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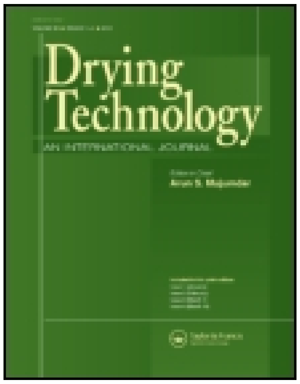

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Physical and Functional Properties of Blackberry Freeze- and Spray-Dried Powders

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The aim of the present work was to develop two products from blackberry juice by freeze and spray drying with potential use as food colorants or healthy ingredients. A characterization of the physical and functional properties of the powdered juices was done. Maltodextrin or a mixture of trehalose and maltodextrin were assessed as carrier matrices. Freeze-dried, maltodextrin-containing powders presented the best retention of bioactive compounds and antiradical activity; however, they showed a narrow relative humidity range for storage in the glassy state. Spray-dried powders showed better physical properties, bearing higher glass transition temperature and lower molecular mobility than freeze-dried formulations.

Keywords Bioactive compounds; Blackberry; Freeze drying; Glass transition; Spray drying

INTRODUCTION

There is a growing trend in consumer demand for berries, given their good taste and health-promoting properties. These fruits are consumed either fresh or frozen, or are incorporated as ingredients in dairy products, cereal bars, soft drinks and tea, among others. The Patagonia area generates over 70% of the blackberry production in Argentina. The perishability characteristics of these fruits impose very specific requirements on post-harvest and transport.[1] Therefore, it is important to develop options to process these fruits and promote their consumption.

One of the major reasons for the increasing popularity of blackberries, raspberries, and other small fruits in the human diet is that they are an excellent source of natural antioxidants.[2–5] The anthocyanins present in blackberries and raspberries are important for the beneficial health effects associated with their antioxidant, anti-inflammatory, and chemo-preventative properties.[6] Extracts of fruits from various blackberry, raspberry, and gooseberry cultivars act effectively as free radical inhibitors.[7–9]

The role of anthocyanins as food-coloring agents is becoming increasingly important. Not only do they contribute to the most important attributes of food—both for aesthetic value and for quality judgement—but they also tend to yield potential positive health effects due to their potent antioxidant properties.[10–13] Anthocyanins are a popular source of food colorants and the red ones, in particular, are normally produced from grapes (Vitis sp.), elderberry (*Sambucus niger*), and red cabbage (*Brassiea oleracea*). The use of anthocaynins may show benefits over that of synthetic colors. However, the use of these colorants in food products may face some problems due to their stability loss during storage, caused by temperature, oxygen, and light.[14] To overcome these problems and improve the bioactive compounds' stability, encapsulation technologies can be applied, such as spray drying[15] and freeze drying. The choice of components of the carrier matrix is important to obtain stable glassy powders. Fruit powders are amorphous materials, susceptible to glass-transition-related changes, including stickiness, caking, and collapse,[16,17] as well as color changes.[18] Maltodextrin (MD) is a low-cost, bland component ideal for the formulation of the carrier matrix.[19,20] Also, the high glass transition temperature (T_g) of low DE MD provides good physical stability to the dried powders.[21,22] Regarding the spray-drying process, it is well known that the type of carrier affects the flavor retention; for this reason, disaccharides, mainly sucrose, are sometimes included in commercial formulations to improve retention characteristics.[23,24] In this sense, the disaccharide trehalose is an alternative to sucrose in the dehydration of fruit juices as it shows a relatively higher T_g. Komes et al.[25,26] observed an improvement in aroma retention in dehydrated strawberry and apricot purees in the presence of trehalose compared to sucrose. Galmarini et al.[27] observed that strawberry puree presented better sensory

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properties when dried with the addition of trehalose in comparison with sucrose and MD.

Stability is greatly influenced by the water sorption behavior, the glass transition, and the molecular mobility characteristics of the powder. Such data can be used for selecting appropriate storage conditions and packaging systems that optimize retention of flavor, color, nutrients, bioactive components, and physical stability.

Encapsulation of anthocyanin-containing products by spray drying was studied by many researchers using different sources (pomegranate,[28] black mulberry,[29] and extracts of *Garcinia indica* Choisy[30] and black carrot[15]). Ferrari et al.[31] analyzed the effect of using different concentrations (5–25%) of maltodextrin (DE 20) as a carrier matrix, and different inlet air temperatures (140°C and 180°C) on the encapsulation of blackberry pulp by spray drying. They found that the optimal processing conditions were an inlet air temperature of 140–150°C and maltodextrin concentration of 5–7%. Bhandari et al.[32] obtained spray-dried powders from different concentrated berry juices using maltodextrin as a carrier matrix. According to their experiments, the best results were obtained for a juice-to-maltodextrin ratio of 65/35 for blackcurrant and 55/45 for raspberry.

The objective of the present work was to characterize the physical and functional properties of freeze- and spray-dried blackberry juices with the potential use as food colorants or functional ingredients. Powdered juices might constitute good alternatives to convenient and healthy food products or ingredients.

MATERIALS AND METHODS

Materials

Frozen blackberries, Black Satin cultivar (Rubus sp), grown in Valentina Norte, Neuquén (Patagonia, Argentina), were purchased from the "Talzauber" farm. The fruit was characterized according to AOAC methods: moisture (925.09), soluble solids (932.12), acidity (945.26), pH (945.27), and ash (940.26).[33]

The used carrier matrices were maltodextrin (MD) DE 12 from Givaudan S.A. (Argentina) and trehalose dihydrate (T) from Cargill Inc. (Wayzata, MN, USA). Analytical-grade reagents were used in all cases.

Powders Preparation

Preparation of Fruit Juice

In order to obtain blackberry juice, the following sequence of steps was followed: thawing of the frozen fruit under controlled conditions (bath at 40–45°C), milling for 1.5 min, centrifugation (6°C, 10,000 rpm) for 15 minutes, and vacuum filtration. After filtration, the juice contained approx. 5.4 g of solids/100 mL, and it was directly mixed with the carrier materials (MD or a 1:1 mixture of MD and T). Two different products were developed: (1) a spray-dried powder having a juice to matrix ratio = 60:40; and (2) a freeze-dried powder having a juice to matrix ratio = 80:20. The differences in carrier matrix proportion were due to the need for a high matrix ratio for spray drying in order to obtain a free-flowing powder, particularly in the presence of trehalose. Instead, in the freeze-dried powder we aimed to develop a more concentrated juice product. In the case of spray drying, this juice was the feed solution. For freeze drying, 2 mL blackberry juice was distributed in 5 mL vials and frozen at −20°C before the drying procedure.

Dehydration

Spray drying. The blackberry juices were spray-dried using a laboratory scale device, Mini Spray Dryer Büchi B290 (Flawil, Switzerland). The operational conditions of the drying process were inlet air temperature of 175 ± 3°C, flow rate 8 mL $\min^{-1}$, air pressure 3.2 bar, and nozzle diameter 1.5 mm. Once obtained, the powders were collected into sealed PVDC bags and then stored at −18°C.

Freeze drying. An Alpha 1–4 LD/2–4 LD-2 freeze drier (Martin Christ Gefriertrocknungsanlagen GMB, Osterode, Germany) was used. It was operated at −84°C at a chamber pressure of 0.04 mbar. The freeze-drying process lasted 48 hours. In order to compare with the spray-dried powders, the freeze-dried cakes were pulverized mechanically (using a glass bar for 30 seconds).

Physical Properties

Water Sorption Isotherms

Humidification. Approximately 0.5 g of the blackberry powders were loaded into 5 mL vials and immediately transferred into evacuated desiccators, which were kept at 20°C over saturated salt solutions that provided constant relative humidities (RH) of 11% (LiCl), 22% (CH_3COONa), 33% ($MgCl_2$), 43% (K_2CO_3), and 52% $Mg(NO_3)_2$. "Equilibrium" conditions were considered to be reached when the difference in weight taken at intervals of three days was less than 0.0005 g. The required time for equilibration was 2–8 weeks for the highest and lowest % RH, respectively.

Water content determination. Karl Fisher (KF) titration was carried out at 20 ± 1°C with a Karl Fischer titrator DL 31 from Mettler-Toledo, applying the one-component technique with Hydranal Titrant Composite 5 from Riedel-de Haën (Germany). Pure methanol or a methanol:formamide mixture (1:1) were used as solvent and they were purchased from Merck (Darmstadt, Germany). Approximately 100 mg samples were analyzed.

Water Activity

Water activity was measured using an electronic dew-point water activity meter Aqualab Series 3TE (Decagon Devices, Pullman, Washington, USA).

Thermal Transitions

Glass transitions were determined by differential scanning calorimetry (DSC; onset values) using a DSC 822e Mettler Toledo calorimeter (Schwerzenbach, Switzerland). The instrument was calibrated with indium (156.6°C), lead (327.5°C), and zinc (419.6°C). All measurements were performed at a heating rate of 10°C/min, in a temperature range between -50 and 100°C. Hermetically sealed 40 µl medium pressure pans were used (an empty pan served as reference). Thermograms were evaluated using Mettler Star^e program. An average value of at least two replicates was reported.

Molecular Mobility

A Bruker PC 120 Minispec pulsed nuclear magnetic resonance (NMR) instrument, with a 0.47 T magnetic field operating at resonance frequency of 20 MHz, was used for measurements. Equilibrated samples were removed from the desiccators, placed into 10 mm diameter glass tubes, and returned to the desiccators for 24 h prior to analysis.

The spin-spin relaxation time (T_2) associated with the solids was measured using a free induction decay analysis (FID) after a single 90° pulse. The decay envelopes were fitted to mono-exponential behavior with the following equation:

$$I = A\exp(-t/T_2) \tag{1}$$

where I represents protons signal intensity, T_2 corresponds to the protons in the polymeric chains of the sample, and A is the signal intensity of protons in T_2 state.

Since no 180° refocus pulse was used in the experiments, the spin-spin relaxation time constants are apparent relaxation time constants; i.e., T_2^*. However, for solid samples (like ours), we can consider that the intrinsic T_2 is very close to the T_2^* as reported previously by Fullerton and Cameron.[34] Therefore, T_2 was used for convenience.

Superficial Color

Superficial color was determined by photocolorimetry using a handheld colorimeter (Minolta Co, model CR400, Japan). Twenty replicates were analyzed. Color functions were calculated for illuminant C at 2° standard observer and in the CIELAB uniform color space. L^*, a^*, and b^* values were obtained. The functions hue angle and chroma were found to be adequate parameters to describe color characteristics in blackberry powders, and were calculated as follows:

$$\text{(1) Hue angle } (h_{ab}): \quad h_{ab} = \arctan\,(b^*/a^*) \tag{2}$$

$$\text{(2) Chroma}: \quad C^*_{ab} = (a^{*2} + b^{*2})^{1/2} \tag{3}$$

On the chromatic circle, h_{ab} takes values from 0° to 360° (magenta red); other reference angles are 90° (yellow), 180° (bluish green), and 270° (blue).

Measurements were performed using glass vials containing enough powder to complete 1 cm height. A white cylindrical cup was used to cover the vial and standardize the measurements.

Frozen blackberries were ground and were placed in Petri dishes; 10 measurements were taken from the fruit pulp.

Solubility

Solubility was determined according to Cano-Chauca et al.[35] with some modifications. 1 g of blackberry juice powder was hydrated in 100 mL distilled water and stirred at high velocity during 5 min. Reconstituted juice was centrifuged at 3000 g during 5 min. Supernatant (25 mL) was transferred to a porcelain capsule and oven-dried at 105°C up to constant weight. Solubility (%) was calculated by weight difference.

Bulk Density

Bulk density (g/mL) was determined by measuring mass with an analytical balance and volume using a graduated cylinder. The volume occupied by 0.5 g of blackberry powders in a 5 mL cylinder was determined after holding the cylinder on a vortex vibrator for 1 min.

Particles Morphology

The microstructural characteristics of powders were analyzed by scanning electron microscopy (SEM) using a Zeiss microscope Supra 40 (Germany). The samples were placed in an aluminum support using a double-sided adhesive tape conductive carbon and then coated with gold nanoparticles using a sputter coater (Cressington Scientific Instruments 108). The images were taken with the detector within the lens, using an acceleration voltage of 3.00 kV.

Chemical and Functional Properties

A spectrophotometer Metrolab 1700 ultraviolet-visible was used in all chemical determinations. In the case of powders, all chemical determinations were done on reconstituted juice, which was prepared as follows: approximately 0.5 g of each powder was dissolved in 25 mL distilled water.

In the case of the control fruit (frozen), an ethanolic extract (80%) was prepared. 15 g of frozen ground fruit were homogenized in 40 mL of absolute ethanol and mixed constantly in a magnetic agitator during 20 minutes and filtered by vacuum. The pellet was extracted again with the same procedure. The extracts were combined and distilled water was added to constitute a total volume of 100 mL.

Monomeric Anthocyanin Content (Acy)

Acy was determined using the pH-differential method.[36] An aliquot of sample was diluted (1:4 v/v) with two buffers, pH 1.0 (0.025 M potassium chloride) and pH 4.5 (0.4 M sodium acetate). After 15 min incubation at room temperature, the absorbance was measured at 510 and 700 nm. Acy content (monomeric anthocyanin) was expressed as cyanidin-3-glucoside (MW: 445.2 and a molar extinction coefficient: 29,600 L cm^{-1} mol^{-1}). Calculations were corrected by dry matter content.

Total Phenolic Content (TPC)

Total phenolic content was determined using the Folin–Ciocalteau reagent according to Singleton and Rossi[37] with some modifications. 150 μL blackberry samples was mixed with 950 μL water, 100 μL Folin–Ciocalteau reagent, and 600 μL 20% sodium carbonate in NaOH 0.1 N. After incubation during 30 min at 40°C, the absorbance was measured at 765 nm. A calibration curve was done with gallic acid as standard. The results were expressed as gallic acid equivalents in milligrams per 100 g of dry matter (mg GAE/100 g of d.m.).

Anthocyanin and Total Phenolic Retention

Anthocyanin (Acy) and total phenolic (TPC) retention after drying were calculated according to Fang and Bhandari[38] using the following formulas (expressed as dry matter):

$$\text{Acy}\ (\%) = \frac{\text{Acy in blackberry powder (mg/100 g)}}{\text{Acy in infeed solution (mg/100 g)}} \times 100 \quad (4)$$

$$\text{TPC retention}\ (\%) = \frac{\text{TPC in blackberry powder (mg/100 g)}}{\text{TPC in infeed solution (mg/100 g)}} \times 100 \quad (5)$$

The monomeric anthocyanin and total phenolic contents corresponding to the infeed solution were: Acy = 54.82 mg mg Cyd-3-glu/100 mL; and TCP = 228 mg GAE/100 mL.

Antiradical Activity (ARA)

Free radical scavenging ability of blackberry powders was measured using the bleaching method of 2,20-azinobis-[3-ethylbenzothiazoline-6-sulfonic acid] radical cation (ABTS$^{+\cdot}$), according to Coria Cayupán et al.[39] with some modifications. ABTS was dissolved in distilled water to yield a 7 mM solution. Radical cation solution was prepared by incubating the ABTS solution with a 2.45 mM potassium persulfate solution for 16 h in the dark at room temperature and subsequently diluted with water to a final absorbance of 1.00 ± 0.01 at 734 nm. For ARA determination, 50 μL of sample solution were added to a cuvette containing 2 mL of the ABTS$^{+\cdot}$ solution. The decrease in absorbance at 734 nm was monitored in cycles of 1 min during 30 min. The percentage inhibition of ABTS$^{+\cdot}$ by the samples was calculated according to Eq. (6).

$$\text{ARA}\% = 100 \times (1 - A_{ss}/A_0) \quad (6)$$

where A_{SS} is the absorbance of the solution in a steady state and A_0 is the absorbance of ABTS$^{+\cdot}$ solution before adding the antioxidant and considering volume variation (2 mL of ABTS$^{+\cdot}$ solution + 50 μL of distilled water). The absorbance of the system at the steady state was estimated by mathematical fitting of kinetic curves performed with Origin 7.0 software.

Total Sugar Content and Reducing Sugars

Total sugar content was determined by an anthrone/sulfuric acid procedure.[40] The anthrone (9,10-dihydro-9-oxoanthracene) with hydroxymethylfurfural (produced by dehydration of carbohydrates by sulfuric acid) give a colored hemiacetal, which is determined spectroscopically at 620 nm.

Reducing sugars were determined spectroscopically at 610 nm according to Somogyi and Nelson.[41]

Both determinations were measured on the ethanolic extract of blackberry frozen fruit and a curve with glucose as standard was used in each case for expressing results.

Experimental Design and Statistical Analysis

The experimental design was a completely randomized design (CRD). For all determinations, except for superficial color and thermal transitions, three replicates were measured, and the results were expressed by mean and standard deviation. Analysis of variance (ANOVA) was done to establish the presence or absence of significant differences between means. Multiple comparisons were performed using the Tukey test and significance level was set at $p < 0.05$. All statistical analyses were carried out using the data analysis software system STATISTICA 8.0.

RESULTS

Frozen Blackberries' Properties

Table 1 shows some physicochemical properties analyzed to characterize the frozen blackberries used in this work. In a review about several blackberry cultivars from the US, Kaume et al.[42] reported a range from 114 to 1056 mg/100 g fresh weight for total phenolics, and pointed out that besides genetics, fruit maturity can influence levels of total phenolics in this fruit. Our results fall within the range reported by Kaume et al.[42]

Different studies on several varieties of blackberry showed that the monomeric anthocyanin pigment content ranged between approx. 30 to 300 mg/100 g.[1,42–44] The anthocyanin content obtained in this work is 106 g/100 g,

TABLE 1
Physicochemical properties of the studied frozen blackberries

Physicochemical properties of blackberries	Mean ± SD
Water content (g H_2O/100 g fresh fruit)	83.5 ± 0.9
Water activity (a_w measured at 25°C)	0.984 ± 0.001
pH	3.03 ± 0.03
Total acidity (g% citric acid)	1.88 ± 0.03
Total soluble solids (°Brix)	9.06 ± 0.06
Ash (%)	0.43 ± 0.07
Total sugar (g glucose/100 g fresh fruit)	7.5 ± 0.5
Reducing sugars (g glucose/100 g fresh fruit)	3.6 ± 0.8
Anthocyanins (mgCyd-3-glu/100 g fresh fruit)	106 ± 20
Total phenolics (mg GAE/100 g fresh fruit)	146 ± 12
Color variables:	
L* value	7.5 ± 0.4
a* value	6.02 ± 0.01
b* value	2.16 ± 0.14
Chroma	6.4 ± 0.3
Hue angle	20 ± 1

and falls within the reported range for blackberries. According to Beattie et al.,[45] the anthocyanin content of blackberry varies due to differences in variety, environmental conditions, cultivation site, degree of ripeness, and processing.

Acidity and total soluble solids values were in the range reported by Fan-Chiang and Wrolstad[43] for 52 samples of blackberries.

Physical Properties of Blackberry Powders

In this section, we analyzed some physical properties of the freeze-dried (FD) and spray-dried (SD) powders, related to the stability of the dehydrated juices. Similar to other fruit juices, blackberries contain sugars (Table 1) and several organic acids[42,43] that would contribute to powder stickiness during spray drying.[46,47] Therefore, maltodextrin (MD) was included as a high molecular weight carrier that would contribute to increasing the glass transition temperature (T_g) of the product and thus provide good product stability.[48,49] Also, trehalose was incorporated into the carrier matrix to assess the performance of this sugar in the retention of bioactive compounds and the appearance characteristics of the juice powders. After some trials, the juice-to-carrier material selected ratio for spray drying was 60:40. In the case of freeze drying, a lower juice-to-matrix ratio was used (80:20) with the aim of developing a more concentrated juice product. The water content and water activity (a_w) were measured after each dehydration process (Table 2). Spray-dried powders presented lower water content than FD ones. This could be related both to the difference in matrix proportion and to the process itself, given that at the high temperatures of the spray drying more water could be removed. In contrast, there were no significant differences in water content between MD and TMD powders.

Figure 1 shows the external morphology of the powders obtained by spray-drying (Fig. 1a–d) and freeze drying (Fig. 1e–f). In the case of spray-dried (SD) powders, MD formulations presented spherical particles with some degree of shrinkage (Fig. 1a,c) compared to the smooth surface spherical particles shown by TMD powders (Fig. 1b,d). The freeze-dried (FD) powders (obtained by pulverization of the FD cake) showed irregular particles of larger size than the size observed for SD powders.

Figure 2 shows the water sorption isotherm at 20°C and the glass transition temperatures as a function of relative humidity (RH) for the FD (Fig. 2a) and SD (Fig. 2b) blackberry powders. Although there were differences in juice-to-matrix ratio, only small differences were observed between the FD and SD powders' water sorption behavior. The FD powders adsorbed slightly more water at each RH than the corresponding SD ones. According to Surana et al.,[50] the preparation method influences the particle size and morphology, affecting the sorption behavior. Upon spray drying, a rapid removal of water occurs, favoring some shrinkage and possibly intermolecular interaction and hydrogen bonding. Therefore, a spray-dried material may have less hydrogen bonding sites available for the sorption of water molecules than freeze-dried materials.[51] In agreement with our results, Giraldo Gómez et al.[52] reported water sorption isotherms at several temperatures for blackberry pulp freeze- and spray-dried powders

TABLE 2
Some physical properties of blackberries powders dehydrated by freeze drying (FD) and spray drying (SD)

Drying process	Formulation	Water content (%, d.b.)	a_w	Solubility (%)	Bulk density (g/mL)
FD	MD	6.11 ± 0.15^a	0.19 ± 0.04^a	99.8 ± 1.0^a	0.45 ± 0.02^a
FD	TMD	$6.05 \pm 0{,}04^a$	0.19 ± 0.02^a	99.5 ± 1.1^a	0.459 ± 0.005^a
SD	MD	3.7 ± 0.3^b	0.163 ± 0.009^a	98.63 ± 0.18^a	0.43 ± 0.03^a
SD	TMD	3.460 ± 0.007^b	0.19 ± 0.02^a	100.0 ± 0.5^a	0.34 ± 0.01^b

In each column, means with the same letter were not significantly different ($p < 0.05$).

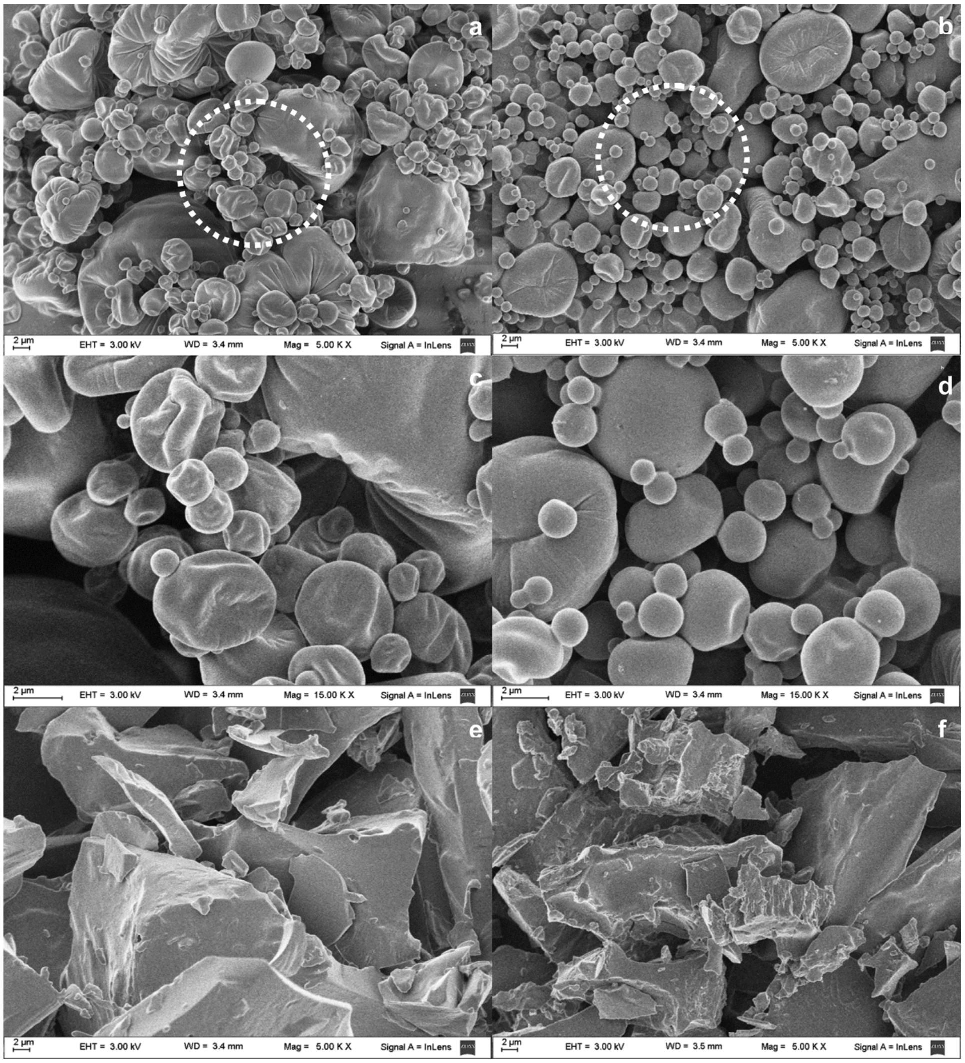

FIG. 1. Scanning electron micrographs of the surface of the blackberry powder particles. Spray-dried powders: (a) MD and (b) TMD at 5000× magnification; the sections indicated by circles in (a) and (b) pictures are magnified at 15000× for MD (c) and TMD. (d) Freeze-dried powders (e) MD and (f) TMD at 5000× magnification.

containing 18% of maltodextrin, and did not observe relevant differences between the used drying methods. Water sorption of maltodextrin[53] and trehalose[54] at low RHs shows an intermediate behavior between the observed values for freeze- and spray-dried blackberry powders. Although pure MD presents higher water sorption all along the RH scale, our blackberry powders did not show significant differences in the isotherms between MD and TMD formulations (Fig. 2). This behavior could be attributed to the relevance of the blackberry components in the water sorption behavior (mainly sugars and organic acids), which probably prevail over the added matrix.

The glass transition temperature (T_g) values were higher for the spray-dried powders than for the freeze-dried ones at the same RH (Fig. 2). This could be due to the higher matrix proportion in the spray-dried powders and also to the lower water contents observed in SD compared to FD powders. Also, the powders containing MD presented higher T_g values than the powders containing the mixture of trehalose and MD. This is attributable to the higher T_g of MD[55] compared to trehalose.[56] SD powders maintained the glassy state at room temperature (20°C) up to 52% RH for MD and 43% for TMD; meanwhile, FD powders kept the glassy state only up to 33% RH for both formulations. It is relevant to note that TMD powders showed a certain amount of trehalose crystallization (as revealed by a fusion peak in the DSC thermograms) at 43 and 52% RH. This fact indicates that the presence of trehalose in these powders limits the storage to RHs lower than 43%.

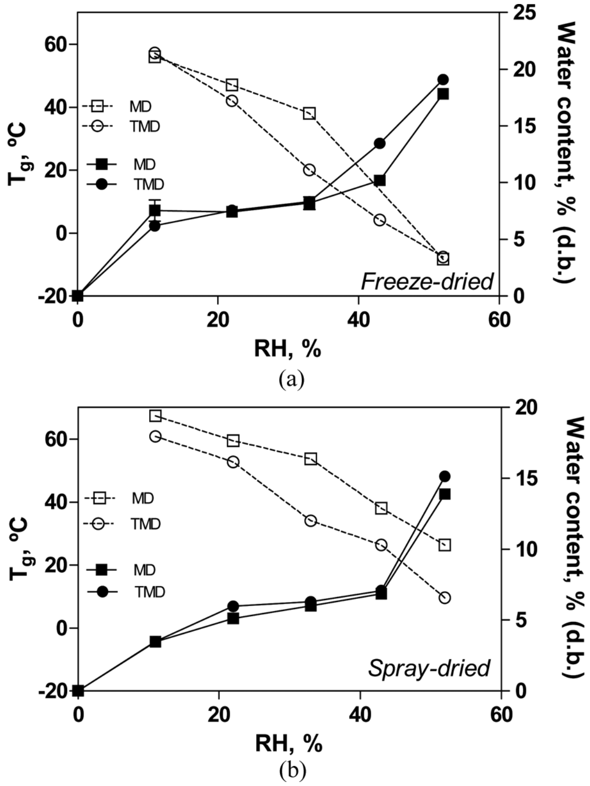

FIG. 2. Water sorption isotherm at 20°C (full symbols and solid line) and glass transition temperature (T_g, open symbols and dashed lines) as a function of relative humidity (RH) for the (a) FD and (b) SD blackberry powders.

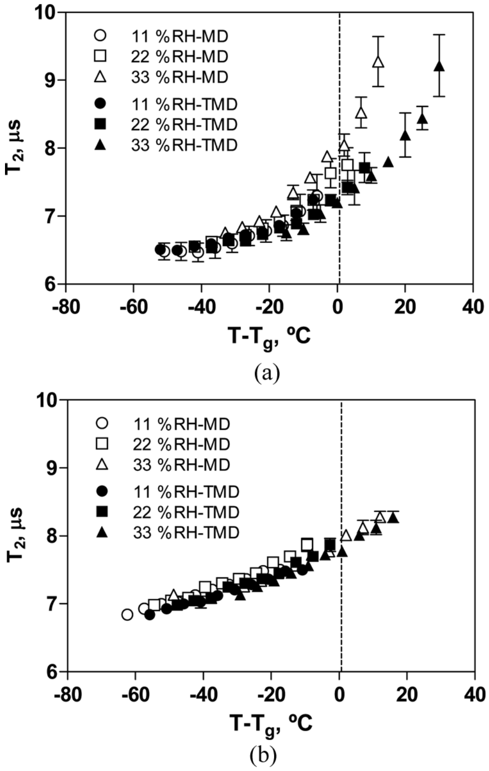

FIG. 3. T_2 relaxation times obtained by ^{1}H NMR as a function of the variable ($T-T_g$), where T is the measurement temperature for NMR, and T_g is the glass transition temperature at the different relative humidities analyzed: (a) FD; (b) SD blackberry powders.

The molecular mobility of the solids and the water tightly bound to the solids was estimated through the determination of the T_2 relaxation times by ^{1}H-NMR measurements. This analysis was done for all the formulations equilibrated at 11, 22, and 33% RH. The choice of RH range was related to having the powders in the glassy state at room temperature (20°C). In order to analyze the effect of temperature on the molecular mobility, the measurements were done in a temperature (T) range between 5 and 50°C, and the T_2 relaxation times were plotted as a function of $T-T_g$(Fig. 3). An increase in the T_2 values with the increment in temperature and RH was observed. In the case of SD powders (Fig. 3b), this T_2 increase was constant all along the analyzed temperature range, both for the glassy and supercooled states. However, it is important to note that only a few samples were above T_g (within the analyzed temperature range) and only up to 16°C. Also, MD powders showed slightly higher T_2 values than TMD ones. Sosa[57] observed higher molecular mobility in maltodextrin-containing systems than in maltodextrin-trehalose mixtures. Freeze-dried powders presented a different behavior (Fig. 3a), showing lower T_2 values than spray-dried powders (particularly in the glassy state), and an important increase in T_2 values around T_g. These differences could be related to the juice-to-matrix ratio that may have influenced the mobility behavior observed in FD and SD powders.

The effect of the drying method and the carrier agents on solubility and bulk density was analyzed (Table 2). All the powders presented very high solubility values. This may be attributed to the fact that both trehalose and maltodextrin have high solubility in water.[35,58] Bulk density values were in the range of the observed values for mulberry powders.[29] Several authors observed an inverse relation between the bulk density and solubility.[29,58] In our work, we observed almost 100% solubility in all cases; however, some differences were observed in bulk density values. Lower bulk density values were observed for the SD formulations, in comparison with the FD powders, particularly for the spray-dried TMD formulation. One of the reasons for this behavior could be the higher proportion of matrix material present in the spray-dried powders. Fazaeli et al.[29] also observed that bulk density showed a decrease with an increase in carrier matrix concentration when analyzing spray-dried black mulberry powders encapsulated with maltodextrins. They ascribed this behavior to the fact that maltodextrin reduces the sticking of particles, and also to the increase in the volume of air trapped in the particles, because maltodextrin is a skin-forming material. It is also important to note that the structural divergences present in freeze- and spray-dried powders (Fig. 1) can affect the bulk density values. During freeze drying, the freezing conditions determine the size of the generated crystals and thus the pore size distribution in the final product.[59] Therefore, the pore size distribution and the conditions of pulverization would be important factors affecting the morphology of freeze-dried powders. An important difference was observed between MD and TMD spray-dried powders. As seen in Figs. 1a and c, MD particles presented certain degree of shrinkage; this fact could explain the possibility of forming a more compact powder when compared to TMD powders (Figs. 1b and d) that present spherical particles. Thus, in one unit of volume TMD particles would leave more void spaces and would have lower density than MD powders.

Table 3 presents the color coordinates determined for the FD and SD blackberry powders. As both carrier materials (maltodextrin and trehalose) are white in the dry state and spray-dried powders have a higher matrix proportion, they showed higher luminosity values than freeze-dried ones. On the other hand, for a specific matrix formulation, the drying method did not affect the chromatic coordinate a*, but the coordinate b* was significantly higher for freeze-dried powders. These changes in chromatic coordinates led to great differences in tonality (hue angle), while saturation (chroma) remained similar. In the presence of trehalose, the powders presented slightly higher values of a* and b* in both drying methods with a visible increase in color saturation. Despite the whiteness of both dried carrier materials, it is likely that trehalose could generate more translucent powders, and thus allow the natural color of the fruit to be more exposed. Duangmal et al.,[60] in a color evaluation of freeze-dried roselle anthocyanin extract using maltodextrin and trehalose as a stabilizers, also showed that a* and b* increased slightly with trehalose addition, producing an increase in chroma values.

The main differences in the pink color of powders (rose-pink for spray-dried and bright pink for freeze-dried) are mainly due to variations in tones and luminosity.

Functional Properties of Blackberry Powders

Table 4 shows the monomeric anthocyanin content (Acy), the total phenolic content (TCP) and the antiradical activity (ARA) of the bioactive compounds in the different powders. FD powders showed much higher values of the three studied parameters compared to the SD powders. This fact could be attributed in part to the higher juice proportion in the FD powders. However, ACY, TCP, and ARA values observed in the SD powders were much lower than expected considering the juice concentration. Therefore, the exposure to high temperatures occurring in the spray-drying process might have caused an important loss of bioactive compounds.

Both for FD and SD powders, the addition of trehalose caused a reduction in bioactive compounds (ACY and TPC) and antiradical capacity. The color parameters (Table 3), however, indicate that in the presence of trehalose the powders showed a more saturated red color. Upon glucose or trehalose addition to blackberry juices, Kopjar et al.[61] observed an increase in the copigmentation effect. Copigmentation causes a hyperchromic effect (absorbance increase) and a bathochromic shift (shift of the maximum absorbance wavelength).[62] The analysis of TMD and MD spectra showed an hypochromic effect when the disaccharide was added (not shown), indicating that our formulations did not present a copigmentation effect.

Duangmal et al.[60] found that maltodextrin provided superior stability than trehalose and retarded anthocyanin degradation in freeze-dried powder of roselle anthocyanin extract. They informed lower stability of anthocyanins with increasing concentrations of trehalose, and attributed this effect to the higher hygroscopicity of the product. Chandra et al.[63] also found that anthocyanin pigments, extracted from tart cherries and stored with dextrins, were more stable than those without additives. They explained that complexing of the flavylium cation form of anthocyanins with dextrins prevented their transformation to other, less stable forms.

The freeze-dried MD blackberry powder presented the highest retention of anthocyanins and phenolics (Acy retention: 75% and TPC retention: 73%). In the presence of trehalose, a reduction of approx. 30% was observed for both determinations, suggesting that trehalose was not efficient in the retention of bioactive compounds. Acy and TPC

TABLE 3
Superficial color parameters of blackberry powders dehydrated by freeze drying (FD) and spray drying (SD)

Drying process	Formulation	L*	a*	b*	Chroma	Hue
FD	MD	53 ± 2^a	25.0 ± 1.4^a	6.4 ± 0.5^a	25.8 ± 1.5^a	14.3 ± 0.4^a
FD	TMD	53 ± 2^a	27.1 ± 1.9^b	6.6 ± 0.9^a	28 ± 2^b	13.7 ± 1.2^a
SD	MD	68.2 ± 0.7^b	24.5 ± 0.6^a	3.01 ± 0.14^c	24.7 ± 0.6^a	7.0 ± 0.3^c
SD	TMD	68.9 ± 0.6^b	27.0 ± 0.5^b	3.73 ± 0.17^b	27.3 ± 0.6^b	7.8 ± 0.2^b

In each column, means with the same letter were not significantly different ($p < 0.05$).

TABLE 4
Monomeric anthocyanin content (Acy), total phenolic content (TCP), and antiradical activity (ARA) of the bioactive compounds in the different powders dehydrated by freeze drying (FD) and spray drying (SD)

Drying process	Formulation	Acy	TPC	ARA%
FD	MD	162 ± 5^a	657 ± 23^a	78 ± 7^a
FD	TMD	112 ± 3^b	493 ± 46^b	63 ± 3^b
SD	MD	70 ± 3^a	340 ± 39^a	38.4 ± 1.5^a
SD	TMD	61 ± 2^b	294 ± 43^a	33.3 ± 0.7^b

In each column, means (for the same drying method) with different letters were significantly different ($p < 0.05$).

retention for spray-dried MD powder were 58 and 68%, whereas for TMD the percentages were 50% and 59%, respectively. In contrast to FD powders, trehalose caused a reduction of retention of about 13% for both determinations in powders obtained by spray drying. This could be related to the higher matrix concentration in SD compared to FD.

CONCLUSIONS

Four powder formulations were analyzed in this work. Freeze drying and spray drying were the dehydration methods assessed to obtain blackberry powders containing maltodextrin or a mixture of trehalose and maltodextrin as carrier matrices. Freeze-dried, MD-containing powders presented the best retention of bioactive compounds and antiradical activity; however, due to the lower matrix proportion, these powders show a narrow RH range for storage in the glassy state. On the other hand, SD powders show better physical properties, bearing higher T_g values and lower molecular mobility than FD formulations.

The addition of trehalose was not favorable both for the physical properties and for the retention of bioactive components. Also, at some RH values the sugar showed a certain degree of crystallization.

The high solubility obtained in all the formulations is a promising result regarding the application of these powders.

Regarding the possible application of the formulations analyzed in this work, freeze-dried powders could be incorporated into beverages or yogurt, considering the higher concentration of functional ingredient per mass unit. In this case, a higher coloring power would be attained compared to the spray-dried powders. On the other hand, spray-dried powders have higher physical stability than FD ones; therefore, they could be considered as ingredients to be incorporated into dehydrated food, which have to withstand different environmental conditions.

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