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Nutritional technological characterization and secondary metabolites in stored carioca bean cultivars

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The recommendation of bean cultivars and the use of appropriate storage techniques allow the quality characteristics of these grains to be preserved for human consumption. The aim of this study was to characterize the effects of storage on three cultivars of the common carioca bean in raw form and to determine the relationships between storage time and technological quality parameters involved in the darkening and hardening of grains, the chemical composition of the beans and the presence of secondary metabolites. The experiment followed a completely randomized design (CRD) with a full factorial scheme consisting of two factors: bean cultivars, with three levels and storage time, with five levels. The color parameters and the storage times significantly differed between the cultivars. The cooking time, when compared to the water absorption index, indicated that the cultivars had, on average, a high percentage of moisture (>95%) and an average cooking time of 17 min., this applies to the control, while values increase during the storage time. Storage under ambient conditions led to a reduction in grain brightness parameters, characterized by darkening and hardening; no reduction in protein and mineral content; and an increase in iron, phosphorous, tannin, and phytic acid contents at 180 days.

Key words: Cooking time, grain color, multivariate analysis, *phaseolus vulgaris*.

INTRODUCTION

The common bean (*Phaseolus vulgaris* L.) is one of the most important foods in the Brazilian diet, as it is an excellent source of essential nutrients, with significant concentrations of protein, carbohydrates (especially starch), fiber, vitamins, and minerals (Borém and Carneiro, 2011). Ensuring and preserving nutritional qualities is a primary and essential condition to safeguard the technological quality of beans, as they are the staple

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food of the Brazilian population in both rural and urban areas (Ramírez-Cárdenasi et al., 2008).

Brazil ranks first and third in the global consumption and production of the common bean, respectively. Among the many commercial groups, beans of the carioca group stand out, as they are a preferred type and represent approximately 70% of the domestic consumer market (Albrecht and Carvalho, 2006). Therefore, they receive greater attention from genetic breeding programs, in which characteristics related to chemical composition (as a function of storage conditions), such as mineral content and secondary metabolites, have been gaining importance for research because they are determinants of the nutritional quality of these legumes.

The quality of beans is determined by two factors: their technological characteristics, which determine acceptance and consumption by consumers, and their nutritional value. Technological characteristics include physical attributes, such as color, brightness, and texture, and they are related to cooking time. Their nutritional value specifies the chemical composition of beans with respect to protein, vitamin, and mineral content. Cooking or technological qualities include, in particular, the ability to be rapidly hydrated, which contributes to reduced cooking time, thick broth, good flavor, and pleasing texture, as well as moderately split beans, thin skin, and good color stability (Bassinello, 2016).

Depending on the variety, the color of the bean tegument is an influential trait at the time of purchase by the final consumer. For example, the carioca cultivar has a light-beige color with brown stripes, and its darkening indicates longer storage time, which contributes to an increase in cooking time (Coelho et al., 2009). The colorful varieties, such as yellow, pink, red, and black beans, have teguments rich in anthocyanins and other phenolic compounds that give the beans antioxidant properties (McGee, 2014), which are associated with desirable nutritional quality by consumers. which are associated with desirable nutritional quality by consumers. This variability is important for diets based on food chemical composition tables, which normally do not have specific values for different bean cultivars or their possible changes in the course of harvest years. In addition, beans of improved nutritional quality and with specific characteristics could be provided to populations worldwide and thus meet their consumption (Prolla et al., 2010) and nutritional needs.

The technological and nutritional quality of different bean cultivars stored under ambient conditions has been little studied. It is important to evaluate the effect of this factor during the storage period at ambient conditions, considering that in Brazil, beans are cultivated for the most part on small, rural properties, where storage conditions are inadequate (Embrapa, 2016). From the point of view of consumers, aspects related to the physical characteristics of beans, such as color, size, shape, and cooking quality, including fast hydration, low cooking time, thick broth, flavor, and texture are the most essential. However, improper storage causes undesirable alterations in the final product (Bassinello, 2008).

This aim of this study was to characterize the effects of storage on three carioca cultivars of the common bean (*P. vulgaris* L.) in its raw form and to determine the relationships between storage and technological quality parameters involved in the darkening and hardening of the beans (color and cooking time), the chemical composition of the beans (proteins, iron (Fe), manganese (Mn), zinc (Zn), and phosphorus (P)), and the presence of secondary metabolites (phytic acid and tannins).

MATERIALS AND METHODS

The experiment was conducted at the Laboratory for Quality Control of Agricultural Products of Western Paraná State University (Universidade Estadual do Oeste do Paraná—UNIOESTE), Cascavel campus, in partnership with The Brazilian Agricultural Research Corporation (EMBRAPA) – Rice and Beans, in Santo Antônio de Goiás, Goiás (GO) and EMBRAPA, Ponta Grossa research station, Paraná (PR), from October 2012 to July 2014.

The samples were three cultivars of the common bean (*P. vulgaris* L.) – carioca commercial group (BRS Estilo, BRS Madrepérola, and BRS Pontal), produced by EMPRAPA – Rice and Beans, from the wet season crop (2012-2013), planted on November 26, 2012 in Ponta Grossa (PR). The area sampled measured 1000 m^2, and the topography was slightly sloping and well drained. It had approximately 25 years of use with prior bean cultivation, and it originally had field vegetation. The area was fertilized with 300 kg per hectare of monoammonium phosphate (MAP) (11% N and 52% P_2O_5), with 0.45 m spacing between rows and 12 plants per linear meter. Plots were manually harvested, and the pods were mechanically threshed. Next, the beans were naturally dried to 13% (wet basis) moisture. After harvest, the samples were allocated into three replicates for each cultivar (for each storage period) and placed in brown paper bags with 500 g capacity each, in their own room, in the Laboratory for Quality Control of Agricultural Products – LACON.

The beans of the three cultivars were stored on open shelves with natural ventilation, at room temperature with an annual mean of 25°C, and away from direct light for a total of 180 days with no humidity control. This location experiences little influence from external conditions (light, temperature, and humidity) and resembles storage in small family farms where, for the most part, the storage environment does not have temperature or humidity control.

In whole beans, the parameters color and water content (moisture) of control cultivars were analyzed at 20 days after harvest. When each storage period was complete, the beans were separated into samples of whole beans and ground beans, packaged in polyethylene bags, and stored in a domestic freezer (-18°C) until analysis.

The tegument color of the recently harvested cultivars (control) and of the stored grains were determined by direct reading in a Konica Minolta® CR-410 colorimeter with an aperture of 50 mm. The colorimeter used the color coordinates L*, a*, and b*. The coordinate L* represent the luminosity, the color parameter a* has positive values for reddish colors and negative values for greenish tones (-60 to 60), and the color component b* has positive values for colors with yellow tones and negative values for blue tones (-60 to 60) (Granato and Masson, 2010). The beans were placed in the granular material attachment (model CR-A50), and the readings were performed in triplicate for each cultivar (Oomah et al., 2011).

From the L*, a*, and b* values, the following colorimetric indices were calculated: chroma (C*), which defines the intensity and purity of a color, and Hue angle (H°). The parameters color angle Hue (H*), Chromaticity (C*), and Δe, which is the total difference in color compared with the initial color, were determined. The color results were expressed in terms of Cielab scale parameters, as follows:

$$H^* = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (1)$$

H* = color angle Hue; a* = color component read-green; b* = color component yellow-blue.

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (2)$$

C* = Chroma; b* = color component red-green; color component yellow-blue.

$$\Delta e^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$

Δe* = difference between the of the sample relative to the standard or control; ΔL*= difference between the luminosity of the sample relative to the control; Δa* = difference between the coordinate a* of the sample relative to the control; Δb* = difference between the coordinate b* of the sample relative to the control. For moisture content, three replicates of 10 g of each sample (whole beans) were weighed, following the standard oven method (Brasil, 2009).

Cooking time was determined with the aid of a modified Mattson cooker method (Proctor and Watts, 1987). The modified Matsson cooker had 25 rods measuring 20 cm in length and weighing 82 g each. Cooking time was considered complete when 50% plus 1 of the beans were pierced by the drop of the 13th rod, that is, by the drop of 52% of the rods.

To evaluate electrical conductivity, the method described by Corrêa and Afonso Júnior (1999), was used. The electrical conductivity of the solution was obtained with a conductivity meter (TECNAL, model TEC–4MP). The values of the reading were divided by the sample weight in grams, and the results are expressed as $\mu S \cdot cm^{-1} g^{-1}$.

The hydrogen potential (pH) was obtained with a portable digital pH meter with automatic temperature compensation, model pH – 221, following the technique described by the Adolfo Lutz Institute (IAL, 2008; Rigueira et al., 2009). The protein content was determined from the total nitrogen (N) content of the samples using the micro-Kjeldahl method (Silva and Queiroz, 2009). The contents of Fe, Mn, and Zn were determined with an atomic absorption spectrophotometer following the method proposed by Malavolta (2006). A 0.2 g aliquot of sample (50 mesh flour). The results for Fe, Mn, and Zn are expressed in $mg \cdot kg^{-1}$.

P was determined by colorimetry (flow injection analysis - FIA) in a spectrophotometer (FEMTO – 700 Plus), was read in a colorimetric (725 nm). The results for P are expressed in $g \cdot kg^{-1}$ (Malavolta et al., 1997). Phytic acid was analyzed using the colorimetric method described by Latta and Eskin (1980), with modification of the resin to DOWEX – AGX-4. After extraction, the samples were read in a spectrophotometer (500 nm). The tannins in the beans were determined using the Folin-Denis spectrophotometric method (Horwitz, 1995), with adaptations. The absorbance was read at 765 nm and the results are expressed in g phenols (tannic acid) g^{-1} ms^{-1}. The experiment followed a completely randomized desig with full factorial scheme, with two factors: carioca bean cultivars (Factor 1) with three levels (BRS Estilo, BRS Madrepérola, and BRS Pontal) and storage time (Factor 2) with five levels (initial period (control) and 60, 90, 135, and 180 days of storage).

An exploratory analysis of the results was conducted, in which the following were calculated: mean, variance, standard deviation, and coefficient of variation. The data obtained were tested for normality (Shapiro-Wilk test) and homogeneity of variances (Hartley test), both at a significance level of 5%. Analysis of variance and comparison of means (Tukey's test) were performed considering a significance level equal to or less than 5% probability ($p<0.05$). After these analyses, the data were subjected to multivariate analysis to determine whether there was a correlation between the studied variables. Multivariate analysis of variance (MANOVA) was used to evaluate whether the effects of the factors on the response variables were significant, with a significance level equal to or less than 5%. All statistical analyses were performed using the software R (Development Core Team R, 2016).

RESULTS AND DISCUSSION

The mean luminosity L* values, indicative of the brightness of the tegument of the three bean cultivars in the five storage periods, decreased over time, contributing to the darkening of the bean, which is considered a negative trait in beans of the carioca class because it can indicate an undesirable, hard texture with increased cooking time. The mean luminosity L* value among the evaluated control cultivars was L* 55.93, which is 2.93 points higher than the L* value of 53.00, the standard mean for carioca beans reported by Carneiro et al. (2000).

The cultivar BRS Madrepérola had the highest brightness, with a mean L* of 58.51. It is worth noting that the evaluated cultivars had higher luminosity values compared with other studies (Silva et al., 2009; Lopes, 2011; Schoeninger et al., 2014; Siqueira et al. 2014), and can be characterized as having light teguments, and consequently may achieve a higher market value. As there was no interaction among cultivars (p-value = 0.4631), Tukey's test was used to compare the mean L* for each cultivar and at each time. Figure 1 (a) and (b) show the differences in color among cultivars and storage times for the parameter L*.

There was a decrease in the variables a* and b* for all cultivars stored for 180 days compared to those stored for 60, 90, and 135 days. The chromaticity a* values of the control beans, whose variation in color ranged from green to red, indicated that BRS Pontal had a higher a* value, 5.04 (reddish coloration), compared to BRS Estilo and to BRS Madrepérola. The chromaticity values a* and b* in carioca beans reported in the literature are on average a* = 7.21 and b* = 12.92 as reported by Silva et al. (2009); a* = 8.20 and b* = 14,36 as reported by Schoeninger et al., (2014); and a* = 6.85 and b* = 12.05 for carioca beans grown in the rainy season as reported by Lopes (2011). Regarding the influence of storage time on b*, the analysis of variance was significant (p-value =

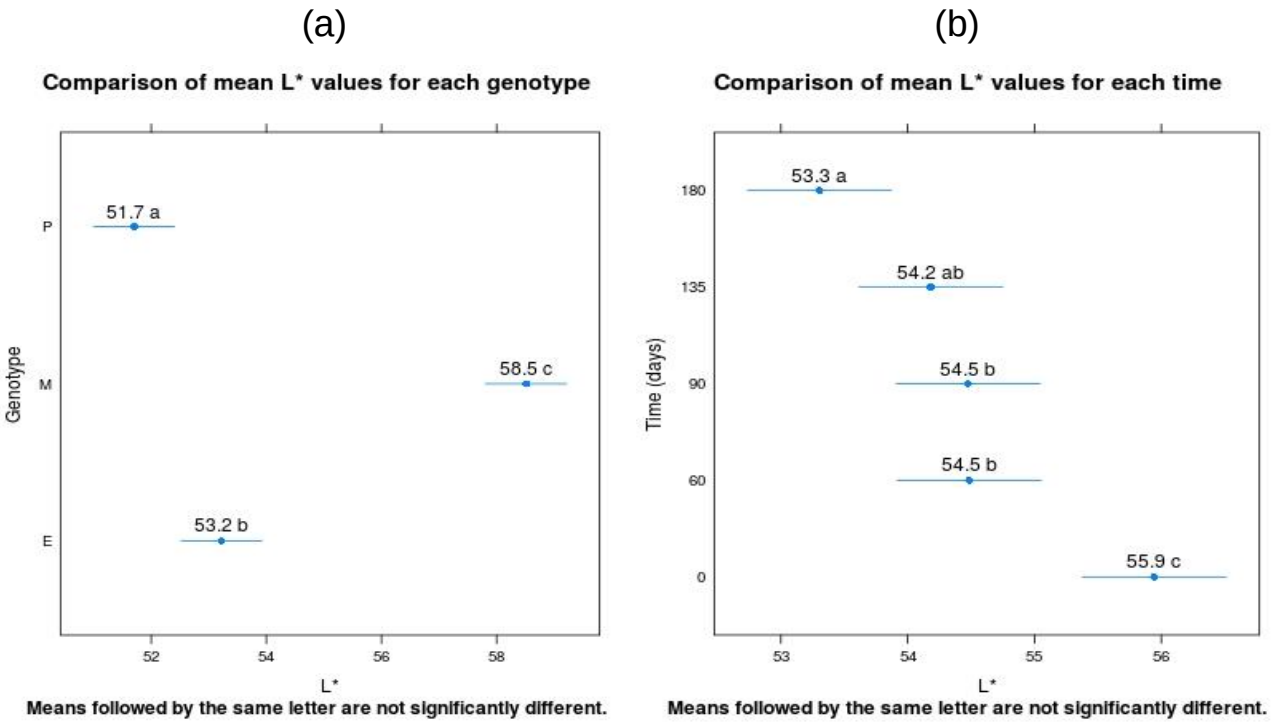

Figure 1. Comparison of mean L* values (a) for each genotype (BRS Estilo (E), BRS Madrepérola (M) and BRS Pontal (P)) and (b) for each storage time (0, 60, 90, 135 and 180 days).

0.0198) for the interaction between cultivar and storage time for the cultivars BRS Estilo, Madrepérola, and Pontal.

For the values that measured the intensity and purity of color, represented by the chroma index C*, beans of the cultivar BRS Estilo had greater color intensity at all storage periods, with values ranging between 11 and 12. The lowest C* value was associated with the shortest storage time, confirming that color intensity increased with the aging of the bean. The higher the C* value, the more noticeable the product will be to human vision (Granato and Masson, 2010). This characteristic could be the differentiating factor in the quality of carioca beans at the time of purchase by the consumer.

For the H° of the three cultivars in the initial period (control), the largest angle was observed for BRS Madrepérola (H° 72.20), with a predominance of yellow color. This result reinforces the value found for chromaticity b* in the same cultivar (BRS Madrepérola), which was close to yellow. The mean value found in this study for the cultivars and storage times was H° = 61.42. A similar H° value (60.27) was reported for raw carioca beans by Schoeninger et al. (2013).

In general, the color parameters (L*, a*, b*, C*, and H°) analyzed for the three cultivars and storage times significantly differed ($p < 0.05$), except for the interaction between cultivar and time for L* and C* (p-value = 0.0681). The total color difference between the control beans and the cultivars in their respective storage periods was calculated by the difference in color between samples, using the values obtained for L*, a*, and b* (Table 1).

The cultivar that had the lowest color variation (Δe*) across the four storage periods was BRS Madrepérola. The longer the storage period, the greater the color difference, that is, the more noticeable the difference was between samples over time and the recently harvested bean (control). The smaller the color difference between carioca beans of the same cultivar over the storage period, especially under ambient conditions, the higher their market value will be.

Table 2 shows the results of the analyses of technological quality. The mean water content values for the three bean cultivars decreased over the five storage times evaluated. This reduction may have been due to hygroscopic equilibrium between the initial moisture content of the beans and the environment in which they were stored, for the three cultivars in time (control, 60, 90, 135 and 180 days).

There was a significant difference ($p = 0.0000$) in the water content of the bean cultivar across storage times. The water absorption percentages before cooking, obtained for the control beans of evaluated cultivars, were, on average, 100.57%. There was an interaction between the factors, indicating differences (p-value = 0.0017) among the cultivars according to time of analysis.

Table 1. Differences in color parameters (ΔL*, Δa*, Δb*, Δe*) of the cultivars BRS Estilo (E), BRS Madrepérola (M), and BRS Pontal (P) at the different storage times (60, 90, 135, 180 days).

Genotype	ΔL*	Δa*	Δb*	Δe*
BRS E60	1.28	2.15	0.45	2.54
BRS E90	1.39	2.15	0.57	2.62
BRS E135	1.83	2.44	0.25	3.07
BRS E180	2.57	2.29	0.04	3.44
BRS P60	2.38	1.60	0.03	2.86
BRS P90	2.27	1.99	0.04	3.02
BRS P135	2.72	1.96	0.01	3.36
BRS P180	3.27	1.13	0.01	3.46
BRS M60	0.71	0.85	1.30	1.72
BRS M90	0.73	0.87	1.14	1.61
BRS M135	0.72	0.96	1.16	1.67
BRS M180	2.08	0.26	0.14	2.10

ΔL* = difference between the L* of the stored sample and the control L*; Δa* = difference between the a* of the stored sample and the control a*; Δb* = difference between the b* of the stored sample and the control b*; Δe* = difference between the color parameters of the stored sample and the control.

When compared with the water absorption index, the results for cooking time demonstrated that the cultivars had, on average, a high percentage of hydration, above 95%, which might have contributed to the rapid cooking time observed, with an overall mean of 17.66 min.

According to the reference values for cooking time proposed by Proctor and Watts (1987), the three cultivars (BRS Estilo, BRS Madrepérola, BRS Pontal) had an average susceptibility level of resistance to cooking (16 to 20 min), with BRS Pontal having the lowest susceptibility to the hardening phenomenon, also known as hard-to-cook (HTC).

Nyakuni et al. (2008) evaluated four common bean cultivars stored at room temperature found that the cooking time increased over storage for 4 cultivars.

It is worth mentioning that the water absorption characteristics of the cultivars had unexpected values, such as the increase in percentage with the increase in days in storage. Therefore, this factor could have influenced the cooking time results starting at 90 days of storage. For the cultivar Pontal, for example, an increase in cooking time was observed at 60 days and a decrease at 90, 135, and 180 days (Table 2).

The values obtained for the parameter electrical conductivity indicated the deterioration of beans during storage. The overall mean electrical conductivity among cultivars in the initial period (control) was 40.23 $\mu S \cdot cm^{-1}$, reaching 76.00 $\mu S \cdot cm^{-1}$ at the end of storage. In the last storage period (180 days), there was an increase in this value for all cultivars, with BRS Pontal leaching the most mineral ions. That is, there was a degradation of the cell wall in this cultivar, suggesting that it is more susceptible to aging when stored under normal ambient conditions. ANOVA confirmed that there was an interaction for electrical conductivity between the factors cultivar and storage time ($p = 0.0000$), confirming the variability among cultivars and during storage.

The mean pH values of the recently harvested (control) and stored (60, 90, 135, and 180 days) beans were close to 7.0 for the three cultivars (pH = 6.69), a required factor for the technological and nutritional quality of beans. An acidic pH value is a characteristic of aged beans, occurring especially due to inadequate storage and/or storage for long periods. The ANOVA results revealed a significant interaction (p-value = 0.0071) between cultivar and storage time, with different performance for both factors.

The reduction in pH stored beans is associate with an increase in acidity over storage time (Coelho et al., 2013) and we believe that the differences reported up to this point can be attributed to genetic differences among the evaluated cultivars. The crude protein content in beans varies according to the genotype, the environment, and the conditions to which they were subjected during cultivation. The average composition of proteins in common raw beans of the carioca group, as reported in national studies, is 20% (Unicamp, 2011). The results obtained in this study were within the expected protein values, with averaging 19% (Table 3). The cultivar BRS Madrepérola had on average the highest protein content (20%) throughout storage. The percentage of protein in the beans was preserved during storage, a required factor considering that the cooking process significantly reduces the protein composition of cooked beans. These results corroborate those reported by Coelho et al. (2012) who found the following protein contents in raw beans stored under normal ambient conditions: control (21.24%), and 12 months (21.37%) of storage. There was a significant interaction for protein content between the factors cultivar and storage time (p-value = 0.0023),

Table 2. Means of the technological quality parameters water content, water absorption, cooking time, electrical conductivity, and pH of carioca bean cultivars stored for 0 (control) 60, 90, 135, and 180 days.

Cultivars/Time	Control	60	90	135	180
			Water Content (%)		
BRS Estilo	18.21±0.08^{Ba}	14.39±0.31^{Cb}	14.45±0.19^{Cb}	11.13±0.10^{Bc}	9.63±0.09^{Ac}
BRS Mpérola	28.32±1.83^{Aa}	12.25±0.04^{Bcb}	13.21±0.50^{Bb}	13.89±3.68^{Bb}	9.62±0.48^{Ac}
BRS Pontal	19.68±1.55^{Ba}	15.67±0.04^{Cb}	14.93±0.36^{Cb}	11.16±0.28^{Bc}	9.26±0.02^{Ac}
Cultivars			**Water Absorption (%)**		
BRS Estilo	94.08±1.06^{Bc}	93.19±0.75^{Bc}	104.18±3.53^{Ab}	100.36±2.64^{Aab}	115.10±6.75^{Aa}
BRS Mpérola	99.52±0.71^{Aa}	99.77±4.06^{Aa}	96.35±2.30^{Aa}	102.83±1.14^{Aa}	105.00±10.01^{Aa}
BRS Pontal	93.61±1.28^{Bb}	93.69±1.49^{ABb}	103.54±4.6^{Aa}	103.92±0.75^{Aa}	103.47±1.17^{Aa}
Cultivars			**Cooking Time (min)**		
BRS Estilo	16.30±0.26^{Cc}	33.57±0.49^{Aa}	30.98±0.69^{Aa}	26.00±2.65^{Bb}	31.33±1.15^{Aa}
BRS Mpérola	19.00±0.00^{Ac}	31.92±0.98^{Aa}	30.71±0.65^{Aa}	30.71±0.65^{Aa}	24.26±1.69^{Bb}
BRS Pontal	17.67±0.58^{Bc}	31.92±0.98^{Aa}	29.50±3.68^{Aa}	19.74±1.46^{Cc}	24.26±1.69^{Bb}
Cultivars			**Electrical Conductivity (µS.cm^{-1})**		
BRS Estilo	36.60±1.64^{Ac}	75.11±4.63^{Aa}	57.55±2.28^{Ab}	70.04±3.36^{Ba}	69.97±4.08^{Ba}
BRS Mpérola	42.79±3.82^{Ac}	37.40±1.30^{Cc}	36.41±2.02^{Bc}	80.67±2.08^{Aa}	63.89±2.10^{Bb}
BRS Pontal	41.32±3.43^{A}d	65.08±2.85^{Bb}	56.08±2.95^{Ac}	55.45±3.07^{Cc}	94.14±1.57^{Aa}
Cultivars			**Hydrogen Potential (pH)**		
BRS Estilo	6.72±0.01^{Aa}	6.58±0.01^{Ab}	6.55±0.07^{ABb}	6.55±0.04^{ABb}	6.57±0.03^{Ab}
BRS Mpérola	6.63±0.05^{Aa}	6.59±0.02^{Aa}	6.63±0.03^{Aa}	6.63±0.04^{Aa}	6.53±0.02^{Aa}
BRS Pontal	6.71±0.12^{Aa}	6.55±0.10^{Ab}	6.47±0.02^{Bb}	6.48±0.02^{Bb}	6.46±0.02^{Bb}

BRS Mpérola = Madrepérola; the mean of three replicates ± standard deviation; the same lowercase letters in rows (time) represent statistically equal means at 5% significance; the same uppercase letters in columns (cultivar) represent statistically equal means at 5% significance.

indicating that at least part of the differences could be attributed to the genetic differences between the evaluated cultivars.

The mineral composition of the cultivars (Table 3) included micronutrients essential to the daily diet, namely Fe, Mn, Zn, and P. Regarding the Fe concentrations, the cultivars BRS Estilo, BRS Madrepérola, and BRS Pontal differed significantly (p-value = 0.0000) among storage periods (60, 90, 135, and 180 days), indicating the existence of an interaction between cultivar and storage time. Storage promoted an increase in the Fe content, with means of 47 to 144 mg·kg^{-1} Fe/sample, with differences among the cultivars (p-value = 0.0000*) and greater variation from 135 to 180 days. This increase could be due to the genetic differences among the cultivars and to the storage time and environment. Buratto (2012) investigated the Fe content in three tissues (cotyledon, embryonic axis, and tegument) in 10 different bean cultivars and found a higher fraction of Fe in the embryonic axis, at 95 to 128 mg·kg^{-1}, and there were differences among cultivars (p-value < 0.01). In the cotyledons, the Fe content was similar in 100% of cultivars (33.69 to 42.17 mg·kg^{-1}).

This increase could be due to the genetic differences among the cultivars and to the storage time and environment. For manganese (Mn), the interaction between cultivar and time was significant (p-value = 0.0000); storage promoted an increase in Mn content, except at 180 days. In 21 strains of beans, Mesquita et al. (2007) found Mn contents of 14.93 to 28.9 mg·kg^{-1}, results corroborated by the present study. Similar results were reported by Silva et al. (2013) for Mn, with means of 17.18 in raw beans (Pontal and commercial). Buratto (2012) evaluated the effect of genetic variability on mineral accumulation in the tegument, cotyledon, and embryonic axis and found Mn concentrations between 3.60 and 5.38 mg·kg^{-1} in the tegument, 11.00 and 18.60 mg·kg^{-1} in the cotyledon, and 14.80 and 17.20 mg·kg^{-1} in the embryonic axis.

Our results for P concentration are close to those reported by Prolla et al. (2010), who reported P contents varying between 3.35 and 3.58 g·kg^{-1} per sample of raw beans in 16 cultivars. The mean content of P in raw beans reported by Oliveira (2009) was 4.73 g·kg^{-1}, and

Table 3. Mean concentrations of the four minerals (Fe, Mn, Zn, P) evaluated in raw beans of the cultivars BRS Estilo, BRS Madrepérola, and BRS Pontal at 0, 60, 90, 135 and 180 days.

Cultivar/Time	0	60	90	135	180
	Fe Content (mg mineral kg^{-1} bean)				
BRS Estilo	52.77±1.89^{Be}	69.08±1.84^{Bd}	88.00±1.30^{Ac}	144.51±11.42^{Aa}	116.55±2.62^{Ab}
BRS Mpérola	104.09±5.17^{Ac}	90.20±2.54^{Ad}	65.29±1.04^{Ce}	132.02±0.54^{Aa}	122.08±3.35^{Ab}
BRS Pontal	105.52±2.27^{Ab}	48.75±5.66^{Ce}	78.66±1.33^{Bc}	62.89±2.47^{Bd}	121.38±1.06^{Aa}
Cultivar			**Mn Content (mg mineral kg^{-1} bean)**		
BRS Estilo	17.93±0.13^{Bb}	19.07 ± 0.13^{Bb}	26.19 ±1.39^{Aa}	21.55 ± 1.82^{Bb}	19.56±0.91^{ABb}
BRS Mpérola	21.11±0.23^{Ab}	22.63 ± 1.22^{Ab}	33.14 ±4.89^{Aa}	21.68 ± 1.66^{Bb}	16.92 ± 1.09^{Bc}
BRS Pontal	18.00±0.14^{Bc}	18.83 ± 0.28^{Bc}	26.89 ±0.27^{Ab}	31.80 ± 1.90^{Aa}	19.76 ± 1.22^{Ac}
Cultivar			**Zn Content (mg mineral kg^{-1} bean)**		
BRS Estilo	42.94±2.05^{Ab}	42.42±0.92^{ABb}	43.94±3.40^{Ab}	49.76±0.79^{Aa}	45.78±2.20^{Aab}
BRS Mpérola	40.72±0.57^{ABc}	43.80±1.70^{Acb}	44.35±3.70^{Acb}	53.93±1.84^{Aa}	48.38±1.58^{Ab}
BRS Pontal	37.55±0.76^{Bbc}	40.00±1.12^{Bbc}	35.79±1.11^{Bc}	41.79±2.25^{Bab}	45.29±2.27^{Aa}
Cultivar			**P Content (g mineral kg^{-1} bean)**		
BRS Estilo	2.14±0.09^{Cc}	3.16±0.21^{Ab}	3.07±0.2^{Ab}	3.20±0.16^{Ab}	4.03±0.30^{Aa}
BRS Mpérola	2.47±0.10^{Bb}	2.75± 0.07^{Bab}	2.88±0.07^{Aab}	2.97±0.03^{Aa}	2.78±0.11^{Bab}
BRS Pontal	3.03±0.05^{Aa}	3.22±0.01^{Aa}	3.23±0.13^{Aa}	3.20±0.09^{Aa}	2.98±0.50^{Ba}
Cultivar			**Proteinas (%)**		
BRS Estilo	17.31±0.38^{Bb}	19.56±0.67^{Aa}	19.19±1.56^{Aa}	17.96±1.01^{Bab}	19.44±0.15^{Aa}
BRS Mpérol^{a}	20.23±0.53^{Aa}	20.35±0.33^{Aa}	19.60±1.38^{Aa}	19.40±0.33^{ABa}	19.57±0.25^{Aa}
BRS Pont^{a}l	19.87±0.41^{Aa}	19.56±0.23^{Aa}	19.73±0.34^{Aa}	20.00±0.45^{Aa}	18.50±0.22^{Ba}

BRS Mpérola = Madrepérola; the mean of three replicates ± standard deviation; the mineral content was calculated in dry weight for each mineral; the same lowercase letters in rows (time) represent statistically equal means at 5% significance; the same uppercase letters in columns (cultivar) represent statistically equal means at 5% significance.

values found by Buratto (2012) were between 2.24 and 11.17 g·kg^{-1}.

According to the Brazilian Table of Food Composition (Tabela Brasileira de Composição de Alimentos – TACO), the fractions of Fe, Mn, P, and Zn in beans are found in higher concentrations in raw beans. The mineral contents for raw carioca beans reported in TACO are 385 mg·100 g^{-1} P, 8.00 mg·100 g^{-1} Fe, and 2.29 mg·100 g^{-1} Zn (UNICAMP, 2011).

The secondary compounds analyzed in the stored carioca bean cultivars were the contents of phytic acid and tannins, which are considered antinutrients in some foods, especially in legumes, which can accumulate high concentrations of these compounds due to long-term storage. The phytates (phytic acid derivatives) can form complexes with proteins and minerals, compromising the absorption of micronutrients important for the human body, such as Fe and Zn. Tannins have adverse effects on the digestibility of proteins, and their characterization in different bean cultivars and under various storage conditions is necessary because of the importance of reducing these chemical compounds in beans. We found an interaction for tannin concentration ($p = 0.0315$) between cultivar and time at the 95% confidence level. There was an increase in their concentration as storage time increased. This phenomenon was expected, considering that the longer the storage time is, the lower the parameter luminosity L*, with the presence of darker pigments. This darkening could be associated with increased tannin content in the tegument. For phytic acid, the interaction between genotype and time was not significant ($p = 0.7434$), and there were no differences among the cultivars ($p = 0.5280$). The mean phytic acid content differed throughout the storage time ($p = 0.0494$) (Table 4). Nyakuni et al. (2008) they found that the development of the HTC defect was associated with a reduction in phytic acid content ($r = -0.802$). The susceptibility to the HTC defect during storage could be attributed to a phytic acid interaction with proteins and carbohydrates, and is also associated with small seed size. Breeding for large seed size could therefore help reduce the development of the HTC defect (Nyakuni et al, 2008).

We found an interaction for tannin concentration (p =

Table 4. Mean tannin (mg·kg^{-1}) and phytic acid (µg·µg^{-1}) content in stored carioca bean cultivars.

Cultivar/Time	0	60	90	135	180
	Tannin Content (mg.100 g^{-1})				
BRS Estilo	243.03^{Bb}	298.72±1.89^{Ab}	234.77±1.20^{Bb}	277.52±1.1^{Bab}	316.30±0.56^{Aa}
BRS Mpérola	237.51^{Bc}	315.15±1.75^{Aab}	275.67±1.45^{ABbc}	273.84±1.03^{Bbc}	342.78±2.02^{Aa}
BRS Pontal	359.21^{Aa}	342.38±1.02^{Aa}	352.10±1.59^{Aa}	314.24±1.49^{Aa}	365.95±0.70^{Aa}
	Phytic Acid Content (µg.µg^{-1})				
BRS Estilo	0.14±0.02^{Aa}	0.11± 0.03^{Aab}	0.14± 0.04^{Aab}	0.10±0.01^{Ab}	0.14± 0.01^{Aa}
BRS Mpérola	0.10±0.04^{Aab}	0.12± 0.01^{Aab}	0.12± 0.01^{Aab}	0.10± 0.01^{Ab}	0.14± 0.01^{Aa}
BRS Pontal	0.10±0.03^{Aab}	0.11± 0.01^{Aab}	0.10± 0.01^{Aab}	0.10± 0.00^{Ab}	0.14± 0.00^{Aa}

BRS Mpérola = Madrepérola; the mean of three replicates ± standard deviation; the tannin and phytic acid contents were calculated in dry weight; the same lowercase letters in rows (time) represent statistically equal means at 5% significance; the same uppercase letters in columns (cultivar) represent statistically equal means at 5% significance.

Table 5. Correlation matrix Spearmann for the variables pH, conductivity and storage time.

Variables	pH	Storage Time
pH	1	-0.809
Storage time	-0.809	1
Variables	**Conductivity**	**Storage Time**
Conductivity	1	0.929
Storage time	0.929	1

in bold are different from 0 with a significance level alpha = 0.05.

0.0315) between cultivar and time at the 95% confidence level. There was an increase in their concentration as storage time increased (Table 4), for all the cultivars. This phenomenon was expected, considering that the longer the storage time is, the lower the parameter luminosity L*, with the presence of darker pigments. This darkening could be associated with increased tannin content in the tegument.

The total content of beans in 50 cultivars studied, phytic acid myo-inositol hexaphosphate, or their phytate salts represented 54 to 82% with an average of 69.30%. The phytic acid content of the beans varies from 0.54 to 1.58%, more than 99% in soluble form, the total phosphorus from 0.26 to 0.56%, the inorganic phosphorus 0.021 to 0.044 and% organic phosphorus, which does not phytic acid, 0.05 to 0.135% (Lolas et al., 1976). It should be noted that phytic acid contains approximately 70% of the phosphate content of legume seeds (Lolas et al., 1976).

Correlation analysis was used to determine which variables were correlated. Our intention was to detect whether the technological and chemical (nutritional) variables were correlated with the cultivar or the storage time. As pH and electrical conductivity are quickly obtainable measurements, in addition to being inexpensive, it is worth noting the behavior of these variables and their respective correlations. Some cultivars had high correlations between various parameters and pH. The cultivar BRS Pontal had a correlation coefficient between L* and pH of 0.63, which means that when the pH increased, the brightness of the bean (L*) was also likely to increase. It also had correlations between pH and moisture content (0.87); pH and weight of 100 beans (0.73); and pH and WA% (-0.92), implying that an increase in the pH of the solution for this genotype causes a decrease in water absorption.

For the chemical variables of the BRS Pontal cultivar, there was a negative correlation between pH and Mn content (-0.64). BRS Estilo had correlations between pH and L* (0.65), pH and a* (-0.62), pH and Fe content (-0.73), and pH and Mn content (-0.65). For the storage periods analyzed, the variable pH and conductivity had a correlation with the variable storage time (0, 60, 90, 135, and 180 days), indicating that pH had a negative correlation (Table 5) with storage time that is, the beans became more acidic with storage time. The variable electrical conductivity had a positive correlation which indicated that electrical conductivity increased as storage time increased (Table 5).

The correlations between the electrical conductivity

values of the cultivars and the availability of minerals was low (< 40.00) to moderate (< 70.00). The following minerals had positive correlations: Fe (0.48), Zn (0.54), and P (0.68) in the cultivar Estilo; iron (0.96), Zn (0.68), and P (0.45) in the cultivar Madrepérola; and P (0.36) and Zn (0.45) in the cultivar Pontal. Fe was the micronutrient that had the highest concentration in each cultivar, and the results of the analyses indicate an increase in this mineral during storage, which corroborates the high positive correlation found for electrical conductivity and iron content, probably due to the analyses having been performed on raw beans without maceration, which preserved some minerals.

The correlations between electrical conductivity and cultivar for secondary metabolites and fractions of fiber were as follows: cultivar BRS Estilo: positive correlations for tannins (0.79); cultivar BRS Madrepérola and cultivar BRS Pontal: positive correlations for phytic acid (0.72) in raw beans. Kon and Sanshuck (1981) studying the quality of baked beans, found a inverse correlation between cooking time and phytic acid content of the beans, that is, higher cooking time less phytate content.

These results confirm that the availability of these compounds did not occur in a similar fashion between cultivars. Another factor that explains these results is the phytic acid content, which had a high positive correlation in the cultivar BRS Pontal, indicating an increase in electrical conductivity associated with an increase in this compound with storage time.

Conclusions

The cultivar BRS Madrepérola is recommended for storage under ambient conditions with no temperature and moisture control, as it had the best performance in the characterization of technological and nutritional variables. The biggest influence on technological and chemical characterization of cultivars found in this study is due to the factor storage time. Overall, storage promoted the increase of these minerals. Multivariate analysis identified important correlations over time for pH and for electrical conductivity, as observed in the color parameters and protein content in the raw beans of the cultivars.

Conflict of Interests

The authors have not declared any conflict of interests.

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