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Influence of non-ionic emulsifier type on the stability of *cinnamaldehyde* nanoemulsions: A comparison of polysorbate 80 and hydrophobically modified inulin

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ABSTRACT

Cinnamaldehyde nanoemulsions were formulated to enable its application in an aqueous environment. The pure cinnamaldehyde nanoemulsions, stabilized by polysorbate 80 (at concentrations > 0.5%), had both a higher stability and smaller droplet size, whereas the emulsions containing hydrophobically modified inulin (HMI) formed a colloidal dispersion with larger particle size. Incorporation of sunflower oil (SO) allowed postponement of Ostwald ripening for a sufficiently long period of time (at least 60 days). Cryo-SEM and droplet size analyses of the nanoemulsions emulsified by HMI revealed no significant changes during storage. Under these conditions, HMI as an emulsifier exhibited a powerful resistance to high salt contents (up to 2 M) and high thermal processing temperatures (90 °C). The surfactant type and SO content had no marked influence on the antimicrobial activity of the nanoemulsions. This study provides precious information for a commercial formulation of nanoemulsions with durable physical stability under severe stress conditions.

1. Introduction

There has been a great interest of food consumers in food products containing natural rather than synthetic products. Food preservatives have always been a critical challenge for food manufacturers but recently essential oils (EOs) are well-known as an alternative solution (Gadea, Glibota, Pérez Pulido, Gálvez, & Ortega, 2017). EOs are natural secondary metabolite compounds of specific plants that can be utilized as antimicrobial, antioxidant, anticancer, antiradical, and flavouring agents (Baschieri, Ajvazi, Tonfack, Valgimigli, & Amorati, 2017). Cinnamaldehyde (CA) is one of the naturally occurring essential oils extracted from cinnamon bark EO that presents strong antimicrobial and antioxidant properties (Chen, Wu, McClements, Li, & Li, 2017; Shen et al., 2015). In terms of antibacterial activity, it has been reported that CA can inhibit the growth of bacterial cells by interaction with the cell membrane and alteration of the physicochemical characteristics of membranes, leading to changes in the permeability of the cells (Gill & Holley, 2004). However, there are limitations to the direct application of such EOs, including poor water solubility, strong scent, bitter taste, customer perception, and skin irritation (Cocchiara, Letizia, Lalko, Lapczynski, & Api, 2005; Jo et al., 2015).

Nowadays, colloidal dispersions, such as emulsions, are widely suggested as delivery systems of lipophilic bioactive compounds. It has also been shown that EO emulsions with smaller droplet size were more efficient in terms of antimicrobial characteristics, in contrast to those having larger droplets with less specific surface area (Speranza, Badan Ribeiro, Cunha, Macedo, & Macedo, 2015). Encapsulation of CA within oil-in-water nanoemulsions may potentially increase its water solubility as well as its bioavailability. In fact, nanoemulsions are colloidal systems with a mean droplet radius of less than 100 nm. They are preferred over conventional emulsions due to their higher transparency and surface area, better stability to gravitational separation and aggregation, and kinetic stability. On the other hand, nanoemulsions suffer from instability phenomena, such as Ostwald ripening (OR), which is the growth of larger droplets at the expense of smaller droplets by molecular diffusivity. OR is reported as the most significant reason for destabilization of EO nanoemulsions (Lim et al., 2011; McClements, 2015; McClements, Henson, Popplewell, Decker, & Choi, 2012). There

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are different ways to overcome this problem, for instance, incorporation of a third hydrophobic compound with poor water solubility in the lipid phase (Sedaghat Doost, Sinnaeve, De Neve, & Van der Meeren, 2017; Sun et al., 2015). Therefore, the influence of a long-chain triglyceride, i.e. high oleic sunflower oil (HOSO), was investigated because of its health beneficial effects and low cost. Nanoemulsions can be produced by either high energy or low energy methods. Microfluidization as a high energy method is frequently employed in the food industry for the formation of nanoemulsions with a low concentration of surfactants.

Generally, the selection of an efficient surfactant to produce oil-in-water nanoemulsions plays a pivotal role. Food products are potentially prone to stress conditions, such as pH, ionic strength, heat treatment, and matrix interaction, during processing, transport, and use by food consumers. Thus, a colloidal delivery system should be designed to maintain its stability and functionality on exposure to severe stress conditions. To the best of our knowledge, there is a lack of information on the fabrication of a stable essential oil (in particular cinnamaldehyde) delivery system under stress conditions, such as high salt content and temperature. The stability of self-emulsified cinnamaldehyde nanoemulsions containing medium-chain triglycerides at different NaCl concentrations (0–0.5 M) was evaluated (Tian, Lei, Zhang, & Li, 2016). Although the salt sensitivity tests revealed that the formed nanoemulsions remained stable in 0.5 M NaCl, the formulated nanoemulsions were not stable at a storage temperature of 37 °C (where severe oiling-off occurred).

In another study, cinnamaldehyde emulsions were prepared using whey protein isolate (WPI) (Chen et al., 2017). The major challenge involving emulsions emulsified with proteins is their pH sensitivity. The CA nanoemulsions were susceptible to droplet flocculation at the isoelectric point of WPI (pH 5). So, in this study, an attempt was made to create a nanoemulsion delivery system with high stability under intensive stress conditions.

Polysorbate 80, as a small molecule non-ionic surfactant with high HLB, was selected; this emulsifier consists of a polysorbate head group as hydrophilic moiety and a oleoyl chain as hydrophobic tail. It has frequently been used to produce EO nanoemulsions because of its low toxicity and cost, biocompatibility, and it being environmentally friendly. It would be expected to effectively maintain the stability of emulsions by steric stabilization in the presence of salt and at acidic pH. However, the hydration of its head groups may be lowered in the presence of high salt content, which may consequently decrease its ability to produce steric stabilization.

Hydrophobically modified inulin (HMI), commercially available as Inutec SP1, is a non-ionic emulsifier with inulin as its backbone. Inutec is a graft copolymer in which alkyl chains are chemically reacted with fructosyl groups of inulin (obtained from chicory) to give it an amphiphilic feature. According to Tadros (2006), Inutec has a number of advantages, such as renewability, biodegradability, and powerful stability of emulsions at high electrolyte concentrations, as well as under high temperature and acidic conditions. Several researches have shown that physically stable oil-in-water nanoemulsions can be effectively produced using Inutec as an emulsifier, even when exposed to stress conditions such as salt, high temperature, or low pH (Sedaghat Doost et al., 2017; Tadros, Vandamme, Booten, Levecke, & Stevens, 2004).

In this study, the aim was to produce CA nanoemulsions with long-term stability when exposed to extreme stress conditions (salt and temperature), potentially applicable as an antimicrobial and flavouring agent. Therefore, the effects of non-ionic surfactant type and concentration on visual appearance and droplet diameter were evaluated. Moreover, the impact of Ostwald ripening inhibitor addition to the lipid phase on the mean droplet size during long-term storage was investigated. Finally, the influence of surfactant type and addition of sunflower oil to the lipid phase on the antimicrobial properties of the formed nanoemulsions was examined.

This study provides a deeper insight into the potential application of cinnamaldehyde nanoemulsions as an alternative antimicrobial agent to enhance the safety of food products.

2. Materials and methods

2.1. Materials

Trans-cinnamaldehyde (*trans*-3-phenyl-2-propenal, 99%), polysorbate 80, and sodium azide (⩾ 99.5%) were purchased from Sigma-Aldrich Co (St. Louis, MO, USA). Hydrophobically modified inulin (Inutec® SP1) was generously provided by BENEO Orafti (Tienen, Belgium). High Oleic Sunflower Oil (HOSO) (iodine value = 87; 82% C18:1) was obtained from Contined B.V. (Bennekom, The Netherlands). Sodium chloride was provided by VWR PROLABO Chemicals (Belgium). Ultrapure water, purified by a Milli-Q filtration system (0.22 µm) (Millipore Corp., Bedford, MA, USA), was used for the analyses and preparation of all aqueous solutions.

2.2. Stock emulsion preparation

A stock oil-in-water nanoemulsion was prepared by weighing the oil phase, consisting of cinnamaldehyde and/or HOSO (5%w/w) and aqueous surfactant solution (0.5 – 5%w/v). Sodium azide (0.02%w/v) was added to all aqueous solutions, except for the samples for antimicrobial activity tests. The mixture was pre-emulsified with a high speed blender (Ultra-Turrax, type S 50N – G 45 F, IKA®-Werke, Germany) for 2 min at 24000 rpm. After pre-emulsification, the mixture temperature was maintained at 20 °C. The mixture was homogenized by passing 10 times through a Microfluidizer (M110-S, Microfluidics Corp., Newton, MA) at a pressure of 112 MPa to form a nanoemulsion. During microfluidization, the emulsion was cooled by placing the heat exchanger coil in an ice-water bath.

The influence of HOSO concentration was examined by homogenizing a 5% (w/w) lipid phase which consisted of variable ratios of cinnamaldehyde and HOSO (CA: HOSO = 100:0, 90:10, 80:20, 70:30, 50:50, 0:100 w/w) with 95%w/w aqueous phase.

2.3. Influences of ionic strength, thermal processing and storage temperature

CA:HOSO (50:50) nanoemulsions were diluted (1:1; v/v) with an appropriate sodium chloride solution to provide a final salt content of 0–2 M and the samples were stored for at least 30 days at ambient temperature (20 °C) to monitor the droplet size variation. The salt solution was added afterwards to ensure that stable nanoemulsions could be initially prepared. In the case of thermal processing, the original samples (without dilution) were kept inside a water bath for 30 min at temperatures ranging from 20 to 90 °C and then cooled to ambient temperature (20 °C). Visual appearance assessment, as well as particle size measurements, were performed. The effect of storage temperature was investigated by incubating the samples at 4, 20 or 40 °C, in order to mimic refrigerator as well as ambient conditions, in addition to accelerated aging conditions.

2.4. Particle size determination

The droplet size distribution of the samples was measured using a Photon Correlation Spectroscope (Model 4700, Malvern Instruments, U.K.) at a scattering angle of 150° at 25 °C. The emulsion was diluted prior to analysis with an appropriate solution to avoid multiple scattering. The light intensity correlation function was analyzed, based on the CONTIN method, whereas the z-average diameter was obtained by cumulant analysis. Each individual measurement was an average of 10 runs. If it was needed, the viscosity values of the salt solutions were applied.