Storage stability of freeze-dried arazá (*Eugenia stipitata* Mc Vaugh) powders. Implications of carrier type and glass transition

Camilo Andrés Reyes-Álvareza,b, María Cecilia Lanari,a,b,∗

a Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET - La Plata, Facultad de Ciencias Exactas Universidad Nacional de La Plata (UNLP), Calle 47 y 116 S/N°, La Plata, B1900AJJ, Buenos Aires, Argentina.

b Members of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

A R T I C L E   I N F O

Keywords:
Arazá
*Eugenia stipitata*
Water-activity
Glass transition
Antioxidant activity

A B S T R A C T

Arazá, a flavousome fruit rich in antioxidants (phenolics/carotenoids/flavonoids/ascorbic acid) may be appropriate for preparing powdered-functional foods and beverages. Variations in water-activity (aw) and matrix physical state (glassy/rubbery) can induce undesirable changes in dehydrated products color antioxidant composition/activity reducing shelf-life. Solving this problem requires a thorough analysis of the aw/physical state effects on the arazá powder physicochemical properties. Objectives were to: (a) analyse aw, glass-transition temperature (Tg) and carrier-type (maltodextrin-DE10/Arabic-gum) effects on freeze-dried arazá color, antioxidant composition/activity; (b) Determine storage-time influence on antioxidant content/activity/polyphenol composition considering the best performing aw values previously determined. Critical aw values calculated from Tg/aw interrelationship overestimated the aw limit corresponding to samples color/antioxidant composition/activity maximum stability, therefore, Tg was not a reliable indicator of the properties stabilities. Antioxidant content/activity/storage behavior (20 °C/aw = 0.11 (best performing aw optimized across all properties)) were satisfactorily predicted by the Weibull equation. Shelf-lives, calculated considering 90% properties retention as the acceptability limit, were 34 (arazá/maltodextrin) and 50 (arazá/Arabic-gum) days. Polyphenolic profile included 6 phenolic acids, one coumaric acid derivative, 4 flavonoids and one ellagittannin. Using a mix of maltodextrin-DE10/Arabic-gum might improve antioxidant content/activity stability obtained with the single carriers and extend their shelf-life.

1. Introduction

Arazá (*Eugenia stipitata* Mc Vaugh) is an amazonian fruit rich in heat-sensitive antioxidants (phenolics/carotenoids/flavonoids/ascorbic acid) with proven antigenotoxic and antimutagenic properties; however, its high perishability hinders its commercialization in regions far from its production zones (Borghi-Virgolin, Fortunato-Seixas & Soares-Janzantti, 2017). Freeze-drying can be a viable solution to this problem since the low processing temperatures used and the absence of liquid water protects heat-sensitive compounds resulting in high quality final product (Marques, Ferreira, & Freire, 2007). However, drying or freeze-drying fruit juices or other products with high sugar content presents technical difficulties, the low glass-transition temperature (Tg) of some components (low molecular weight sugars and organic acids) and their high hygroscopicity causes stickiness, collapse and flow problems during processing and storage (Orjuela-Palacio & Lanari, 2016). Since in comparison with other tropical fruits, arazá's level of low molecular weight sugars (0.48 g glucose 100 mL−1; Borghi-Virgolin, Fortunato-Seixa, & Soares-Janzantti, 2017) is 9–10 times less, the incidence of these issues in the powder might be lower. Several researchers reported that incorporating carrier agents like maltodextrin (MD) and/or Arabic-gum (AG) before drying increased Tg, prevented caking, reduced hygroscopicity and improved physical stability of vacuum-dried mango (Jaya & Das, 2004) and spray-dried acai (Tonon et al., 2009).

Water-activity (aw) and physical state (glassy/rubbery) of the matrix play a fundamental role in dehydrated food stability. The glassy/rubbery transition occurs at a specific temperature (glass-transition temperature, Tg) which depends on the aw/water content of the powder. At T < Tg, the dehydrated food system is in the highly viscous glassy state associated to low levels of molecular mobility and diffusion-controlled reaction rates. At T > Tg, the product is in the rubbery state which...
implies a sharp viscosity decrease and an enhancement in certain processes rates. Water content/a_w increments can also reduce T_g through water plasticization and consequently induce glass-transition (Syamaladevi, Sablani, Tang, Powers, & Swanson, 2011).

Although food stored under glossy state conditions can be shelf stable, discoloration caused by non-enzymatic browning, antioxidant content/activity losses may still occur (Syamaladevi et al., 2011) therefore optimum product stability requires a thorough analysis on the T_g/a_w effect on the product physicochemical stability within the glossy and rubbery states ranges.

The aim of this study was to determine the relative humidity/a_r necessary for preserving color, antioxidant content and activity of arazá samples freeze-dried with maltodextrin or Arabic gum stored at 20 °C. Specific objectives were:

(a) To analyse the relationship between a_u, glass-transition and carrier type (maltodextrin DE 10 and Arabic-gum) at 20 °C on the stability of freeze-dried arazá color, antioxidant concentration and activity.

(b) To determine the effect of storage time on the antioxidant content and activity and polyphenol composition considering the best performing a_u values previously determined.

2. Materials and methods

2.1. Fruit selection and processing

Fresh arazá (moisture (H) 96 ± 2.4%, totals soluble solids (TSS) 3.9 ± 0.4°Brix) purchased at a local market in Ibagué (Colombia), was selected according to its color (yellow-green) and size (10–14 cm diameter). After washing, peeling and cutting, the fruit was manually pressed to form a paste and mixed with different salts (LiCl (11.3%); CH₃COOK (23.4%); MgCl₂ (33%); K₂CO₃ (43.2%); Mg(NO₃)₂ (54.4%) and NaCl (76%)). The samples were weighed every 3 days until content/activity losses may still occur (Syamaladevi et al., 2011). The powder T_g/water content relationship was predicted with the Gordon–Taylor equation (Eq. (2); Gordon & Taylor, 1953) considering T_g = T_g onset-

\[ T_g = \frac{X_{T_g} + k_{X_w} T_{gw}}{X_w + k_{X_w}} \]

where X_w and X_r represent the solids and water weight fractions (kg*(kg d.m)^{-1}), T_gw and T_{gw} (°C) the glass-transition temperatures of the water (-135 °C; Tonon et al., 2009) and the anhydrous matrix respectively and k_{X_w} a constant related to the matrix/water interaction. Eqs. (1) and (2) parameters were estimated using nonlinear regression analysis with the OriginPro v 8.0 (OriginLab Corp., Northampton, MA USA) and Systat 12 (Systat Software Inc; San Jose, CA USA) softwares. Models performance were evaluated with the mean relative deviation modulus (%E) and the adjusted determination coefficient (R_{adj}²).

The critical moisture content (C_w) and water-activity (C_{aw}) values corresponding to the glass/rubbery transition at 20 °C were determined as described by Tonon et al. (2009).

2.3. Physico-chemical analysis

2.3.1. Water-activity, moisture content

All determinations were done at least in triplicate. Water-activity was measured at 25 °C in an AquaLab series 3 (Decagon Device, Pullman, Washington, USA) calibrated with the saline solutions used for the sorption experiments.

2.3.2. Microstructure

The powders microstructure was analyzed by scanning electron microscopy (SEM; FEI Quanta 200 microscope, Netherlands) under high-vacuum conditions and 20 kV acceleration voltage (Deladino, Anbinder, Navarro, & Martino, 2007) The samples, attached to stubs with two-sided adhesive tape, were coated with a gold layer (40–50 nm).

2.3.3. Flowability, hygroscopicity and degree of caking

The powder bulk densities (g (cm^3)^{-1}) were evaluated measuring the volume occupied by a given weight of powder (40 g) in a graduated cylinder with (compact density (CD)); (100 taps, rate = 60 taps min^{-1}) and without compacting loose density (LD); (Deladino, Navarro, & Martino, 2007). The powders flowability was determined with the dynamic repose angle chamber (Solids handling study bench, CEN, Armfield, UK; Geldart, Abdullah, Hassanpour, Nwoke, & Wouters, 2006) and the Hausner index (Ha), defined as the compact to loose bulk density ratio (CD (LD)^{-1}).

Samples hygroscopicity (Hyg; Eq. (3)) and degree of caking (DC; Eq. (4)) were determined as described by Jaya and Das (2004).

\[ H_y = \frac{W_f}{W_i} + W_{t, 100} \]

\[ D_r = \frac{W_f}{W_i} \]
2.3.4. Color, pH, total soluble solids (TSS) and solubility in cold water

Color was expressed with the CIE L*a*b* coordinates and measured with a Minolta CR-400 Chroma Meter (Minolta, Osaka, Japan), each value was the average of 9 measurements on triplicate samples. The total color difference (ΔE) were calculated from Eq. 5
to measure the pH and the TSS ('Brix), the powders were reconstituted with a H2O volume similar to that lost during drying. Determinations were done by duplicate at 25 °C with a pHmeter (Hach Sension + pH3 Lab; Hach Company, Lovely, CO, USA) or a refractometer Atago N2 (Tokyo, Japan).

Samples solubility (Sol) (Eq. (6)) in water at 4 °C was determined in duplicate according to Chen and Jane (1994).

\[
\text{Sol} = \frac{p_{sa} + FD \times 100}{pt}
\]

d (g) and c (g) are the total and filter-retained powder weights.

2.3.5. Total/reducing sugars content and antioxidant composition

Total and reducing sugars concentration (g Glu (glucose equiv-\textsuperscript{1}) were analyzed with the anthrone/sulfuric acid colorimetric test (Leyva et al., 2008) using a UVmini-1240 UV–Vis Spectrophotometer (Shimadzu Scientific Instruments, Japan).

Antioxidants were extracted with a methanol/H\textsubscript{2}O (50:50 v/v, pH = 2.0) mixture (Saura-Calixto, Serrano, & Goñi, 2007). The total phenolic content of the extracts (TP; mg GAE (gallic acid equivalents) (g d.m\textsuperscript{-1}) was assessed with the Folin-Ciocalteu method (Schesler, Hawat, Böhm & Bitsch, 2002).

Total flavonoids (TF; mg CAT (catechin eq) (g d.m\textsuperscript{-1}) and carotenoids levels (TC; mg β-carotene eq(g d.m\textsuperscript{-1}) were determined according to Chang, Yang, and Wen (2002) and Ordoñez-Santos, Hurtado-Aguilar, Ríos-Solarte, and Arias-Jaramillo (2014).

Ascorbic acid (AA; mg AA*(100 g d.m\textsuperscript{-1}) concentration was analyzed by high performance liquid chromatography (Waters, model R-414, Milford, MA, USA; Orjuela-Palacio & Lanari, 2016).
Polyphenol composition was determined following Soares et al. (2019) protocol with a Waters Model 6000 A LC system (Milford, MA, USA) equipped with a diode array detector (DAD) and a C-18 Altex-Ultrosphere™-ODS column (250 mm × 4.6 mm i.d, 5 μm part size). Compound identification was done comparing their DAD spectra and retention times with those from commercial standards (Caffeic (CAF), Cinnamic (CIN), Chlorogenic (CLO), Coumaric (COU) trans-Ferulic (tFER), Gallic (GA)) acids and Rutin tri-hydrate (R3H2O; Sigma-Aldrich, Argentina) and from Soares et al. (2019) publication.

2.3.6. Antiradical activity and ferric reducing antioxidant power

The AMD and AAG antiradical activities (ARA; Eq. (7)) were determined with the DPPH scavenging assay (Brand-Williams, Cuvelier, & Berset, 1995).

\[
AR = \frac{[(\text{Absb}_0 - \text{Absss}) \times \text{Absb}_0^{-1}]}{100}
\]

Absb₀ and Absss are the absorbancies of the blank (b) and the sample (s) at time = 0 and at t = 120 min.

Ferric Reducing Antioxidant Power (FRAP; μM Fe²⁺(g d.m.)⁻¹) was evaluated according to Pulido, Bravo, and Saura-Calixto (2000) after 30 min of reaction time.

2.4. Storage stability

To analyse the influence of storage time and its interaction with carrier type on the powders antioxidant composition, ARA and FRAP, the samples were stored as described in Sect. 2.2 for 90 days at 20 °C using the RH/aₗ that provided maximum stability to all properties obtained from the aₗ/glass-transition relationship with color, antioxidant concentration and activity analysis.

Antioxidant content and activity retention (RY) during storage was analyzed using the Weibull equations (Eqs. (8) and (9); Oms-Oliu, Odrizola-Serrano, Soliva-Fortuny, & Martín-Belloso, 2009).

\[
\text{RY}_t = RY_0 \exp\left(-kt\right)^\gamma
\]  

(8)

\[
\text{RY}_t = RY_0 - \left(RY_0 - RY_f\right) \exp\left(-kt\right)^\gamma
\]  

(9)

\[
\text{RY}_t = \frac{Y}{Y_0}
\]  

(10)

\(\text{RY}_t\) represents the fraction of the property Y (TP, TC, TF, AA, ARA, FRAP) retained at t days, RY₀ and RY₀ correspond to the RY value at days 0 and 90 while k (days⁻¹) and γ are the kinetic and shape constants respectively.

Eq. (8), and (9) parameters were determined by regression analysis with the OriginPro v8.0. The model “goodness of fit” was evaluated considering the highest adjusted regression coefficients (R²adj) and minimal error of the parameters.

2.5. Statistical analysis

Results were expressed as the mean ± standard error of at least three replicates. The effect of temperature, carrier type and water-activity on the color, antioxidant content, antiradical activity and FRAP were analyzed with the Infostat (v. 2013) software. Significant differences among means were determined by analysis of variance followed
et al. (2006) reported that powders with repose angles > 50° or therefore individual AAG and AMD results were replaced by their

(Ara, Frap) were independent of the carrier type (P > 0.05), solids (TSS), ascorbic acid concentration (AA) and antioxidant activities

color parameters (L*, SI, HA) as well as solubility (Sol), total soluble

(50°), the di

listed in Table 1;

Fig. 3. a, b Water activity (Aaw - \Delta; Amd -\circ) and Tgaw-Tg (AAG - ▲; AMD

△) in

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water plasticization e

movement problems during processing.

The AMD and AAG samples prepared with 5% carrier showed lower

aw levels (0.08–0.09; Table 1) than those obtained with 0 or 2.5% (0.36–0.13) therefore, this concentration was used in the rest of the experiments.

3. Results and discussion

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3.1. Samples characterization

AAG and AMD physicochemical properties before equilibration are listed in Table 1; flow capacity Hauser index (Ha), repose angle and color parameters (L*, SI, HA) as well as solubility (Sol), total soluble solids (TSS), ascorbic acid concentration (AA) and antioxidant activities (ARA, FRAP) were independent of the carrier type (P > 0.05), therefore individual AAG and AMD results were replaced by their average.

UPS United States Pharmacopeia Convention (2012) and Geldart et al. (2006) reported that powders with repose angles > 50° or Hauser index > 1.5 have flow problems during processing.

Although the samples repose angle was 6.4% higher than the limit (50°), the difference was not significant (P > 0.05); in addition, AMD/ AAG Hauser ratio (Table 1) also fulfilled Geldart et al. (2006) conditions (Ha > 1.5), indicating that the samples flowability was acceptable

for manufacturing purposes.

AAG and AMD microstructures before equilibration (Appendix Fig. 1a and b non-eq) were consistent with the samples low humidity since the particles shapes and sizes were highly irregular with sharp edges and shriveled surfaces suggesting absence of agglomeration even though AAG particles were bigger and thicker.

Juliano and Barbosa-Cánovas (2010) concluded that powders fluidity depended on particle size, shape and surface characteristics. Compared with smooth round particles, those with smaller size, irregular shapes and rough surfaces have more inter-particles contact points resulting in a higher cohesiveness and a lower flowing capacity (Juliano & Barbosa-Cánovas, 2010). AMD and AAG irregular flaky shape and rough surfaces (Appendix Fig. 1a and b) fulfilled this condition, therefore their flow behavior could be partially explained by their morphology.

3.2. Glass-transition temperature/equilibrium water content/water-activity relationships

Table 1 shows the aaw moisture content, hygroscopicity and degree of caking levels of the non-equilibrated samples. Water-activity values were within the range (aaw < 0.25) recommended by Labuza and Altunakar (2007) for preserving biochemical stability and microbiological safety. Moisture level (H), hygroscopicity (Hyg; Eq. (3)) and degree of caking (DC; Eq. (4)) were higher in AAG than in AMD, possibly due to AG higher content of hydrophilic groups. According to GEA Niro Research Laboratory. (2003), Hyg and DC values indicated that, the samples were very hygroscopic and prone to caking.

Both products had high Tg, possibly due to their low level of reducing sugars (Table 1), Tonon et al. (2009) reported similar results for spray dried açai with 6% MD10.

Fig. 1 shows the water-activity effect on AAG and AMD equilibrium water content and Tg at 20°C. For aaw ranging 0.08–0.23, AMD moisture content remained stable but further enhancements up to 0.76 increased it by 464%; in contrast, AAG moisture gain was continuous reaching 529%.

Both isotherms were satisfactorily predicted by the GAB equation (Eq. (1)), Table 2 presents the regression parameters, the determination coefficient (R2 adj) and the mean relative deviation modulus (%E).

Wm AAG was higher than Wm AMD (P < 0.05), this could be caused by AG higher concentration of hydrophilic groups in comparison with MD10 which favor a greater interaction solute/sorbent (Silva, Kurozawa, Park, & Hubinger, 2012).

Wm represents the moisture level corresponding to optimum food stability (Orjuela-Palacio & Lanari, 2016), Labuza and Ball (2002) concluded that Wm > 0.1 kg H2O (kg d.m.)−1 may compromise food stability. Results showed that the predicted Wm values satisfied this condition (Table 2) therefore the processing conditions used in the current study were appropriate for producing powders with good stability.

Water-activity and carrier type strongly (P < 0.05) affected Tg (Fig. 1); at aaw = 0.11, Tg drop in AMD was 3 times higher than in AAG. Further aaw increments to 0.33 reduced the sample Tg by 26.5%, however, at aaw 0.43–0.76, Tg AAG stability was 14% lower.

The Gordon-Taylor equation (Eq. (2)) satisfactorily predicted the Tg/aaw relationship (Fig. 1; Table 2). kGT represents the effectiveness of water plasticizing capacity in a given matrix (Ramoned, Ponce-Cevallos, Buera, & Elizalde, 2011) therefore an enhancement of this property implies a faster Tg drop at low water contents. Statistical analysis showed that AMD and AAG kGT values were similar (P > 0.05) hence the plasticization effect was independent from the carrier type.

The critical moisture content (CW; Caw) and water-activity (Caaw) values corresponding to the samples glass/rubbery transition at 20°C (Table 2; Fig. 1) indicated that to preserve the AMD or AAG glassy state during the whole storage period, samples should be kept at relative
humidities < 61 or 49% respectively.

To determine the influence of physical state (glassy/rubbery) on \( \Delta E \) (Appendix Fig. 2), antioxidant concentration (Fig. 2a–d) and activity (Fig. 3a–b), the \( T_g \) effect was analyzed considering \( \Delta T = T_{\text{stor}} - T_g \) \( (T_{\text{stor}} = 20 \, ^\circ C) \).

Results showed that within the glassy-state zone, discoloration and antioxidant content/activity losses were considerable. At \( a_w = 0.43 \), \( \Delta E_{\text{AAG}} \) and \( \Delta E_{\text{AMD}} \) values increased 14.75 and 1.75 times respectively in comparison with their levels in non-equilibrated samples. Karmas, Buera, and Karel (1992) observed significant discoloration caused by non-enzymatic browning in freeze-dried potatoes under glassy-state conditions.

Antioxidant retention decreased by 26% for TP and 20% for TC and TF (Fig. 2a–c). Carrier-type influence on AA content was highly significant (P < 0.05), at \( a_w = 0.43 \), AAG and AMD retention dropped 19 and 37% respectively (Fig. 2d). Ismail and Mauer (2019) detected significant ascorbic-acid degradation in glassy state model systems whereas Prado, Buera, and Elizalde (2006) showed that \( \beta \)-carotene degradation was faster in the glassy than in the rubbery state.

In accordance with antioxidant content results, ARA and FRAP also diminished in the glassy area (P < 0.05; Fig. 3a, b), at \( a_w = 0.43 \), antioxidant activities retention decreased by 14% and was not affected by carrier type (P > 0.05).

Syamaladevi et al. (2011) reported that although molecular mobility were greatly reduced in the glassy state, undesirable chemical reactions may still occur caused by changes in water-activity. Bell and Hageman (1994) reported that aspartame degradation was more affected by \( a_w \) than by \( T_g \).

Deladino, Navarro, & Martino, (2005) concluded that although maltodextrin and Arabic-gum can encapsulate the bioactives protecting them from adverse environmental conditions, their efficiency is reduced because spray or freeze-drying encapsulation leaves a significant proportion of the antioxidants unprotected in the microcapsule surface resulting in increments of the degradation rates.

Results showed that to retain 90% of the color, antioxidant content/activity values from the samples before equilibration, the powders must be kept at \( a_w \leq 0.11 \).

The SEM micrographs (Appendix Fig. 1a and b) shows the water-activity effect on the microstructure of the powders, \( a_w \) increments up to 0.33 (GLASSY STATE) did not produced visible signs of agglomeration; particles had wrinkled surfaces, pores and visible dents. In contrast, in the phase transition \( (0 \, ^\circ C < \Delta T \leq 20 \, ^\circ C - T_{\text{gend}}) \) and rubbery state \( (T-T_g > 20 \, ^\circ C - T_{\text{gend}}) \) regions, the formation of inter-particle bridges was noticeable at \( a_w = 0.54 \) and enhanced at 0.76.

### 3.3. Storage stability

To determine the antioxidant content and activity variations during storage, AAG and AMD samples were kept for 90 days at 20 °C and \( a_w = 0.11 \). Results showed that antioxidant concentration/activity losses were: 10% (TP/TC/TF), 6–9% (AA), 9–12% (ARA) and 10–14% (FRAP; Fig. 4a–d, Fig. 5a–b).

Degradation rates followed two different patterns:

a) Continuous decline \( (T_{\text{AMD/AAAG}}, T_{\text{AAG}}, T_{\text{AMD}}, A_{\text{AAG}} \text{ and } \text{FRAP}_{\text{AAG}}) \) or

b) An initial stable period followed by a sharp drop until reaching an asymptotic level \( (T_{\text{AMD}}, T_{\text{CAAG}}, A_{\text{AAG}}, \text{FRAP}_{\text{AAG}} \text{ and } \text{ARA}_{\text{AAG/}}\text{AMD}) \).

Results were satisfactorily predicted by Eq. (8) in the first case and Eq. (9) in the latter. Table 3 shows the regression parameters and their corresponding errors along with the models adjusted determination coefficients (\( R^2_{\text{adj}} \)).
From days 30–90 (TC) or days 36–157 (AA), TC and AA stabilities were more pronounced in AMD than in AAG (P < 0.05) whereas, between days 22–67, TF retention was higher in AAG than in AMD (P < 0.05). Following these periods, AAG had higher TP, TC and AA and lower TF concentrations than AMD (P < 0.05).

FRAP and ARA stabilities during storage followed similar behaviors: an initial 30 days period with no changes (P > 0.05) followed by a drop where the stability order was:

- ARA_{AMD} > ARA_{AAG} (31–77 days)
- FRAP_{AMD} > FRAP_{AAG} (31–92 days)

After these periods, AAG presented higher levels of both ARA and FRAP than AMD (P < 0.05).

AAG and AMD shelf lives (SL) were calculated assuming 90% retention of the different properties as the acceptability limit. The results (Table 3) indicated that using AG as the carrier increased SL from 34 to 50 days; however, if only antioxidant activity contribution is taken into consideration then the shelf-life values were 99 and at least 200 days for AMD and AAG respectively.

Storage time and carrier type produced significant changes (P < 0.05) in the arazá polyphenolic profile (Table 4). In accordance with Soares et al. (2019), we detected 6 phenolic acids: gallic (GAL), chlorogenic (CLO), coumaric (COU), cinnamic (CIN), caffeic (CAF) and transferulic (tFER) as well as one coumaric acid derivative identified as coumaric acid hexoside (COUHex). In addition, both samples contained 4 flavonoids (rutin mono-hydrate (RH2O) and trihydrate (R3H2O); Quercetin-3-O-rutinoside (QRut), eriodictyol-7-O-glucoside (EGlu) and one ellagitannin; di-HHDP (hexahydroxydiphenol)-galloyl-glucose (casuaricitin/protentillin) derivative (CPDer).

Carrier type affected the freeze-drying influence on polyphenols content (Table 4; P < 0.05). Comparison between both samples showed that AAG contained 130–204% more Ga, QRut, R3H2O and RH2O whereas CAF, CLO, CIN, COUHex and CPDer were 172–283% higher in AMD.

At day 90, phenolic acids losses were 16–68% (AAG) and 16–70% (AMD) while in the case of the flavonoids and the di-HHDP-galloyl-glucose derivative the reductions were: 4–51% (AAG) and 10–71% (AMD; Table 4), in contrast, rutin monohydrate content remained constant through the whole storage period.

Polyphenols stability ranking was:

- AAG
  - tFER > COUHex ≈ GAL > COU ≈ CLO ≈ CIN ≈ CAF
  - RH2O > QRut > R3H2O > CPDer > EGIU
- AMD
  - GAL > tFER > COUHex > CLO > CAF ≈ CIN ≈ COU
  - RH2O > QRut > EGIU > R3H2O > CPDer

Results obtained from contrasting the carrier effects on polyphenol stability showed that using AG reduced QRut, COU, CPDer and RH2O/R3H2O storage losses 28–59% whereas MD10 improved COUHex, GA and EGIU stabilities 20–58%.

4. Conclusions

The critical water-activity values determined from the Tg/aw inter-relationship (0.61 (AMD), 0.49 (AAG)) overestimated the aw limits corresponding to the samples color and antioxidant content/activity stability levels therefore, in these cases, Tg was not a reliable criterion for stability prediction.

Assuming 90% retention of all the different properties as the acceptability limit, AAG and AMD shelf-lives (20 °C, aw = 0.11) were 50 and 34 days.

Total flavonoids and total carotenoids levels were key factors in determining the samples shelf-lives. Although AAG had the longest
Table 4
Storage time effect on polyphenol composition of freeze-dried araçá pulp encapsulated with Arabic gum (AAG) or maltodextrin DE10 (AMD) 5% (w/w).

<table>
<thead>
<tr>
<th>Bioactives</th>
<th>Rt (min)</th>
<th>0 days</th>
<th>90 days</th>
<th>AMD</th>
<th>0 days</th>
<th>90 days</th>
<th>Stor. Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeic acid (CAF)</td>
<td>11.3</td>
<td>66.49 ± 5.52</td>
<td>21.14 ± 3.09</td>
<td>3.24</td>
<td>187.87 ± 7.07</td>
<td>70.64 ± 4.62</td>
<td>68.21</td>
</tr>
<tr>
<td>Chlorgencic acid (GA)</td>
<td>9.6</td>
<td>96.94 ± 1.83</td>
<td>38.12 ± 4.15</td>
<td>11.69</td>
<td>166.98 ± 4.76</td>
<td>71.70 ± 7.48</td>
<td>60.68</td>
</tr>
<tr>
<td>Cinnamic acid (CIN)</td>
<td>27.5</td>
<td>126.58 ± 2.54</td>
<td>41.82 ± 0.84</td>
<td>7.05</td>
<td>288.95 ± 5.07</td>
<td>87.72 ± 1.29</td>
<td>66.96</td>
</tr>
<tr>
<td>Coumaric acid (COU)</td>
<td>15.1</td>
<td>128.55 ± 3.48</td>
<td>67.86 ± 2.04</td>
<td>3.54</td>
<td>354.23 ± 6.19</td>
<td>121.24 ± 7.25</td>
<td>47.21</td>
</tr>
<tr>
<td>Coumaric acid-O-hexoxide (COUHex)</td>
<td>13.9</td>
<td>57.15 ± 1.79</td>
<td>36.60 ± 1.54</td>
<td>11.89</td>
<td>95.31 ± 9.25</td>
<td>85.51 ± 0.94</td>
<td>35.96</td>
</tr>
<tr>
<td>Gallic acid (GA)</td>
<td>4.4</td>
<td>166.02 ± 3.39</td>
<td>106.01 ± 0.86</td>
<td>8.01</td>
<td>81.08 ± 2.45</td>
<td>68.19 ± 1.83</td>
<td>36.15</td>
</tr>
<tr>
<td>Trans-furanic acid (SFR)</td>
<td>0.44</td>
<td>35.10 ± 10.98</td>
<td>109.15 ± 5.12</td>
<td>11.69</td>
<td>524.68 ± 6.99</td>
<td>419.15 ± 6.41</td>
<td>15.63</td>
</tr>
<tr>
<td>Di-HBD-pally-gluco-gluco (casuarictin/potentillin)derivate (CPD)</td>
<td>14.7</td>
<td>235.21 ± 6.94</td>
<td>164.22 ± 2.57</td>
<td>586.78 ± 3.69</td>
<td>170.06 ± 10.79</td>
<td>30.17</td>
<td>71.02</td>
</tr>
<tr>
<td>Eriodictyol-7-O-glucoside (EGlu)</td>
<td>3.1</td>
<td>699.75 ± 11.82</td>
<td>643.63 ± 5.14</td>
<td>417.51 ± 4.02</td>
<td>347.27 ± 4.28</td>
<td>8.02</td>
<td>18.02</td>
</tr>
<tr>
<td>Rutin (tribhydrate; R3H2O)</td>
<td>18.9</td>
<td>171.81 ± 8.14</td>
<td>143.21 ± 3.68</td>
<td>132.53 ± 8.57</td>
<td>100.81 ± 3.06</td>
<td>16.65</td>
<td>23.93</td>
</tr>
<tr>
<td>Rutin (hydrate for; RH2O)</td>
<td>3.5</td>
<td>413.33 ± 12.24</td>
<td>395.75 ± 5.99</td>
<td>214.79 ± 4.97</td>
<td>192.72 ± 5.14</td>
<td>4.25</td>
<td>10.26</td>
</tr>
</tbody>
</table>

1: COUHex: mg COU eq (100 g d.m)−1; 2: CPD: mg Gallic acid eq (GAE) (100 g d.m)−1; 3: EGlu: mg GAE (100 g d.m)−1; 4: R3H2O: mg R3H2O eq (100 g d.m)−1.

- Storage loss.
- Rt: retention time.
- mg (100 g dry matter (d.m))−1.

shell-life, AMD had a higher TP, TF and TC content therefore using a mix of maltodextrin-DE10/Arabic-gum might improve the antioxidant content/activity stabilities and extend the samples shelf-life.

Declaration of competing interest

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Acknowledgements

We thank Eng. Chris Young for assisting with the English translation, Claudio Reyes for the ascorbic-acid analysis, Dr Juliana Orjuela-Palacio, Dr Jonh Mendez and Universidad del Tolima for their contribution. C.A. Reyes-Álvarez was supported by the Argentinian Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2019.108842.

References

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