

Evaluation of new strategies to reduce the total content of α -solanine and α -chaconine in potatoes

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ABSTRACT

Potatoes are a staple food for over a billion people worldwide, a primary dietary source of carbohydrates, and a vital crop to the agricultural economy of South America, Africa, East Asia and Central Asia. Potatoes occupy third place (after rice and wheat) on the list of foods on which the world depends for food security. In particular, glyco-alkaloids contents in potatoes are potentially toxic and secondary metabolites such as α -solanine and α -chaconine are reported to be dangerous to human health. This paper describes new methods for α -solanine and α -chaconine reduction in the potato cultivar known as Marabel. The potatoes were incubated at room temperature in the dark for 24 h and the optimal experimental condition was achieved with NaOH solution at pH 12. In the assayed samples, α -solanine and α -chaconine reduction was 43% and 27% respectively. The process proposed here allows to minimize the total content of glyco-alkaloids, with respect to mode of collection, storage and cleaning of Marabel potatoes.

1. Introduction

Potatoes (*Solanum tuberosum* L.), belongs to the Solanaceae family, are native to South America and they were cultivated in the pre-Columbian period, although several wild species were spread in North America. The spontaneous varieties still until now enigmatic. Potatoes are a staple food and the main source of carbohydrates in the diets of hundreds of millions of people, as well as a crop vital to the economy of South America, Africa, East Asia and Central Asia. Potatoes occupy third place (after rice and wheat) on the list of foods on which the world depends for food security. The potato was considered as an ornamental plant and the flowers was used to adorn the hair of fashionable ladies.

Despite the beneficial uses, potatoes contain toxic secondary metabolites to the human health, such as α -solanine and α -chaconine (Yamashoji and Matsuda, 2013), while other glycoalkaloids, α -tomatine, α -solasonine and α -solamargine are present in negligible quantities (Fig. 1). The compounds α -solanine and α -chaconine possess an effective chemical defence against animals, insects (e.g., Colorado beetle), fungi (e.g., potato blight, *Fusarium*, *Alternaria*), worms and bacteria (Andrivon et al., 2003; Friedman, 2006). Certain wild *Solanum* species containing high levels of glycoalkaloids, which are used in reproduction studies to introduce unique features into cultivable species,

such as a high resistance to pathogens (Meziani et al., 2015; Nitithamyong et al., 2010). The stressful factors that occur before and after the harvest potatoes could cause a rapid increase the concentration of α -solanine and α -chaconine. Small sized and immature tubers were often associated with high levels of glycoalkaloids. In fact, the levels decrease with growth and maturation of the plant (Senguel et al., 2004). Even post-harvest conditions, such as exposure to light, heat and storage times, are able to influence the levels of glycoalkaloids (Haase, 2010). Prolonged exposure to light rapidly stimulates the production of glycoalkaloids. It has been shown that exposure of the tubers to sodium and fluorescent light increases their concentration (Roch et al., 2015; Romanucci et al., 2016a). These substances, often simply referred to generically as “solanine” or, for greater precision, as Total GlycoAlkaloids (TGA), can be considered as a group because of their similar chemical structures are quite similar, and when they are metabolized, they release the same few alkaloids (Mendel et al., 2010). TGA are not evenly distributed in the potato (approximately 10 mg per 100 g) (Romanucci et al., 2016a), but a large portion is concentrated under the skin, and it is preferable to remove it (Friedman and Dao, 1992). Furthermore, these two glycoalkaloids are poorly soluble in water and are not eliminated by normal cooking processes because they are degraded only at temperatures above 243 °C. Baking at 170 °C (as in the case of

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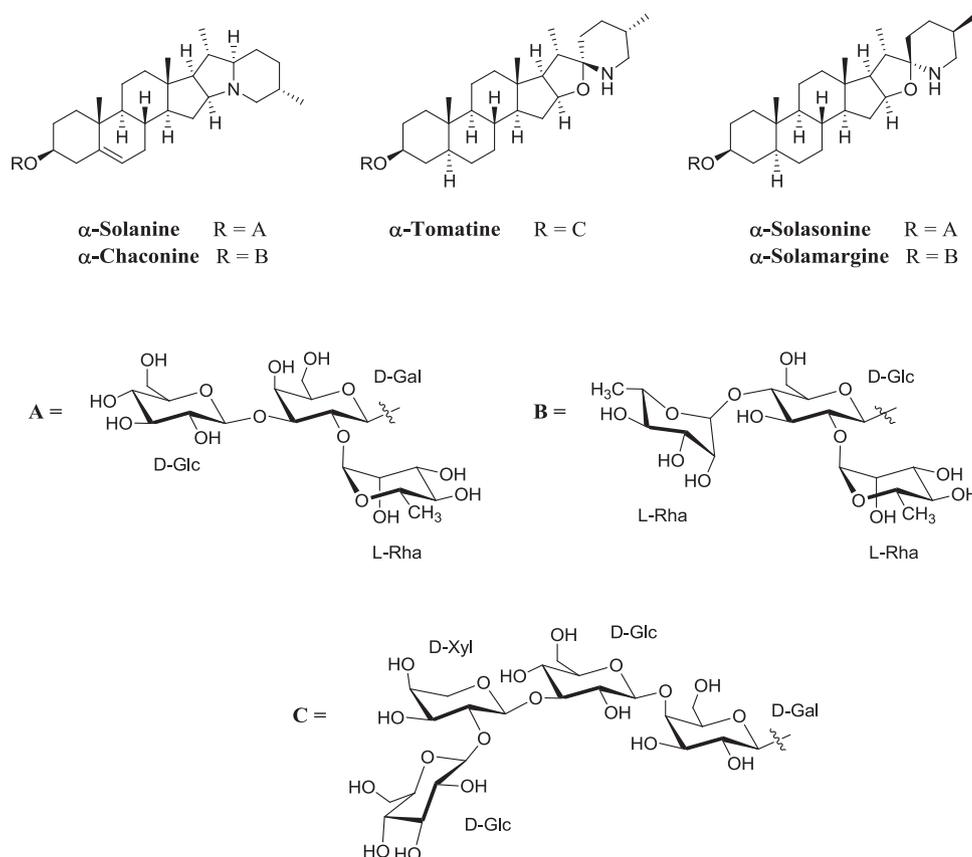


Fig. 1. Chemical structures of glycoalkaloids.

Table 1
Concentrations^a of α -solanine and α -chaconine of Marabel potatoes.

Experimental conditions	α -solanine (α -S) ^a	α -chaconine (α -C) ^a	(α -S) + (α -C) ^a
A Potatoes not treated	7.54 ± 0.43	1.20 ± 0.18	8.74
B Aqueous solution containing the following nutrients: phosphate (10 mg/L), nitrate (10 mg/L), nitrite (10 mg/L), sodium carbonate (10 mg/L)	7.62 ± 0.19	1.45 ± 0.10	9.07
C Solution of sodium bicarbonate at a concentration of 1.1 g/L	9.39 ± 0.38	1.50 ± 0.32	10.9
D Solution of sodium bicarbonate at a concentration of 6.5 g/L	11.01 ± 0.56	2.16 ± 0.16	13.2
E In a nitrogen atmosphere	6.96 ± 0.64	1.16 ± 0.10	8.12
F At pH 12 for a solution of NaOH 0.1 M	4.27 ± 0.93	0.88 ± 0.10	5.15
G At pH 3 to a solution of acetic acid	5.50 ± 0.44	1.12 ± 0.10	6.62
H In a solution of cyanamide at a concentration of 1 mg/L	7.82 ± 0.45	1.50 ± 0.15	9.32
I In a solution of sodium tartrate and potassium at a concentration of 6.5 g/L	6.70 ± 0.30	1.06 ± 0.11	7.76
L Potatoes illuminated with a lamp mimicking the conditions to which they are exposed in supermarkets	15.84 ± 0.55	2.36 ± 0.16	18.2

^a In mg/kg of potatoes.

frying) might reduce the amount of these substances, although it does not completely eliminate them. A recent study showed that daily consumption of potatoes leads to the accumulation of glycoalkaloids. Poisoning by α -solanine and α -chaconine was noted primarily from gastrointestinal disorders and neurological issues. Symptoms include nausea, diarrhoea, vomiting, stomach cramps, burning throat, heart arrhythmia, headaches and dizziness. In severe cases, hallucinations, loss of sensation, paralysis, fever, jaundice, dilated pupils, hypothermia, drowsiness and apathy, confusion, weakness, unconsciousness and death have been reported (Phillips et al., 1996). Severe poisoning can cause paralysis, respiratory failure, heart failure, and coma (Ji et al., 2012; Mendel et al., 2010; Roddick, 1989). In this context, Madiwale G.P. reports some precautions to minimize alkaloid content in potatoes (Madiwale et al., 2012), but a systematic study is still needed. Continuing our studies concerning the characterization (Cuttillo et al., 2004, 2006; D'Abrosca et al., 2005; Della Greca et al., 2002, 2003, 2004; Di Fabio et al., 2012; Fiorentino et al., 2007; Romanucci et al., 2014), as

well as the analysis of metabolites in staple foods and nutraceuticals (Romanucci et al., 2016b; Davinelli et al., 2015), the aim of this manuscript is directed to determine some industrial processes which could serve to minimize the content of glycoalkaloids arousing the interest of producers and a wide and safe consumption.

2. Results and discussion

In this study we determine some industrial processes which could serve to minimize the content of glycoalkaloids α -solanine and α -chaconine. For the tests, potatoes were chosen from a single batch (potatoes harvested on the same day, from the same soil, and were transported and stored in the same manner). The potatoes used in the tests were approximately the same size (by weight), and those that were damaged, had green spots on the surface or were shrivelled or sprouted were discarded. All potatoes were cleaned by removing soil residue and were washed and dried before weighing. Ten different tests were

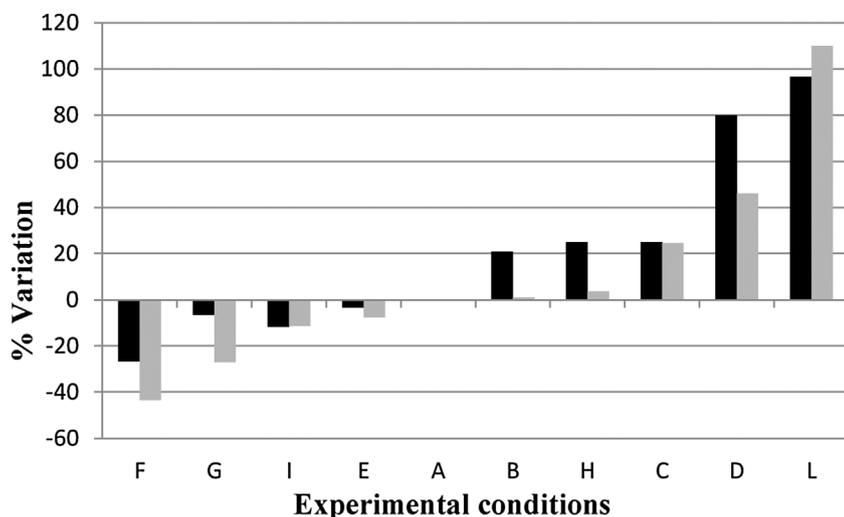


Fig. 2. Percentage variation of α -solanine (gray bar) and α -chaconine (black bar) after industrial treatments.

prepared for different potato storage conditions, as reported in Table 1. The tests were performed in triplicate at room temperature in the dark for 24 h. After treatment, the potatoes were removed from the containers and dried and peeled. The sample skins were lyophilized and finely chopped for three tests for each condition. Table 1 show the results of the concentration of α -solanine and α -chaconine for each different conditions after 21 days and non-significant values were discarded. In addition we reported the total concentration of α -chaconine and α -solanine for different experimental conditions.

The test results in Fig. 2 indicate that the concentration of the two alkaloids is minimal if the tubers are washed with an alkaline solution with a pH equal to 12 (entry F) or with an acid solution at a pH equal to 3 (entry G). However, the content of the two glyco-alkaloids is slightly lower than of the reference value (8.74 mg/kg of potatoes, entry A) corresponding to the product preserved, as necessary, in a dark, cool and clean place, also when the potatoes are stored in a nitrogen atmosphere (entry E) or when they are rinsed with a solution of sodium tartrate and potassium (entry I). On the contrary, the content of the two alkaloids increases in all other cases (entries B–D and H), and above all if the potatoes are subjected to continuous artificial light (entry L), such as when exposed for sale in supermarkets.

3. Experimental

3.1. Reagents and materials

α -Solanine was purchased from Sigma-Aldrich (Shanghai, China); α -chaconine was purchased from ChromaDex (Irvine, CA, USA). HPLC-grade acetonitrile, methanol, formic acid, ammonium formate, and anhydrous magnesium sulphate were purchased from Dikma Technologies Inc. (Lake Forest, CA, USA). Analytical-grade ammonium hydroxide was obtained from Beijing Chemical Plant (Beijing, China). Ultra-pure-quality water, which was generated in the laboratory using a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used throughout the experiments.

3.2. Collection and selection of samples

Potatoes of Marabel variety were harvested in November 2016. For analysis, potatoes of the same lot were selected; the potatoes were harvested in the same day, from the same soil and were transported and stored by identical methods. The selected potatoes had similar sizes (by weight); those that were damaged or that had green stains on the surface were discarded. All potatoes were cleaned by removing any soil residue and were washed, dried and weighed. The α -solanine and α -chaconine contents were measured after 21 days by RP-HPLC analysis.

The potatoes were stored in the dark at room temperature to simulate the usual conditions in which potatoes are preserved.

3.3. Selection of treatment processes

Potatoes have been stored in 10 different conditions: in the dark, at room temperature, in a place without moisture avoiding any shocks, cuts or cruscings (entry A), ideal for preserving the product until it is consumed; washed with a solution containing different nutrients such as phosphate, nitrate, nitrite and sodium carbonate (entry B) or with a solution containing sodium tartrate and potassium (entry I), conditions similar to those in which the plant grows; with two different concentrations of sodium bicarbonate, chosen for its mild disinfectant and antiseptic properties (entries C and D); preserved in an inert atmosphere for nitrogen (entry E); washed with a solution at pH 12 for NaOH (entry F), at pH 3 for acetic acid (entry G) and with a dilute solution of cyanamide (entry H) to avoid mold growth and harmful microorganisms; exposed in the light of a neon miming the conditions in which they are sold in supermarkets (entry L).

3.4. Extraction procedure

The dried and lyophilized skins were extracted three times with 100 mL of 80% ethanol/water (1:1, v/v) at room temperature. The solutions were filtered, combined and dried under vacuum and finally, the obtained crude product was weighed. The extract of the fraction containing the alkaloids was obtained according to the procedure for selective extraction published by Henriques et al. (2004). The crude dry hydroalcoholic infusion was resumed with a solution of 0.2 M hydrochloric acid and left to macerate for one night at room temperature. The solution was filtered, and the pH was adjusted 12 with addition of 2 M NaOH, resulting in a slight precipitate. The precipitate was separated from the supernatant by centrifugation (3000 rpm for 7 min at 4 °C), suspended in ethanol (1 mL) and injected into the HPLC for determination of α -solanine and α -chaconine.

3.5. HPLC analysis protocol

HPLC was performed on a Shimadzu LC-10AD using the UV–vis detector Shimadzu RID-10A (Kyoto, Japan). A semi-preparative HPLC was performed using an RP18 (LiChrospher 10 mm, 250 × 10 mm i.d., Merck). The content of α -chaconine and α -solanine present in the alkaloidic fraction was determined via HPLC analysis under isocratic conditions, using an eluent mixture of acetonitrile and sodium phosphate buffer at pH 7, at a concentration 0.01 M (36.5: 63.5), with a flow of 1.0 mL per minute.

4. Conclusion

In conclusion, we have evaluated the concentration of two glycoalkaloids, contained most of all in the skin of potatoes, after treatment with aqueous solutions containing nutrients or light disinfectants or phytotoxic compounds or miming the conditions of the exposition in the supermarkets. We have established a simple industrial process, which is also economical, easy to apply and compatible with food that helps significantly to decrease the contents of two toxic glyco-alkaloids in potatoes. Potatoes should be harvested at full maturity (after the plant has dried), cleaned and stored, and before the embedding washed with a solution of acidic pH (~3, for acetic acid), or better, basic pH (~12, for NaOH). A number of unpublished tests, but whose results are perfectly consistent with similar experiments reported in the literature, indicated that potatoes should avoid bumps or cuts, and be sold in closed envelopes (and not on usual screens) to avoid light and slightly larger than necessary to avoid impact or crushing when moved. These results are very interesting particularly in consideration that in many countries potatoes are widely eaten in the daily diet and often without being peeled. The promising results could also find application in other food products such as tomatoes and aubergines, containing the same glyco-alkaloids or molecules with similar structure.

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References

- Andrivon, D., Corbiere, R., Lucas, J.M., Pasco, C., Gravouelle, J.M., Pelle, R., Dantec, J.-P., Ellisèche, D., 2003. Resistance to late blight and soft rot in six potato progenies and glycoalkaloid contents in the tubers. *Am. J. Potato Res.* 80, 125–134.
- Cuttillo, F., D'Abrosca, B., Della Greca, M., Zarrelli, A., 2004. Chenoalbicin, a novel cinnamic acid amide alkaloid from *Chenopodium album*. *Chem. Biodiver.* 1, 1579–1583.
- Cuttillo, F., Della Greca, M., Gionti, M., Previtiera, L., Zarrelli, A., 2006. Phenols and lignans from *Chenopodium album*. *Phytochem. Anal.* 17, 344–349.
- D'Abrosca, B., Della Greca, M., Fiorentino, A., Monaco, P., Natale, A., Oriano, P., Zarrelli, A., 2005. Structural characterization of phytotoxic terpenoids from *Cestrum parqui*. *Phytochemistry* 66, 2681–2688.
- Davinelli, S., Scapagnini, G., Bertoglio, J.C., Zarrelli, A., Riccardo, P., Scapagnini, G., 2015. A randomized clinical trial evaluating the efficacy of an anthocyanin-Maqui Berry extract (Delphinol[®]) on oxidative stress biomarkers. *J. Am. Coll. Nutr.* 34, 28–33.
- Della Greca, M., Fiorentino, A., Monaco, P., Previtiera, L., Zarrelli, A., 2002. A new dimeric 9,10-dihydrophenanthrenoid from the rhizome of *Juncus acutus*. *Tetrahedron Lett.* 43, 2573–2575.
- Della Greca, M., Fiorentino, A., Monaco, P., Previtiera, L., Temussi, F., Zarrelli, A., 2003. New dimeric phenanthrenoids from the rhizomes of *Juncus acutus*: structure determination and anti-algal activity. *Tetrahedron* 59, 2317–2324.
- Della Greca, M., Isidori, M., Lavorgna, M., Monaco, P., Previtiera, L., Zarrelli, A., 2004. Bioactivity of phenanthrenes from *Juncus acutus* on *Selenastrum capricornutum*. *J. Chem. Ecol.* 30, 867–879.
- Di Fabio, G., Malgieri, G., Isernia, C., D'Onofrio, J., Gaglione, M., Messere, A., Zarrelli, A., De Napoli, L., 2012. A novel synthetic strategy for monosubstituted cyclodextrin derivatives. *Chem. Commun.* 48, 3875–3877.
- Fiorentino, A., Della Greca, M., D'Abrosca, B., Oriano, P., Golino, A., Izzo, A., Zarrelli, A., Monaco, P., 2007. Lignans, neolignans and sesquilignans from *Cestrum parqui* l'Her. *Biochem. Syst. Ecol.* 35, 392–396.
- Friedman, M., Dao, L., 1992. Distribution of glycoalkaloids in potato plants and commercial potato products. *J. Agric. Food Chem.* 40, 419–423.
- Friedman, M., 2006. Potato Glycoalkaloids and metabolites: roles in the plant and in the diet. *J. Agric. Food Chem.* 54, 8655–8681.
- Haase, N.U., 2010. Glycoalkaloid concentration in potato tubers related to storage and consumer offering. *Potato Res.* 53, 297–307.
- Henriques, A.T., Lopes, S.O., Paranhos, J.T., Gregianini, T.S., Von Poser, G.L., Fett-Neto, A.G., Schripsema, J., 2004. N, β -D-Glucopyranosyl vincosamide, a light regulated indole alkaloid from the shoots of *Psychotria leiocarpa*. *Phytochemistry* 65, 449–454.
- Ji, X., Rivers, L., Zielinski, Z., Xu, M., Erinn, M.D., Jancy, S., Zhang, S., Wang, Y., Chapman, R.G., Keddy, P., George, S.R., Christopher, W., Kirby, C.W., Embleton, J., Worrall, K., Murphy, A., De Koeyer, D., Tai, H., Yu, L., Charter, E., Zhang, J., 2012. Quantitative analysis of phenolic components and glycoalkaloids from 20 potato clones and in vitro evaluation of antioxidant cholesterol uptake, and neuroprotective activities. *Food Chem.* 133, 1177–1187.
- Madiwale, G.P., Reddivari, L., Stone, M., Holm, D.G., Vanamala, J., 2012. Combined effects of storage and processing on the bioactive compounds and pro-apoptotic properties of color-fleshed potatoes in human colon cancer cells. *J. Agric. Food Chem.* 60, 11088–11096.
- Mendel, F., McDonald, G.M., Filadelfi-Keszi, M.A., 2010. Potato glycoalkaloids: chemistry, analysis, safety, and plant physiology. *Crit. Rev. Plant Sci.* 16, 55–132.
- Meziani, S., Oomah, B.D., Zaidi, F., Simon-Levert, A., Bertrand, Zaidi-Yahiaoui, R., 2015. Antibacterial activity of carob *Ceratonia siliqua* L. extracts against phytopathogenic bacteria *Pectobacterium atrosepticum*. *Microb. Pathog.* 78, 95–102.
- Nitithamyong, A., Vonelbe, J.H., Wheeler, R.M., Tibbitts, T.W., 2010. Glycoalkaloids in potato tubers grown under controlled environments. *Am. Potato J.* 76, 337–343.
- Phillips, B.J., Hughes, J.A., Phillips, J.C., Walter, D.G., Anderson, D., Tahourdin, C.S.M., 1996. A study of the toxic hazard that might be associated with the consumption of green potato tops. *Food Chem. Toxicol.* 34, 439–448.
- Roch, A.B.O., Honori, S.L., Messias, C.L., Oton, M., Gomez, P.A., 2015. Effect of UV-C radiation and fluorescent light to control postharvest soft rot in potato seed tubers. *Sci. Hortic.* 181, 174–181.
- Roddick, J.G., 1989. The acetylcholinesterase-inhibitory activity of steroidal glycoalkaloids and their aglycons. *Phytochemistry* 28, 2631–2634.
- Romanucci, V., Milardi, D., Campagna, T., Gaglione, M., Messere, A., D'Urso, A., Crisafi, E., La Rosa, C., Zarrelli, A., Balzarini, J., Di Fabio, G., 2014. Synthesis, biophysical characterization and anti-HIV activity of d(TG₃AG) quadruplexes bearing hydrophobic tails at the 5'-end. *Bioorg. Med. Chem.* 22, 960–966.
- Romanucci, V., Pisanti, A., Di Fabio, G., Davinelli, S., Scapagnini, G., Guaragna, A., Zarrelli, A., 2016a. Toxin levels in different variety of potatoes: alarming contents of α -chaconine. *Phytochem. Lett.* 16, 103–107.
- Romanucci, V., D'Alonzo, D., Guaragna, A., Di Marino, C., Davinelli, S., Scapagnini, G., Di Fabio, G., Zarrelli, A., 2016b. Bioactive compounds of *Aristotelia chilensis* stuntz and their pharmacological effects. *Curr. Pharm. Biotechnol.* 17, 513–523.
- Senguel, M., Keles, F., Keles, M.S., 2004. The effect of storage conditions temperature, light, time and variety on the glycoalkaloid content of potato tubers and sprouts. *Food Control* 15, 281–286.
- Yamashoji, S., Matsuda, T., 2013. Synergistic cytotoxicity induced by α -solanine and α -chaconine. *Food Chem.* 141, 669–674.