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Role of the phases composition on the incorporation of gallic acid in O/W and W/O emulsions

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ABSTRACT

This work aimed to study the incorporation and preservation of gallic acid (GA) in emulsions formulated using soybean oil as oil phase, polyoxyethylene sorbitan (Tween 20) and polyglycerol polyricinoleate (PGPR) as surfactants. The systems evaluated were oil-in-water (O/W) and water-in-oil (W/O) emulsions prepared using the same aqueous to oily phases weight ratio (3:1). The volume fraction of surfactant was 0.01, 0.02 or 0.04 and gallic acid concentration in the final emulsions was 0 or 0.5% w/w. Increasing GA concentration did not show any effect on the initial or equilibrium interfacial tension (22 mN/m) in GA solution/soybean oil systems but reduced the average diameter of the droplets in both emulsions. The W/O emulsions showed bimodal droplet size distribution, pseudoplastic behavior and the presence of GA decreased the phase separation. The O/W emulsions exhibited kinetic stability, monomodal droplet size distribution and Newtonian fluid behavior. Results showed that the emulsification process was an efficient method to protect the bioactive against oxidation. Fresh O/W emulsions showed higher GA retention but during the storage time, the W/O emulsions showed a better capacity to retain the gallic acid. However, both emulsions exhibited high retention of bioactive (>86.61%) after 7 days of storage showing that this strategy could be used in different emulsified food products.

1. Introduction

Researches aiming at the application of polyphenols have attracted great interest of the pharmaceutical, nutraceutical and functional food industries, considering the potential benefits of these bioactive compounds to the human health (Fang and Bhandari, 2010). Polyphenols show antioxidant capacity, which is associated with anti-inflammatory, antibacterial and antiviral functionality (Quideau and Feldman, 1996). These compounds also have applications in food products due to its ability to protect oxygen sensitive compounds (Rakić et al., 2006). Gallic acid, a polyphenol class of phenolic acids, shows effective action in the treatment of diabetes and albuminuria (Hsieh et al., 2007), can be used as an antifungal and antiviral (Uozaki et al., 2007) and offers cytotoxicity against cancer cells (de Mejia et al., 2006). However, the antioxidant properties of polyphenols are also responsible for the instability of these compounds in the presence of light, heat and under certain conditions of pH. Furthermore, their low bioavailability is mainly attributed to a low solubility in water (Manach et al., 2004) and many of these molecules have a bitter and astringent taste, limiting its use in food or oral medications (Munin and Edwards-Lévy, 2011).

Several encapsulation and preservation methods have been studied in order to overcome these drawbacks and maximize the benefits of polyphenols (Deladino et al., 2008). Encapsulation promotes the protection of bioactive during the production process, storage and consumption until its release in a specific site within the body, ensuring their bioavailability and efficacy (Acosta, 2009; Chen et al., 2006). Emulsions are dispersions that present polar and nonpolar regions, low production cost and relative easy preparation, are protective systems with high potential for encapsulation of bioactive compounds. However, the emulsions are thermodynamically unstable systems that tend to destabilize with time. Therefore, the use of intense mechanical forces and/or addition of surfactants/stabilizers are necessary to increase the kinetic stability of emulsions (McClements et al., 2007).

The development of O/W and W/O emulsions manufactured by different processes and phase composition are interesting alternatives to encapsulate gallic acid for their use on systems with unlike properties. Therefore, the aim of this study was to evaluate O/W and W/O emulsions formulated with different surfactant concentrations using the same aqueous to oily phases weight ratio (3:1) in order to identify the most stable system that provide greater

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protection to the gallic acid. In order to understand the influence of gallic acid addition in emulsions the following analyses were performed: interfacial tension analysis, kinetic stability, average size of droplets, microscopy and rheology. Furthermore, color, total phenols and antioxidant capacity of emulsions were evaluated to identify the system that promoted greater protection of gallic acid.

2. Material and methods

2.1. Material

The ingredients used to prepare the emulsions were gallic acid (GA) obtained from Sigma Aldrich Co. (St. Louis, EUA) and surfactant polyoxyethylene sorbitan monolaurate (Tween 20) purchased from Dinamica Quimica Contemporanea Ltda (Diadema, Brazil). Polyglycerol polyricinoleate (GRINDSTED® PGPR) was kindly donated by Danisco Brasil Ltda (Brazil) and soybean oil (Bunge Alimentos S.A., Brazil) was purchased in the local market.

2.2. Preparation and characterization of the gallic acid solution

The aqueous gallic acid solution (0.1–3.5% w/w) was prepared by dispersing gallic acid in deionized water (Millipore®) using a magnetic stirrer for 3 h at 25 °C (Noubigh et al., 2013). The solubility of gallic acid was evaluated at 25 °C and atmospheric pressure from visual presence or absence of precipitate. The pH of these solutions was measured at 25 °C using a pH meter (827 pH lab, Metrohm Autolab B.V., Switzerland) in duplicate.

The interfacial tension between soybean oil and aqueous gallic acid solution (0.1–3.5% w/w) was measured at 25 °C using a tensiometer Tracker-S (Teclis, Longessaigne, France), by the pendant (W/O) and rising (O/W) drop methods, aiming to evaluate the effect of the gallic acid concentration on the interfacial tension. The initial drop volume was 6 µl for both methods.

The effect of Tween 20 or PGPR concentration on the interfacial tension was also evaluated with the concentration of gallic acid fixed at 0.5% (w/w). For this purpose, Tween 20 (0.1, 1, 2 and 4% w/w) was dissolved into the gallic acid solution by magnetic stirring at room temperature and PGPR (1, 2, 3 and 4% w/w) was dissolved in soybean oil at 42 ± 2 °C for 5 min under magnetic stirring, with subsequent cooling at room temperature. The measurements were performed at 25 °C and the initial drop volume was 2 µl. Measurements were performed in duplicate.

2.3. Emulsion preparation

The oil-in-water (O/W) emulsions were prepared at 25 ± 2 °C by pre-mixing the oily and aqueous phase using an Ultra Turrax model T18 (IKA, Staufen, Germany) for 4 min at 14,000 rpm, followed by homogenization at 30 MPa/5 MPa using a Panda 2K NS1001L double-stage homogenizer (Niro Soavi, Parma, Italy). The oily phase was composed by soybean oil and Tween 20, while the aqueous phase was gallic acid solution or water. For the water-in-oil emulsion (W/O), the emulsifier PGPR, was previously dissolved into the soybean oil for 5 min using a magnetic stirrer at 42 ± 2 °C. Then, the dispersion was added to a jacketed vessel attached to a thermostatic bath (Quimis, Brasil) at 25 ± 2 °C. After that the aqueous phase was added dropwise to the dispersion (soybean oil + PGPR) using a peristaltic pump Masterflex L/S (Cole-Parmer Instrument Company, EUA) with a mean flow rate of 2.5 ml/min during homogenization in a rotor–stator system (Ultra Turrax T18, IKA, Germany) at 14,000 rpm. When the aqueous phase was completely incorporated into the emulsion (after 85 min), the rotational speed was decreased to 11,000 rpm and the system was homogenized for 4 min. Both oil-in-water (O/W) and water-in-oil (W/O) emulsions were prepared using the same aqueous to oily phases weight ratio (3:1 or 75:25) and volume fraction of surfactant was 0.01, 0.02 or 0.04. The gallic acid concentration in the final emulsions was 0 or 0.5% w/w. Emulsions were evaluated by kinetic stability, optical microscopy, particle size distribution, rheological behavior, color, total phenols, antioxidant activity and gallic acid retention. Gallic acid solutions freshly prepared under mild conditions of mixing and subjected to the same process conditions to produce O/W and W/O emulsions were used as control samples of oxidation process. The solutions were evaluated for color.

2.4. Kinetic stability

Immediately after preparation, 100 ml of each emulsion was poured into a cylindrical glass tube (internal diameter = 27 mm, height = 173 mm), sealed with a plastic cap and stored at 25 °C for 7 days. The O/W emulsion stability was measured by the height of the bottom phase (H_b) and expressed as creaming index (CI). The W/O emulsion stability was expressed as sedimentation index (SI) and it was measured by checking the oil top layer height (H_t) during storage. The creaming and sedimentation indexes were determined according to Eqs. (1) and (2), respectively.

$$CI(\%) = \left(\frac{H_b}{H_0}\right) * 100 \tag{1}$$

$$SI(\%) = \left(\frac{H_t}{H_0}\right) * 100 \tag{2}$$

where H_0 represents the initial height of the emulsion. The analyses were carried out in duplicate.

2.5. Optical microscopy

The emulsion microstructure was observed in an optical microscope (Axio Scope.A1, Carl Zeiss, Germany) with 100× oil immersion objective lens. The images were captured with the software AxioVision Rel. 4.8 (Carl Zeiss, Germany). The optical microscopy was performed on the freshly prepared emulsions and after 7 days of storage.

2.6. Particle size distribution

The droplet size distribution was determined by the laser diffraction method using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, UK). The emulsions were dispersed in water (O/W) or soybean oil (W/O). For W/O emulsion, ultrasound was applied for 5 min in order to avoid the presence of bubbles. The size of the droplets was expressed as the volume-surface mean diameter (D_{32}) and the polydispersity index (PDI), according to Eqs. (3) and (4), respectively. Measurements were performed just after emulsions preparation and 7 days after storage in duplicate.

$$D_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{3}$$

$$PDI = \frac{d_{(90)} - d_{(10)}}{d_{(50)}} \tag{4}$$

where n_i is the droplets number with diameter d_i and d_{10}, d_{50} and d_{90} are the diameters at 10%, 50% and 90% of cumulative volume, respectively.