Evaluation and modeling of the properties and antioxidant characteristics of a new potato variety (Primavera) during storage at 4 °C

Evaluación y modelado de las propiedades y características antioxidantes de una nueva variedad de papa (Primavera) durante su almacenamiento a 4 °C

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ABSTRACT

Keywords:
Antioxidants
New potato variety
Phenolic compounds
Storage tubers
Shelf-life

Potatoes are one of the crops with the greatest influence worldwide, and Colombia is the most important exporter of "Criolla" or diploid potato. Universidad Nacional de Colombia has developed varieties of new diploid potatoes with high antioxidant properties and colored flesh: Primavera, Paola, Violeta, Milagros, and Paysandú. The aim of this research was to characterize and evaluate the stability of physicochemical properties of the raw potato cv Primavera during storage at 4 °C. It was used the potato variety Primavera grown in Santa Elena, Antioquia, during season mayo-august 2016. The evaluated properties were the antioxidant capacity (DPPH and ABTS), phenolic compounds (Folin-Ciocalteu method), moisture, texture in whole tuber and slices, and color in the pulp (CIELab). Samples were stored in bags at a constant temperature of 4 °C and were evaluated for 0, 7, 14, 21, and 30 d. Polynomial regression was performed for each variable vs time. In general, properties for potato variety Primavera did not show a defined trend; otherwise, they were fluctuating; this may be associated with various factors such as primary production and the interaction of physic-chemical phenomena of the matter with its environment. Potato presented an important content of antioxidant compounds compared with other varieties (ABTS: 2.89→2.94 mg Trolox g^{-1}; DPPH: 2.33→1.48 mg Trolox g^{-1}; phenolic compounds: 6.09→6.27 mg gallic acid equivalent g^{-1}). The "criolla" potato cv Primavera has a lot of important antioxidant properties which could confer it an agro-industrial potential in a short and medium term.

RESUMEN

Palabras clave:
Antioxidantes
Nueva variedad de papa
Compuestos fenólicos
Almacenamiento tubérculos
Vida útil

La papa es uno de los cultivos con mayor influencia a nivel mundial y Colombia se destaca por ser el primer exportador de papa criolla o diploide. Nuevas variedades de papa diploide con propiedades antioxidantes y coloración en su pulpa han sido desarrolladas por la Universidad Nacional de Colombia: Primavera, Paola, Violeta, Milagros y Paysandú. El objetivo del presente estudio fue caracterizar y evaluar la estabilidad de las propiedades fisicoquímicas de la papa variedad Primavera, en estado fresco, durante su almacenamiento a 4 °C. Se utilizó papa variedad Primavera, cultivada en Santa Elena, Antioquia, durante los meses de mayo-agosto de 2016. Las propiedades fueron evaluadas mediante la capacidad antioxidante (DPPH y ABTS), fenoles totales (método de Folin-Ciocalteu), humedad, textura en la papa entera y en rodajas, y el color en la pulpa (CIELab). Las muestras fueron almacenadas en bolsas a una temperatura constante de 4 °C y fueron analizadas en los tiempos de control 0, 7, 14, 21 y 30 d. Se realizó una regresión polinomial para cada variable en función del tiempo. En general, las propiedades evaluadas de la papa variedad Primavera no presentaron una tendencia definida, por el contrario, fueron fluctuantes, lo cual podría estar asociado a diversos factores desde la producción primaria; así como a la interacción de fenómenos químicos y físicos de la materia con su entorno. La papa presentó un contenido importante de compuestos antioxidantes comparada con otras variedades (ABTS: 2,89→2,94 mg Trolox g^{-1}; DPPH: 2,33→1,48 mg Trolox g^{-1}; fenoles totales: 6,09→6,27 mg ácido gálico equivalente g^{-1}). La papa criolla variedad Primavera es un alimento que posee importantes propiedades antioxidantes, lo cual le podría conferir un potencial de agro-industrialización a corto y mediano plazo.

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Potato is one of the crops with the highest production worldwide. China is one of the biggest producer, with 95 million tons produced annually. In Colombia, 3 million tons are produced annually (FAOSTAT, 2016). Potatoes are a desired and targeted product because of its high nutritional value, presenting high content of starch and micronutrients. Besides, it is versatile during steaming, allowing to prepare different recipes with it.

An advantage of *Solanum phureja* Juz. et Buk (Andean ancient species) is that have a better capacity to be pollinated with other potato species, resulting in a wide range of wild-type species from the Andes. This tuber has been used widely in programs of crop genetic improvement (Juyó *et al.*, 2011).

With this selection process, diploid potatoes with antioxidant properties and resistant to diseases, such as powdery scab and late blight, have been obtained (Singh and Kaur, 2016). The potato variety Primavera is part of these new varieties; it was developed at Universidad Nacional de Colombia, and its main characteristics is a colored peel and pulp with red and purple colors (Figure 1) (ICA, 2016).

Figure 1. Potato (*S. phureja* cv Primavera).

One of the most important attributes in colored potatoes is the high antioxidant content including phenolic compounds like anthocyanins (Kita *et al.*, 2015). Although this kind of potato is a versatile gastronomic alternative, because of its color and bioactive compounds, this product has a short lifespan after being harvested (Molina *et al.*, 2015). This short lifespan limits its storage for long periods; therefore, fast processing is required, representing a problem for industries that likely discard them because it does not meet the current quality standards in parameters like texture, dry matter and color (van Dijk *et al.*, 2002a).

Considering the lifespan characteristics of potato variety Primavera, the aim of this research was to characterize a new potato variety (Primavera), in a fresh state, in terms of moisture, phenolic compounds, color, texture, antioxidant activity, and evaluate its stability during storage at 4 °C.

MATERIALS AND METHODS
Raw material
Potato (*S. phureja* cv Primavera), which is a diploid potato, was collected from an in-field and non-technified crop in Santa Elena, Antioquia. The place is located at an altitude of 2300 m.a.s.l., and presents an average temperature of 14.5 °C and average relative humidity of 89% during may-august, 2016. The potatoes were processed the fifth day after harvest, previously cleaned and disinfected with water and organic acids Citrosan® to eliminate pathogen microorganism (1 mL L^{-1}); this day was considered as the storage day 0.

A completely randomized experimental design was used; where samples were evaluated for 0, 7, 14, 21, and 30 d. This elapse let evaluate the stability of the whole potato in real time. The potatoes were stored in low-density polyethylene bags with holes to enable air exchange in a refrigerator at 4 °C and local atmospheric pressure (640 mm Hg). The amount of potatoes stored were 1 kg each lot.

To determinate the antioxidant activity, moisture, and total phenolic compounds the potatoes were chopped and grind in order to not have differences between the measurements.

Methods
Moisture content. 2 g of macerated potato were weighed and taken to a forced convection oven at 105 °C for 5 h; the moisture content was reported as the loss of weight in moisture base (AOAC, 2005).

Antioxidant activity. The measurement of antioxidant activity was done with indirect methods of DPPH (α, α-diphenyl-β-picrylhydrazyl) and ABTS (2, 2'-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid). The antioxidants extraction was done by mixing 3.5 mL of Methanol reactive grade with 3 g of potato variety Primavera previously macerated with peel; then the sample was sonicated for 20 min and centrifuged for 20 min at 9000 rpm (Repo de Carrasco and Encina Zelada,

2008). The extracts were covered from light and stored at 2 °C until used.

The ABTS method was reported by Re *et al.* (1999). For it, 20 µL of methanolic extract was taken and mixed with 2000 µL of ABTS radical. After 7 min in darkness, the data of absorbance at 734 nm was registered, and the concentration was reported in mg Trolox g^{-1} dry basis. A calibration curve was previously made to determine the percentage of inhibition. It was made from 9 points of concentration of trolox in the cell between 0 and 16 µM Trolox, and this yielded a zero-order equation (Y=4.2163X+1.2276 with R^2=0.9956)

The DPPH method was done according to the methods reported by Brand-Williams *et al.* (1995). 20 µL of methanolic extract was mixed with 1980 µL DPPH radical and were registered at an absorbance of 517 nm after 30 min in darkness, the results were reported in mg Trolox g^{-1} dry basis. A calibration curve was previously made to determine the percentage of inhibition. It was made from five points of concentration of trolox in the cell between 0.0016 and 0.0046 mg Trolox mL^{-1}, and this yielded a zero-order equation (Y=2398X-23.654 with R^2=0.9865)

Total phenolic compound. The measurement was done according to the methods reported by Wang *et al.* (2016); the extraction of fresh potato phenols was performed by mixing 3 g of potato with 4 mL of Methanol: Water (60:40) solution. The mix was sonicated for 20 min and centrifuged for 30 min at 9000 rpm; 20 µL of the extract was taken and mixed with 480 µL of distilled water, 1250 µL of calcium carbonate 20% and 250 µL of diluted Folin-Ciocalteau reagent (1:1). The absorbance was read at 760 nm, after 2 h of reaction in darkness. A calibration curve was previously made from 13 points of concentration of GAE in the cell between 0 and 24 mg GAE L^{-1}, and this yielded a zero-order equation (Y=0.0186X+0.00032 with R^2=0.9939). The results were reported as mg GAE g^{-1} dry basis.

Texture. Fracture and resistance assays were performed using a texture analyzer TA-XT2i Stable Micro Systems (SMS) and the Software Texture Exceed, version 2.64. During measurements, whole and longitudinal sliced potatoes of 2 mm thickness were placed on a reference surface SMSP/35, and an awl with a spherical terminal

(SMS P/0.25s) was used to measure fracturability of the chopped potatoes; an awl SMS P/2 was used to measure the whole potato.

Color. The color measurements were determined in the center of pulp (reddish zone) with a spectrophotometer X-Rite (SP64 model), which works with CIELab coordinates, illuminate D65, 10º observer, specular included (SPIN). The ΔE quantity was computing as follow:

$$\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2} \quad (1)$$

Where L_0^*, a_0^*, and b_0^* are the parameters of color in CIELab coordinates at time 0.

Statistical analysis. The measure for each quality attribute of potato during each time of control was performed as follow: moisture, a$_w$, antioxidant capacity, total phenolic compounds (three samples, one measure/sample); color and texture (six samples, one measure/sample). The polynomial regression was used to estimate the performance of each quality attribute versus the time. The experimental error was partitioned in lack of fit and pure error (Walpole *et al.*, 2012). For the parameter of color (L*, a*, b*) a multi-response model with the correlated error was used, and a secondary parameter ΔE based on predicted values was calculated (Hadfield, 2010). All statistical analyses were performed in the R environment (R Core Team, 2016) and the packages MCMCglm (Hadfield, 2010), and coda (Plummer *et al.*, 2006) were used.

RESULTS AND DISCUSSION

The moisture values for the potato variety Primavera during storage were adjusted to a cubic model (Table 1). As can be seen in Figure 2A, a general water loss occurred in the tuber throughout storage, a change of direction in the slope indicated a gain of moisture of the product at 14 d. Moisture was fitted to a cubic model. For both, the whole potato and the slices, the model that best fit was the quadratic one. Similar results were reported by Rivero *et al.* (2003) for potatoes from Tenerife, which lost water after 20 weeks of storage at 12 °C. This process of water loss happens through the periderm layer because of its high permeability (Singh and Kaur, 2009). Mass transfer occurs because of the difference in water chemical potential that exists between the potato and the environment and for breathing processes and transpiration of the tuber

(Kaya *et al.*, 2016). Near 14 d, a change of direction in the slope indicated a gain of moisture of the product, this can be due to changes in environmental conditions, as relative moisture, which was not controlled during the experiment.

The initial values of moisture of fresh potato variety Primavera were similar to those reported by Bártová *et al.* (2015), (81%) in fresh *S. phureja* diploid potatoes,

and by Cerón-Lasso *et al.* (2018), who reported moisture between 72.06% and 77.24% for genotypes G2589, G2585, G1997, G0204, G2599, and G1781 of native diploid potatoes (*Solanum phureja*).

In the case of the whole potato, a slight increase in the slope F/D is observed until 7 d. Figure 2 shows an increase in the slope F/D until 14 d, which is followed by a subsequent decrease in the values for the sliced potato.

Table 1. Coefficients of the polynomial that models each of the quality attributes of the potato variety Primavera and its respective adjustment coefficient (R^2).

Property	Coefficients				R^2
	β_0	β_1	β_2	β_3	
L	37.46**	0.410	-0.070	0.0020	0.99
a*	18.52**	1.610*	-0.180**	0.0040**	0.99
b*	5.24+	-0.230	0.005	0.0001	0.73
ΔE	----	----	----	----	0.99
ABTS	2.70*	-0.298	0.032+	-0.0007+	0.92
DPPH	2.30***	-0.249***	0.015***	-0.0003***	0.96
Phenolic compounds	6.43***	-0.613+	0.050+	-0.0010+	0.39
Moisture	80.79***	1.100**	0.064**	-0.0010*	0.99
Texture (Whole tuber)	4.42***	0.072+	-0.005**	----	0.97
Texture Slices	0.12	0.085*	-0.003*	----	0.85

+, *, **, *** represent a significance level of 0.10, 0.05, 0.01, and 0.001, respectively.

The increase in the slope F/D for the whole potato indicates a less turgor of the tissue. This behavior would be due to the degradation of pectins and changes in monovalent and divalent ions in the cell wall of the tuber, which causes a decrease in the cell adhesion and therefore a lower resistance to breaking by puncture (van Dijk *et al.*, 2002b). This result was similar to the one reported by Solomon and Jindal (2005) for crossed potatoes stored at 24 °C.

The results for texture analysis at time zero for the whole potatoes identified a product with an important firmness that contributes to greater resistance to the mechanical damages during its postharvest handling, which could be attributed to the important pectic compounds present in the cell walls of the potato peels' tissue (Bordoloi, 2012). The penetration strength values found in the potato variety Primavera were higher than those reported by Castro Lara (2008), in fresh potatoes from the Hermes variety,

stored at 4 °C, but lower than those reported by Espinosa *et al.* (1998).

The texture of the sliced potato identified in greater detail the level of deformation of the internal matrix, showing an important elastic component (slope F/D<45°). This result suggests that the potato's interior may be less turgid and firm (Singh *et al.*, 2016). This last situation may be due to the plasticizing effect of water present in the matrix (Salvador, 2009). For the sliced potato, the behavior was consistent with the loss of water that the tuber suffered during the first 15 d, which makes it less elastic., and is also related to changes in starch content, which is degraded to simple sugars, making the sliced potatoes tend to be fractured (van Dijk *et al.*, 2002a).

The values of penetration strength in potato's slices were lower than those found by García-Segovia *et al.* (2008)
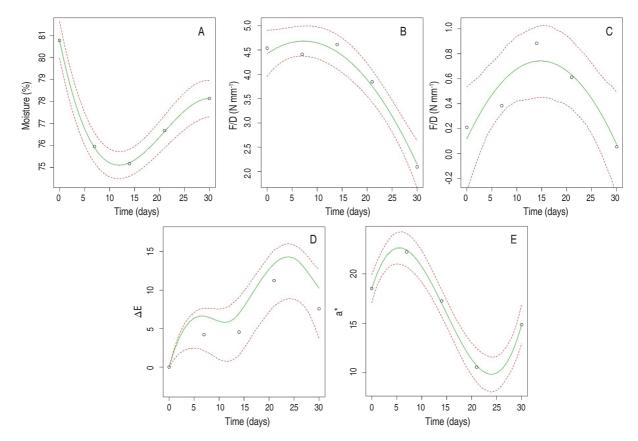
Figure 2. Mean values (o) and predicted values (green line) by the polynomial model for changes in potato physical attributes during storage time. A. Moisture; B. Texture for the whole tuber; C. Texture for slices; D. ΔE (color inside slice); E. a* (red-green chromaticity). Dashed red line shows both lower and upper boundary of the highest posterior density interval at 95% of probability.

for Monalisa variety of 20 mm diameter (397±35 N); therefore, it will be expected a less turgid, more elastic and collapsed structure product.

Changes in texture and moisture influenced the appearance of the tuber. From 14 d the tuber began to be rougher and brightness, this situation increased along the storage time (Figure 3).

The color change was adjusted to a cubic model. Figure 2 shows a gradual increase of ΔE in periods of 7 d, reaching its maximum value of 12.3 in 21 d, followed by a decrease of ΔE until 30 d.

The changes for ΔE are attributed mainly to three phenomena: initially to the sowing, geographical and environmental conditions that provide in potatoes a high variability between lots, in terms of size, pigmentation, and shape. On the other hand, and consistent with the

above, to the greater or lesser density of pigments that the equipment captures in the observation window used in the spectrophotometer (ϕ=11 mm), which is random and uncontrollable. Finally, to the changes mainly in chromaticity a* attributable to the degradation of anthocyanins and carotenoid pigments present (Šulc *et al.*, 2017). The ΔE property showed an increase at the end of storage concerning 0 d of storage; this result is in agreement with the result obtained by Nourian *et al.* (2003) who found an increase in the color of the pulp for the Chieftain Potato variety, stored at different temperatures including 4°C.

The changes in pulp potatoes color during the storage should be due to chemical reactions, in the case of brightness, this change is usually seen during the transformation of amyloplasts to chloroplasts (Grunenfelder *et al.*, 2006), because of the light presence during storage. In the case of chromaticity a*, its variation is mainly changes suffered in colored compounds, like anthocyanins. These reddish

compounds are transformed in other types of compounds, by hydroxylation, methylation, and glycosylation; which

generate color changes, by pH effects, temperature, and light (Reyes and Cisneros, 2007).

A

B

C

D

E

Figure 3. Photographs of potato cv Primavera during storage. A. 0 d; B. 7 d; C. 14 d; D. 21 d; E. 30 d.

The fit to the model for ABTS, DPPH and phenolic compounds (PC) was cubic (Figure 4). In the case of DPPH, there was a decrease in values up to 14 d (from 2.33 to 1.20 mg Trolox g^{-1}) followed by a slight increase (from 1.28 to 1.48 mg Trolox g^{-1}) (Figure 4B). Overall, a decrease of 50% in the antioxidant activity is observed by the DPPH method, and a decrease and subsequent increase in this quality attribute is observed with ABTS method (from 2.89 mg Trolox g^{-1} at 0 d to 2.94 mg Trolox g^{-1} at 30 d) and PC (6.09 mg GAE g^{-1} at 0 d to 6.27 mg GAE g^{-1} at the end of the storage).

The behavior of the parameters associated with the antioxidant capacity of the diploid potato (ABTS, DPPH, total phenols) did not show a specific correlation with the color parameters, probably due to the same variability mentioned for the ΔE. However, there are other factors not controlled in the research that may be affecting, such as those associated with primary production and the chemical and physical phenomena of the interaction of the matter with the environment.

The differences in both measures, ABTS and DPPH, occur because of the type of antioxidant assessed with each method. In general, ABTS measures hydro- and lipophilic compounds (Kuskoski *et al.*, 2005). DPPH measures hydrophobic antioxidant systems; Floegel *et al.* (2011) found great differences between both methods in highly pigmented foods, which is the case of potato variety Primavera. Similar behavior for antioxidant capacity is observed for colored potatoes, especially clone 'CO97227-2P/P', reported by Külen *et al.* (2013), in which antioxidant activity by ABTS showed a considerable increase during storage at refrigeration conditions for 7 months; in contrast, with DPPH, the antioxidant capacity was constant over time.

DPPH and ABTS values, at time 0 d, were higher than the one reported by Molina *et al.* (2015) (DPPH: 458 μmol Trolox 100 g^{-1} for clon 2 of native potatoes), and the ones reported by Burlingame *et al.* (2009) for *S. pinnatisectum* wild Andean species (43-892 μg Trolox g^{-1}).
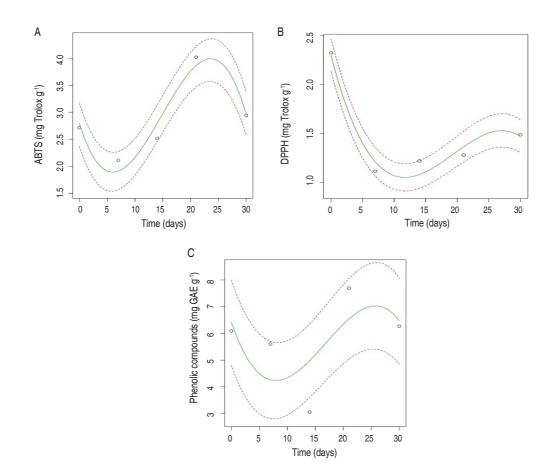
Figure 4. Mean values (o) and predicted values by the polynomial model in potato chemical attributes during storage time. A. ABTS; B. DPPH; C. Total phenolic compounds. Dashed red line shows both lower and upper boundary of the highest posterior density interval at 95% of probability.

An outstanding feature of this potato variety is its number of antioxidants, as well as phenolic compounds. Figure 4 presents a behavior similar to that one reported by Singh and Kaur (2016), which shows an increase in a number of total phenolic compounds, specifically the p-cumaric acid and quercetin, during potato storage, especially at temperatures of 4°C. Low temperatures, light, and some pathogens during storage could induce the generation of phenolic compounds, by the phenylalanine ammonia lyase, that regulates the synthesis of these compounds –considering that the majority of phenolic compounds in reddish diploid potatoes are anthocyanins (Rytel *et al.*, 2014). The increase in total phenolic compounds with time in refrigeration conditions can be explained partly by enzyme anthocyanin synthase activity, which increases in lower temperatures (Dios-López *et al.*, 2011) the degradation of the complex phenolic structures into phenolic acids, and de breakdown of cell structure which have the phenolic compounds strongly linked (Türkben *et al.*, 2010).

CONCLUSIONS

Potato variety Primavera has antioxidant properties and total phenolic content higher than the found in other potatoes with similar features, making it food with great potential for industrial exploitation. The stability study allowed the evaluation of some properties of the potato during the storage time. A well-defined tendency of antioxidant activity and total phenolic compounds was not observed. At 21 d, the potatoes displayed considerable rugosity and loss of turgor, along with color deterioration, making the product a perishable food that requires fast consumption and processing after harvest. In the models evaluated, none showed a lack of fit.

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