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Yerba mate antioxidant powders obtained by co-crystallization: Stability during storage

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ABSTRACT

The interest on yerba mate has increased in the last years due to its high content of bioactive compounds related to health benefits. Antioxidant aqueous extracts of yerba mate were entrapped into a sucrose matrix by co-crystallization. The products were characterized in terms of their morphology, entrapment yield, loading capacity, water activity, moisture content, antioxidant activity, thermal behavior, solubility and hygroscopicity. It was found that the co-crystallization process led to high entrapment yield and maintained the antioxidant activity of the yerba mate extract towards DPPH radical. Also, the co-crystallized powders showed values of water activity, moisture content, hygroscopicity and flowability indicative of high stability and good handling properties. The total polyphenols content of the co-crystallized products remained almost constant along storage at 75% RH and 20 °C, however, fluctuations in their DPPH radical scavenging activity were observed.

1. Introduction

Yerba mate (*Ilex paraguariensis*) is highly consumed as infusion in several South American countries and has been recognized by FDA as GRAS (generally recognized as safe). The extract of yerba mate could be considered as a natural antioxidant to preserve food by retarding deterioration, rancidity, or discoloration and also, has the advantage of being effective at very low concentrations (De Campos et al., 2007; Valerga et al., 2013). Various pharmacological activities inherent to the yerba mate extract have been attributed to their content of polyphenols, flavonoids and xanthines including caffeic acid, chlorogenic acids, rutin, caffeine and theobromine (Anesini et al., 2012; Bravo et al., 2007; Jaiswal et al., 2010). Recent studies have demonstrated that the phenolic compounds act in the prevention and treatment of health disorder due to its antioxidant, hepatoprotective, choleretic, diuretic, hypocholesterolemic, antirheumatic, antitrombotic, antiinflammatory, antiobesity and antiageing properties (Bracesco et al., 2011; Marques and Farah, 2009).

Natural antioxidants may be added to a wide range of food such as baked goods, biscuits, chewing gum, dry snacks, fruit drinks, mayonnaise, meat products, nuts, oils and fats, among others. However, it is well known that the aqueous extracts obtained from plants, exhibit low stability and some of them have an unpleasant flavor, therefore, only a few extracts are currently employed in the food industry (Kosaraju et al., 2008; Makris and Rossiter, 2000; Wanasundara and Shahidi, 2005).

Encapsulation technologies become an actual choice applied to preserve and/or protect numerous ingredients from adverse environmental conditions (light, moisture, and oxygen) and to prevent undesirable interactions with the carrier food matrix (Gouin, 2004; Onwulata, 2011). Recently, Fang and Bhandari (2010) and Munin and Edwards-Lévy (2011) published interesting reviews focused on the techniques employed for the encapsulation of polyphenols such as spray drying, coacervation, liposome entrapment, inclusion complexation, co-crystallization, nanoencapsulation, freeze drying and emulsion. Spray drying is the most widely applied process mainly for the preparation of dry, stable food additives and flavors (Desai and Jin Park, 2005). Co-crystallization offers an economic and flexible alternative for the incorporation of active compounds into powder foods. In this process, the crystalline structure of sucrose is modified from perfect to irregular agglomerated crystals, to provide a porous matrix in which a second active ingredient can be incorporated. These agglomerates have a sponge-like appearance, with considerable void space and an increased surface area (Awad and Chen, 1993; Chen et al., 1988). Co-crystallization with sucrose could improve the solubility, dispersibility, wettability, anticaking, antidusting, antiseparation, homogeneity, flowability and stability of food materials. Nevertheless, few studies have been carried out on this technique dealing with flavors, natural extracts, essential oils, honey, glucose and fructose (Astolfi-Filho et al., 2005; Beristain et al., 1996; Bhandari et al., 1998; Bhandari and Hartel, 2002; Maulny et al., 2005; Sardar and Singhal, 2013).

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Previously, we have obtained co-crystallized products working with mineral salts and freeze-dried yerba mate extract which results demonstrated that the co-crystallization was a good alternative for the handling of these materials (Deladino et al., 2007, 2010). Further studies are necessary for co-crystallization to reach industrial applications. In this regard, simplifications of the co-crystallization steps would favor scaling up of the process. In the present work, an improvement in the production of the co-crystallized powders was carried out: the aqueous extract of yerba mate was employed as the solvent of the supersaturated sucrose solution. The physicochemical characterization of the antioxidant powders was performed and their stability during storage was evaluated, as well.

2. Materials and methods

2.1. Preparation of the yerba mate extract

Different amounts (3, 5 and 10 g) of commercial yerba mate (Las Marías, Corrientes, Argentina) were mixed with 100 mL of distilled water and placed in a thermostatic bath (Viking, Argentina) at 100 °C for 40 min. Once obtained, the extracts were filtered, cooled and kept in dark flasks until used.

2.2. Preparation of the co-crystallized products

A blend of commercial sucrose (50 g) (Ledesma, Argentina) and yerba mate extract (10 mL) was heated to 132 °C on a hot plate and stirred with a vertical agitator (IKA Labortechnik, Staufen, Germany). When a slight turbidity was detected in the syrup, indicating the beginning of crystallization process, the mix was removed from the heat, maintaining the agitation. Then, co-crystallized products were dried in a convection oven (SanJor, Argentina) at 40 °C for 15 h, milled and transferred to polyethylene bags for storage in desiccators with silica gel until use. Three batches of co-crystallized powders were prepared as described above. A supersaturated sucrose solution without the active compound was processed in the same manner as described above to act as a control. Agglomerates were sieved with a set of meshes between 2 and 0.250 mm. Size distribution of the agglomerates was calculated by the weight of the powder retained in each sieve. Specifically, the particles retained in the meshes of 0.5 and 1 mm were used to determine the solubility, flowability, hygroscopicity and the chemical stability during storage.

2.3. Total polyphenols content

Total polyphenols content (TPC) was determined by the Folin–Ciocalteu method (Singleton et al., 1999). Briefly, 2 mL of Na_2CO_3 (2 g/100 mL) (Anedra, Argentina) were mixed with 200 μL of the sample and 200 μL of Folin–Ciocalteau reagent (Anedra, Argentina, 1:1 diluted). After 30 min, sample absorbance was measured at 725 nm in a spectrophotometer (Shimadzu, UV-mini 1240, Japan). Chlorogenic acid (Fluka, USA) was used as standard.

2.4. Loading capacity and entrapment yield

Loading capacity (L_c) was calculated as the TPC of the yerba mate extract loaded in 1 g of co-crystallized material. The entrapment yield (%EY) was calculated as follow:

$$\%\mathrm{EY} = \left(\frac{L_c}{L_0}\right) \times 100 \qquad (1)$$

where L_0 is the initial TPC of the yerba mate extract per gram of raw mix.

2.5. Antioxidant activity of the yerba mate co-crystallized powders

The antioxidant activity was determined measuring the free radical scavenging activity towards the 1,1-diphenyl-2-picryl-hydrayl reagent (DPPH·) (Sigma–Aldrich, USA) according to the method described by Brand-Williams et al. (1995). One gram of co-crystallized product was dissolved in 10 mL of distilled water. An aliquot of 100 μL of dissolution was mixed with 3.9 mL of DPPH· ethanol solution (25 mg DPPH·/L). Absorbance was determined at 517 nm until the reaction reached a plateau. Antioxidant activity was expressed as the percentage of inhibition (I%) of the DPPH· free radical, calculated with the following equation:

$$I(\%) = \left(\frac{\mathrm{Abs_b} - \mathrm{Abs_s}}{Abs_b}\right) \times 100 \qquad (2)$$

where $\mathrm{Abs_b}$ is the absorbance of control reaction (without the sample) and $\mathrm{Abs_s}$ is the absorbance of the sample.

2.6. Characterization of the co-crystallized products

2.6.1. Scanning electronic microscopy (SEM)

Morphological analysis was performed by SEM using a FEI, Quanta 200 microscope (Netherlands). Samples were attached to stubs using a two-sided adhesive tape, then coated with a layer of gold (40–50 nm) and examined using an acceleration voltage of 20 kV.

2.6.2. Color attributes

Color was measured using a tristimulus Minolta colorimeter (Konica-Minolta CR-400, Japan) and was reported in CIELab scales (L^*, a^* and b^* values), where L^* was used to denote lightness, a^* redness and greenness, and b^* yellowness and blueness. Chroma and hue angle values were calculated using Eqs. (3) and (4), respectively.

$$\mathrm{Chroma} = [a^{*2} + b^{*2}]^{1/2} \qquad (3)$$

$$\mathrm{Hue\ angle} = \tan^{-1}(b^*/a^*) \qquad (4)$$

2.6.3. Moisture content and water activity

Moisture content (%) was measured gravimetrically by drying the grounded samples in a vacuum oven at 70 °C, until constant weight (AOAC, 1998). Values of water activity (a_w) were determined using an AquaLab Serie 3 TE (USA) equipment.

2.6.4. Solubility

Solubility was determined by blending 1 g of co-crystallized powder with 10 mL of distilled water at ambient temperature with continuous stirring (IKA RH1 magnetic stirring, Germany). Aliquots were removed at different times and the dissolved sucrose mass in the solution was determined using a HI96801 digital refractometer (Hanna Instruments, USA).

2.6.5. Flowability tests

Flowability of the co-crystallized powders was determined by both, dynamic angle of repose and Hausner ratio (H). The angle of repose was determined with a rotating cylindrical chamber, which was tilted gradually until slipping occurred and the angle measured (Solids handling study bench, CEN, Armfield, United Kingdom) (Geldart et al., 2006).

The value of H was calculated by the ratio of the tap bulk density to the loose bulk density (Hausner, 1967). The loose bulk density was determined by pouring a known mass of co-crystallized product delivered freely by gravity into a measuring cylinder, and it was calculated by dividing the mass by the bulk volume.