

1 **The impact of moisture sorption properties on the color and bioactives**  
 2 **concentrations of black currant-yerba mate instant drinks**

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11  
 12 **Abbreviations**

|                                     |                                                                                         |
|-------------------------------------|-----------------------------------------------------------------------------------------|
| YM                                  | Yerba mate                                                                              |
| BC                                  | black currant                                                                           |
| MD <sub>10</sub>                    | Maltodextrin Dextrose Equivalent 10                                                     |
| d.m.                                | Dry matter                                                                              |
| a <sub>w</sub>                      | Water activity                                                                          |
| RH                                  | Relative humidity                                                                       |
| W <sub>c</sub>                      | Equilibrium moisture content (kg H <sub>2</sub> O (kg d.m) <sup>-1</sup> )              |
| W <sub>m</sub>                      | Equilibrium monolayer moisture content (kg H <sub>2</sub> O (kg d.m) <sup>-1</sup> )    |
| X <sub>s</sub>                      | Security water contents; Caurie model (kg H <sub>2</sub> O (kg d.m) <sup>-1</sup> )     |
| q <sub>0</sub>                      | Net isosteric heat of the first water molecule (kJ mol <sup>-1</sup> )                  |
| A / B                               | Halsey and Oswin models constants                                                       |
| %E                                  | Mean relative deviation modulus                                                         |
| K <sub>GAB</sub> / C <sub>GAB</sub> | GAB model constants                                                                     |
| v                                   | Caurie model constant                                                                   |
| T                                   | Absolute temperature (K).                                                               |
| T <sub>hm</sub>                     | Harmonic mean temperature (K)                                                           |
| T <sub>β</sub>                      | Isokinetic temperature (K)                                                              |
| R                                   | Universal gas constant (0.008314 kJ mol <sup>-1</sup> K <sup>-1</sup> )                 |
| q <sub>stn</sub>                    | Net isosteric heat (kJ mol <sup>-1</sup> )                                              |
| Q <sub>st</sub>                     | Total heat of sorption (kJ mol <sup>-1</sup> )                                          |
| ΔH <sub>vap</sub>                   | Free water's latent heat of vaporization (kJ mol <sup>-1</sup> )                        |
| ΔS <sub>d</sub>                     | Differential entropy (kJ mol <sup>-1</sup> K <sup>-1</sup> )                            |
| ΔG <sub>β</sub>                     | Free energy (kJ mol <sup>-1</sup> ) at T <sub>β</sub>                                   |
| TP                                  | Total phenolic content (mg gallic acid equivalents (g d.m (dry matter)) <sup>-1</sup> ) |

|            |                                                                                                |
|------------|------------------------------------------------------------------------------------------------|
| MAC        | Monomeric anthocyanin content<br>(mg cyanidin-3-glucoside equivalents (g d.m.) <sup>-1</sup> ) |
| L*, a*, b* | CIELab color coordinate                                                                        |
| ΔE*        | Total color difference                                                                         |
| SI         | saturation index                                                                               |
| HA         | hue angle                                                                                      |
| AA         | Ascorbic acid content (mg AA (100 g d.m.) <sup>-1</sup> )                                      |

1

1 **Abstract**

2 **BACKGROUND:** Black currant (BC) and yerba mate (YM) have high contents of  
3 polyphenolic antioxidants beneficial for health. Obtaining freeze-dried BC/YM instant  
4 drinks can be a means for providing their advantages to consumers. However, their high  
5 sugar contents make them very hygroscopic causing undesirable changes in color and  
6 bioactives concentration.

7 **OBJECTIVE:** To solve this problem it is necessary to determine the powder's sorption  
8 properties and the temperature/relative humidity's (RH) influence on their color and  
9 polyphenol, ascorbic acid and anthocyanins's concentrations.

10 **METHODS:** We analyzed the sorption isotherms of freeze-dried  
11 YMI/BC/maltodextrin/sugar powder at 10/20/40°C and compared them with those from  
12 YM/maltodextrin.

13 **RESULTS:** Of all models tested (Caurie, GAB, Halsey, Oswin) GAB was the best.  
14 Monolayer moisture values ( $W_m$ ) were  $\leq 0.1 \text{ kg H}_2\text{O}(\text{kg d.m})^{-1}$  indicating good stability.  
15 Due to its higher sugar content, BC/YM powders were more hygroscopic and with  
16 higher exothermic isosteric sorption heat ( $Q_{st}$ ) than YM powders.  $Q_{st}$  and differential  
17 entropy decreased exponentially with increasing moisture levels. Within the  
18 experimental conditions, isokinetic theory indicated that the whole sorption process was  
19 enthalpy controlled. Temperature and RH strongly modified BC/YM's color and  
20 ascorbic acid and monomeric anthocyanins concentrations. At all temperatures,  
21 optimum levels of these properties required  $\text{RH} \leq 33\%$ . To achieve maximum  
22 physicochemical quality and stability the powder's moisture content must be  $\leq W_m$ , in  
23 this case, RH dropped to 9% (10°C) and 11.3% (20°C/40°C).

24 **Keywords:** Black currant; Yerba mate; sorption properties, anthocyanins, ascorbic acid,  
25 color.

26

## 1 **1. Introduction**

2 Black currant (*Ribes nigrum*; BC) is an excellent source of antioxidants [1] with a wide  
3 range of health benefits including antioxidant, antimicrobial, anti-carcinogenic and  
4 neuroprotective activities, vision improvement and induction of apoptosis [2, 3, 4]. BC  
5 has a particularly high content of phenolic compounds and anthocyanins and is the  
6 richest source of vitamin C among all berry fruit species [5].

7

8 Yerba mate (*Ilex paraguariensis*; YM), a native plant from South America, has a high  
9 content of polyphenols and flavonoids with antioxidant and hepatoprotective properties  
10 [6], as well as the capacity to improve the cardiovascular [7] and central nervous  
11 systems [8]. Moreover, its high caffeine content makes it a good ingredient for the  
12 preparation of natural energy drinks.

13 Consumption of yerba mate infusions alone or combined with juices is popular in  
14 Argentina, Brasil and Uruguay. Producing a beverage combining mate infusions with  
15 black currant juice can be a simple and effective mean for providing their health  
16 benefits to many consumers.

17 Drying is one of the most common methods used for preserving fruit juices; dried juices  
18 have several advantages compared to the fresh product, including, reduced  
19 transportation and distribution's costs, extended shelf life at room temperatures and  
20 overall convenience. They can be consumed as final products per se or used as  
21 ingredients or additives (colorants or flavoring agents) in other foods. In the case of  
22 yerba mate infusions, the dried product can also be used as an ingredient in energy  
23 drinks.

1 Black currant is a highly perishable, thermally sensitive seasonal product therefore; a  
2 drying technique like freeze-drying can be applied to minimize the loss of its nutritional  
3 and sensory properties.

4 Drying or freeze-drying fruit juices or other products with high sugar content presents  
5 technical difficulties, the low glass transition temperature of some components (low  
6 molecular weight sugars and organic acids) and their high hygroscopicity causes  
7 stickiness, collapse and flow problems during processing and storage [9]. Although the  
8 addition of carrier agents like maltodextrin before drying can help to reduce this  
9 problem, to obtain powders with optimum quality and stability during storage the  
10 moisture sorption properties of the powder must be considered [10].

11 Moisture sorption isotherms describe the relationship between water activity and  
12 equilibrium moisture content of a particular food at specified pressures and  
13 temperatures. They are important for calculating the moisture level corresponding to  
14 optimum food stability [11] and other thermodynamic functions like the isosteric heat of  
15 sorption, the differential entropy and the mechanisms that control the sorption process  
16 [10]. These properties are used in the design, modeling and optimization of the drying  
17 process as well as for predicting the powder's stability and quality during packaging and  
18 storage [12]. Variation of heat of sorption with moisture provides valuable information  
19 for energy requirements calculations and knowledge of the extent of the water/solid vs  
20 water/water interaction.

21 Color and color stability are key factors in consumers' acceptability of berry juices [1].

22 In addition, Tuorilla and Cardello[13] reported that providing information regarding the  
23 health benefits of certain food product may increase its acceptance and facilitate its  
24 marketing.

1 The attractive red color of the black currant juice is mainly due to the presence of  
2 anthocyanins; these compounds, as well as ascorbic acid and the polyphenols are the  
3 most important antioxidants in this drink and their stability is highly affected by  
4 temperature and the powder's humidity content [14]. Therefore, to obtain a high quality  
5 instant drink based on YM and BC juice a thorough analysis of the color, polyphenol,  
6 ascorbic acid and anthocyanins relationship with temperature and the moisture sorption  
7 capacity of the powders is needed.

8 The objectives of this study were (a) to determine and model the adsorption isotherms  
9 of freeze-dried black currant juice combined with yerba mate extracts at 3 temperatures  
10 (10 °C, 20 °C and 40°C); (b) to calculate the isosteric heat of sorption and the  
11 differential entropy, (c) to determine the mechanism that controls the moisture sorption  
12 process and (d) to analyze the relationship between moisture sorption capacity, color  
13 and total polyphenols, anthocyanins and ascorbic acid contents

14

## 15 **2. Materials and Methods**

### 16 2.1 Raw materials and beverage preparation

17 Figure 1 describes the process followed for the beverages preparation. To prepare the  
18 freeze-dried yerba mate infusion, 60g /L of commercial yerba mate leaves (*Ilex*  
19 *paraguariensis* St Hil; La Unión Suave, Est. Las Marias SAIC, Gob. Virasoro,  
20 Argentina) were extracted at 100°C for 15 min, decanted for 15 min at 25°C and  
21 filtered. A fraction of the filtrate (3°Brix; pH 5.5) was mixed with 15% w/v  
22 Maltodextrin Dextrose Equivalent 10 (MD; Productos de Maíz S.A., Buenos Aires,  
23 Argentina) and freeze dried at room temperature with a FIC L1-1-E300-CRT freeze  
24 dryer (Buenos Aires, Argentina) operated with a freezing plate at -35 °C and a vacuum  
25 below 100 µm.

1 The organic ripe black currant berries (*Ribes nigrum* cv. Silvergieter;) provided by  
2 Chacras Cuyen, (El Bolson, Chubut, Argentina) were harvested during January 2012  
3 and stored at - 20°C for 270 days. 24 h before the beverage preparation, the fruit was  
4 defrosted and processed in an industrial fruit pulper (Filter net pore diameter: 2 mm).  
5 The pulp (BC; 40°Brix; pH 3.21) was mixed with the yerba mate filtrate in a 3:1 ratio,  
6 MD (15% w/v) and passion fruit aroma (0.01% w/w) and freeze-dried in the same  
7 conditions as the YMI. After freeze-drying the powders were homogenized with sugar  
8 (4.95%) and a commercial diet sweetener (0.05%; Ciclamate 5700mg/100g; Sacarin  
9 2000 mg/Dextrose).

10

## 11 2.2 Water sorption isotherms

12 The adsorption isotherms of the YM and BC/YM freeze-dried powders were determined  
13 with the static gravimetric method [15, 16] at 10°C, 20°C and 40°C. The powder  
14 samples (in triplicate) were placed in hermetic containers filled with saturated solutions  
15 of different salts that provided environments with a constant relative humidity (RH)  
16 (*LiCl* (11.3%); *CH<sub>3</sub>COOK* (23.4%); *MgCl<sub>2</sub>* (33%); *K<sub>2</sub>CO<sub>3</sub>* (43.2%); *Mg(NO<sub>3</sub>)<sub>2</sub>* (54.4%)  
17 and *NaCl* (76%)) and were kept in a temperature-controlled chamber. The samples were  
18 weighed every 3 days until reaching equilibrium (difference between 2 consecutive  
19 weights < ± 0.003g), the equilibration period lasted 2 to 3 weeks. At this point, the  
20 equilibrated sample's water activity ( $a_w$ ) can be considered equal to the corresponding  
21 RH/100 [17].

22

23

24

25

### 2.3 Water activity and moisture content analysis

The water activity was measured at 25°C in an AquaLab serie 3 (Decagon Device, Pullman, Washington, USA), calibrated with the saline solutions used for the sorption experiments.

The moisture content was analyzed gravimetrically with the AOAC method [18]. The lyophilized samples were dried in a vacuum oven (Sanjor serie SL DB; Buenos Aires, Argentina) at  $105 \pm 1^\circ\text{C}$  until constant weight. Both assays were done in triplicate.

### 2.4 Mathematical modelling of the water sorption isotherm and statistical

comparisons

The relationship between the equilibrium moisture content ( $W_c$ ) and the  $a_w$  of the powder drinks was predicted using 2 (Caurie; Halsey and Oswin) and 3 parameters (Guggenheim-Anderson-de Boer (GAB)) models commonly used for food (Table 1; [10]). In these equations,  $W_c$ ,  $W_m$  and  $X_s$  represent the equilibrium monolayer and security water contents respectively while  $C$ ,  $K$ ,  $A$  and  $B$  are all dimensionless constants present in the different models [10].

The 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. The selection of the most appropriate model was based on its goodness of fit, evaluated with the mean relative deviation modulus (%E) defined by Eqn. (5) [17].

$$\%E = \frac{100}{N} \sum_{i=1}^n \frac{|W_c - W_{pc}|}{W_c} \quad (5)$$

$W_c$  and  $W_{pc}$  represent the experimental and predicted equilibrium moisture levels ( $\text{kg H}_2\text{O (kg d.m)}^{-1}$  (dry matter)) respectively and “N” the number of observations.



1 Lomauro et al. [17] reported that for practical purposes %E<10 can be considered as  
 2 indicative of a good fit.

3 In the case of the GAB equation, Lewicki [19] concluded that for a good description of  
 4 sigmoidal type isotherms and to assure that the difference between the true and  
 5 predicted Wm results is less than  $\pm 15\%$ , the  $K_{GAB}$  and  $C_{GAB}$  values must comply with:  
 6  $0.24 < K_{GAB} \leq 1$  and  $5.67 \leq C_{GAB} \leq \infty$ .

7

## 8 2.5 Thermodynamic properties

9 The net isosteric heat or differential enthalpy of sorption ( $q_{stn}$ ;  $\text{kJ mol}^{-1}$ ), the total heat of  
 10 sorption ( $Q_{st}$ ,  $\text{kJ mol}^{-1}$ ) and the differential entropy ( $\Delta S_d$ ;  $\text{kJ mol}^{-1} \text{K}^{-1}$ ) were calculated  
 11 from the equilibrium data using the following equations[20].

$$12 \quad \ln a_w |_{W_c} = \frac{\Delta S_d}{R} - \frac{q_{stn}}{RT} \quad (6)$$

$$13 \quad Q_{st} = q_{stn} + \Delta H_{vap} \quad (7)$$

14  $a_w$  represents the predicted water activity value for a specific equilibrium moisture  
 15 content ( $W_c$ );  $\Delta H_{vap}$  is the free water's latent heat of vaporization calculated at the  
 16 average temperature between 283 and 313K (298K;  $44.05 \text{ kJ mol}^{-1}$ ), R the universal gas  
 17 constant ( $0.008314 \text{ kJ mol}^{-1} \text{K}^{-1}$ ) and T the absolute temperature (K).

18  $q_{stn}$  and  $\Delta S_d$  were calculated from the slope ( $-q_{stn}/R$ ) and the intercept ( $\Delta S_d/R$ ) of the  
 19  $\ln(a_w)$  vs  $1/T$  plot (Eq 6) at each  $W_c$ .

20 The relationship between  $q_{stn}$  or  $Q_{st}$  and the equilibrium moisture content was  
 21 determined with the empirical equation proposed by Tsami et al. [21] (Eqn. (8)).

$$22 \quad q_{stn} = q_0 e^{\left(\frac{-W_c}{W_0}\right)} \quad (8)$$

$$23 \quad Q_{st} = q_0 e^{\left(\frac{-W_c}{W_0}\right)} + \Delta H_{vap} \quad (9)$$

1  $q_0$  represents the net isosteric heat ( $\text{kJ mol}^{-1}$ ) of the first water molecule and  $W_0$  the  
 2 characteristic moisture content of the food material ( $\text{kg water (kg d.m)}^{-1}$  (dry matter)).  
 3 Eqns. (6), (8) and (9) parameters were determined by regression analysis with the  
 4 OriginPro v 8.0 and the Systat 12 software.

5

## 6 2.6 Enthalpy-entropy compensation theory

7 The enthalpy-entropy compensation theory proposes a linear relationship between  $q_{\text{stn}}$   
 8 and  $\Delta S_d$  according to Eq. (10)[22].

$$9 \quad \mathbf{q_{stn}} = \Delta S_d \mathbf{T_\beta} + \Delta G_\beta \quad (10)$$

10  $T_\beta$  is the isokinetic temperature (K) and represents the temperature at which all reactions  
 11 proceed at the same rate and  $\Delta G_\beta$  is the free energy ( $\text{kJ mol}^{-1}$ ) at  $T_\beta$ . Both parameters  
 12 were estimated by fitting Eqn. 10 to the  $q_{\text{stn}}$  and  $\Delta S_d$  results calculated previously.

13 Krug et al. [23] concluded that a linear chemical compensation pattern also requires that  
 14  $T_\beta$  must be different from the harmonic mean temperature ( $T_{\text{hm}}$ ) defined as:

$$15 \quad T_{\text{hm}} = \frac{\mathbf{n}}{\sum_{i=1}^{\mathbf{n}} (1/T)} \quad (11)$$

16  $n$  = total isotherms number

17 An approximate  $(1-\alpha)100\%$  confidence interval for  $T_\beta$  was calculated using equations  
 18 (12), (13) and (14) [24]

$$19 \quad \mathbf{T_\beta} = \hat{\mathbf{T}_\beta} \pm t_{m-2, \frac{\alpha}{2}} \sqrt{\text{Var}(\mathbf{T}_\beta)} \quad (12)$$

$$20 \quad \hat{\mathbf{T}_\beta} = \frac{\sum[(\mathbf{q_{stn}})_T - (\overline{\mathbf{q_{stn}}})_T][(\Delta S_d)_T - (\overline{\Delta S_d})_T]}{\sum[(\Delta S_d)_T - (\overline{\Delta S_d})_T]^2} \quad (13)$$

$$21 \quad \text{Var}(\mathbf{T}_\beta) = \frac{\sum[(\mathbf{q_{stn}})_T - \Delta G_\beta - \mathbf{T}_\beta(\Delta S_d)_T]^2}{(m-2)\sum[(\Delta S)_T - (\overline{\Delta S_d})_T]^2} \quad (14)$$

1 m is the number of  $q_{\text{stn}}/\Delta S$  data pairs,  $t_m$  is the t(Student) at (m-2) degrees of freedom,  
2  $\overline{(q_{\text{stn}})}$  and  $\overline{\Delta S_d}$  are the mean values of  $q_{\text{stn}}$  ( $\text{kJ mol}^{-1}$ ) and the differential entropy  
3 ( $\text{kJmol}^{-1} \text{K}^{-1}$ ).

#### 4 2.7 Total polyphenols and monomeric anthocyanins contents

5 The total phenolic content of the extracts (TP; mg GAE (gallic acid equivalents) (g d.m.  
6 (dry matter))<sup>-1</sup> was assessed with the Folin-Ciocalteu method reported by Schlesier et  
7 al. [25], using a UVmini-1240 UV-Vis Spectrophotometer (Shimadzu Scientific  
8 Instruments, Japan).

9 The monomeric anthocyanin (MAC) content of the BC/YM powder was determined  
10 with the pH differential method [26]. The monomeric anthocyanins were extracted with  
11 ethanol: HCl 0.1N (85:15). After diluting the extracts with buffer to achieve an  
12 appropriate concentration range, the absorbancies were read at 520 ( $\lambda_{\text{max}}$ ) and 700 nm  
13 with a spectrophotometer U-1900 (HITACHI, Japan).

$$14 \quad A = (A_{\lambda_{\text{vis-max}}} - A_{\lambda_{700}})_{\text{pH } 1.0} - (A_{\lambda_{\text{vis-max}}} - A_{\lambda_{700}})_{\text{pH } 4.5} \quad (15)$$

$$15 \quad \text{MAC (mg L}^{-1}\text{)} = \frac{A * MW * DF * 1000}{\epsilon * 1} \quad (16)$$

16 MAC was expressed as mg CyGE (cyanidin-3-glucoside equivalents) (g d.m.)<sup>-1</sup>;  
17 molecular weight (MW) = 449.2  $\text{g mol}^{-1}$ ; extinction coefficient ( $\epsilon$ ) = 26900  $\text{L cm}^{-1} \text{mol}^{-1}$ ;  
18 <sup>1</sup>; DF = dilution factor [26].

19

#### 20 2.8 Color analysis

21 Color was measured on triplicate samples with a Minolta CR-400 Chroma Meter  
22 (Minolta, Osaka, Japan), each value was the average of 9 measurements on duplicate  
23 samples.

1 Color was expressed by CIE L\* (lightness), a\* (redness), b\* (yellowness), saturation  
2 index (SI) and hue angle (HA).[27] SI, a measure of color intensity, was computed as:

$$3 \quad SI = \sqrt{a^{*2} + b^{*2}} \quad (17)$$

4 HA represents the psychometric hue and was calculated as:

$$5 \quad HA = \tan^{-1} \left( \frac{b^*}{a^*} \right) \quad (18)$$

6 An increase in HA towards more positive values or a reduction to more negative  
7 indicated an enhancement in yellowness or blueness respectively.

8 The total color difference ( $\Delta E^*$ ) with respect to the samples color coordinates before  
9 equilibration ( $L^*_0, a^*_0; b^*_0$ ) was determined with equation (19)[27]:

10

$$11 \quad \Delta E^* = \sqrt{\left( (L^*_0 - L^*)^2 + (a^*_0 - a^*)^2 + (b^*_0 - b^*)^2 \right)} \quad (19)$$

12

### 13 2.9 Ascorbic acid analysis

14 To analyze moisture sorption's influence on the ascorbic acid (AA) content, the  
15 equilibrated samples (0.5 g) were extracted with an aqueous solution of metaphosphoric  
16 acid ( $HPO_3$ ; 50 g L<sup>-1</sup>; Carlo Erba S.A, BCN, España) followed by centrifugation at 2000  
17 rpm (Rolco CM 2036, Buenos Aires, Argentina).

18 AA concentration was determined by high performance liquid chromatography  
19 (Waters, model R-414, Milford, MA, USA). The method consisted of an isocratic  
20 elution procedure with UV-Visible detection at 245 nm using AA (Food grade,  
21 Parafarm) as external standard. Before injection, the extracts were filtered with a pre-  
22 filter and a 0.45  $\mu$ m millipore membrane.

23 Separations were carried out on a 5 mm RP C18 column of 150 mm - 4.6 mm  
24 (Symmetry, Waters, Dublin, Ireland) at 25°C. The mobile phase was a mixture of 5 g L<sup>-1</sup>

1 <sup>1</sup> HPO<sub>3</sub> metaphosphoric acid–acetonitrile (93:7) [28] with a flow rate = 1 mL min<sup>-1</sup>. To  
2 prevent the loss of AA, standard solutions and extracted samples were protected from  
3 light.

4 Quantitation was performed by comparing the chromatographic peak area with that of  
5 the external standard. The calibration curve was plotted in the concentration range of  
6 0.5–200 mg L<sup>-1</sup> and based on a 10-point calibration.

7

## 8 2.10 Statistical Analysis.

9 The effect of temperature and water activity on the color, TP, ascorbic acid and  
10 anthocyanins content was analyzed using the SYSTAT 12 and Infostat (v. 2013)  
11 software. Significant differences among means were determined by analysis of variance  
12 followed by pairwise comparisons with the Tuckey test. P values < 0.05 were  
13 considered statistically significant.

14

## 15 3. Results and Discussion

### 16 3.1 Moisture sorption isotherms

17 The initial a<sub>w</sub> and moisture content values of the freeze-dried beverages were 0.089 and  
18 0.0354 kg H<sub>2</sub>O (kg d.m)<sup>-1</sup> for the BC/YM and 0.065 and 0.0216 kg H<sub>2</sub>O (kg d.m)<sup>-1</sup> for  
19 the YM. Figs 2 (a) and (b) show the a<sub>w</sub> influence on the BC/YM and YM powder  
20 drinks' equilibrium moisture content (W<sub>c</sub>; kg H<sub>2</sub>O (kg d.m)<sup>-1</sup>) at 10°C, 20°C and 40°C.

21 A comparison between the YM and BC/YM isotherms indicated that the incorporation  
22 of BC and commercial sucrose significantly increased (P < 0.05) the powder's  
23 hygroscopicity, the effect was particularly strong for a<sub>w</sub> between 0.54 and 0.76 where  
24 the W<sub>c</sub><sup>BC/YM</sup> levels were 35-40% higher. This behavior was expected as sugars are well

1 known humectants [29]; similar results had been reported in high sugar content products  
2 like pineapple pulp [12], blueberry [10] and orange juice [30] powders.

3 In agreement with Al-Muhtaseb et al. [31] temperature increase reduced the equilibrium  
4 moisture content in both samples; Ferrari et al. [32] and Mosquera et al. [11] reported  
5 similar results working with spray dried blackberry or freeze-dried strawberry powders  
6 respectively. Pahlevanzadeh and Yazdani [33] suggested that the temperature rise  
7 enhanced the kinetic energy associated with the water molecules resulting in a reduction  
8 of the attractive forces H<sub>2</sub>O/sorbent and consequently in lower hygroscopicity levels.

9 The parameters obtained from the regression analysis of the different models (GAB;  
10 Caurie; Halsey and Oswin), the determination coefficient (R<sup>2</sup>) and the mean relative  
11 deviation modulus (%E) for BC/YM and YM are presented in Table 3. The GAB  
12 equation was the only one that satisfied [17] Lomauro et al. (1985) conclusions regarding  
13 goodness of fit criteria (E% < 10 and highest R<sup>2</sup>) for the complete a<sub>w</sub> and temperature  
14 ranges. Additionally, the K<sub>GAB</sub> and C<sub>GAB</sub> values of the YM and BC/YM also fulfilled  
15 Lewicki's (1997) [19] recommendations (Sec. 2.4), therefore this model was considered  
16 the most appropriate for all the thermodynamic properties analysis.

17 The experimental and predicted results (GAB equation) of the adsorption isotherms at  
18 the 3 working temperatures for the a) YM and b) BC/YM powders are presented in  
19 Figs. 2(a) and (b).

20 Monolayer moisture contents are of particular importance as they represent the moisture  
21 level corresponding to optimum food stability [11]; Labuza [34] concluded that W<sub>m</sub>  
22 levels higher than 0.1 kg H<sub>2</sub>O (kg d.m)<sup>-1</sup> may compromise food stability. Results  
23 showed that for all temperatures, the predicted W<sub>m</sub> values of the YM and BC/YM  
24 samples were equal or less than that limit (Table 3) hence, the powders' stability could  
25 be considered good.

1 Temperature increase reduced the monolayer moisture concentration of both beverages  
2 (Table 3), Vega-Gálvez et al.[10] and Perez-Alonso et al. [35] working with blueberries  
3 or pure MD, respectively, reported a similar effect, conversely, studies done with  
4 vacuum-dried lemon juice [36] or freeze-dried pineapple pulp[37] using 18% MD as a  
5 carrier did not show a clear trend.

6 At 10°C or 20°C, the YM's  $W_m$  values were higher than those from the BC/YM  
7 samples, however, this difference was not significant ( $P>0.05$ ) in the 40°C isotherms.  
8 The BC/YM monolayer moisture content results at 20°C and 40°C were lower than  
9 those reported by Perez-Alonso, et al.[35], for pure MD<sub>10</sub> (0.07-0.073 kg H<sub>2</sub>O (kg d.m)<sup>-1</sup>)  
10 and by Gabas et al.[12], and Carvalho et al.[38], for vacuum dried persimmon or  
11 pineapple with 18% d.m MD<sub>10</sub> (0.06-0.069 kg H<sub>2</sub>O (kg d.m)<sup>-1</sup>) at the same temperatures

### 12 3.2 Thermodynamic properties

13 The net differential isosteric heat of sorption ( $q_{stn}$ ), the differential heat of sorption and  
14 the differential entropy were estimated with equations (6), (7) and (8) and the  
15 equilibrium moisture concentrations predicted from the GAB model (Eqn. 1). In  
16 accordance with previous publications [12, 10], we detected a strong reduction in  $Q_{st}$   
17 with increasing  $W_c$  levels in both samples (Fig 3) that were satisfactorily fitted with  
18 Eqn.(9) ( $R^2= 0.998$ ; [21]). For all the  $W_c$  range tested,  $Q_{st}^{BC/YM}$  was more negative than  
19  $Q_{st}^{YM}$  indicating that water binding in the BC/YM powders was stronger than in the  
20 YM. This is probably due to the greater concentration of sugars rich in free hydroxyl  
21 groups (capable of forming strong hydrogen bonds) in BC/YM than in the YM powders.  
22 Increasing  $W_c$  from 0.059 to 0.1 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup> reduced the isosteric heat of both  
23 samples 4 to 5 times. This was expected since the range corresponded to the monolayers  
24 moisture contents of the powders (Table 3) and in these conditions the binding energy

1 between sorbate and sorbent is very high [20]. The predicted  $Q_{st}$  results at the estimated  
2  $W_m$  values were:

3 • BC/YM: 93.82 (0.041 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>), 74.23, (0.056 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>)  
4 and 67.95 kJ mol<sup>-1</sup> (0.063 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>)

5 • YM: 103.51 (0.039 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>), 66.12 (0.064 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>) and  
6 47.52 kJ mol<sup>-1</sup> (0.104 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>)

7 The values between parentheses corresponded to the BC/YM and YM monolayer  
8 moisture levels (Table 3).

9 A further increase in moisture content (0.1 to 0.15 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>) diminished the  
10  $Q_{st}$  of both samples,, although it was still higher than  $\Delta H_{vap}$ , indicating that the energy  
11 sorbate/sorbent is greater than the energy between water molecules therefore new layers  
12 of water molecules are formed in the powder's surface (multilayer sorption).

13 Results from Fig. 3 showed that at  $W_c$  contents between 0.18-0.3 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>,  
14  $Q_{st}^{BC/YM}$  reached an asymptotic level similar to  $\Delta H_{vap}$  therefore it could be considered as  
15 the limit of bound water[39, 21] for this sample. In the case of the YM powders,  $Q_{st}$  was  
16 similar to  $\Delta H_{vap}$  at 0.15 kg H<sub>2</sub>O (kg d.m.)<sup>-1</sup>.

17 Table 4 presented the net isosteric heat of the first water molecule ( $q_0$ ; kJ mol<sup>-1</sup>) and the  
18 characteristic moisture content of the food material ( $W_0$ ; kg water (kg d.m.)<sup>-1</sup>).

19 The differential entropy ( $\Delta S_d$ ; kJ mol<sup>-1</sup> K<sup>-1</sup>) was calculated from Eqn. (6) using the  $W_c$   
20 values predicted by the GAB equation (see Section 2.4). The relationship between  $\Delta S_d$   
21 and  $W_c$  was satisfactorily modeled ( $R^2 = 0.996$ ) with Eqn. (15) using the SigmaPlot  
22 software (Systat Inc; Fig.4.)

23 
$$\Delta S_d = a e^{-bW_c} \quad (15)$$

24 The YM and BC/YM “a” and “b” parameters and their respective coefficients of  
25 determination ( $R^2$ ) are presented in Table 4.



1 To test the applicability of the isokinetic theory to the moisture sorption process of the  
2 YM and BC/YM powders, Eqn. (10) (See Section 2.6) was fitted to their respective  $q_{\text{stn}}$   
3 and  $\Delta S_d$  values (Fig. 5).  
4 Table 4 shows the isokinetic temperature ( $T_\beta$ ), the free energy ( $\Delta G_\beta$ ) and the  
5 determination coefficient ( $R^2$ ) values calculated by regression analysis for both samples.  
6 Validity of the theory requires that  $T_\beta$  must be significantly different from the harmonic  
7 mean temperature ( $T_{\text{hm}}$ ) calculated with Eqn. 11 [23]. The isokinetic temperatures and  
8 their 95% confidence intervals of the YM and BC/YM powders were  $329.99 \pm 0.70$  K  
9 and  $339.99 \pm 0.02$  K significantly different ( $P < 0.05$ ) from the harmonic mean  
10 temperature (301.52 K) used in this study. This fact combined with the high degrees of  
11 linearity ( $R^2 > 0.999$ ) obtained confirms the existence of  $q_{\text{stn}}/\Delta S_d$  compensation; hence  
12 the isokinetic theory is a valid mean for describing the water sorption mechanism in  
13 both samples within the experimental conditions used.  
14 The YM and BC/YM samples presented only one line of compensation each (Fig 5),  
15 indicating that there is no change of mechanism in the whole moisture and temperature  
16 ranges studied. According to Leffler [40] if  $T_\beta > T_{\text{hm}}$ , the process is enthalpy driven  
17 whereas in the opposite situation ( $T_\beta < T_{\text{hm}}$ ) it is entropy controlled. Since our results  
18 comply with the former condition the process can be considered to be enthalpy driven  
19 i.e. the moisture sorption mechanism is controlled by the energy interactions related to  
20 the chemical composition of the YM and BC/YM powders. Beristain et al. [22] reached  
21 similar conclusions regarding the sorption process of dried figs, currants, apricots,  
22 plums and raisins.  
23

1           3.3 Temperature and relative humidity effects on ascorbic acid, total  
2 polyphenols and monomeric anthocyanins concentrations and the color of the BC/YM  
3 powders

4 The water activity, TP, MAC and color of the BC/YM powders before equilibration  
5 were:

$$6 \quad a_w = 0.089 \quad TP = 33.56 \text{ mg GAE/g d.m} \quad MAC = 354.02 \text{ mg CyGE g d.m}^{-1}$$

$$7 \quad L^* = 52.46; a^* = 21.57; b^* = -2.83; SI = 21.76; HA = -0.13^\circ$$

8 Equilibration diminished TP by 20%-33%. Statistical analysis of the  
9 temperature/relative humidity influence on total polyphenol (TP) contents (Table 5)  
10 demonstrated that at each temperature, TP was not affected by RH ( $P > 0.05$ ). In  
11 addition, no significant effect ( $P > 0.05$ ) was detected by increasing the temperature at a  
12 given RH value.

13 Fig 6 showed the MAC relationship with temperature and relative humidity. Results  
14 showed that although initially MAC (40°C) values were the highest ( $P < 0.05$ ),  
15 increasing RH beyond 33% had an extremely negative impact on MAC(40°C)'s  
16 stability, at RH = 54% and 76%, MAC(40°C) dropped to 54 % and 8.6% of their  
17 original values respectively. In contrast, for  $11\% \leq RH < 54\%$ , no losses ( $P > 0.05$ )  
18 were detected in the samples kept at 10°C / 20°C; nevertheless, the effects of enhancing  
19 RH to 76 % were as detrimental as those observed at 40°C

20 Figure 7 shows the ascorbic acid / RH relationship of the BC/YM powders at 10°C,  
21 20°C and 40°C. In comparison with the fresh pulp, processing and equilibration at the  
22 selected temperatures resulted in 80-83% losses in AA content.

23 Temperature and relative humidity had a significant effect ( $P > 0.05$ ) on the ascorbic  
24 acid concentration (Fig. 7). In accordance with Sablani et al. [41], AA retention  
25 diminished with increasing temperatures; for  $23\% \leq RH \leq 76\%$ , the ranking was:

1 
$$AA(10^{\circ}C) = AA(20^{\circ}C) \gg AA(40^{\circ}C) (P < 0.05)$$

2 At 10°C and 20°C and RH between 11- 54%, AA remained stable; on the other hand,  
3 at 40°C, increasing RH to 23% caused an AA loss of 37%, additional RH increments up  
4 to 54% did not affect AA(40°C) At all temperatures, AA concentration in samples  
5 equilibrated to 76%RH, fell to a minimum level of 99.58 mg AA (100 g d.m.)<sup>-1</sup>.

6 Figure 8A, B and C show the L\*, SI and HA relationship with temperature and relative  
7 humidity. For RH ranging from 11% to 43%, the lightness (Fig. 8A) values at 10°C and  
8 20°C were constant (P> 0.05), further increments in RH to 54% enhanced L\* by 8%  
9 (P< 0.05). In the case of powders kept at 40°C, no effect (P > 0.05) was detected for RH  
10 between 11% - 33%, nevertheless at 43% RH the lightness levels were 7.7 % greater.  
11 Equilibrating with relative humidity's between 11% - 54% enhanced L\* 5.8% to 14.2%,  
12 in contrast, using 76% RH was extremely damaging; the lightness dropped 25% - 35%  
13 compared with the samples before equilibration.

14 Within each temperature, RH variations between 11% - 54% did not influence (P>  
15 0.05) the saturation index (SI) levels (Fig 8B); additionally, the temperature factor was  
16 significant only at 40°C (P< 0.05), SI values at 10°C and 20°C were 7 % higher than  
17 those at 40°C indicating a drop in color vividness in the latter temperature. At 76%  
18 relative humidity, the saturation indexes at all temperatures fell to 10% of their levels  
19 before equilibration.

20 Humidity increments from 11% to 54% did not modify HA at 10°C or 20°C nevertheless,  
21 when the temperature was raised to 40°C, the upper limit of the RH range  
22 corresponding to constant HA fell to 33% (Fig. 8C). At 76%RH, HA(10°C) diminished  
23 (P < 0.05) from -5.65° to -29.32° indicating a shift towards a greater blue input.  
24 HA(20°C) did not change (P > 0.05) and HA(40°C) increased (P < 0.05) from 5.79° to  
25 40.26° which means a higher contribution of yellow. These differences could be

1 explained considering that although for all temperatures  $b^*$  (76%RH) values indicated  
2 an increment in yellowness ( $P < 0.05$ ; data not shown), in the resulting HAs this effect  
3 was overcompensated ( $10^\circ\text{C}$ ) or suppressed ( $20^\circ\text{C}$ ) by their corresponding  $a^*$  values.  
4 Comparison of Figs. 8A, B, C and Fig. 6 showed that within 285.76 - 299.94 mg CyGE  
5 ( $\text{g d.m.})^{-1}$  at  $10^\circ\text{C}/20^\circ\text{C}$  and 347.72 - 335.25 mg CyGE ( $\text{g d.m.})^{-1}$  at  $40^\circ\text{C}$ ,  $L^*$ ,  $SI$  and  
6 HA were independent of RH. Lowering MAC levels down to 30 - 60 mg CyGE ( $\text{g}$   
7  $\text{d.m.})^{-1}$  resulted in undesirable alterations in the 3 color parameters.  
8 Relative humidity's influence was also strong in other powder's properties like caking  
9 and agglomeration. Visual observation of the BC/YM samples showed that enhancing  
10 RH values to 33% did not produce any noticeable stickiness, collapse or caking  
11 formation at any of the temperatures used in the current study. However at 43.2%RH,  
12 slight degrees of stickiness and caking were detected that increased with temperature, in  
13 addition, at 76%RH water sorption was so high that the sample behaved like a leather.  
14 In conclusion, to obtain the best results regarding the color, MAC and ascorbic acid  
15 contents at the selected temperatures, the BC/YM powders must be kept at relative  
16 humidities equal or less than 33%. However several reports [11, 34] recommended the  
17 use of  $W_c = W_m$  as a condition for obtaining maximum food stability; in this case, the  
18 RH values calculated with the GAB model (Eqn 1) were:  $\text{RH}(10^\circ\text{C}) = 9\%$  and  
19  $\text{RH}(20^\circ\text{C}/40^\circ\text{C}) = 11.31\%$ .

20

#### 21 **4. Conclusions**

22 Comparison of the goodness of fit of the Caurie; Halsey, Oswin and GAB models  
23 indicated that that the latter one was the best for predicting the equilibrium moisture  
24 content of the YM and BC/YM samples at all the temperatures and water activities  
25 tested. The  $K_{\text{GAB}}$  and  $C_{\text{GAB}}$  estimated by regression analysis allowed an appropriate

1 description of the YM and BC/YM isotherms and assured differences between the true  
2 and predicted  $W_m$  results lower than  $\pm 15\%$ .

3 Due to their greater content of sugars, the BC/YM freeze-dried powders were more  
4 hygroscopic than the YM, the effect was particularly noticeable at  $a_w$  ranging 0.54 -  
5 0.76, where the  $W_c^{YMBC}$  levels were 35 - 40% higher. This difference in the formulation  
6 also affected the differential isosteric heat of sorption;  $Q_{st}^{BC/YM}$  was more negative than  
7  $Q_{st}^{YM}$  indicating that water binding in the BC/YM powders was stronger than in the  
8 YM.

9 The  $Q_{st}$  and  $\Delta S_d$  dependence with moisture levels were modeled with empirical  
10 exponential equations.  $Q_{st}$  reached an asymptotic level similar to  $\Delta H_{vap}$  at 0.15 kg  $H_2O$   
11  $(kg\ d.m)^{-1}$  and 0.18 - 0.3 kg  $H_2O\ (kg\ d.m)^{-1}$  for the YM and BC/YM samples  
12 respectively.

13 Within the experimental conditions used, the isokinetic theory is a suitable mean for  
14 describing the water sorption mechanism in both samples, results suggested that this  
15 process occurs by enthalpy controlled mechanisms.

16 Temperature and water activity had a strong impact in the powders color as well as in  
17 their ascorbic acid and monomeric anthocyanins concentrations. To obtain a product  
18 with optimum properties at the selected temperatures samples must be exposed to  $RH \leq$   
19 33%. However, maximum quality and stability of food powders requires that  $W_c \leq W_m$   
20 which corresponds to relative humidity values of 9% (10°C) and 11.31% (20°C /  
21 40°C).

22

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4  
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1 **Table 1.** Sorption models for predicting moisture sorption isotherms.

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| Model  | Equation                                                                               | Parameters                                                                                                                                |
|--------|----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|
| GAB    | $W_c = \frac{W_m K C a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$                 | $W_m$ , monolayer moisture content<br>C: constant related to monolayer sorption heat.<br>K: constant related to multilayer sorption heat. |
| OSWIN  | $W_c = A \left[ \frac{a_w}{(1 - a_w)} \right]^B \quad (2)$                             | A / B: constants                                                                                                                          |
| HALSEY | $W_c = \left[ \frac{A}{\ln\left(\frac{1}{a_w}\right)} \right]^{\frac{1}{B}} \quad (3)$ |                                                                                                                                           |
| CAURIE | $W_c = \exp \left[ a_w * \ln(v) - \frac{1}{4.5 * X_s} \right] \quad (4)$               | V: constant<br>$X_s$ : Security water content                                                                                             |

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**Table 2.** Equilibrium moisture content (kg H<sub>2</sub>O (kg d.m)<sup>-1</sup>) of freeze-dried YM (yerba mate) and BC/YM (yerba mate/black currant) powders at 10, 20 y 40°C.

| Salt/<br>a <sub>w</sub> (RH/100) <sup>a</sup>             | 10°C          |               | 20°C          |               | 40°C         |              |
|-----------------------------------------------------------|---------------|---------------|---------------|---------------|--------------|--------------|
|                                                           | BC/YM*        | YM*           | BC/YM*        | YM*           | BC/YM*       | YM*          |
| LiCl<br>(0.113) <sup>a</sup>                              | 0.058±0.0004  | 0.029±0.0040  | 0.055 ±0.0006 | 0.043 ±0.0030 | 0.044±0.0005 | 0.020±0.0050 |
| KCH <sub>3</sub> COO<br>(0.234) <sup>a</sup>              | 0.071±0.0005  | 0.062 ±0.0040 | 0.070 ±0.0010 | 0.059 ±0.0060 | 0.050±0.0020 | 0.043±0.0030 |
| MgCl <sub>2</sub><br>(0.33) <sup>a</sup>                  | 0.089±0.0007  | 0.074 ±0.001  | 0.079 ±0.0008 | 0.068± 0.0070 | 0.059±0.0001 | 0.049±0.0060 |
| K <sub>2</sub> CO <sub>3</sub><br>(0.432) <sup>a</sup>    | 0.102±0.0005  | 0.089 ±0.001  | 0.097 ±0.0087 | 0.09±0.003    | 0.071±0.0016 | 0.006±0.0010 |
| Mg(NO <sub>3</sub> ) <sub>2</sub><br>(0.544) <sup>a</sup> | 0.119±0.0029  | 0.104±0.0010  | 0.116 ±0.0003 | 0.100±0.0060  | 0.088±0.0008 | 0.007±0.0010 |
| NaCl<br>(0.760) <sup>a</sup>                              | 0.222 ±0.0048 | 0.157±0.001   | 0.20 ±0.0120  | 0.154±0.001   | 0.195±0.0090 | 0.144±0.0010 |

<sup>a</sup>RH relative humidity; Reported values correspond to the mean ± standard deviation of at least 3 replicates.

**Table 3.** Regression parameters and statistical tests ( $R^2$ ; %E) of the equations used for modelling the BC/YM and YM sorption isotherms at 10°C, 20 °C and 40°C.

| Equations     | Parameters           | 10°C   |        | 20°C  |        | 40 °C  |        |
|---------------|----------------------|--------|--------|-------|--------|--------|--------|
|               |                      | BC/YM  | YM     | BC/YM | YM     | BC/YM  | YM     |
| <b>GAB</b>    | <b>W<sub>m</sub></b> | 0.063  | 0.104  | 0.056 | 0.064  | 0.041  | 0.039  |
|               | <b>K</b>             | 0.946  | 0.560  | 0.95  | 0.822  | 1.04   | 0.971  |
|               | <b>C</b>             | 57.40  | 5.80   | 50.05 | 10.09  | 20     | 10.53  |
|               | <b>R<sup>2</sup></b> | 0.9919 | 0.9990 | 0.996 | 0.997  | 0.994  | 0.9957 |
|               | <b>E%</b>            | 2.64   | 3.96   | 4.42  | 5.69   | 4.22   | 9.12   |
| <b>Oswin</b>  | <b>A</b>             | 0.1222 | 0.0991 | 0.112 | 0.0961 | 0.089  | 0.0715 |
|               | <b>B</b>             | 0.488  | 0.425  | 0.477 | 0.457  | 0.637  | 0.587  |
|               | <b>R<sup>2</sup></b> | 0.969  | 0.97   | 0.956 | 0.982  | 0.927  | 0.976  |
|               | <b>E%</b>            | 8.59   | 10.79  | 9.47  | 6.04   | 17.33  | 10.89  |
|               | <b>A</b>             | 0.029  | 0.013  | 0.024 | 0.016  | 0.04   | 0.024  |
| <b>Halsey</b> | <b>B</b>             | 1.48   | 1.70   | 1.50  | 1.578  | 1.16   | 1.246  |
|               | <b>R<sup>2</sup></b> | 0.991  | 0.930  | 0.977 | 0.970  | 0.963  | 0.979  |
|               | <b>E%</b>            | 4.03   | 16.65  | 5.26  | 9.85   | 11.78  | 13.11  |
| <b>Caurie</b> | <b>V</b>             | 9.093  | 6.899  | 8.674 | 7.943  | 17.163 | 14.058 |
|               | <b>Xs</b>            | 0.069  | 0.061  | 0.068 | 0.059  | 0.058  | 0.050  |
|               | <b>R<sup>2</sup></b> | 0.977  | 0.948  | 0.961 | 0.972  | 0.937  | 0.969  |
|               | <b>E%</b>            | 6.99   | 14.82  | 7.89  | 9.04   | 15.61  | 13.53  |

**Table 4.** Regression parameters of the equations (8), (10) and (15) for freeze-dried YM and BC/YM.

| <b>Parameters</b>                                   | <b>YM</b> | <b>BC/YM</b> |
|-----------------------------------------------------|-----------|--------------|
| $q_0$ (kJ mol <sup>-1</sup> )                       | 326.97    | 195.14       |
| $W_0$ (kg H <sub>2</sub> O (kg d.m) <sup>-1</sup> ) | 0.023     | 0.03         |
| $R^2$                                               | 0.973     | 0,991        |
| a                                                   | 1.31      | 0.68         |
| b                                                   | 48.80     | 36.47        |
| $R^2$                                               | 0.998     | 0.996        |
| $T_\beta$ (K)                                       | 329.99    | 339.16       |
| $\Delta G_\beta$ (kJ mol <sup>-1</sup> )            | 0.84      | 0.83         |
| $R^2$                                               | 0.999     | 0.999        |

**Table 5.** Effect of temperature and relative humidity (RH) on the total polyphenol content of the **BC/YM**powders.

| <b>RH (%)</b> | <b>10°C</b>                | <b>20°C</b>                | <b>40°C</b>                |
|---------------|----------------------------|----------------------------|----------------------------|
| 11.3          | 21.78 ± 0.91 <sup>ab</sup> | 22.71 ± 0.20 <sup>ab</sup> | 21.85 ± 3.23 <sup>ab</sup> |
| 23.4          | 22.78 ± 1.52 <sup>ab</sup> | 23.50 ± 0.10 <sup>ab</sup> | 26.85 ± 1.82 <sup>ab</sup> |
| 33.0          | 24.14 ± 5.86 <sup>ab</sup> | 26.14 ± 3.43 <sup>ab</sup> | 28.21 ± 4.95 <sup>b</sup>  |
| 43.2          | 26.57 ± 4.04 <sup>ab</sup> | 25.07± 2.93 <sup>ab</sup>  | 31.00 ± 0.20 <sup>b</sup>  |
| 54.4          | 20.78 ± 0.30 <sup>ab</sup> | 25.43± 4.24 <sup>ab</sup>  | 29.07 ± 0.71 <sup>b</sup>  |
| 76.0          | 17.14 ± 0.20 <sup>ab</sup> | 23.21± 0.51 <sup>ab</sup>  | 24.43 ± 0.20 <sup>ab</sup> |

Results are expressed as mean ± standard deviation of at least 2 replicates Means with different superscripts are significantly different (P < 0.05)

## Figure captions

**Fig. 1.** Process followed for preparing the freeze-dried YM and BC/YM drinks.

**Fig. 2.** Temperature influence on the sorption isotherms of freeze-dried BC/YM (a) and YM (b) at 10, 20 and 40°C. The lines represent the equilibrium moisture contents predicted by the GAB model.

**Fig. 3.** Changes of the BC/YM and YM sorption heat with equilibrium moisture content. The lines represent the sorption heat predicted by Eqn. (9).

**Fig. 4.** Equilibrium moisture content effect on the differential entropy of the BC/YM and YM freeze dried drinks. The lines represent the differential entropy values predicted by the exponential equation.

**Fig. 5.** Enthalpy-entropy linear relationship for freeze-dried BC/YM and YM.

**Fig. 6.** Monomeric anthocyanins concentration (MAC) changes with temperature and relative humidity (%).

**Fig. 7.** Ascorbic acid (AA) content changes with relative humidity (%) and temperature

—○— 10 —□— 20 —△— 40 °C.

**Fig.8 A, B, C.** Lightness ( $L^*$ ; A), Saturation Index (SI; B) and Hue Angle ( $HA$ , °; C) dependence with temperature and relative humidity (%).



Fig. 1.

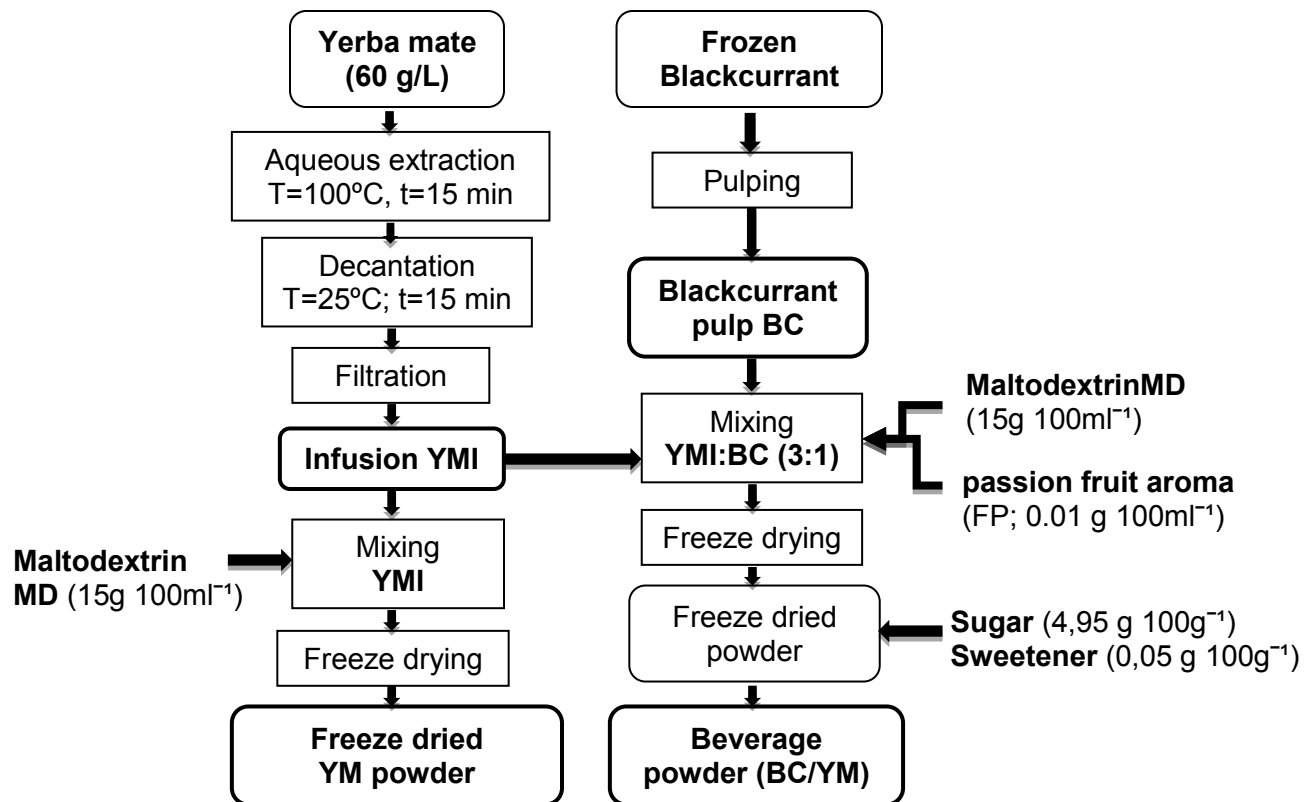


Fig. 2.

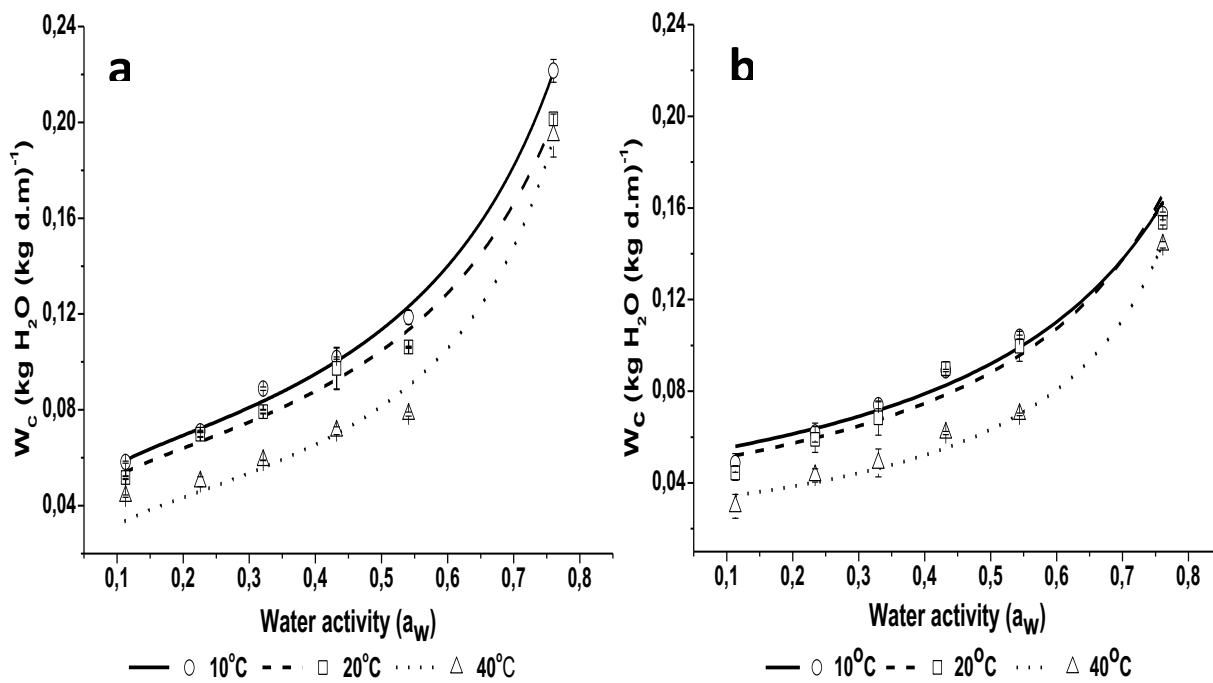


Fig. 3.

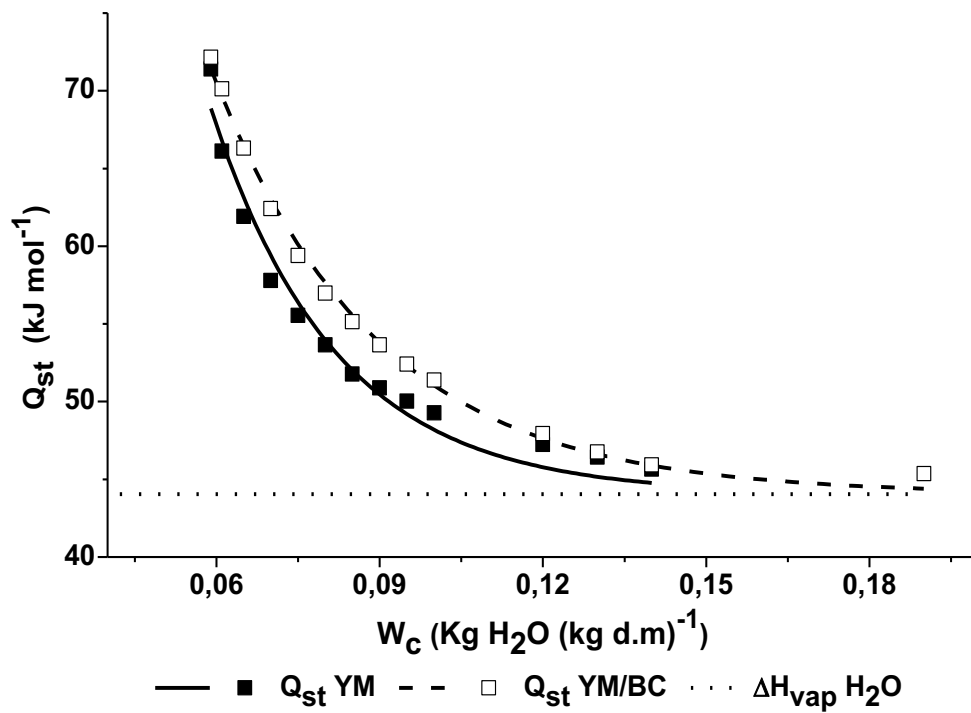


Fig. 4.

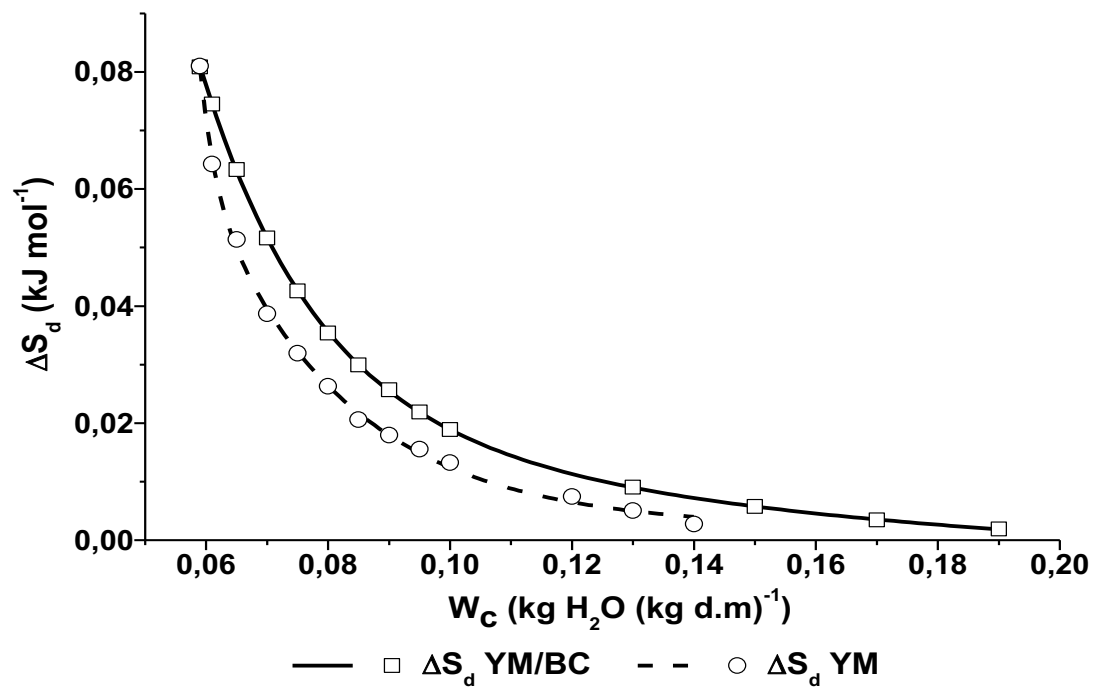


Fig. 5.

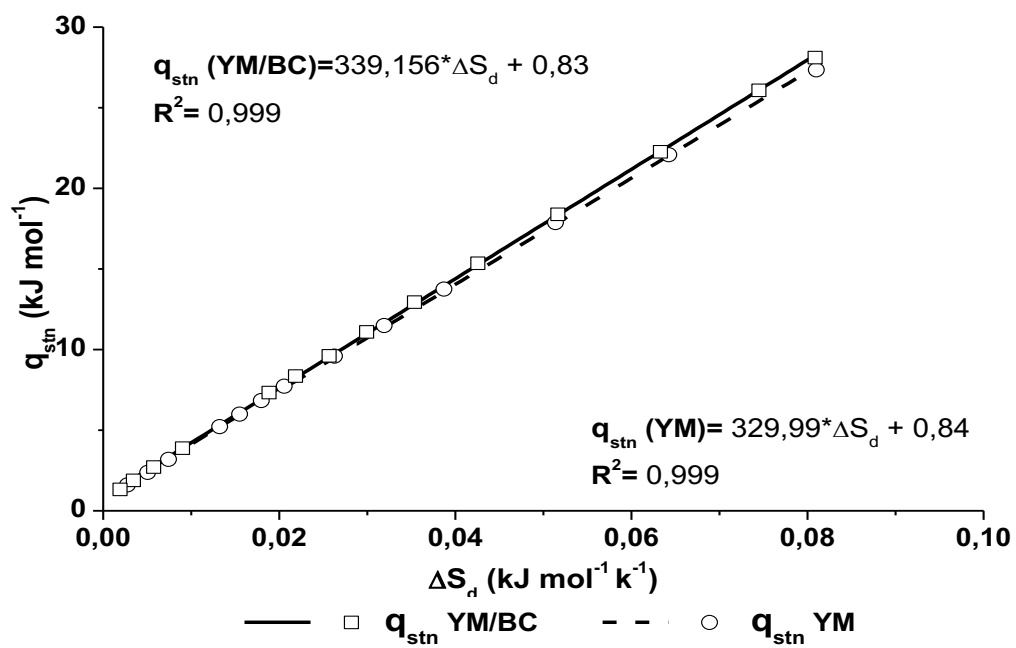


Fig. 6.

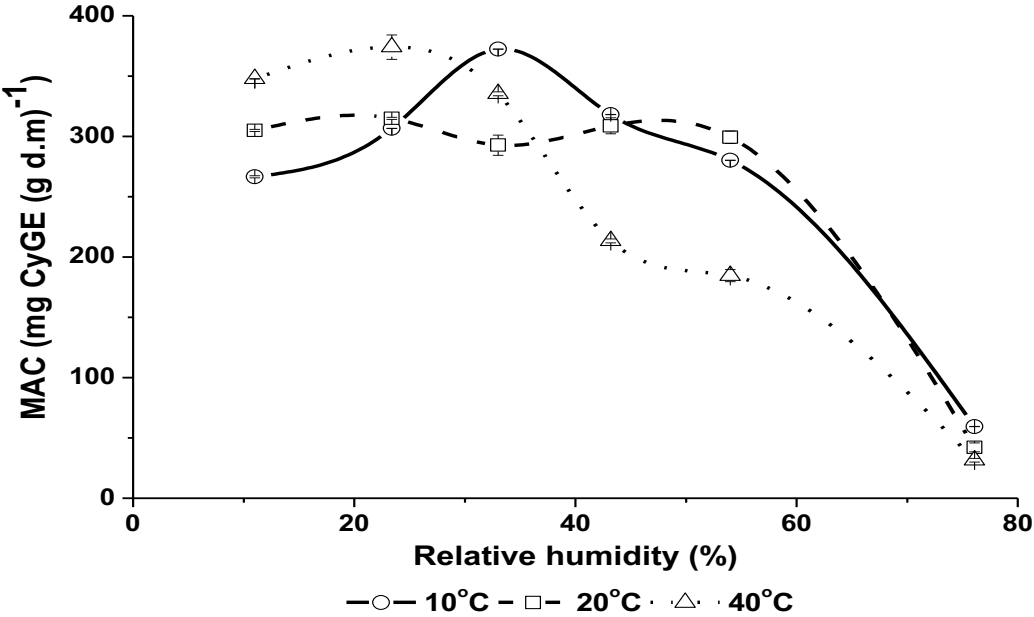


Fig. 7.

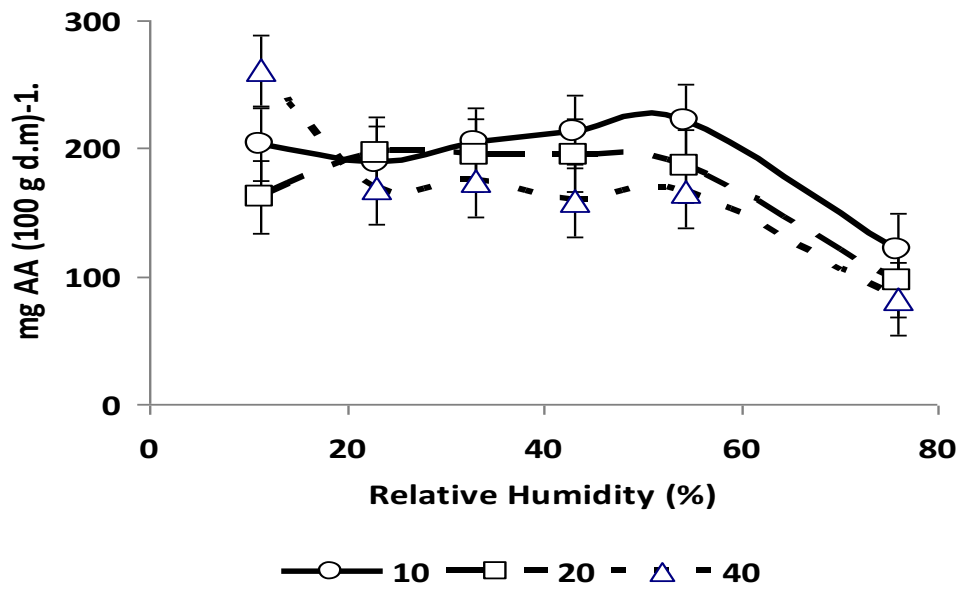


Fig. 8.

