Food Research International 65 (2014) 27–34

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Extraction and fractionation of phenolic acids and glycoalkaloids from potato peels using acidified water/ethanol-based solvents

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ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form 3 June 2014
Accepted 4 June 2014
Available online 20 June 2014

Keywords:
Potato peels
Phenolic acids
Glycoalkaloids
Water/ethanol-based extraction
Solid-phase extraction
UFLC–MS

ABSTRACT

Potato processing generates potato peels as byproducts. Methanolic extracts from the peels result in mixtures of phenolic acids and glycoalkaloids. Phenolic acids have potential for food applications owing to their antioxidant and antibacterial properties. However, when extracted from potatoes, their separation from toxic glycoalkaloids is needed prior to their applications in foods. Moreover, glycoalkaloids may be used as feedstock for synthesis of pharmaceuticals. This study aimed to develop a method for the extraction and fractionation of phenolic acids and glycoalkaloids from potato peels using food grade water/ethanol-based solvents. Samples were analyzed by ultrafast liquid chromatography (UFLC) and/or ultrafast liquid chromatography–mass spectrometry (UFLC–MS). A methanol-based solvent for extraction was used as a control to be compared with two aqueous ethanolic solvents acidified with acetic acid. The recovery of the predominant compounds from potato peels was comparable for all three solvents. Extraction yielded per 100 g of potato peel fresh weight 17.0 mg α-chaconine, 7.1 mg α-solanine, 0.1 mg solanidine, 4.8 mg caffeic acid, 13.3 mg neochlorogenic acid, and 77.6 mg chlorogenic acid. More than 90% of these compounds were recovered after two consecutive extractions. The crude extract was fractionated by solid-phase extraction at pH 7 and eluted with aqueous ethanol. Quantitative recovery of the phenolic acids and glycoalkaloids was achieved in their corresponding fractions. Hydrolysis followed by solid-phase fractionation of the crude extract allowed recovery of 139 μmol caffeic acid/100 g potato peel fresh weight. Partial degradation of caffeic acid and glycoalkaloids occurred during the process. Degradation of caffeic acid can be likely mitigated by the addition of antioxidants and metal chelators. The method developed in this study allows the sustainable recovery of secondary plant metabolites from potato peels and their fractionation using food grade water/ethanolic solvents for application of phenolic extracts free of toxic glycoalkaloids for food preservation, and of glycoalkaloid extracts for synthesis of pharmaceuticals.

1. Introduction

Potatoes (*Solanum tuberosum* L.) are among the most important staple crops consumed by humans (Mattila & Hellstrom, 2007). The production of value-added potato products has increased to satisfy the demand of consumers for convenience foods, whereas fresh potato consumption is continuously decreasing. Processing leads to the production of significant amounts of waste (FAO, 2008; Schieber & Aranda Saldaña, 2009). Processed potato products account only for 50 to 60% of the raw material. The byproducts include cull potatoes and processing waste (Charmley, Nelson, & Zvomuya, 2006). Peels constitute the main fraction of the processing waste. While considered waste, potato peels also contain valuable components (Mäder, Rawel, & Kroh, 2009). Phenolic compounds and glycoalkaloids are particularly interesting because they are suitable for application in the food and pharmaceutical industries after extraction and purification (Mäder et al., 2009; Schieber & Aranda Saldaña, 2009).

Phenolic acids are the main phenolic compounds in potatoes (Mäder et al., 2009; Schieber & Aranda Saldaña, 2009; Singh & Saldaña, 2011). They have shown antioxidant and antibacterial activities (Rodriguez de Soltillo, Hadley & Wolf-Hall, 1998; Sánchez-Maldonado, Schieber, & Gänzle, 2011; Svensson, Sekwati-Monang, Lopes Lutz, Schieber, & Gaenzle, 2010). Therefore, these compounds hold promise for application as preservatives in foods, feeds, and packing materials. Plant extracts containing phenolic acids were suitable as food preservatives (Corrales, Han, & Tauscher, 2009; Ejechi & Akpomedaye, 2005; Elegir, Kindl, Sadocco, & Orlandi, 2008). However, chlorogenic acid constitutes 90% of the phenolic compounds in potato peels (Im et al., 2008; Schieber & Aranda Saldaña, 2009). Chlorogenic acid exists in the form of three main isomers, which include chlorogenic acid (5-*O*-caffeoylquinic acid), neochlorogenic acid (3-*O*-caffeoylquinic acid) and cryptochlorogenic acid (4-*O*-caffeoylquinic acid) (Lee & Finn, 2007; Nandutu, Clifford, & Howell, 2007; Shui, Leong, & Wong, 2005). Chlorogenic acid isomers do not have strong antibacterial activity but can be hydrolyzed to quinic

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http://dx.doi.org/10.1016/j.foodres.2014.06.018
0963-9969/

and caffeic acids (Fig. 1). Caffeic acid shows antimicrobial activity against gram positive and gram negative bacteria at concentrations ranging from 0.1 to 1 g/L (Rodriguez de Soltillo et al., 1998; Sánchez-Maldonado et al., 2011). Quinic acid, the second product of chlorogenic acid hydrolysis, is a starting material for the synthesis of drugs such as Oseltamivir for influenza treatment (Yeung, Hong & Corey, 2006; Satoh, Akiba, Yokoshima, & Fukuyama, 2007).

Glycoalkaloids are plant steroids that contain nitrogen and a sugar moiety attached to the 3-OH position (Fig. 2). α-Chaconine and α-solanine are the main glycoalkaloids found in potatoes (Friedman, 2004). They are suitable for utilization in pharmaceutical industry. The aglycone solanidine is an intermediate for the synthesis of hormones such as progesterone and cortisone derivatives (Nikolic & Stankovic, 2003). Additionally, glycoalkaloids and their aglycones have been shown to possess anti-allergic, antipyretic, anti-inflammatory, hyperglycemic, and antibiotic properties (Friedman, 2006). Furthermore, potato glycoalkaloids have antifungal activities (Fewell & Roddick, 1993, 1997). However, they are toxic for humans and should be absent in potato products or potato extracts used for food applications (Rodriguez-Saona, Wrolstad, & Pereira, 1999). For fresh potatoes, a maximum of 200 mg of glycoalkaloids per kilogram is acceptable for human consumption (Fewell & Roddick, 1993; Friedman, 2006).

Conventional methods for the extraction of phenolic compounds from plant material use organic solvents such as methanol, acetone, ethanol and ethyl acetate (Dai & Murpher, 2010; Svensson et al., 2010). Glycoalkaloids from potatoes are traditionally extracted with chloroform/methanol mixtures (Bushway & Ponnampalam, 1981; Friedman, Roitman, & Kozukue, 2003). These methods are detrimental for the environment. Water and ethanol are alternatives for the recovery of phenolic compounds from potato peels, facilitating food applications (Kannat, Chander, Radhakrishna, & Sharma, 2005; Onyeneho & Hettiarachchy, 1993; Singh & Rajini, 2004). Water/acetic acid mixtures have been used to extract glycoalkaloids (Friedman et al., 2003; Machado, Toledo, & García 2007; Sotelo & Serrano, 2000). However, to our knowledge there is no method for the simultaneous recovery and subsequent separation of phenolic acids and glycoalkaloids to obtain food grade phenolic extracts free of toxic glycoalkaloids and the corresponding glycoalkaloids fraction for pharmaceutical purposes. In addition, recovery of these compounds from potato peels using food grade solvents would be an advantage for the food industry since it reduces the organic waste that causes disposal problems (Kim & Kim, 2010) and minimizes the environmental impact of toxic solvents. Therefore, this study aimed to develop a sustainable method for the simultaneous extraction of these compounds from potato peels using food grade acidified water/ethanol based solvents. Furthermore, experiments aimed to achieve separation of polyphenols and glycoalkaloids from potato peels to allow applications of both fractions in the food and pharmaceutical industries, respectively.

2. Materials and methods

2.1. External standards

Chlorogenic acid (5-*O*-caffeoylquinic acid) and caffeic acid were purchased from Sigma (St. Louis, MO, USA). α-Chaconine, α-solanine and solanidine were obtained from Extrasynthese (Genay, France).

2.2. Extraction of potato peels

Potatoes from the cultivar "Russet" purchased in a local grocery store in Edmonton, Alberta, Canada were used for this study. After manual peeling, 30 g of fresh peels was simultaneously crushed and mixed with 75 mL of extraction solvent in a domestic blender. Peels and solvent were left in the dark for 30 min, stirred for an additional 30 min, sonicated for 20 min, and centrifuged at 4696 *g*. The supernatant was recovered and filtered. Extraction was performed three times per batch and samples from each extraction were collected. Three different solvents were used for extraction; acetic acid was used to equal the pH to that of the control solvent (3.2). Solvent A contained 25% water, 70% methanol, and 5% acetic acid; solvent B contained 24% water, 67% ethanol, and 9% acetic acid; and solvent C contained 46% water, 51% ethanol and 3% acetic acid. The organic solvent was evaporated under vacuum at 40 °C using a Rotavapor RE21 (Büchi, Flawil, Switzerland). The dry potato peel extract was resuspended in 15 mL of water. A 40 mg/L standard solution of chlorogenic acid was extracted under the same conditions as the potato peels in order to evaluate stability of chlorogenic acid during the process.

2.3. Fractionation of phenolic acids and glycoalkaloids by solid-phase extraction

Phenolic acids were fractionated from the glycoalkaloids using a Sep Pak Vac 6 cc C18 cartridge. Solvents and water were adjusted to pH 7. Prior to use, the column was conditioned by elution with 5 mL of ethanol followed by 5 mL of water. Two milliliters of the extract previously resuspended in water was passed through the column and washed with 5 mL of water (pH 7). Subsequently, 20 mL of the corresponding solvent was added, phenolic acids were eluted with water/ethanol (80:20, v/v) and glycoalkaloids were eluted with water/ethanol (20:80, v/v). To determine the volume of solvent required for complete elution, the fractions were collected successively in 2 mL tubes, and the concentration of phenolic acids and glycoalkaloids was determined subsequently.

2.4. Alkaline hydrolysis of chlorogenic acid

Three mL of the extract obtained from solvent C, previously dissolved in 15 mL of water, was centrifuged and the supernatant was mixed with 750 μL of NaOH solution (10 M) and flushed under nitrogen for 2 min. The vial was hermetically closed and the solution was stirred for 4 hours at room temperature. Subsequently, the solution was adjusted to pH 4 with HCl and used for fractionation as described in Section 2.3. To evaluate whether alkaline hydrolysis results in the loss of caffeic acid, a 40 mmol/mL standard solution of chlorogenic acid was subjected to alkaline hydrolysis under the same conditions as previously mentioned.

2.5. Quantification of phenolic acids and glycoalkaloids

The separation and quantification of phenolic compounds from potato peels were performed using an ultrafast liquid chromatography (UFLC) system consisting of a LC 20 AD XR pump, SIL-20 AC XR

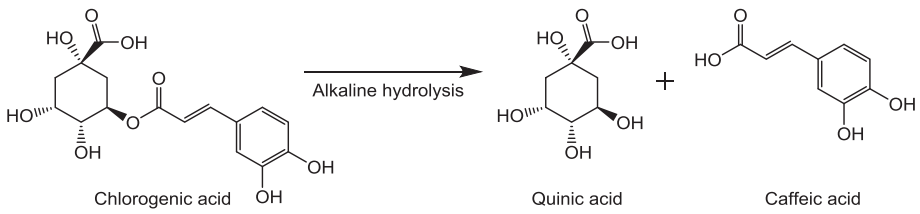

Fig. 1. Products of alkaline hydrolysis of chlorogenic acid.