding antioxidant activities.

2. Materials and methods

2.1. Materials

Peels from Russet and Innovator variety of potatoes were procured from McCain Foods Limited, Florenceville, NB, Canada; while the Yellow and Purple potatoes were purchased from local markets in St. John's, NL, Canada.

Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was purchased from Acros Organics (Fair Lawn, NJ, USA). Organic solvents and reagents such as methanol, acetone and sodium carbonate were purchased from Fisher Scientific Co. (Nepean, ON, Canada). 2,2′-Azobis (2-methylpropionamidine) dihydrochloride (AAPH), 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS), Folin and Ciocalteau's phenol reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), and all phenolic standards with purity (⩾96%) were obtained from Sigma–Aldrich Canada Ltd. (Oakville, ON, Canada).

2.2. Sample preparation

Yellow and Purple potatoes were peeled manually, and their skins freeze dried for 3 days at −48 °C and 30×10^{-3} mbar (Freezone 6, model 77530, Labconco Co., Kansas City, MO, USA). The flesh of Russet, Purple and Yellow potatoes was also separated, cut and freeze dried. Peels from Russet and Innovator variety of potatoes, procured from McCain, were also immediately freeze dried; these were received as fresh-frozen samples). The dried samples were then ground and to pass through a 0.5 mm sieve, vacuum packed and stored in a freezer at −20 °C until analysed. All experiments were carried out in triplicates and the results were reported as means ± standard deviation. The methodologies followed are described below.

2.3. Extraction of the phenolic fractions

Free, esterified, and insoluble-bound phenolic compounds were extracted and fractionated as described by Krygier, Sosulski, and Hogge (1982). Freeze dried potato peels (10 g) were ultrasonicated for 20 min at 30 °C with 150 mL of a mixture of methanol–acetone–water (7:7:6, v/v/v) The resulting slurries were centrifuged at 4000*g* (ICE Centra MS, International Equipment Co., Needham Heights, MA, USA) for 5 min and the supernatants collected. The residue was re-extracted under the same conditions. After centrifugation, the combined extracts were retained for determination of soluble phenolics which included free phenolic acids and soluble phenolic esters; while the residue was kept for determination of insoluble-bound phenolic acids. The combined supernatants were evaporated under vacuum at 40 °C to remove the organic solvents, and the aqueous phase was adjusted to pH 2 before extraction with hexane to remove interfering lipids (Krygier et al., 1982). The free phenolic acids were then extracted with diethyl ether–ethyl acetate (1:1, v/v) 4 times, dried under vacuum using a rotary evaporator and the extract was dissolved in 5 mL of 80% methanol (HPLC grade). The esters remaining in the aqueous phase were hydrolysed with 4 M NaOH and the liberated phenolic acids were extracted with diethyl ether–ethyl acetate, dried and dissolved in 5 mL methanol as in the case of free phenolics. The residues were initially dispersed in 50 mL of 4 M NaOH and stirred for 4 h under nitrogen. The solution was then acidified to pH 2, centrifuged and the bound phenolics were extracted with diethyl ether–ethyl acetate (1:1, v/v) as described for esterified phenolics.

2.4. Estimation of total phenolic content

The total phenolic content was determined according to an improved version of the procedure explained by Singleton and Rossi (1965). Folin Ciocalteu's phenol reagent (0.50 mL) was added to test tubes containing 0.5 mL of methanolic extracts. Contents were mixed thoroughly and 1 mL of sodium

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