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Original article

Influence of carrier agents on the physicochemical properties of blackberry powder produced by spray drying

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Summary The aim of this work was to study the effect of different carrier agents (maltodextrin, gum arabic or a blend of both carrier agents) on the physicochemical properties of blackberry powder produced by spray drying. Moisture content, anthocyanin retention, antioxidant activity, colour parameters, bulk and absolute density, porosity, wettability, sorption isotherms, particle size and morphology of blackberry powders were evaluated. The use of maltodextrin resulted in less hygroscopic powders with lower moisture content and better reconstitution properties. Powders produced with maltodextrin or a blend of maltodextrin and gum arabic presented the best anthocyanin retention and the highest antioxidant activity. Experimental data of water adsorption were well fitted to GAB model. All the samples exhibited a large number of irregular particles with spherical shapes. However, particles produced with gum arabic were smaller and showed more dented surfaces, which probably contributed to the increase in wettability values and lower pigments retention.

Keywords Anthocyanin, antioxidant activity, atomisation, gum arabic, maltodextrin, *Rubus* spp.

Introduction

Several studies around the world have shown that diets rich in fruits and vegetables protect humans against cancer and cardiovascular diseases. Plant foods contain a great variety of phenolic compounds, which are considered bioactive compounds with functional benefits, because of their high antioxidant activity. The blackberry (*Rubus* spp.) is a small fruit that is native to Asia and cultivated in Europe, North America and in temperate regions of Brazil. Blackberries are a good source of antioxidants, showing considerable levels of phenolic compounds, mainly anthocyanins, which are responsible for their attractive colour (Koca & Karadeniz, 2009). Despite their large potential for food industry, the fragility and high post-harvest respiration rate of blackberries contributes significantly to their nutritional and microbiological deterioration, resulting in limited shelf-life and reduced quality. Furthermore, the processing and storage of blackberries accelerate the degradation of monomeric anthocyanins, mainly through polymerisation reactions, causing colour loss (Wu *et al.*, 2010).

Spray drying is a widely used technique that turns liquid food into a powder form. This method is commonly used in food and pharmaceutical manufacturing processes. Its short production time and the use of lower temperatures make spray drying suitable for heat-sensitive food components, such as anthocyanins found in blackberry, because it promotes a higher retention of flavour, colour and nutrients (Masters, 1991). In this context, spray drying process can be used as an alternative to improve the product shelf life and better preserve blackberry anthocyanins. Previous researches have demonstrated the antioxidant properties of blackberries, because of the presence of anthocyanin pigments (Koca & Karadeniz, 2009; Wu *et al.*, 2010; Gancel *et al.*, 2011). Studies concerning the determination of antioxidant activity of spray dried blackberry powder have not been reported yet.

According to Goula & Adamopoulos (2010), the spray drying of fruit juices has great economical potential, because the transformation of these products into a dry form results in reduced volume and packaging, easier handling and transportation, and longer shelf

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life. On the other hand, fruit juices are very difficult to spray dry. The low glass transition temperature of some juice components (low molecular weight sugars and organic acids) and their high hygroscopicity result in stickiness and flowing problems. Furthermore, the adhesion of droplets to the dryer chamber walls decreases process yield. To prevent these problems, the addition of carrier agents, such as maltodextrin or gum arabic, to the feed solution before the atomisation is recommended, to produce free flowing powders, avoiding stickiness, reducing powder hygroscopicity and enhancing process yield. Moreover, the carrier agents also can protect sensitive food components against unfavourable environmental conditions (Bhandari *et al*., 1997).

The purpose of this work was to evaluate the effect of different carrier agents (maltodextrin, gum arabic or a blend of both carrier agents) on the physicochemical properties of blackberry powder produced by spray drying. Moisture content, anthocyanin content, antioxidant activity, colour parameters, bulk and absolute density, porosity, wettability, sorption isotherms, particle size and morphology of blackberry powders were analysed.

Materials and methods

Materials

Frozen blackberry pulp (De Marchi Ltd., Jundiaí, Brazil) was stored in a freezing chamber at −18 °C and thawed in a refrigerator (4–5 °C) for 18 h, according to the amount required for each experiment. Table 1 presents its physicochemical properties. The carrier agents used were maltodextrin Maltogill® 20 (Cargill, Uberlândia, Brazil) with 20 DE and gum arabic Instantgum® (Colloides Naturels, São Paulo, Brazil).

Table 1 Physicochemical properties of blackberry pulp subjected to the spray drying process

Analysis	Mean value	Method
Moisture content (% wet basis)	91.96 ± 0.14	AOAC (2006)
Ash (%)	0.20 ± 0.01	AOAC (2006)
Protein (%)	<0.1	AOAC (2006)
Lipid (%)	0.10 ± 0.01	AOAC (2006)
Reducing sugars (%)	5.35 ± 0.26	AOAC (2006)
Total sugars (%)	6.43 ± 0.13	AOAC (2006)
Titratable acidity (% citric acid)	0.76 ± 0.01	AOAC (2006)
Anthocyanins (mg/100 g dry matter)	969.04 ± 26.19	AOAC (2006)
Antioxidant Activity (μmol TE g^{-1} dry matter)	281.06 ± 18.49	Ou *et al.* (2001)
pH	3.31 ± 0.02	pH metre

All data are the mean of triplicate measurements ± standard deviation values.

Sample preparation and spray drying process

The carrier agent – maltodextrin, gum arabic or a blend (1:1 w/w) of both carrier agents – was added to the pulp in a final concentration of 7 g/100 g fresh juice (w/w), which corresponds to 48 g/100 g total solids. Then, the pulp and the carrier agent were homogenised in a colloid mill (Meteor, São Paulo, Brazil) until complete dissolution. About 2 kg of blackberry pulp was used for each experiment.

The process was performed using a laboratory-scale spray dryer (model B290; Büchi, Flawil, Switzerland) at a drying rate of 1.0 kg of water h^{-1}. The mixture was fed into the drying chamber at room temperature (25 °C) through a peristaltic pump with the flow rate adjusted to 0.49 kg h^{-1}. The inlet air temperature was 145 °C and the outlet air temperature varied from 75 to 80 °C. Spray drying was carried out with a concurrent regime, using a two-fluid nozzle atomiser (0.7 mm diameter), a drying air flow rate of 0.36 m^3 h^{-1} and an aspirator flow rate of 35 m^3 h^{-1} (100% of its maximum capacity). These conditions have been established in a previous work (Ferrari *et al*., 2011). The different powders produced were placed in hermetic containers and stored in desiccators containing silica gel until utilisation.

Analytical methods

Moisture content

The moisture content of the powder was determined gravimetrically. Samples were weighed and dried in a vacuum oven at 70 °C for 24 h (AOAC, 2006).

Anthocyanin content

The anthocyanin content of the samples was determined according to the spectrophotometric pH differential method (AOAC, 2006), which is based on the anthocyanin structural transformation that occurs with a change in pH (coloured at pH 1.0 and colourless at pH 4.5). Two dilutions of each sample were prepared with potassium chloride (0.025 M) and sodium acetate (0.4 M), which were used as buffer solutions at pH 1.0 and 4.5, respectively. Anthocyanins were extracted with an acetone solution (70%), according to the methodology described by Falcão *et al.* (2007), with some modifications. These extracts were used for both anthocyanin and antioxidant activity determinations. Absorbance was measured in a spectrophotometer (model 700Plus; Femto, São Paulo, Brazil) at 520 and 700 nm. Total anthocyanin content was calculated using the molar extinction coefficient of 26 900 L cm^{-1} mol for cyanidin-3-glucoside (cyd-3-glu), which is the predominant anthocyanin found in blackberry pulp (Koca & Karadeniz, 2009). Results were expressed as mg cyd-3-glu/100 g dried juice (excluding the mass of carrier agents). Total anthocyanin content in the mixture fed into the spray dryer was also determined. Anthocyanin retention (AR) after the process was calculated according to eqn 1.

$$\mathrm{AR} = \frac{\text{TAC in spray dried powder}}{\text{TAC in feed solution}} \times 100 \qquad (1)$$

where AR is anthocyanin retention (%) and TAC is the total anthocyanin content (mg/100 g dried juice).

Antioxidant activity

Antioxidant activity was determined by Oxygen Radical Absorbance Capacity (ORAC) method (Ou *et al.*, 2001), using a microplate fluorescence reader containing a 96-well plate (NOVOStar; BMG Labtech, Ortenberg, Germany). ORAC is a kinetic assay that measures the loss of fluorescein fluorescence over time because of the peroxyl-radical formation by the breakdown of 2,2′-azobis(2-amidino-propane) dihydrochloride (AAPH) at 37 °C. Trolox, a water soluble vitamin E analogue, acts as a positive control inhibiting fluorescein decay. Fluorescence is continuously monitored for 80 min, when it remained constant, with an excitation wavelength of 485 nm and an emission wavelength of 520 nm. AAPH solution (153 mM) was used as free radical initiator and fluorescein solution (8.16×10^{-5} mM) as oxidisable substrate. Both solutions were prepared in 75 mM phosphate buffer (pH 7.4) and kept at 4 °C in dark conditions. The extraction was also performed using an acetone solution (70%). Each well was filled with 20 μL of blackberry extract (at different dilutions), 120 μL of fluorescein solution and 60 μL of AAPH solution. The same analysis was done to Trolox methanolic solutions, in some dilutions ranging from 0 to 700 μM, which allowed the construction of a standard Trolox curve. Results were expressed as μmol Trolox Equivalent (TE) per gram of dried juice (excluding the mass of carrier agents).

Colour

The colour of the blackberry powder was measured using a colorimeter (model CR400; Konica Minolta, Osaka, Japan), with a CIELab scale (L^*, a^* and b^*), D65 as an illuminant and a 10° observer angle as a reference system. The colour measurements were expressed in terms of lightness L^* ($L^* = 0$ for black and $L^* = 100$ for white) and the chromaticity parameters a^* [green (−) to red (+)] and b^* [blue (−) to yellow (+)]. C^* (chroma) and H^* (hue angle) were calculated from these parameters, as the following equations (eqns 2 and 3). Chroma indicates colour intensity, whereas hue angle values vary from 0° (pure red colour), 90° (pure yellow colour), 180° (pure green colour) to 270° (pure blue colour). The measurements were performed in triplicate and three reading were done for each replicate.

$$C* = (a*^2 + b*^2)^{1/2} \qquad (2)$$

$$H^* = \arctan\left(\frac{b^*}{a^*}\right) \qquad (3)$$

Bulk density, absolute density and porosity

The bulk density (ρ_{bulk}) of the powders was measured by weighing 1 g of sample and placing it in a 10 mL graduated cylinder. The cylinder was tapped by hand five times from a height of 10 cm and the bulk density was calculated as the ratio between the mass of powder contained in the cylinder and the volume occupied (Goula & Adamopoulos, 2004). The absolute density (ρ_{abs}) was determined in a picnometer, using 99% ethanol as the immiscible liquid (Souza *et al.*, 2009). Porosity (ϵ) was calculated as follows (Lewis, 1987):

$$\varepsilon = 1 - \frac{\rho_{bulk}}{\rho_{abs}} \qquad (4)$$

Wettability

The wettability was evaluated according to the method described by Vissotto *et al.* (2010), considering the time required for 1.0 g of powder deposited on liquid surface to become completely submersed in 400 g of distilled water at 25 °C.

Particle size distribution

The particle size was determined using a laser light diffraction instrument (Mastersizer S, model MAM 5005; Malvern Instruments, Malvern, UK). A small amount of powder was dispersed in 99% isopropanol under magnetic agitation, and the distribution of particle size monitored during three successive measurements. The particle size was expressed as D[4,3] (De Brouckere mean diameter), the mean diameter over the volume distribution, which is generally used to characterise a particle.

Scanning electron microscopy (SEM)

The microstructure of the particles was evaluated using SEM. Powders were attached to SEM stubs using a double-sided adhesive tape and coated with gold/palladium under vacuum in a Sputter Coater Polaron (model SC7620; VG Microtech, Ringmer, UK) at a coating rate of 0.51 Å s^{-1}, 3–5 mA, 1 V and 0.08–0.09 mbar for 180 s. The coated samples were observed with a LEO440i scanning electron microscope (LEICA Electron Microscopy Ltd., Oxford, UK). SEM was operated at 20 kV and 150 pA with magnification of 1000×.

Sorption isotherms

Sorption isotherms were determined by the gravimetric method. Approximately 1 g of each spray dried blackberry powder was weighed in aluminium vials and equilibrated over some saturated salt solutions in dessicators at 25 °C (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl and KCl) to provide relative humidity values of 11.3%, 22.6%, 32.8%, 43.2%, 52.9%, 68.9%, 75.3% and 84.3%, respectively. The sample weights were controlled until a constant value ($< \pm 0.001$ g) was reached (around 4 weeks), where the equilibrium was assumed. The equilibrium moisture content was determined from the initial water content data and the change in the registered weight until equilibrium. These values were used to construct the sorption isotherms (Mosquera *et al.*, 2011).

GAB model was used to predict the water sorption behaviour of spray dried samples, according to eqn 5.

$$W_e = \frac{X_m C_{GAB} K_{GAB} a_w}{[(1 - K_{GAB} a_w)(1 - K_{GAB} a_w + C_{GAB} K_{GAB} a_w)]} \quad (5)$$

where W_e is the equilibrium moisture content (g water/g dry matter), X_m is the monolayer moisture content (g water/g dry matter), a_w is the water activity, C_{GAB} and K_{GAB} are constants.

A non-linear regression analysis was carried out using the software STATISTICA® 8.0 (StatSoft, Inc., Tulsa, OK, USA) to obtain the model parameters.

Statistical analysis

The experiments were carried out in duplicate, and all the analyses were done in triplicate. Results were presented as mean values with standard deviations. Different mean values were statistically evaluated by analysis of variance (ANOVA), using the software STATISTICA® 8.0 (StatSoft, Inc., Tulsa, OK, USA). Mean separation was determined using the Tukey test at $P \leq 0.05$.

Results and discussion

Moisture content

Moisture content is an important powder property, which is related to the drying efficiency. Furthermore, lower moisture content limits the ability of water to act as a plasticiser and to reduce the glass transition temperature. Moisture content of blackberry powders varied from 1.74% to 3.32% (Table 2), close to the values reported by Tonon *et al.* (2009a,b), Quek *et al.* (2007) and Saénz *et al.* (2009), working with spray dried açaí, watermelon and cactus pear powder, respectively. Blackberry powder produced with 7% maltodextrin showed significant lower moisture content ($P \leq 0.05$) in comparison to other samples, meaning that the combination of maltodextrin and gum arabic did not affect this response. In a similar study, Kurozawa *et al.* (2009) did not observe a significant effect of maltodextrin or gum arabic on the moisture content of spray dried chicken meat protein hydrolysate. Righetto & Netto (2005) verified that maltodextrin was more effective in the reduction of moisture content of acerola powder produced by spray drying. This behaviour was probably due to the differences between the chemical structure of both carrier agents, because gum arabic is a complex heteropolysaccharide with a highly ramified structure, containing shorter chains and more hydrophilic groups.

Anthocyanin content and antioxidant activity

Total anthocyanin content of spray dried blackberry powder varied between 628 and 642 mg/100 g dried juice (Table 2). These values are higher than those obtained for purple sweet potato flour (from 520 to

Table 2 Moisture content, anthocyanin content, anthocyanin retention, antioxidant activity and colour parameters of spray dried blackberry powders produced with maltodextrin (MD), gum arabic (GA) or a blend of both carrier agents

	Samples		
Analysis	**7%MD**	**7%GA**	**3.5%MD + 3.5%GA**
Moisture content (%)	1.74 ± 0.05^a	3.32 ± 0.03^b	3.20 ± 0.07^b
Anthocyanin content (mg/100 g dried juice)	642.73 ± 0.78^a	628.16 ± 0.16^b	639.02 ± 0.75^a
Anthocyanin retention (%)	84.17 ± 0.50^a	78.24 ± 0.41^b	85.02 ± 0.37^a
Antioxidant activity (μmol TE g^{-1} dried juice)	266.58 ± 12.16^a	213.34 ± 4.76^b	257.22 ± 13.57^a
Lightness *L**	36.83 ± 1.04^a	39.96 ± 1.09^b	36.01 ± 1.11^a
Parameter *a**	23.45 ± 1.54^a	19.08 ± 1.99^b	22.87 ± 1.07^a
Parameter *b**	3.84 ± 0.31^a	3.58 ± 0.32^a	3.87 ± 0.21^a
Chroma *C**	22.99 ± 1.73^a	18.89 ± 1.94^b	23.08 ± 1.07^a
Hue angle (°)	8.81 ± 0.21^a	10.67 ± 0.20^b	8.69 ± 0.19^a

Mean ± standard deviation values with different letters in the same line indicate significant differences at $P \leq 0.05$.

570 mg/100 g dry matter) and bayberry powder (around 570 mg/100 g dry matter), both produced by spray drying process using maltodextrin as the carrier agent (Ahmed *et al*., 2010; Fang & Bhandari, 2011). Antioxidant activity of blackberry powders ranged from 213 to 266 μmol TE g^{-1} dried juice. In a similar work, Tonon *et al*. (2010) reported that anthocyanin content and antioxidant activity of spray dried açai powder was about fivefold higher (approximately 3400 mg/100 g dried juice and 1100 μmol TE g^{-1} dried juice, respectively), because açai has higher antioxidant capacity than other anthocyanin-rich fruits, such as blackberry, blueberry and others.

Powders produced with maltodextrin or a blend of maltodextrin and gum arabic showed higher pigment retention (around 85%), whereas the use of gum arabic resulted in lower anthocyanin retention (around 78%). The same trend was verified for antioxidant activity of spray dried powder, suggesting that anthocyanins found in blackberry are mainly correlated to its antioxidant capacity. Studying the microencapsulation of guava juice by spray drying, Osorio *et al*. (2011) concluded that maltodextrin better preserved fruit vitamin C content. Guava powder encapsulated with maltodextrin showed higher vitamin C content (about 50%) in comparison to the results obtained for samples produced using a mixture of gum arabic and maltodextrin (1:5 w/w). Tonon *et al*. (2010) evaluated the use of maltodextrin, gum arabic and tapioca starch as carrier agents during the spray drying process of açai pulp. No significant differences were observed between the maltodextrin and gum arabic with regard to anthocyanin content and antioxidant activity. However, açai powder produced with tapioca starch showed the lowest anthocyanin retention and antioxidant capacity. According to the authors, highly insoluble materials, such as tapioca starch, did not provide high microencapsulation efficiency, and consequently, lower anthocyanin retention and antioxidant activity were verified in this case.

Colour parameters

According to the results, the colour parameters of blackberry powders were located in the first quadrant of CIELAB colour diagram ($+a^*$ and $+b^*$), corresponding to the region of red and yellow.

Lightness values were significantly lower ($P \leq 0.05$) for the samples produced using 7% maltodextrin or both carrier agents, indicating that these powders were slightly darker. Parameter b^* did not show statistical differences, regardless of carrier agent. The use of maltodextrin significantly increased parameter a^* and chroma C^* values, decreasing hue angle H^* and leading to the formation of more red powders. This behaviour can be related to anthocyanin content and antioxidant activity results, because powders produced with maltodextrin showed better pigment retention and higher antioxidant activity (Table 2).

Bulk density, absolute density and porosity

Table 3 shows the results of bulk density, absolute density, porosity, wettability and mean diameter of powders produced using different carrier agents.

Blackberry powder produced with the blend of both carrier agents exhibited the highest bulk density, whereas the use of maltodextrin resulted in significantly lower bulk density values. Tonon *et al*. (2010) observed higher bulk density values for spray dried açai powder, when tapioca starch was employed as carrier agent. The authors attributed this behaviour to the highest molecular weight of tapioca starch in comparison to maltodextrin and gum arabic. The heavier the material, more easily it accommodates into the spaces between the particles, occupying less space and resulting in higher bulk density values. Furthermore, the polymer interactions between the carrier agents and powder product also affect bulk density, meaning that the combination of maltodextrin and gum arabic used in the present work contributed to the increase in powder bulk density. Similar results were also pointed out by Osorio *et al*. (2011), working with guava powder produced by spray drying. Powder encapsulated with maltodextrin exhibited a minor bulk density than that obtained with a blend of maltodextrin and gum arabic. Chegini & Ghobadian (2005) reported that spray dried powders with higher moisture content tend to have a higher bulking weight, because of the presence of water, which is considerably denser than the dry solid. This behaviour can be associated with the results observed in our study, because blackberry powders produced with gum arabic or both carrier agents showed higher moisture content and higher bulk density.

With respect to absolute density, all the samples showed similar values, not significantly differing

Table 3 Bulk density (ρ_{bulk}), absolute density (ρ_{abs}), porosity (ϵ), wettability and mean diameter (D[4,3]) of spray dried blackberry powders produced with maltodextrin (MD), gum arabic (GA) or a blend of both carrier agents

	Samples		
Analysis	**7%MD**	**7%GA**	**3.5%MD + 3.5%GA**
ρ_{bulk} (g cm^{-3})	0.409 ± 0.005^a	0.424 ± 0.001^b	0.443 ± 0.007^c
ρ_{abs} (g cm^{-3})	1.487 ± 0.010^a	1.512 ± 0.010^a	1.502 ± 0.010^a
ϵ (%)	72.47 ± 0.10^a	71.98 ± 0.58^b	70.50 ± 0.35^c
Wettability (s)	82.20 ± 12.30^a	134.20 ± 12.52^b	116.20 ± 8.53^b
D[4,3] (μm)	48.89 ± 5.71^a	10.98 ± 0.47^b	28.45 ± 0.79^c

Mean ± standard deviation values with different letters in the same line indicate significant differences at $P \leq 0.05$.

between each other. The knowledge of food density is important for processing, packaging, storage and shipping. Absolute density corresponds to the real solid density and does not consider the spaces between the particles, in contrast to the bulk density, which takes into account all these spaces. The lower the bulk density, the more occluded air within the powders and therefore, a greater possibility for product oxidation and reduced storage stability. Lower bulk density also implies in greater volume for packaging (Lewis, 1987).

Porosity is also related to the bulk density, because this property measures the fraction of the total volume which is occupied by the air. Blackberry powder produced with maltodextrin showed higher porosity values (Table 3), which indicates the presence of a larger number of spaces between the particles, containing oxygen available for degradations reactions. Nevertheless, as the differences between the porosity values were quite small (ranging from 70.50% to 72.47%), this property did not have a significant effect on the anthocyanin retention and antioxidant activity (Table 2) of spray dried blackberry powder. Tonon *et al.* (2010) reported that spray dried açai powder produced with tapioca starch presented lower porosity values (around 68%), in comparison to the samples encapsulated with maltodextrin or gum arabic (around 75%). Despite the small number of interparticle spaces observed for açai powder produced with tapioca starch, maltodextrin was the carrier agent that showed the best pigment protection and the highest antioxidant activity.

Wettability and particle size

Wettability can be defined as the ability of a powder bulk to be penetrated by a liquid because of the capillary forces (Hogekamp & Schubert, 2003). As observed in Table 3, blackberry powder produced with 7% maltodextrin showed the lowest wettability values and the highest mean diameter. Wettability is inversed related to the particle size, because larger particles show more spaces between them, being more easily penetrated by water. On the other hand, smaller particles are less porous, making more difficult the liquid penetration into the food matrix, which results in poor reconstitution properties.

According to Gong *et al.* (2007), spray-dried powders often have a small particle size (< 50 µm), with poor handling and reconstitution properties. To improve these properties, bayberry powder produced by spray drying was subjected to the agglomeration process, using a fluidised bed granulator and dryer. Wettability markedly increased from the wetting time of 120 s to a satisfactory value of 15 s after agglomeration, whereas particle size increased from 74 µm to about 200 µm. In a similar work, Quek *et al.* (2007) reported that the agglomeration decreases the powder exposure to oxygen, protecting lycopene and beta-carotene present in spray dried watermelon powder from oxidation. Rodríguez-Hernández *et al.* (2005) verified that the increase in the particle surface area because of decreased particle size accelerated the degradation of vitamin C content in cactus pear juice produced by spray drying. Therefore, it is possible that the higher mean diameter obtained for spray dried blackberry powder produced with maltodextrin or both carrier agents (around 49 and 28 µm, respectively) may have contributed to the greater anthocyanin retention and higher antioxidant activity observed in these conditions (Table 2).

Figure 1 shows the particle size distribution of spray dried blackberry powders produced using different carrier agents. A bimodal distribution was observed, indicating two predominant sizes: one with a lower volume (< 2%) and smaller particle diameters (predominant sizes of 0.8–1.0 µm). The second peak, with larger volume (around 7–10%) and larger particle size, varied according to each carrier agent used. Particle size of powders produced with maltodextrin, gum arabic and both carrier agents ranged from 0.1 to 477.0, 0.1 to 41.4 and 0.1 to 351.5 µm, respectively, whereas the predominant sizes were 26, 9 and 22 µm, respectively. According to Tonon *et al.* (2009a,b), bimodal distribution is important for powder products, because the smaller particles can penetrate into the spaces between the larger ones and occupy less space. The presence of larger particles may be attributed to the beginning of the agglomeration process.

Particle size can be also related to the powder bulk density. In general, bulk density decreases when particle size increase. The higher the particle mean diameter, the higher is the interstitial air content between the particles and, consequently, the higher is the volume occupied, resulting in lower bulk density (Goula & Adamopoulos, 2010). This behaviour can also explain the lowest bulk density values of powders produced with 7% maltodextrin.

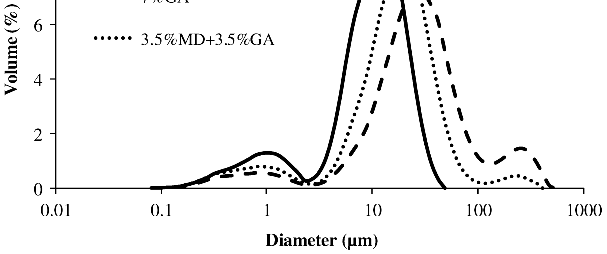

Figure 1 Particle size distribution of spray dried blackberry powders produced using different carrier agents.

Scanning electron microscopy

The morphological characteristics of spray dried blackberry powders produced using different carrier agents are presented in Fig. 2. Particles showed spherical shapes and various sizes, which is a characteristic of powders obtained by spray drying process.

Particles produced with 7% gum arabic were more heterogeneous with a shrivelled surface (Fig. 2b), whereas the blackberry powder produced with maltodextrin had a large number of smooth particles (Fig. 2a,c). In a similar study with pitaya seed oil powder (PSOP), Lim *et al.* (2011) observed that particles encapsulated with blends of maltodextrin and gum arabic showed smooth surfaces and they also were more agglomerated, while the surface of the PSOP samples produced with lactose and gum arabic showed a wrinkled and more porous structure. According to Osorio *et al.* (2010), smooth spheres are desirable for the stability of encapsulated ingredients and also for the controlled release. Loksuwan (2007) reported that maltodextrin with 20–24DE contains a great amount of low molecular weight sugars, which may act as plasticisers, preventing the shrinkage of the surface during the spray drying and leading to the formation of more smooth particles.

Osorio *et al.* (2011) verified the formation of more regular spherical particles for guava particles encapsulated with gum arabic. However, Kurozawa *et al.* (2009), working with spray drying of chicken meat protein hydrolysate, observed that the particles produced with gum arabic presented more irregular shape and dented surfaces. According to Saénz *et al.* (2009), dents are formed because of the shrinkage of particles during drying and cooling, and the presence of these dents has as adverse effect on the flow properties of powder particles. Thus, this could be related to the higher wettability values (around 135 s) obtained for blackberry powder produced with 7% gum arabic, as observed in Table 3.

The use of 7% maltodextrin resulted in a strong adherence of smaller particles to the surface of larger ones, forming many agglomerates (Fig. 2a). This fact can be related to the increase in particle size, as seen in Table 3. Besides, these agglomerates also contributed to the lower bulk density values and better anthocyanin protection verified in this sample, as discussed earlier.

Sorption isotherms

Figure 3 shows the experimental sorption isotherms for the spray dried blackberry powder produced using different carrier agents. The sorption isotherms showed an increase in equilibrium moisture content with increasing water activity, at constant temperature. Similar trend was observed for açai, acerola and strawberry powders (Righetto & Netto, 2005; Tonon *et al.*, 2009a,b; Mosquera *et al.*, 2011). According to Fig. 3, the blackberry powder produced with maltodextrin showed the lowest water adsorption, while the samples produced with gum arabic were the most hygroscopic ones. Similar behaviour was pointed out

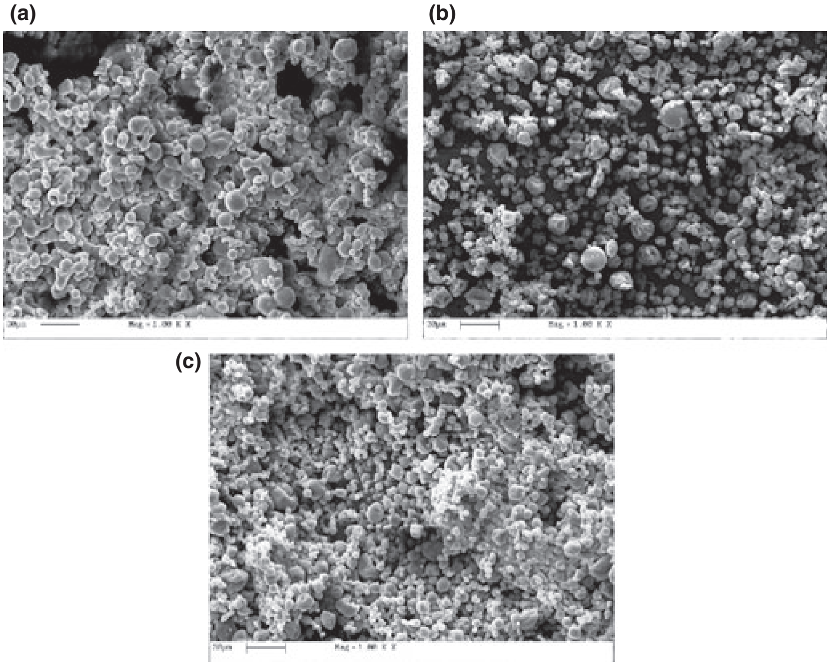

Figure 2 Scanning electron microscopy micrographs of spray dried blackberry powders produced using different carrier agents. (a) 7% maltodextrin, (b) 7% gum arabic and (c) 3.5% maltodextrin + 3.5% gum arabic. Magnification = 1000×.

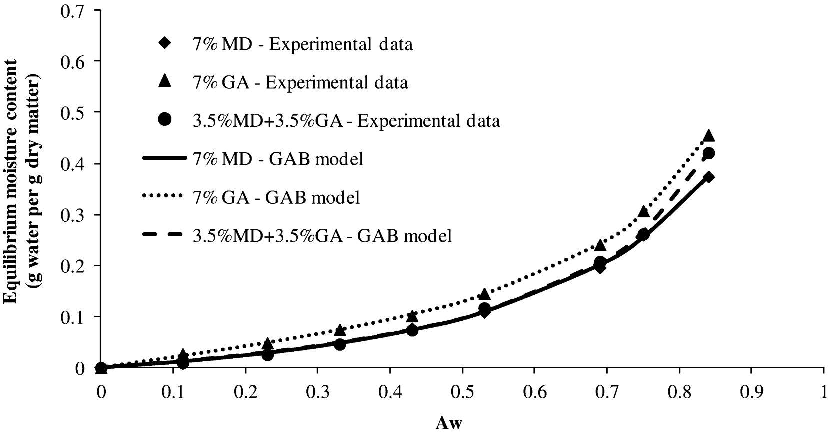

Figure 3 Sorption isotherms of spray dried blackberry powder produced using different carrier agents.

Table 4 Estimated GAB parameters for spray dried blackberry powders produced with maltodextrin (MD), gum arabic (GA) or a blend of both carrier agents

	Parameters			
Samples	**X_m (g water/g dry matter)**	**C_{GAB}**	**K_{GAB}**	**R^2**
7%MD	0.071	6.006	0.989	0.999
7%GA	0.087	5.928	0.988	0.999
3.5%MD + 3.5%GA	0.086	5.735	0.970	0.998

by Kurozawa *et al.* (2009), which can be attributed to the ramified structure of gum arabic, as previously discussed, promoting greater moisture adsorption.

The estimated parameters of GAB model are presented in Table 4. The model showed a good fit to experimental data, with high coefficients of determination (R^2 > 0.99). The values of C_{GAB} and K_{GAB} constants were in accordance with the limit values suggested by Lewicki (1997), based on the mathematical analysis of the model. For sigmoidal type curves, the author stated that the constants should assume values in the range $0.24 \leq K_{GAB} \leq 1.00$ and $5.6 \leq C_{GAB} \leq \infty$ to guarantee a relatively good description of the isotherms by GAB model. The K_{GAB} values of all the blackberry powder samples were close to 1, demonstrating multilayer properties which are similar to liquid water (Pérez-Alonso *et al.*, 2006; Mosquera *et al.*, 2011), while the C_{GAB} values were around 5.7–6.0 (Table 4), close to the upper limit values reported by Lewicki (1997). Mosquera *et al.* (2011) and Comunian *et al.* (2011) also obtained a good fit for the experimental data of the sorption isotherms for strawberry and chlorophyllide powders, respectively, using GAB model.

The X_m parameter (monolayer moisture content) corresponds to the amount of water strongly absorbed to specific sites at the food surface and is considered as the optimum value to assure food stability. The X_m values for spray dried blackberry powder ranged from 0.071 to 0.087 g water g^{-1} dry matter (Table 4), being lower for powders produced with maltodextrin, which is in agreement with Righetto & Netto (2005) and Comunian *et al.* (2011). Pérez-Alonso *et al.* (2006) attributed these results to a combination of factors, which include the conformation and topology of molecule and the hydrophilic/hydrophobic sites adsorbed at the interface.

Conclusions

Maltodextrin was more effective in the preservation of physicochemical characteristics of spray dried blackberry powder, because powders produced with this carrier agent were less hygroscopic, showed higher anthocyanin retention and higher antioxidant activity, lower moisture content and better reconstitution properties. Experimental data of water adsorption were well fitted to GAB model, showing high coefficients of determination. With respect to morphology, all the samples exhibited a large number of irregular particles with spherical shapes. Particles produced with gum arabic were smaller and more shrivelled, which contributed to the increase in wettability values and lower pigments protection. The use of maltodextrin resulted in powders rich in anthocyanins, with high antioxidant activity and good quality, which can be used as natural food colourants in the production of dry mixes, beverages, desserts, jellies, jams and other products.

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References

Ahmed, M., Akter, M.S., Lee, J.C. & Eun, J.B. (2010). Encapsulation by spray drying of bioactive components, physicochemical and morphological properties from purple sweet potato. *LWT – Food Science and Technology*, **43**, 1307–1312.

AOAC (2006). *Official Methods of Analysis of the Association of Official Analytical Chemists*, 18th edn. Gaithersburg, MD: Association of Official Analytical Chemists.

Bhandari, B.R., Data, N. & Howes, T. (1997). Problems associated with spray drying of sugar-rich foods. *Drying Technology*, **15**, 671–684.

Chegini, G.R. & Ghobadian, B. (2005). Effect of spray-drying conditions on physical properties of orange juice powder. *Drying Technology*, **23**, 656–668.

Comunian, T.A., Monterrey-Quintero, E.S., Thomazini, M. *et al.* (2011). Assessment of production efficiency, physicochemical properties and storage stability of spray-dried chlorophyllide, a natural food colourant, using gum Arabic, maltodextrin and soy protein isolate-based carrier systems. *International Journal of Food Science and Technology*, **46**, 1259–1265.

Falcão, A.P., Chaves, E.S., Kuskoski, E.M., Fett, R., Falcão, .L.D. & Bordignon-Luiz, M.T. (2007). Total polyphenol index, total anthocyanins and antioxidant activity of a model system of grape jelly. *Ciência e Tecnologia de Alimentos*, **27**, 637–642 (in Portuguese).

Fang, Z. & Bhandari, B. (2011). Effect of spray drying and storage on the stability of bayberry polyphenols. *Food Chemistry*, **129**, 1139–1147.

Ferrari, C.C., Germer, S.P.M. & Aguirre, J.M. (2011). Effects of spray-drying conditions on the physicochemical properties of blackberry powder. *Drying Technology*, **30**, 154–163.

Gancel, A.L., Feneuil, A., Acosta, O., Pérez, A.M. & Vaillant, F. (2011). Impact of industrial processing and storage on major polyphenols and the antioxidant capacity of tropical highland blackberry (*Rubus adenotrichus*). *Food Research International*, **44**, 2243–2251.

Gong, Z., Zhang, M., Mujumbar, A.S. & Sun, J. (2007). Spray drying and agglomeration of instant bayberry powder. *Drying Technology*, **26**, 116–121.

Goula, A.M. & Adamopoulos, K.G. (2004). Spray drying of tomato pulp: effect of feed concentration. *Drying Technology*, **22**, 2309–2330.

Goula, A.M. & Adamopoulos, K.G. (2010). A new technique for spray drying orange juice concentrate. *Innovative Food Science and Emerging Technologies*, **11**, 342–351.

Hogekamp, S. & Schubert, H. (2003). Rehydration of food powders. *Food Science and Technology International*, **9**, 223–235.

Koca, I. & Karadeniz, K. (2009). Antioxidant properties of blackberry and blueberry fruits grown in the Black Sea Region of Turkey. *Scientia Horticulturae*, **121**, 447–450.

Kurozawa, L.E., Park, K.J. & Hubinger, M.D. (2009). Effect of carrier agent on the physicochemical properties of a spray dried chicken meat protein hydrolysate. *Journal of Food Engineering*, **94**, 326–333.

Lewicki, P. (1997). The applicability of the GAB model to food water sorption isotherms. *International Journal of Food Science and Technology*, **32**, 553–557.

Lewis, M.J. (1987). *Physical Properties of Foods and Food Processing Systems*. Pp. 51–64. Chichester, UK: Ellis Horwood Ltd.

Lim, H.K., Tan, C.P., Bakar, J. & Ng, S.P. (2011). Effects of different wall materials on the physicochemical properties and oxidative stability of spray-dried microencapsulated red-fleshed pitaya (*Hylocereus polyrhizus*) seed oil. *Food and Bioprocess Technology*, doi: 10.1007/s11947-011-0555-1.

Loksuwan, J. (2007). Characteristics of microencapsulated β-carotene formed by spray drying with modified tapioca starch, native tapioca starch and maltodextrin. *Food Hydrocolloids*, **21**, 928–935.

Masters, K. (1991). *Spray Drying Handbook*, 5th edn. Pp. 241–327. London, UK: Longman Scientific and Technical.

Mosquera, L.H., Moraga, G. & Martínez-Navarrete, N. (2011). Critical water activity and critical water content of freeze-dried strawberry powder as affected by maltodextrin and arabic gum. *Food Research International*, doi: 10.1016/j.foodres.2011.05.019.

Osorio, C., Acevedo, B., Hillebrand, S., Carriazo, J., Winterhalter, P. & Morales, A.L. (2010). Microencapsulation by spray drying of anthocyanin pigments from corozo (*Bactris guineensis*) fruit. *Journal of Agricultural and Food Chemistry*, **58**, 6977–6985.

Osorio, C., Forero, D.P. & Carriazo, J.G. (2011). Characterization and performance assessment of guava (*Psidium guajava* L.) microencapsulates obtained by spray drying. *Food Research International*, **44**, 1174–1181.

Ou, B., Hampsch-Woodill, M. & Prior, R.L. (2001). Development and validation of an improved oxygen radical absorbance capacity assay using fluorescein as the fluorescent probe. *Journal of Agricultural and Food Chemistry*, **49**, 4619–4626.

Pérez-Alonso, C., Beristain, C.I., Lobato-Calleros, C., Rodríguez-Huezo, M.E. & Vernon-Carter, E.J. (2006). Thermodynamic analysis of the sorption isotherms of pure and blended carbohydrate polymers. *Journal of Food Engineering*, **77**, 753–760.

Quek, S.Y., Chok, N.K. & Swedlund, P. (2007). The physicochemical properties of spray-dried watermelon powders. *Chemical Engineering and Processing*, **46**, 386–392.

Righetto, A.M. & Netto, F.M. (2005). Effect of encapsulating materials on water sorption, glass transition and stability of juice from immature acerola. *International Journal of Food Properties*, **8**, 337–346.

Rodríguez-Hernández, G.R., González-García, R., Grajales-Lagunes, A., Ruiz-Cabrera, M.A. & Abud-Archila, M. (2005). Spray-drying of cactus pear juice (*Opuntia streptacantha*): effect on the physicochemical properties of powder and reconstituted product. *Drying Technology*, **23**, 955–973.

Saénz, C., Tapia, S., Chávez, J. & Robert, P. (2009). Microencapsulation by spray drying of bioactive compounds from cactus pear (*Opuntia ficus-indica*). *Food Chemistry*, **114**, 616–622.

Souza, A.S., Borges, S.V., Magalhães, N.F., Ricardo, H.V., Cereda, M.P. & Daiuto, E.R. (2009). Influence of spray drying conditions on the physicochemical properties of dried pulp tomato. *Ciência e Tecnologia de Alimentos*, **29**, 291–294.

Tonon, R.V., Baroni, A.F., Brabet, C., Gibert, O., Pallet, D. & Hubinger, M.D. (2009a). Water sorption and glass transition temperature of spray dried açai (*Euterpe oleracea* Mart.) juice. *Journal of Food Engineering*, **94**, 215–221.

Tonon, R.V., Brabet, C., Pallet, D., Brat, P. & Hubinger, M.D. (2009b). Physical and morphological characterization of açai (*Euterpe oleraceae* Mart.) powder produced with different carrier agents. *International Journal of Food Science & Technology*, **44**, 1950–1958.

Tonon, R.V., Brabet, C. & Hubinger, M.D. (2010). Anthocyanin stability and antioxidant activity of spray dried açai (*Euterpe oleracea* Mart.) juice powder produced with different carrier agents. *Food Research International*, **43**, 907–914.

Vissotto, F.Z., Jorge, L.C., Makita, G.T., Rodrigues, M.I. & Menegalli, F.C. (2010). Influence of the process parameters and sugar granulometry on cocoa beverage powder steam agglomeration. *Journal of Food Engineering*, **97**, 283–291.

Wu, R., Frei, B., Kennedy, J.A. & Zhao, Y. (2010). Effects of refrigerated storage and processing technologies on the bioactive compounds and antioxidant capacities of 'Marion' and 'Evergreen' blackberries. *LWT – Food Science and Technology*, **43**, 1253–1264.