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Assessing the stabilizing effect of xanthan gum on vitamin D-enriched pecan oil in oil-in-water emulsions

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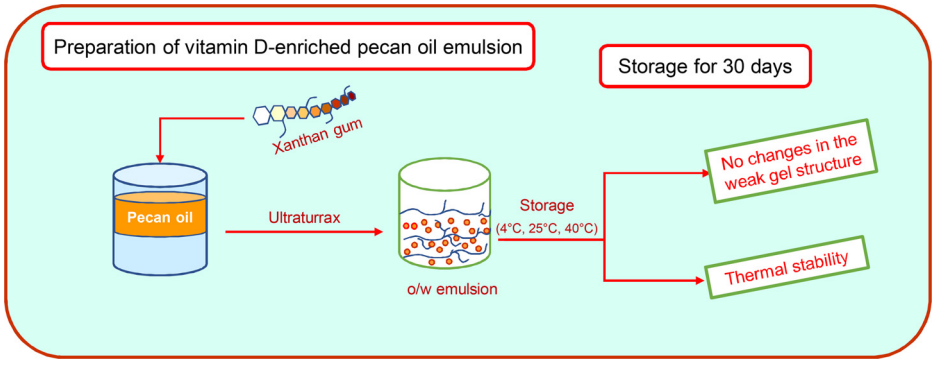
GRAPHICAL ABSTRACT



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ABSTRACT

Oil-in-water emulsions of vitamin D incorporated in pecan oil were developed, using xanthan gum (XG) as a stabilizer. Fourteen formulations, composed of 2% surfactants, 5% pecan oil/vitamin D3 and 93% water were prepared in the presence of the hydrophilic Tween 20® and lipophilic Span 80® surfactants at different compositions. The hydrophilic/lipophilic balance (HLB = 10.70) of the oil phase, which led to the slowest rate of creaming and the lowest amount of creaming after 90 days, was chosen as the best composition of the nonionic surfactants. Using XG as stabilizing agent at 0.25, 0.5 and 1.0% concentrations, preliminary tests were carried out to evaluate the rheological properties and droplet size distribution of the emulsions. Their stability were also investigated after being submitted to environment stresses (centrifugation cycles, and storage at varying temperatures for 30 days). The emulsions prepared with XG at 0.5% concentration maintained their stability after five centrifugation cycles at 3000 rpm for 30 min, and after storage at 4, 25 and 40 °C, as revealed by rheological and droplet size measurements.

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1. Introduction

The two forms of vitamin D (D2, ergocalciferol, and D3, cholecalciferol) are essential for human beings. Worldwide, low levels, insufficiency or deficiency of vitamin D are associated to increased risk of rickets in children and fractures in adults, hypertension, cancer, cardiovascular disease, type 2 diabetes mellitus and other chronic diseases [1]. The main source of vitamin D is its precursor, which is synthesized in the skin upon exposure to the sun or UVB irradiation. However, many factors may lead individuals to a very limited amount of this source of vitamin D. In such cases, oral supplementation of vitamin D is recommended. However, the poor palatability of vitamin D makes its intake rather difficult, especially by children.

Pecan nut (*Carya illinoinensis*) is a well-appreciated nut, native of North America and well-adapted to several countries. Pecan nut oil is rich in monounsaturated fatty acids (predominantly oleic acid) and bioactive substances with antioxidant activity, including vitamin E. Improved palatability and bioavailability of vitamin D would be achieved by incorporating vitamin D in pecan nut oil emulsions.

Generally, the closely interrelated physicochemical mechanisms of creaming, flocculation, coalescence, phase inversion and Ostwald ripening contribute to destabilize thermodynamically unstable emulsions. To overcome this tendency, emulsifiers are always added. These surface-active substances are adsorbed at the oil/water interface, favor emulsion formation by lowering the interfacial tension, and prevent droplets coalescence [2,3]. Most proteins may be adsorbed at the oil-water interface and are used as emulsifiers and short-term stabilizers. Natural polysaccharides, with the exception of gum Arabic and some kinds of pectins, which have emulsifying properties, act as long-term stabilizers, by modifying the viscosity of the continuous phase [4].

Xanthan gum (XG), the water-soluble heteropolysaccharide produced by *Xanthomonas campestris,* has been used as a stabilizing agent for emulsions, slowing down or preventing creaming [2]. Xanthan gum consists of a main chain formed by (1,4)-β-D-glucose repeating units, with alternating trisaccharide substituents, composed of α-D-mannose, β-D-glucuronic acid and β-D-mannose residues. A pyruvate moiety is linked to the 4- and 6- positions of the β-D-mannose terminal unit, whereas the internal mannose is acetylated. XG is nontoxic and has been widely used in food and pharmaceutical products. It forms pseudoplastic weak-gel networks, which inhibit gravity-induced creaming and/or phase separation [5–7].

Recently, coalescence and phase separation by creaming or sedimentation, the main factors affecting long-term stability of emulsions, were investigated by adding XG at several concentrations. Creaming was prevented up to 8 months with XG concentrations higher than 0.5 mass%, for a poly(ethylene oxide-*co*-propylene oxide)-emulsifier system [8]. Using octenyl succinate-modified waxy cornstarch (OSA) as an emulsifier for sunflower oil emulsions, addition of XG concentrations higher than the critical viscosity concentration (0.08 mass%) prevented creaming for a period of 15 days [9]. Smaller concentrations of XG (0.03 – 0.3 mass%) significantly decreased the droplet size of omega-3 vegetable oil emulsions, using a soy soluble polysaccharide as the unique emulsifier. However, probably because of the very low concentrations, creaming was observed [10]. Generally, aging of emulsions were accompanied by microscopy techniques and rheological measurements under invariable conditions, at ambient temperature. Known to be stable under a broad range of temperature and pH [11], XG at 0.25 wt% concentration was shown to preserve, for 14 days, the stability at pH 3 of high-oleic O/W emulsions, in which a protein concentrate was used as an emulsifier [12].

In this work, the effect of XG as a stabilizing agent to vitamin D-enriched pecan oil emulsions was investigated. The nonionic surfactants Tween 20® and Span 80® were added as emulsifiers. To the best of the authors' knowledge, this emulsion formulation has not been addressed before to encapsulate vitamin D. Physical stability was evaluated during storage and also when formulations were submitted to common environment stresses, such as changes in temperature and centrifugation. Visual observation, rheology and light scattering (mean droplet size and droplet size distribution) measurements were the techniques used to evaluate phase separation and stability in the XG-stabilized emulsions.

2. Materials and methods

2.1. Materials

Food grade xanthan gum (XG) was supplied by CP Kelco (Limeira, SP, Brazil). Pecan oil was provided by Vital Atman (São Paulo, SP, Brazil). Vitamin D3 (Cholecalciferol) was produced by Galena Química e Farmacêutica (Campinas, SP, Brazil). The nonionic surfactants Tween 20® and Span 80® were provided by Comércio e Indústria Farmos (Rio de Janeiro, RJ, Brazil) and Sigma Aldrich (São Paulo, SP, Brazil), respectively.

2.2. Determination of the hydrophilic/lipophilic balance (HLB) of the oil phase

To determine the HLB of the oil phase, the methodology reported by some authors [13] was followed with some modifications. Emulsions were prepared without the addition of XG, in the presence of the surfactants Tween® 20 (hydrophilic character, HLB = 16.7) and Span® 80 (lipophilic character, HLB = 4.3). For this, emulsions (total mass of 5 g) were prepared by mixing 2% surfactants, 5% pecan oil containing dissolved vitamin D3 (80 mg, 4000 IU) and 93% water. The mixtures were prepared with varying amounts of surfactants, suitable for obtaining HLB values in the range 4.3–16.7and their HLB_m values were calculated by Eq. (1).

$$HLB_m = \frac{(M_a \times HLB_a) + (M_b \times HLB_b)}{M_t} \quad (1)$$

where HLB_m is the HLB value of the mixture, HLB_a is the HLB value of the surfactant a, HLB_b is the HLB value of the surfactant b; M_a is the mass (g) of the surfactant a; M_b is the mass (g) of the surfactant b, and M_t is the total mass (g) of surfactants.

The two phases were heated separately at 75 ± 5 °C; then, the aqueous phase was poured slowly into the oil phase at 10,000 rpm in a Ultra Turrax IKA T25 (Ika Works, Wilmington, NC, USA), for 4 min. After complete addition, stirring was reduced to 6000 rpm until room temperature (25 °C ± 5 °C) was reached. The dispersions were visually evaluated after 24 h and for 90 days. The HLB value calculated for the most stable emulsion was taken as the final HLB value. Table S1 of the Supplementary material shows the amounts of surfactants used to prepare the formulations, as well as their HLB values.

2.3. Preparation of emulsions in the presence of XG

To prepare the emulsions stabilized by XG, the same methodology was followed, with 2% surfactants, 5% pecan oil containing dissolved vitamin D3 (80 mg, 4000 IU) and 93% XG gum aqueous solution at 0.25%, 0.5% and 1.0% (m/v) concentrations. In all cases, the surfactants composition was maintained constant at 51.6% of Tween 20 and 48.4% of Span 80 (HLB = 10.70), which had led to the most stable emulsion obtained in the previous HLB experiment. XG solutions were prepared in water, under magnetic stirring at room temperature, for 16 h.

2.4. Physical stability

The stability of the final emulsions was evaluated as they were submitted to environment stresses, to which they might be exposed during production, transport, storage and use.