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Physicochemical and technological properties of common bean cultivars (*Phaseolus vulgaris* L.) grown in Brazil and their starch characteristics

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ABSTRACT: A great diversity of bean cultivars is developed each year, but, to our knowledge, there is a dearth of information regarding the physicochemical and technological properties of the grains, as well as its starch characteristics. Therefore, this study aims to evaluate the physicochemical and technological properties of five cultivars from the carioca bean group and five cultivars from the black bean group as freshly harvested grains. Moreover, the physicochemical, crystallinity and pasting properties of isolated starch were also determined. The results showed differences in all of the studied properties as a function of genotype. High grain thickness and low seed coat percentage were associated with the low cooking time. The highest protein and starch content were exhibited by grains from the "Pérola" and "Estilo" cultivars, respectively. Similar crystalline structure was observed in all starches, but the relative crystallinity and the physicochemical and pasting properties were dependent on the cultivar.

Key words: black bean; carioca bean; cooking time; pasting properties

Propriedades físico-químicas e tecnológicas de cultivares de feijão comum (*Phaseolus vulgaris* L.) cultivadas no Brasil e suas características de amido

RESUMO: Uma grande diversidade de cultivares de feijão é cultivada a cada ano, mas, para o nosso conhecimento, há uma escassez de informações sobre as propriedades físico-químicas e tecnológicas desses grãos, bem como de suas características de amido. Portanto, este estudo tem como objetivo avaliar as propriedades físico-químicas e tecnológicas de cinco cultivares do grupo de feijão carioca e cinco cultivares do grupo de feijão preto. Além disso, as propriedades físico-químicas, de cristalinidade e colagem de amido isolado também foram determinadas. Os resultados mostraram diferenças em todas as propriedades estudadas em função do genótipo. Maior espessura de cotilédone e menor percentagem de tegumento foram associadas com baixo tempo de cocção. O maior teor de proteína e amido foi exibido por grãos das cultivares "Pérola" e "Estilo", respectivamente. Estrutura cristalina semelhante foi observada em todos os amidos, mas a cristalinidade relativa e as propriedades físico-químicas e de colheita dependeram da cultivar.

Palavras-chave: feijão preto; feijão carioca; tempo de cocção; propriedades de pasta

Introduction

Beans are an important source of carbohydrates, proteins, minerals, and vitamins, mainly those from the B complex (Słupski, 2012). The high protein content and good amino acid balance make beans attractive for consumers in developing countries because the low-cost bean protein can replace high-cost meat protein. Moreover, when beans are consumed with rice, they provide the ideal amino acid balance to the consumer because they support each other in the essential amino acids of lysine and methionine. On one hand, although rice is poor in lysine, beans are rich in lysine. On the other hand, beans are deficient in methionine, whereas rice is rich in methionine. However, beans are no longer viewed as merely a protein source for poor people. Studies have demonstrated the health benefits of bean constituents as antioxidant, anti-carcinogenic, and anti-inflammatory agents (García-Lafuente et al., 2014).

In Brazil, common beans are one of the most popular food products, being considered together with rice as the basis of the Brazilian diet. In 2013, the country was the third world's largest dry beans producer, behind only Myanmar and India (FAO, 2014). Common beans from the carioca group are responsible for approximately 70% of Brazilian's common bean production, whereas 30% is from black beans. These two groups, carioca and black beans, possess a large variability of physicochemical, technological and nutritional properties. These properties are mainly affected by the genetic characteristics and the growing conditions (Oomah et al., 2010; Ovando-Martínez et al., 2011); as a result, knowledge regarding the physicochemical, technological, and nutritional properties as a function of, for example, the genotype and the growing and storage conditions, is essential for supporting the decisions of geneticists, plant breeders, and industries.

Starch is the main bean constituent, accounting for approximately 45% of the bean composition (Hoover & Ratnayake, 2002). Bean starch possesses a C-type crystalline structure, whereas cereal and tuber starches present an A-type and a B-type crystalline structure, respectively (Vanier et al., 2012). Previous studies have reported differences in the physicochemical and rheological properties of oat (Hoover et al., 2003), wheat (Yoo & Jane, 2002), rice (Sodhi & Singh, 2003), maize (Singh et al., 2006), potato (Alvani et al., 2011), barley (Song & Jane, 2000), and field pea (Wang et al., 2010) starches as a function of genotype. However, similar studies with starches isolated from carioca and black beans cultivated in Brazil are limited. According to Hoover et al. (2010), there is a great variability of bean cultivars in the world; however, few studies have reported differences in the composition, structure, and properties among the starches from different cultivars.

The present study aims to characterize the physicochemical and technological properties of the main carioca and black bean cultivars grown in Brazil and also to characterize the physicochemical, crystallinity, and pasting properties of their isolated starch.

Materials and Methods

Materials

Carioca bean cultivars (Estilo, Horizonte, Pérola, Requinte and Pontal) and black bean cultivars (Campeiro, Esplendor, Grafite, Supremo and Valente) were provided by Embrapa Rice and Beans, in the city of Santo Antônio de Goiás, State of Goiás, Brazil (Supplementary data S1). Carioca and black beans grains were cultivated under the irrigation system at Capivara's farm of Embrapa Rice and Beans. The seeding was performed with a row spacing of 50 cm and 450 kg of the fertilization formula 5: 30: 16 (N: P: K). The grains were harvested with 13% moisture content and then immediately subjected to cleaning process, with just the whole grains without defects being selected. Later, the grains were transported to the *Postharvest, Industrialization and Quality of Grains Laboratory of the Federal University of Pelotas*, where the physicochemical and technological properties of the grains, as well as the physicochemical and rheological properties of their isolated starches were evaluated.

Physicochemical properties

Physical properties of grains

The one-thousand grains mass (1000 grain mass) was determined by manually counting one-thousand grains and weighting them using an analytical balance. The grain dimensions (length × width × thickness) were determined for 60 grains using a digital caliper. The seed coat content, expressed as a percentage (%), was determined by manual removal of the seed testa of 100 g of grains. The seed coat was then dried at 105 °C for 1 h and weighted.

Proximate composition and fiber content

The moisture content of the bean was determined using a drying oven set at 105 ± 3 °C with natural air circulation for 24 h, following the recommendations of the American Society of Agricultural Engineers (ASAE, 2000). The moisture content was expressed as a percentage (%). The fat content was determined following method 30-20 of the American Association of Cereal Chemists (AACC, 1995). The nitrogen content was determined according to AACC method 46-13 (AACC, 1995), and the protein content was obtained using a conversion factor of nitrogen to protein of 6.25. The ash content was determined according to AACC method 08-01 (AACC, 1995). The dietary fiber content was determined following the analytical protocol described by Angelucci et al. (1987). Total carbohydrates excluding dietary fiber were estimated by the difference of the total content versus the sum of the protein, ash, fat, and dietary fiber contents.

Protein solubility (%)

The protein solubility in water was determined according to the method described by Paraginski et al. (2014). One gram of bean flour was dispersed in 50 mL of distilled water at constant stirring for 1 h. The slurry was centrifuged at 5300 × *g* for 20 min, and 2.0 mL of supernatant was collected for the determination of the protein content. The nitrogen content was determined by the Kjeldahl method, and the resulting nitrogen value was converted to protein using the factor of 6.25. The protein solubility, expressed as a percentage (%), was calculated by the ratio of the soluble protein content to the crude protein content.

Electrical conductivity

The electrical conductivity was determined from four replicates of 25 grains, weighed, immersed in 75 mL of distilled water, placed in an incubator at a constant temperature of 20 °C, and then incubated for 24 h (Vieira et al., 1999). The solutions were shaken gently, and the electrical conductivity was determined from an unfiltered solution. The results were expressed in µS cm^{-1} g^{-1}.

Technological properties

Hydration coefficient before cooking

The hydration coefficient was determined by soaking 20 g of grains at room temperature (25 °C) in 100 mL of deionized water (ratio 1: 5). After 12 h, the beans were removed from the water and then centrifuged at 1000 rpm for 1 min to remove the free water before being weighed again. The grain in weight was taken as the amount of water absorbed and expressed as the hydration coefficient (Nasar-Abbas et al., 2008).

Cooking time

The cooking time was determined using the method described by Burr et al., (1968), with some further modifications. Prior to cooking, grain samples (25 beans) were soaked in 100 mL of deionized water for 12 h. A Mattson-modified cooker was used to determine the cooking time of the individual beans. This cooker utilized 25 stainless steel cylindrical plungers, with 82-g piercing tip rods in contact with the surface of the bean. The cooker was then placed into a 2-L beaker containing 400 mL of boiling water. The bean grains were judged as 'cooked' when the 2-mm diameter piercing tip of the brass rods passed through the beans. The cooking time was reported as the time required for 50% of the grains to be cooked, as indicated by the plungers dropping and penetrating individual beans.

Starch characteristics

Starch isolation

The starch was isolated from bean grains using the procedure of Rupollo et al. (2011). A total of 100 g of grains were used to determine the percentage extraction yield by weighing the starch obtained after drying. After the isolation process, all starches exhibited less than 0.45% (d.b.) of protein content.

Starch color

The color evaluation was performed on the surface of the starches. The color was measured five times for each treatment. A Minolta Colorimeter (Milton Roy; Color Mate, City) color analyzer was used. The colorimeter was calibrated using a white tile, and the L* parameter value was then obtained.

Swelling power and solubility

The swelling power and solubility at 90 °C of the starches were determined using the method described by Vanier et al. (2012). The solubility was expressed as the percentage of the dried solid weight based on the dry sample weight. The swelling power was represented as the ratio of the wet sediment weight to the initial dry sample weight (subtracting the amount of soluble starch).

X-ray diffraction

X-ray diffractograms of the starches were obtained using an x-ray diffractometer (XRD-6000, Shimadzu, Kyoto, Japan). The scanning region of the diffraction ranged from 5° to 45°, with a target voltage of 30 kV, a current of 30 mA, and a scan speed of 1° min^{-1}. The relative crystallinity (RC) of the starch granules was calculated via the method described by Lopez-Rubio et al. (2008) using the following equation: $RC (\%) = (Ac / (Ac + Aa)) \times 100$; where Ac is the crystalline area, and Aa is the amorphous area on the x-ray diffractograms.

Pasting properties

The pasting properties of the starch samples were determined using a Rapid Visco Analyzer (RVA–4, Newport Scientific, Australia) with the Standard Analysis 1 profile. The viscosity was expressed in rapid visco units (RVUs). Starch (3.0 g with 12% moisture content) was weighted directly in the RVA canister, and 25 mL of distilled water was then added to the canister. The sample was held at 50 °C for 1 min, heated to 95 °C in 3.5 min, and then held at 95 °C for 2.5 min. The sample was cooled to 50 °C in 4 min and then held at 50 °C for 1 min. The rotating speed was held at 960 rpm for 10 s, and it was subsequently maintained at 160 rpm during the remaining process. The parameters of pasting temperature, peak viscosity, holding viscosity, breakdown (the difference between peak viscosity and holding strength), final viscosity, and setback (the difference between final viscosity and peak viscosity) were recorded.

Statistical analysis

The experimental design was completely randomized. Analytical determinations for the samples were performed in triplicate, except the grain dimensions and the electrical conductivity, which were recorded sixty and four times, respectively. The data were subjected to analysis of variance (ANOVA), followed by Tukey's test at a 5% significance level.

Results and Discussion

Physical properties of the grains

The 1000-grain mass, the grain dimensions, and the seed coat percentage are presented in Table 1. The highest 1000-grain mass ($p < 0.05$) was determined to be the "Pérola"

Table 1. Physical properties of different carioca and black bean cultivars grown in Brazil.

Cultivars	1000 grains mass (g)*	Dimensions**			Seed coat (%)***
		Length (mm)	Width (mm)	Thickness (mm)	
Carioca bean					
Estilo	241.3±0.08 d	10.12±0.48 ef	6.78±0.57 bcd	4.94±0.43 ab	9.14
Horizonte	245.6±0.06 c	11.65±0.67 a	6.84±0.37 abcd	4.77±0.32 bcd	9.95
Pérola	262.4±0.02 a	11.35±1.00 ab	7.08±0.61 a	4.96±0.46 a	9.62
Pontal	210.0±0.02 f	9.86±0.79 fg	6.53±0.37 e	4.46±0.23 de	10.63
Requinte	198.1±0.07 g	8.97±0.47 h	6.63±0.37 de	4.66±0.34 c	9.47
Black bean					
Campeiro	256.2±0.05 b	10.93±0.78 bc	7.05±0.43 a	4.73±0.37 c	9.32
Esplendor	175.9±0.05 i	9.64±0.58 g	6.21±0.29 f	4.22±0.25 f	10.46
Grafite	246.1±0.01 c	10.60±0.81 cd	6.94±0.54 ab	5.02±0.33 a	9.13
Supremo	196.3±0.02 h	9.39±0.67 gh	6.63±0.45 cde	4.64±0.31 cd	10.07
Valente	224.4±0.03 e	10.37±1.04 de	6.97±0.44 ab	4.41±0.27 e	10.03

* Results are the means of three determinations ± standard deviation. ** Results are the means of sixty determinations ± standard deviation. *** Results are the means of two determinations. Values followed by different letters in the same column statistically differ byTukey test ($p < 0.05$).

and "Campeiro" cultivars, whereas the lowest ($p < 0.05$) was determined to be the "Esplendor" cultivar. The 1000-grain mass varies as a function of cultivar and is well-associated with the grain dimensions (Length × Width × Thickness). The carioca bean cultivars "Horizonte" and "Pérola" exhibited the highest values of length ($p < 0.05$), whereas the cultivars "Estilo", "Pérola" and "Grafite" exhibited the highest values of thickness ($p < 0.05$). The black bean cultivar "Esplendor" exhibited the lowest values of width and thickness ($p < 0.05$) (Table 1.).

Wang et al. (2010) reported that the 1000-grain mass, grain dimensions and proximate composition of pea seeds (*Pisum sativum*) are influenced by cultivar, growing location, growing year and also climate factors. Oomah et al. (2010) compared 13 different cultivars of faba bean (*Vicia faba* L.) grown in different locations of Alberta, Canada, and found variations in the grain dimensions, hydration capacity, tegument color, total phenolic content, tannin content and anthocyanin content, depending on the growing region. The seed coat percentage was in the range of 9%-11%, and the highest content was determined to be in the "Pontal" (10.63%) and "Esplendor" (10.46%) cultivars. According to Oomah et al. (2010), the seed coat of beans constitute 7% to 13% of the grain mass and is a rich source of dietary fibers, minerals, and phenolic compounds with high antioxidant activity. In the present study, the cultivars were grown in the same experimental field, and, thus, the differences in the grain dimensions and seed coat percentage may only be attributed to genotype.

Proximate composition and fiber content

The proximate composition and the fiber content of the different carioca and black bean cultivars grown in Brazil are presented in Table 2. The protein content varied from 21.07% to 27.40%. The highest protein content ($p < 0.05$) was observed in the "Pérola" cultivar, whereas the lowest protein content ($p < 0.05$) was observed in the "Estilo" cultivar. Interestingly, both "Pérola" and "Estilo" are from the carioca group.

Siddiq et al. (2010) studied some physical and functional properties of red kidney beans, small red kidney beans, cranberry beans, and black beans and determined the protein content of the beans to be between 20.93% and 23.62%. Shimelis & Rakshit (2005) evaluated the physicochemical properties of eight bean cultivars from Ethiopia and reported the protein content of the beans to vary from 17.95% to 22.07%. In the present study, several cultivars exhibited higher crude protein content than those studied by Siddiq et al. (2010) and Shimelis & Rakshit (2005). Beans with high protein content are desired in those regions worldwide where

Table 2. Proximate composition and dietary fiber content of different carioca and black bean cultivars grown in Brazil.

Cultivars	Protein	Fat	Ash	Dietary fiber	Total carbohydrates
			(%)*		
Carioca bean					
Estilo	21.07±0.13 f	1.52±0.02 b	3.93±0.00 e	18.54±0.78 ef	54.05
Horizonte	26.06±0.24 b	1.20±0.01 de	4.19±0.10 bc	18.70±1.09 def	49.82
Pérola	27.40±0.01 a	1.10±0.08 f	4.21±0.06 bc	21.66±0.66 abc	45.11
Pontal	23.99±0.11 d	1.20±0.03 de	4.01±0.07 de	23.36±0.96 a	47.43
Requinte	23.74±0.26 d	1.16±0.00 de	4.11±0.01 bcd	20.79±1.16 abcde	49.40
Black bean					
Campeiro	23.08±0.10 e	1.23±0.04 d	4.25±0.06 ab	22.83±0.85 ab	48.59
Esplendor	25.36±0.25 c	1.37±0.00 c	3.94±0.02 e	17.63±1.33 f	51.67
Grafite	23.81±0.01 d	1.22±0.01 d	4.06±0.03 cde	20.32±0.32 bcde	50.56
Supremo	26.00±0.00 b	1.68±0.04 a	4.39±0.06 a	21.15±0.73 abcd	46.76
Valente	23.89±0.15 d	1.22±0.06 d	4.20±0.01 bc	19.93±0.53 cdef	50.74

* Results are the means of three determinations ± standard deviation. Values followed by different letters in the same column statistically differ by Tukey test ($p < 0.05$). ** Results estimated by difference from protein, fat, ash and dietary fiber contents.

beans are the only source of proteins. Higher protein content is accompanied by better essential amino acids intake, which reduces some health problems related to meat consumption (Mathres, 2002). Moreover, high protein content may be an interesting parameter for industries working on bean protein extraction.

The fat and ash contents varied in the ranges of 1.10 to 1.68% and 3.93 to 4.39%, respectively. A similar fat content was reported by Wani et al. (2013), who studied the composition of three different Indian black gram (*Phaseolus mungo* L.) cultivars. The ash content was similar to those reported by Barampama & Simard (1993), who determined the ash content to be between 3.8 and 4.5% in four bean cultivars grown in Burundi. According to Tiwari & Singh (2012), pulses are a good source of phosphorus, potassium, calcium, and magnesium, along with a small amount of iron and selenium. Moreover, most beans possess higher calcium content than wheat, rice, and some corn cultivars. The dietary fiber content of the different carioca and black bean cultivars grown in Brazil ranged from 17.63 and 23.36%, as presented in Table 2. Tiwari & Cummins (2011) reported that the pectin fraction corresponds to 55% of the dietary fiber in the cotyledon fraction, whereas cellulose is the main dietary fiber component in the seed coat fraction (35 to 57%). The dietary fiber passes through the small intestine and goes directly to the colon, where the fiber is fermented by bacteria, producing short-chain fatty acids. These short-chain fatty acids fulfill a very important role in protecting the colon against cancer (Mathres, 2002).

The total carbohydrate content was estimated as the difference between the total content and the sum of the contents of protein, fat, ash, and dietary fiber constituents. The total carbohydrates content varied from 45.11 to 54.05% (Table 1.). The carioca bean cultivar “Estilo” exhibited the highest total carbohydrates content, whereas the “Pérola” cultivar exhibited the lowest total carbohydrates content. Starch was isolated from each bean cultivar and further characterized for physicochemical, crystallinity and pasting properties.

Protein solubility and electrical conductivity

The protein solubility and electrical conductivity of the different carioca and black bean grains are presented in Table 3. The protein solubility can affect the emulsion capacity, the foam formation and the gelation characteristics of bean flours when used as raw material for product development (Wani et al., 2013). The protein solubility of carioca and black beans varied from 30.19 to 61.22%. Low protein solubility can be the result of a greater extent of disulfide linkages within the bean structure. Moreover, low protein solubility can be the result of the greater interaction of proteins with starch and phenolic compounds, which leads to a more stable and more insoluble structure of the proteins (Paraginski et al., 2014).

The electrical conductivity is an indicator of the integrity of the cell membrane. The highest ($p < 0.05$) electric conductivity was determined in the “Estilo” and “Pontal” cultivars, both of which are from the carioca bean group. The “Esplendor” cultivar exhibited the highest ($p < 0.05$) electrical conductivity value between black bean cultivars. In contrast, the lowest electric conductivity was observed in the “Horizonte”, “Pérola”, “Campeiro” and “Grafite” cultivars (Table 3.). High electrical conductivity indicates that a greater amount of electrolytes have leached from the grains to the soaking water as a consequence of the damage of cell membranes (Berrios et al., 1999). The loss of cell membrane integrity is considered one of the primary physiological events of the grain deterioration process.

Technological properties

The results obtained from the hydration capacity and cooking time evaluations are presented in Table 3. Cooking time and hydration capacity are quality factors associated with the bean hardness grains with high hydration capacity and low cooking time are preferred by industries and consumers. The hydration capacity of the grains ranged from 1.98 to 2.10 g g^{-1}. The water is retained in the large intercellular spaces and small adhesion areas between the cells of cotyledon (Berrios et al., 1998). The “Pérola” and “Horizonte” cultivars, which had longer lengths (Table 1.), exhibited higher hydration capacities

Table 3. Protein solubility, electrical conductivity and technological properties of different carioca and black bean cultivars grown in Brazil.

Cultivars	Protein solubility (%)*	Electrical condutivity (µS.cm-1)*	Hydration capacity (g g^{-1})*	Cooking time (minutes)*
Carioca bean				
Estilo	61.22±4.44 a	101.5±1.5 a	2.00±0.004 f	15.25±0.75 g
Horizonte	52.27±3.50 bc	78.6±3.3 de	2.10±0.007 a	21.69±0.45 b
Pérola	55.30±1.77 ab	71.8±1.2 e	2.09±0.003 a	19.88±0.69 cde
Pontal	50.33±3.10 bc	104.1±6.6 a	2.05±0.001 b	25.11±0.84 a
Requinte	50.14±0.26 bc	91.0±1.8 bc	1.98±0.001 g	19.38±0.33 cde
Black bean				
Campeiro	55.06±4.31 ab	75.9±1.3 de	2.05±0.004 bc	19.10±0.78 de
Esplendor	30.19±1.09 e	91.6±3.5 b	2.04±0.005 cd	20.95±0.70 bc
Grafite	47.95±1.81 cd	80.5±0.9 de	2.02±0.001 e	16.53±0.17 fg
Supremo	42.46±0.75 d	82.2±4.4 cd	2.04±0.002 d	18.17±0.76 ef
Valente	47.36±2.03 cd	80.9±2.9 d	2.04±0.002 bcd	20.45±0.35 bcd

* Results are the means of three determinations ± standard deviation. Values followed by different letters in the same column statistically differ by Tukey test ($p < 0.05$).

(Table 3.), in agreement with the results presented by Singh et al. (1990). The authors reported a positive correlation between the size of the chickpea (*Cicer arietinum*) grains and their hydration capacity. The cooking time ranged from 15.25 to 25.11 min and 16.53 to 20.95 min for the cultivars from the carioca and black bean groups, respectively (Table 3.). In beans stored under inappropriate conditions, a reduction in hydration capacity of the grains occurs, followed by an increase in the cooking time (Vanier et al., 2014). The increase in both the cooking time and the hardness of beans as a result of storage was explained by Coelho et al. (2007). The authors reported that a portion of the phosphate esters groups of phytic acid is hydrolyzed by phytase enzyme. Because these phosphate esters are partially hydrolyzed, they will no longer chelate with divalent cations (Ca^{2+} and Mg^{2+}). Thus, the calcium and magnesium ions will crosslink with some pectin from medium lamella, hindering the separation of cellular medium lamella from cotyledons during the cooking process, leading to an increase in the cooking time. However, the differences in cooking time of freshly harvested beans observed in the presented study may be related to the seed coat percentage and the grain thickness (Table 1.). In general, grains with high thickness values and low seed coat percentages, such as “Estilo”, “Pérola” and “Grafite”, have shorter cooking times, compared with the cooking times of the other cultivars.

Physicochemical properties of isolated starch

The extraction yield, residual protein content, whiteness, swelling power and solubility of starch isolated from carioca and black beans are presented in Table 4. The extraction yield ranged from 14.48 to 20.50% for carioca bean cultivars and from 18.17 to 28.06% for black bean cultivars (Table 4.).

Hoover et al. (2010) postulated that the extraction yield of pulse starches can vary from 18 to 49%, which is in agreement with the results presented in Table 4. However, the “Estilo” cultivar, the “Pontal” cultivar, and, in particular, the “Horizonte” cultivar exhibited lower extraction yields than the minimum of 18% reported by Hoover et al. (2010). Zhou et al. (2004) and Hoover & Ratnayake (2002) observed starch extraction yields between 16.4 and 22.2% for black beans. Higher values of the starch extraction yields were determined in the present study for the “Campeiro”, “Grafite” and “Supremo” cultivars. The residual protein content of isolated starches was lower than 0.40% for all cultivars, except for “Pérola”, which exhibited a protein content of 0.45%. Hoover et al. (2010) reported residual protein contents between 0.01 and 0.43% in starches isolated from legumes. Even exhibiting higher ($p < 0.05$) protein content than starches isolated from other bean cultivars (Table 4.), starch from “Pérola” exhibited the highest ($p < 0.05$) whiteness. In contrast, the starches of “Estilo”, “Grafite”, “Supremo” and “Valente” cultivars exhibited the lowest whiteness. According to Vanier et al. (2012), starches with high whiteness values may be more attractive for applications in the paper industry.

Swelling power and solubility were determined from 90 °C gelatinized starches (Table 4.). The swelling power varied from 8.58 to 10.72 g g^{-1}, with the highest ($p < 0.05$) value determined to be for the “Estilo” cultivar. A similar swelling power range was reported by Rupollo et al. (2011) in starch isolated from carioca beans stored under different conditions for 360 days. Starch solubility is a result of amylose dissociation and leaching from the granule during heating and soaking at 90 °C. Starch solubility was very similar between all studied bean cultivars (Table 4.), ranging from 4.36 to 5.40 g g^{-1}. According to Tester & Morrison (1990), the amylose leaching is a result of the structural transition of the starch granule from an organized to a non-organized state as a consequence of hot water absorption.

X-ray diffraction of isolated starch

The X-ray diffractograms and the relative crystallinity of the different carioca and black bean cultivars are presented in Figure 1. According to Vanier et al. (2012), bean starch exhibits a C-type crystalline structure, which is a mixture of A- and B-type crystalline structures. The C-type pattern is characterized by a small peak at the diffraction angle 2θ of 5.6°, and stronger peaks at diffraction angle 2θ of 17, 23, and 26º. However, in the present study, the small peak at the

Table 4. Extraction yield, protein content, color, swelling power and solubility of the starches isolated from different carioca and black bean cultivars.

Cultivars	Extraction yield (%)*	Protein content (%)**	Whiteness (L value)**	Swelling power (g g^{-1})**	Solubility (g g^{-1})**
Carioca bean					
Estilo	17.88	0.33±0.00 b	86.91±2.03 cd	10.72±0.14 a	4.84±0.16 ab
Horizonte	14.48	0.34±0.02 b	88.01±2.74 bc	8.71±0.15 fg	4.74±0.05 ab
Pérola	19.58	0.45±0.00 a	92.41±2.19 a	9.07±0.12 defg	5.07±0.25 ab
Pontal	17.96	0.38±0.02 b	89.16±2.41 bc	9.62±0.19 bcd	4.49±0.26 b
Requinte	20.50	0.37±0.02 b	87.37±1.55 bcd	9.36±0.18 bcde	4.66±0.01 ab
Black bean					
Campeiro	25.50	0.32±0.02 b	89.84±2.01 b	9.29±0.29 cdef	4.54±0.41 b
Esplendor	18.17	0.35±0.07 b	88.08±1.51 bc	8.58±0.29 g	4.36±0.17 b
Grafite	28.06	0.33±0.00 b	87.28±0.62 bcd	9.88±0.12 b	5.25±0.49 ab
Supremo	24.97	0.34±0.00 b	86.75±0.98 cd	9.78±0.27 bc	5.40±0.07 a
Valente	21.17	0.34±0.00 b	85.20±1.99 d	9.03±0.15 efg	4.52±0.43 b

* Results are the means of two determinations. ** Results are the means of three determinations ± standard deviation. Values followed by different letters in the same column statistically differ by Tukey test ($p < 0.05$).

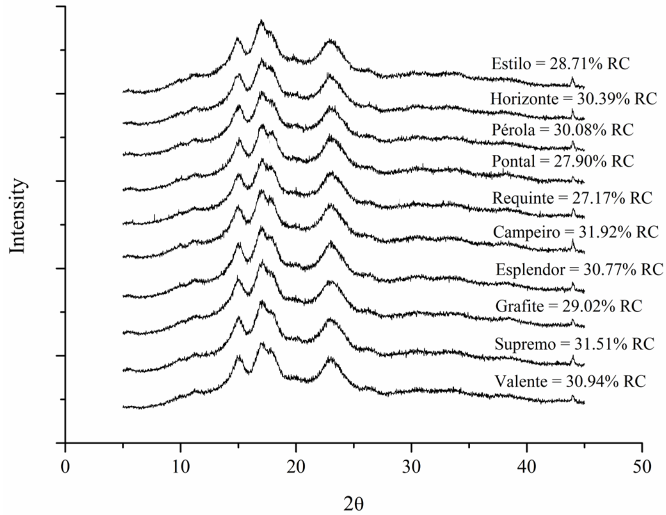

Figure 1. X-ray diffraction pattern and relative crystallinity of starches isolated from different carioca and black bean cultivars.

diffraction angle 2θ of 5.6° was not perceived for all studied bean cultivars. The X-ray diffractograms of the different cultivars revealed similar peaks at diffraction angles 2θ of 15, 17, 20, 23 and 26° (Figure 1.).

Similar results were reported by Ovando-Martínez et al. (2011) in their study of starches isolated from pinto and black beans were grown under different conditions in Mexico. The authors observed peaks at diffraction angles 2θ of 5.4, 15, 17, 20, 23.2, and 26.6°. In the present study, there was no difference in the peak positions among the starches from all the studied cultivars.

As observed in Figure 1, the relative crystallinity (RC) of the starches varied in the ranges of 27.17 to 30.39% and 29.02 to 31.92% for the carioca and black bean groups, respectively, depending on the cultivar. The highest RC was exhibited by the "Campeiro" cultivar and the lowest RC was exhibited by the "Requinte" cultivar. Our results are in agreement with the findings of Hoover et al. (2010), who reported an RC variation from 17 to 34% in bean starches. The authors attributed the differences to (1) crystallite size, (2) the number of crystallites that are arranged in the crystalline array, (3) moisture content, and (4) polymorphic content. Hoover & Ratnayake (2002) characterized three starches from the Canadian black bean cultivar and two from the Canadian pinto bean cultivar and reported RC values varying from 17 to 21.7% for the black bean cultivar and from 25 to 25.5% for the pinto bean cultivar. According to the authors, the value of RC mainly depends on: (1) the extent of interaction between the double helices of amylopectin; (2) the extent and perfection of the orientation of the crystallites; and (3) the amylopectin chain length.

Pasting properties of isolated starch

The pasting curves of the different bean groups and cultivars were very similar (data not shown). The collected data from the pasting profile analyses are presented in Table 5. The pasting temperature of the ten different bean cultivars ranged between 72.22 and 78.15 °C. The highest (p < 0.05) pasting temperatures were detected for the "Horizonte", "Pérola" and "Esplendor" cultivars, whereas the lowest was observed for the "Campeiro" cultivar (Table 5.). The pasting temperature is the temperature required to start the gelatinization process and increase the starch viscosity. A high pasting temperature is an indication of a greater extent of intragranular forces and strengthening bonds, which requires higher heat for the structural disintegration of starch and paste formation. Singh et al. (2004) characterized starch granules isolated from different cultivars of the Indian chickpea (*Cicer arietinum* L.) and related the highest pasting temperature for the CL-769 cultivar to the high resistance of their starch granules to swelling and breakage.

Starch from the "Campeiro" cultivar exhibited the highest (p < 0.05) peak viscosity, whereas starch from the "Pontal" cultivar exhibited the lowest (p < 0.05) peak and holding viscosities (Table 5.). The highest (p < 0.05) holding viscosity was determined in starch isolated from the "Horizonte" and "Esplendor" cultivars, with the first cultivar from the carioca group and the second one from the black group. This result clearly indicates that the pasting properties are dependent on the cultivar and not on the group. The breakdown viscosity depends on the starch granule stability whereas submitted to continuous shearing and constant heating. The highest (p

Table 5. Pasting properties of starches isolated from different carioca and black bean cultivars.

Cultivars	Pasting temperature (°C)	Peak viscosity (RVU)	Holding viscosity (RVU)	Breakdown (RVU)	Setback (RVU)	Final viscosity (RVU)
Carioca bean						
Estilo	73.40±0.05d	234.75±1.92 ef	160.58±3.08 c	74.16±1.16cd	197.87±0.04 a	358.45±3.12 bcd
Horizonte	78.15±0.05a	263.91±2.08bc	204.54±2.12a	59.37±4.20fg	169.71±0.04 c	374.25±2.08 a
Pérola	77.47±0.07ab	261.12±0.37c	179.21±2.54b	80.40±3.65bc	165.79±0.04 c	345.00±2.50 ef
Pontal	76.62±0.07b	205.75±2.50g	151.91±0.16d	53.83±2.66g	154.54±1.46 d	306.46±1.29 h
Requinte	73.85±0.35d	238.29±0.21e	159.62±2.95c	78.67±2.75bc	170.75±0.33 c	330.37±2.62 g
Black bean						
Campeiro	72.22±0.37e	305.58±4.16a	179.62±5.29b	125.95±1.12a	182.54±6.62 b	362.16±11.91abc
Esplendor	77.40±0.80ab	267.29±1.12b	197.83±1.33a	69.46±0.21de	153.25±4.33 d	351.08±3.00 cde
Grafite	75.10±0.00c	264.08±0.83bc	178.50±2.50b	85.58±3.33b	190.50±4.00 ab	368.77±1.27 ab
Supremo	75.07±0.02c	229.33±1.91f	166.71±0.96c	62.62±0.95ef	171.20±0.62 c	337.91±1.58 fg
Valente	76.60±0.10b	253.87±0.04d	176.00±0.67b	77.87±0.70c	171.54±0.37c	347.54±0.29 def

* Results are the means of three determinations ± standard deviation. Values followed by different letters in the same column statistically differ by Tukey test (p < 0.05).

< 0.05) breakdown and the peak viscosity were determined in starch isolated from “Campeiro” black bean, indicating that the granules are more resistant to damage during shearing and heating, compared with starches from other cultivars. The “Pontal” and “Horizonte” cultivars provided starches with the lowest ($p < 0.05$) breakdown values. Singh et al. (2006) observed higher breakdown in starches with higher relative crystallinity and low amylose content when studying normal, sugary and waxy maize starches. In the present study, no direct correlation between the breakdown and the relative crystallinity was observed (Figure 1. and Table 5.). Starch granules from the “Estilo” and “Grafite” cultivars exhibited the highest ($p < 0.05$) setback among all the studied bean cultivars, whereas the lowest ($p < 0.05$) setback was determined to be in the “Pontal” and “Esplendor” cultivars (Table 5.). According to Hughes et al. (2009), high breakdown and setback viscosities may be the result of the superior swelling power of starch granules and fast aggregation of the leached amylose chains, respectively. The setback is also influenced by the amount of leached amylose, the granule size, and the presence of defragmented and rigid granules on the leached amylose network.

The final viscosities of the bean starches ranged from 306.46 to 375.25 RVU, depending on the cultivar (Table 5.). Starches isolated from “Horizonte”, “Campeiro” and “Grafite” cultivars exhibited the highest ($p < 0.05$) final viscosity, whereas starch isolated from the “Pontal” cultivar exhibited the lowest ($p < 0.05$) final viscosity. In general, according to Hoover et al. (2010), the pasting properties of bean starches reflect their high amylose content, the presence of only trace quantities of lipid-amylose complexes, the strong interaction between starch chains (amylose–amylose and/or amylose–amylopectin) within the native granule, and the orientation of amylose chains.

Conclusions

The provided data may support plant breeders and industries in selecting carioca and black bean genotypes for different applications in the food industry.

The higher protein content of the “Pérola” cultivar and the higher starch extraction yield of the “Grafite”, cultivar, compared with all ten studied bean cultivars, make them more attractive sources for extraction of the respective components.

The lowest cooking time exhibited by the “Estilo” and “Grafite” cultivars is indicative of their superior technological properties.

Isolated starch with low residual protein content and high whiteness values were observed, regardless of bean color group and cultivar.

All starches exhibited similar crystalline structure, with the relative crystallinity and the pasting properties varying as a function of genotype.

Studies dealing with the application of bean protein and starch into food products are necessary in order to broaden bean constituents’ use in food industry.

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