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Original Research Article

Distribution of phenolic compounds and other polar compounds in the tuber of *Solanum tuberosum* L. by HPLC-DAD-q-TOF and study of their antioxidant activity

Ana López-Cobo [a], Ana M. Gómez-Caravaca [a,b], Lorenzo Cerretani [c], Antonio Segura-Carretero [a,b,*], Alberto Fernández-Gutiérrez [a,b]

[a] Research and Development of Functional Food Centre (CIDAF), PTS Granada, Avda. del Conocimiento s/n, Edificio Bioregión, 18016 Granada, Spain
[b] Department of Analytical Chemistry, University of Granada, c/Fuentenueva s/n, 18071 Granada, Spain
[c] Pizzoli S.p.A., Via Zenzalino Nord n. 1, 40054 Budrio (BO), Italy

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ABSTRACT

Potato (*Solanum tuberosum* L.) is one of the most widely grown crops worldwide. It represents a staple source of nutrients including carbohydrates, high-quality proteins, minerals, vitamins and polyphenols. This study aimed to identify mainly polyphenols in flesh, peel, and whole tuber of two potato cultivars (Blue Bell and Melody) by high performance liquid chromatography-diode array detector-electrospray ionization-quadrupole-time of flight-mass spectrometry (HPLC-DAD-ESI-q-TOF-MS) analysis and to quantify the main polyphenols by ultraviolet–visible (UV–vis) in order to evaluate their distribution. The antioxidant activity of the three fractions of both cultivars by ferric reducing antioxidant power (FRAP), trolox equivalent antioxidant capacity (TEAC) and oxygen radical absorbance capacity (ORAC) was also studied. A total of 24 polar compounds were identified in less than 25 min. Three caffeoylquinic acid isomers, caffeic acid, 3,5-dicaffeoylquinic acid, and *N*-[2-hydroxy-2-(4-hydroxyphenyl) ethyl] ferulamide were the main phenolic compounds in the three fractions of the two potato cultivars. Blue Bell was the cultivar with the highest phenolic-compound content, while the peels were the part with the highest phenolic-compound content as well as the highest antioxidant activity. The results established potato peels as an attractive by-product of the potato industry because they can be used as an alternative source of polyphenols in the food industry and used in other food products.

1. Introduction

Potato (*Solanum tuberosum* L.) is one of the most widely grown crops worldwide, and the fourth largest in terms of fresh produce, after rice, wheat, and maize (FAO, 2011). Representing the staple source of nutrients and energy in many different countries, potato is an appealing crop due to its fast growth, adaptability to different environments, high yield, and response to low fertilizer input. In addition, its characteristics (up to 85% of the plant is edible as compared to ~50% in cereals) and ability to produce high yields under harsher climates and using less land than any other major crop make potato a suitable staple food in many countries (FAO, 2008). Furthermore, potato is a major source of carbohydrates, high-quality proteins (proteins with a large number of essential amino acids), minerals such as potassium, sodium, iron, magnesium, and vitamins such as C, B1, B6, and B9. Furthermore, some potato cultivars are a rich source of polyphenolic compounds (Zhu et al., 2010).

Phenolic compounds are secondary metabolites that are synthesized during normal plant development (Cheynier, 2012) and in response to stress conditions such as infection, wounding, and UV radiation, among others (Beckman, 2000). These metabolites play a decisive role in the sensory quality of fruits, vegetables, and other plants such as bitterness, astringency, color or smell (Cheynier, 2005). They have attracted increasing attention in recent years due to their health benefits, as their consumption has been linked to lowering the risk of diseases associated with oxidative stress, such as cancer and cardiovascular diseases

* Corresponding author at: Research and Development of Functional Food Centre (CIDAF), PTS Granada, Avda. del Conocimiento s/n, Edificio Bioregión, 18016 Granada, Spain. Tel.: +34 958 637206; fax: +34 958 637083.
E-mail address: ansegura@ugr.es (A. Segura-Carretero).

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(Scalbert et al., 2005). Potatoes contribute to the daily intake of polyphenols and therefore their consumption may be beneficial for human health.

Recent works have reported that major phenolic compounds in potato are hydroxycinnamoylquinic/hydroxycinnamoyl derivatives, mainly 5-caffeoylquinic acid, 1-caffeoylquinic acid, 3-caffeoylquinic acid (or chlorogenic acid), caffeic acid, and caffeoyl-putrescine. In addition, Mohdaly et al. (2013) have also reported low amounts of vanillic, sinapic, *p*-coumaric, and cinnamic acid. However, the phenolic-compound composition in potato depends on different factors such as cultivation site, climatic conditions, agricultural practices, and genotype (Hejtmándová et al., 2013; Lombardo et al., 2013).

Phenolic compounds are distributed mostly between the outer tissues and the skin (peel) of potato tubers (Al-Weshahy and Venket-Rao, 2009). Therefore, recycled potato peel, as a by-product of the food industry, could be considered as a source of polyphenol compounds and could be used to produce other food products including functional foods and nutraceuticals.

In this work, the flesh, peel, and whole tuber of two cultivars of *S. tuberosum* L. (Blue Bell and Melody) were analyzed by HPLC-DAD-ESI-q-TOF-MS (high performance liquid chromatography-diode array detector-electrospray ionization-quadrupole-time of flight-mass spectrometry) to identify and quantify their phenolic and other polar compound content and were subjected to several *in vitro* methods based on single electron transfer mechanisms (Trolox equivalent antioxidant capacity [TEAC] and ferric reducing antioxidant power [FRAP]); and on a hydrogen-atom transfer mechanism (oxygen radical absorbance capacity [ORAC]) to measure their antioxidant activity. The distribution of phenolic compounds was also determined in the different parts of the potato tuber.

2. Materials and methods

2.1. Chemicals and reagents

HPLC-grade acetonitrile and methanol were purchased from Labscan (Dublin, Ireland). Glacial acetic acid, ABTS (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)) (98%), potassium persulfate (99%), Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) (97%), TPTZ (2, 6-tripyridyl-s-triazine) (99%), ferric chloride (99%), ferrous sulfate (99%), AAPH (2,2′-azobis-2-methyl-propanimidamine, dihydrochloride) (97%), fluorescein (95%), monobasic sodium phosphate (99%), dibasic sodium phosphate (99%), caffeic acid (99%), 3-caffeoylquinic acid (or chlorogenic acid) (95%), rutin (94%), and ferulic acid (99%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Absolute ethanol, sodium acetate (99%), and hydrochloric acid (37%) were from Panreac (Barcelona, Spain). Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Samples

Two potato cultivars of *S. tuberosum* L. were analyzed: "Blue Bell" and "Melody". Blue Bell has yellow flesh and yellow peel with blue spots on it, and Melody has yellow flesh and yellow peel. Potatoes of the two different varieties were grown in 2012 (from March to July) under the same agricultural conditions in open fields in Emilia-Romagna (northern Italy) in accordance with integrated pest management guidelines of the Food and Agriculture Organization of the United Nations (FAO, 2012). Three accessions of each variety were analyzed. The peel (removed manually from the potatoes), the flesh, and whole potato were analyzed separately. Samples were frozen at −80 °C for two days and then freeze-dried. Every accession was extracted three times and each extract was analyzed three times.

2.3. Extraction of the polar fraction

Freeze-dried samples (3 g flesh and entire potato, 2 g peel) were placed in an ultrasonic bath (15 min) with 20 mL of a solution of methanol/water (4:1, v/v) with 1% acetic acid. After centrifugation at 1000 × *g* for 15 min, the supernatant was removed, and the extraction was repeated three more times. The supernatants were collected, evaporated, and reconstituted with 1 mL of methanol/water (4:1, v/v) with 1% acetic acid. The final extracts were filtered through 0.2-μm nylon syringe filters and stored at −18 °C until analyzed.

2.4. HPLC-DAD-ESI-q-TOF-MS analyses

The phenolic compounds were separated from the potato extracts using an Agilent 1200 series Rapid Resolution LC system (Agilent Technologies, CA, USA) consisting of a vacuum degasser, an autosampler, and a binary pump. This instrument was equipped with an Agilent Poroshell 120 EC-C18 column (4.6 mm × 100 mm, 2.7 μm) from Agilent Technologies. A gradient elution was programmed using as a mobile phase A, acidified water (0.5% acetic acid), and as a mobile phase B, acetonitrile. The program was as follows: 5–7% B in 2 min, 7–9% B in 2 min, 9–12% B in 3 min, 12–15% B in 1 min, 15–16% B in 1 min, 16–18% B in 3 min, 18–20% B in 2 min, 20–22% in 1 min, 22–25% in 1.50 min, 25–28% B in 1.10 min, 28–30% B in 1 min, 30–31% B in 1 min, 31–32% B in 1.50 min, 32–100% B in 3.10 min, 100–100% in 2 min. The flow rate was set at 0.80 mL min^{-1} throughout the gradient. The injection volume was 10 μL, and UV spectra were recorded from 200 to 600 nm using the DAD detector, whereas the chromatograms were registered at 240, 280, and 330 nm. The effluent from the HPLC column was split using a T-type phase separator before introducing it into the mass spectrometer (split ratio 1:3).

The HPLC system was coupled to a microTOF-q-MS (Bruker Daltonics, Bremen, Germany), equipped with an ESI interface. Analysis parameters were set using negative and positive ion modes with spectra acquired over a mass range from *m*/*z* 50 to 1100. The optimum values of ESI-q-TOF-MS parameters in negative mode were: capillary voltage, −4 kV; drying gas temperature 210 °C; drying gas flow 8 L min^{-1}; and nebulizing gas pressure of 2 bar. The optimum values of the parameters in positive mode were: capillary voltage +4.5 kV; drying gas temperature 210 °C; drying gas flow 8 L min^{-1}; and nebulizing gas pressure of 2 bar.

The accurate mass data of the molecular ions were processed using the software DataAnalysis 4.0 (Bruker Daltonics GmgH, Bremen, Germany), which provided a list of possible elemental formulas by using the SmartFormula Editor. The SmartFormula Editor uses a CHNO algorithm, which provides standard functionalities such as minimum/maximum elemental range, electron configuration, and ring-plus double-bond equivalents, as well as a sophisticated comparison of the theoretical with the measured isotopic pattern (Sigma-Value) for increased confidence in the suggested molecular formula. The widely accepted accuracy for confirmation of elemental compositions has been established to be 5 ppm (Ferrer et al., 2005).

During the use of the HPLC method, an external instrument calibration was performed using a Cole Palmer syringe pump (Vernon Hills, IL, USA) directly connected to the interface, passing a solution of sodium acetate cluster containing 5 mM sodium hydroxide and 0.2% acetic acid in water/isopropanol 1:1 (v:v). With this method, an exact calibration curve was based on numerous cluster masses each differing by 68 Da ($NaCHO_2$).