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Propolis encapsulation by spray drying: Characterization and stability

V.M. Busch [a, b], A. Pereyra-Gonzalez [c], N. Šegatin [d], P.R. Santagapita [a, b], N. Poklar Ulrih [d], M.P. Buera [a, b, *]

[a] Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Dptos. de Industrias y de Química Orgánica, Buenos Aires, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina
[c] MEDEX d.o.o., Ljubljana, Slovenia
[d] Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia

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ABSTRACT

Propolis extracts have shown to possess several health beneficial properties attributed to their phenol composition. Several pharmaceutical formulations are based on propolis as active ingredient and it could also be a potential component of functional foods. The main drawback for its application as food ingredient is its low water solubility, strong taste and aroma. In this work, an encapsulated Argentine alcohol-free propolis powder was obtained by spray drying, by using different maltodextrin matrices, with or without added gums. Besides, physicochemical characterization of powders and biocompound stability studies towards humidification at different water activities were done. Galangin and pinocembrin were the major components identified by HPLC in propolis before and after the drying process. The SEM images analysis showed that the addition of gums improved the particles integrity and size homogeneity. Furthermore, a higher degree of encapsulation of some polyphenols (such as quercetin), higher antioxidant activity measured by the reducing power assay, and higher physical stability toward humidification and physical collapse were also achieved especially in gum-added systems. The use of propolis as an encapsulated powdered additive widens its alcohol-free dosage applications.

1. Introduction

Propolis is a natural resinous mixture produced by honey bees from substances collected from parts of plants, buds, and exudates. Propolis extracts have shown to possess several health beneficial properties, such as antimicrobial, anti-inflammatory, healing, anesthetic, anticariogenic, antiviral, anticarcinogenic and antioxidant (Bodini, Sobral, Favaro-Trindade, & Carvalho, 2013; Chaillou & Nazareno, 2009). These properties are due to their chemical composition, more specifically to the presence of phenolic compounds, such as flavonoid aglycones, phenolic acids and their esters, aldehydes and ketones (Bodini et al., 2013). Isla, Nieva Moreno, Sampietro, and Vattuone (2001) found a positive correlation between flavonoid content of some Argentine propolis and percentage of inhibition of malon dialdehyde (MDA) by lipid oxidation. Although some specific propolis like Brazilian propolis type 6 or geopropolis lacks on phenolic acids and/or flavonoids compounds (Da Cunha et al., 2013; Duarte et al., 2003; Huang, Zhang, Wang, Li & Hu, 2014), in general the flavonoid content represents the major propolis components, and it was proposed as a good marker of propolis quality (Gardana, Scaglianti, Pietta, & Simonetti, 2007; Sampietro, Sampietro Vattuone, & Vattuone, 2016).

Several pharmaceutical formulations are based on propolis as active ingredient and it could also be a potential component of functional foods. Nevertheless, the application of propolis as a food ingredient is limited by its alcohol solubility, strong taste and aroma (Bodini et al., 2013; Nori et al., 2011).

Propolis encapsulation by spray-drying appears as an option to avoid undesirable sensory characteristics, protect bioactivity and widen the dosage by a water soluble encapsulation matrix (Bruschi, Cardoso, Lucchesi, & Gremião, 2003; Da Silva et al., 2013). Since bioactive compounds often present very low solubilities and bioavailabilities due to their hydrophobic character, spray-dried powder shows a considerable importance as it enhances the flavonoid compounds' solubility and absorption (Di Battista, Constenla, Ramírez-Rigo, & Piña, 2015; Fujimori et al., 2016), besides of reducing their thermal degradation (Pang, Mashitah,

* Corresponding author. Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2160, Ciudad Universitaria, C1428EGA, Ciudad Autónoma de Buenos Aires, Argentina.
E-mail address: pilar@di.fcen.uba.ar (M.P. Buera).

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Yusoff, & Gimbun, 2014). Among all water-soluble matrices, maltodextrin is commonly used as a spray-drying agent for its high solubility and good bioactive compounds' retention (Franceschinis, Salvatori, Sosa, & Schebor, 2015; Pang et al., 2014). This property has been related to its rate of dehydration, which produces a rapid formation of dense skin and a good protection of core ingredient against oxygen transfer and possible deterioration (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007; Matsuno & Adachi, 1993). The physicochemical properties of powders and the retention of bioactive compounds can be modified by the addition of another ingredient (Da Silva et al., 2013; Krishnan, Kshirsagar, & Singhal, 2005). The use of gums as second matrix ingredients has proved to change release-kinetics in several encapsulation systems (Guan & Zhong, 2015; Kim, Choi, Kim, & Lim, 2015). Krishnan et al. (2005) showed that a blend of Arabic gum and maltodextrin protected cardamom oleoresin better than Arabic gum alone. Similarly, spray-dried powders with modified wall materials (tapioca starch and maltodextrin) showed differences in water solubility, surface morphology and β-carotene retention efficiency (Loksuwan, 2007).

In this context, the aim of this work was to obtain an encapsulated Argentine alcohol-free propolis (from a Biosphere Reserve) powder by spray drying, by using different maltodextrin matrices. A non-conventional galactomannan gum (*vinal* gum) and Arabic gum were employed as secondary encapsulation agents. The physicochemical characteristics and the antioxidant capacity of powders were determined and the main polyphenol compounds were quantified prior and after encapsulation.

2. Materials and methods

2.1. Materials

Propolis from Tigre (*Delta del Paraná* Biosphere Reserve, declared protected zone by UNESCO in 2000, unesco.org), was studied. It was obtained by honey bees from the buds and resin of many trees: poplar (*Populus alba*), willow (*Salix* spp.), cockspur coral tree (*Erythrina crista-galli*), Australian acacia (*Acacia mearnsii*) and pecan (*Carya illinoinensis*) (Burkart, 1957; Kalesnik & Aceñolaza, 2008). Maltodextrin (MD) dextrose equivalent 13 from Saporiti S.A. (Buenos Aires, Argentina), and Arabic gum from Biopack S.A. (Zárate, Argentina) were also employed.

2.1.1. Propolis purification

14 g of propolis were dissolved in 100 mL of ethanol and stirred for 24 h. Then it was filtered with a Buchner doing vacuum with 0.42 μm pore size paper filter. In order to remove all remaining wax, the ethanolic extract was kept at freezer (−20 °C) for 10 h and centrifuged at −5 °C at 4500 rpm for 10 min twice. The clear supernatant was evaporated in rotavap at 40 °C to a final volume of 40 mL. The final concentration of the ethanolic extract was 0.123 g/mL of purified propolis.

2.1.2. Vinal gum extraction and purification

Separation of *vinal (Prosopis ruscifolia)* seeds, extraction and purification of the gum were done according to previous work (Busch, Kolender, Santagapita, & Buera, 2015). Briefly, seeds were separated by milling the pods and passing through several sieves. Then, the endosperm was manually separated after alkaline treatment (Chaires-Martinez, Salazar-Montoya, & Ramos-Ramírez, 2008). The purification was done through water solubilization of the endosperm and flocculation of the gum into absolute ethanol twice. *Vinal* gum was freeze-dried by using a Heto Holten A/S, cooling trap model CT 110 freeze-dryer (Heto Lab Equipment, Alleroed, Denmark) operating at a condenser plate temperature of −111 °C, a chamber pressure of 30 Pa, and shelf temperature of 25 °C. *Vinal* gum has molecular weight of 1.43 ± 0.04 × 10^6 Da (viscometric), a mannose/galactose ratio determined by GC-MS of 1.6 and an apparent viscosity of 600 mPa s at 0.1 g/100 mL (Busch et al., 2015).

2.2. Encapsulation of propolis by spray drying

Three systems were prepared: maltodextrin propolis system without added gum (w-oG), maltodextrin - *vinal* gum propolis system (VG), and maltodextrin - Arabic gum propolis system (GA). Each system was prepared by stirring 30 g of MD, 0.3 g of Arabic gum or *vinal* in 100 mL of bi-distilled water at 500 rpm for 24 h. Then, each system was homogenized by an Ultra-Turrax T18 (IKA, Königswinter, Germany) at 15,000 rpm for 2 min and then 10 mL of the propolis ethanolic extract (0.123 g/mL solids) was added dropwisely, and suspended in the Ultra-Turrax for 2 min more. Each system was filtered twice to get rid of remaining solids, in order to prevent the clogging of the spray dryer nozzle. The operational conditions of a mini spray dryer (Büchi B290, Flawil, Switzerland) were: flow rate: 8 mL/min; air pressure: 3.2 kPa; nozzle diameter: 1.5 mm; inlet temperature: 120 °C. Outlet temperatures were between 70 °C and 74 °C for the three systems.

2.3. Propolis compounds analyzed by HPLC

A high-performance liquid chromatograph Agilent series 1100 equipped with UV detector was used (Agilent Technologies, Waldbronn, Germany). Separation was done by a purosphere STAR RP- 18 endcapped; 5 μm 150 × 4.6 mm column (Merck Millipore, Darmstadt, Germany). Temperature of column oven was set at 25 °C, flow rate was 0.7 mL/min, injection volume for both standards and extracts was 10 μL, and detection was performed at 290 nm. Elution was performed using acetonitrile-1% phosphoric acid solvent system using a linear gradient. Calibration curves for each particular standard (HPLC quality) were done using caffeic acid, p-coumaric acid, ferulic acid, quercetin, cinnamic acid, apigenin, naringenin and galangin (from Sigma-Aldrich Co., St. Louis, MO, USA); chrysin and pinocembrin (Fluka, from Sigma-Aldrich Co.); and pinocembrin derivate (pinocembrin-7-methylether, Roth, from Carl Roth GmbH, Karlsruhe, Germany). The encapsulation efficiency (called % encapsulation) was calculated by equation (1).

$$\%encapsulation_i = \frac{X_i \cdot 100}{Y_i} \quad (1)$$

where X_i is the amount of each compound found in the spray dried powder (mg/g of dry powder), and Y_i is the quantity of that compound in the propolis extract added to the solution entering the spray dryer (mg/g of solids).

2.4. Physicochemical characterization of powders

2.4.1. Water dispersibility (WD)

WD was evaluated by suspending 0.5 g of the spray-dried systems in 50 mL of bi-distilled water, stirring 5 min (vortex), and centrifuging at 5000 rpm for 5 min. A 20 mL supernatant aliquot was dried in oven at 105 °C for 2 h (adapted from Da Silva et al., 2013). WD was calculated following equation (2).

$$WD\ (\%) = \frac{weight\ (g) of\ solid\ supernatant\ \times 2.5}{weight\ of\ sample\ (g)} \quad (2)$$