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Influence of interfacial composition on oxidative stability of oil-in-water emulsions stabilized by biopolymer emulsifiers

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ABSTRACT

The objective of this research was to evaluate the influence of storage pH (3 and 7) and biopolymer emulsifier type (Whey protein isolate (WPI), Modified starch (MS) and Gum arabic (GA)) on the physical and oxidative stability of rice bran oil-in-water emulsions. All three emulsifiers formed small emulsion droplets (d_{32} < 0.5 μm) when used at sufficiently high levels: 0.45%, 1% and 10% for WPI, MS and GA, respectively. The droplets were relatively stable to droplet growth throughout storage (d_{32} < 0.6 μm after 20 days), although there was some evidence of droplet aggregation particularly in the MS-stabilized emulsions. The electrical charge on the biopolymer-coated lipid droplets depended on pH and biopolymer type: −13 and −27 mV at pH 3 and 7 for GA; −2 and −3 mV at pH 3 and 7 for MS; +37 and −38 mV at pH 3 and 7 for WPI. The oxidative stability of the emulsions was monitored by measuring peroxide (primary products) and hexanal (secondary products) formation during storage at 37 °C, for up to 20 days, in the presence of a pro-oxidant (iron/EDTA). Rice bran oil emulsions containing MS- and WPI-coated lipid droplets were relatively stable to lipid oxidation, but those containing GA-coated droplets were highly unstable to oxidation at both pH 3 and 7. The results are interpreted in terms of the impact of the electrical characteristics of the biopolymers on the ability of cationic iron ions to interact with emulsified lipids. These results have important implications for utilizing rice bran oil, and other oxidatively unstable oils, in commercial food and beverage products.

1. Introduction

Rice bran oil is finding increasing utilization in food, cosmetic, pharmaceutical and animal feed applications (Naivikul, Klinkesorn, & Santiwattana, 2008). Rice bran oil is primarily used as a frying oil, because of its relatively high flavour and oxidative stability compared to alternative oils (Naivikul, Klinkesorn, & Santiwattana, 2008; Van Hoed et al., 2006). The fatty acid composition of rice bran oil is similar to peanut oil in terms of total saturated and unsaturated fatty acids, except that there are more long chain fatty acids in peanut oil. Oleic, linoleic, and palmitic fatty acids are the major fatty acids in rice bran oil making up >75% of the total. The levels of *trans*-fatty acids have been reported to be very low in natural rice bran oil (Orthoefer & Eastman, 2004).

Rice bran oil has a relatively high concentration of unsaturated fatty acids, and is therefore susceptible to lipid oxidation. The oxidative deterioration of lipids affects the quality of foods, influencing their flavour, odour, and nutritive value (Frankel, Satué-Gracia, Meyer, & German, 2002). The rate at which oxidation takes place is dependent on several factors, such as the molecular structure of the lipids, the storage temperature, the presence of pro-oxidants and antioxidants, and the structural organization of the lipids (McClements & Decker, 2000; Nawar, 1996). Lipids are often present in food products in the form of emulsions. Many common food products exist as oil-in-water emulsions (e.g., beverages, dressings, sauces, soups, and deserts); in these products, the lipid portion is dispersed as miniscule droplets dispersed within an aqueous continuous phase (McClements, 2005). The susceptibility of these emulsified lipids to oxidation depends not only upon the factors mentioned previously, but also upon the surrounding molecular environment and interactions with other molecules within their immediate vicinity (Kellerby, Gu, McClements, & Decker, 2006a). A number of studies have highlighted the importance of transition metal catalysis as a major factor responsible for promoting lipid oxidation in emulsion systems (Berton, Ropers, Viau, & Genot, 2011; Guzun-Cojocaru et al., 2011; Waraho, Cardenia, Rodriguez-Estrada, McClements, & Decker, 2009). Iron, a transition metal, is a strong pro-oxidant that is ubiquitous in food systems. Transition metals that are in close proximity to surface-active lipid hydroperoxides at the lipid droplet

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interface will promote hydroperoxide degradation. Iron can decompose hydroperoxides (LOOH) into alkoxyl (LO•) and peroxyl (LOO•) radicals. In lipid systems, these highly reactive radicals abstract hydrogen from unsaturated fatty acids (LH) within their immediate vicinity, forming new radicals that can further promote oxidation, eventually leading to rancidity. The ability of iron to breakdown lipid hydroperoxides depends on its physical location relative to the surface of the emulsified lipid phase, since oxidation usually occurs at the oil–water interface (Demetriades, Coupland, & McClements, 1997b). This ability may be either hindered or promoted, due to the presence of an adsorbed emulsifier layer at the lipid droplet surfaces (Mancuso, McClements, & Decker, 2000).

In this study, we examined the influence of three different surface-active biopolymers on the oxidative stability of emulsified rice bran oil. These biopolymers were selected based on differences in their molecular characteristics: whey protein isolate is a mixture of amphoteric globular proteins (Dalgleish, 1997; Wilde, 2000); gum arabic is a mixture of anionic polysaccharides and protein fractions (Al-Assaf & Phillips, 2008; Dickinson, 2003; Garti & Leser, 2001); modified starch consists of starch molecules that have been chemically reacted with octenyl succinic anhydride (OSA) to give them some hydrophobic character (Given, 2009; Tan, 2004; Trubiano, 1995). Recent work in our laboratory showed that these three biopolymers could be used to successfully form and stabilize rice bran oil-in-water emulsions (Charoen et al., 2011). We hypothesized that the oxidative stability of emulsified rice bran oil would depend on the nature of the biopolymer emulsifier coating the lipid droplets, due to differences in the composition, structure, and properties of the interfacial layer. The aim of this study was therefore to test this hypothesis by comparing the oxidative stability of lipid droplets coated by different biopolymer emulsifiers at pH 3 and 7.

2. Materials and methods

2.1. Materials

Rice bran oil (RBO) was purchased from a food ingredient manufacturer (Thai Edible Oil Co., Ltd, Bangkok, Thailand). This RBO was isolated from various rice bran sources using a solvent extraction method. The composition of this product has previously been reported by other researchers (VanHoed et al., 2006). The fatty acid composition of the product was reported to be 19.8% palmitic acid, 44.6% oleic acid, 30.2% linoleic acid, and 0.9% linolenic acid. The lipophilic functional components in the RBO were reported to be: total sterol (1.83 g/100 g); oryzanol (0.3 g/100 g); total tocopherol and tocotrienol (0.062 g/100 g). The density of this oil was 915.30 ± 0.03 kg/m^3. The RBO was stored in a refrigerator prior to utilization. Whey protein isolate (WPI, 97.7 wt.% protein) was donated by Davisco Foods International (Le Sueur, MN, USA). Gum arabic (GA) was donated by TIC Gums (Philadelphia, USA). Modified starch (MS, PURITY GUM™ Ultra) was donated by the National Starch LLC (Bridgewater, NJ, USA). Sodium chloride, sodium citrate, sodium azide, ethylenediaminetetraacetic acid (EDTA), ferrous sulphate, and barium chloride were purchased from Sigma Chemical Company (St. Louis, Mo., USA). Double-distilled water was used to prepare all solutions and emulsions, which was obtained from a water purification system (Barnstead NANO pure infinity ultra pure Dubuque, Iowa). Ferrous iron-EDTA solutions were made by dissolving 200 μM EDTA and 200 μM ferrous sulphate in buffer solutions (10.0 mM sodium citrate, 0.01 wt.% sodium azide).

2.2. Methods

2.2.1. Emulsion Preparation

Aqueous phases were prepared by dispersing 0.45%WPI, 10.0%GA or 1.0%MS in aqueous buffer solutions (10.0 mM sodium citrate, 0.01 wt.% sodium azide), with and without ferrous iron-EDTA (200 μM) followed by stirring at room temperature overnight to ensure complete dispersion and hydration. These levels of emulsifier were selected based on our recent previous study (Charoen et al., 2011), *i.e.,* they were the minimum amounts required to form relatively small droplets (d < 0.6 μm) during homogenization. Rice bran oil-in-water emulsions were prepared by homogenizing 5.0 wt.% oil phase with 95.0 wt.% aqueous phase at ambient temperature. An emulsion pre-mix was prepared using a high-speed blender (2 min, Biospec Products Inc., Bartlesville, USA), which was then passed through a high pressure homogenizer (Model 101, Microfluidics, Newton, Massachusetts, USA) three times at 9320 psi. Samples of emulsions were then adjusted to either pH 3.0 or 7.0 using NaOH and/or HCl.

2.2.2. Emulsion characterization

Particle size and charge were measured using the approaches described previously (Charoen et al., 2011). The particle size distribution (PSD) of the emulsions was measured using a laser light scattering instrument (MalvernSizer2000, Malvern Instruments Ltd., Worcestershire, UK). The electrical charge (ζ-potential) of lipid droplets was determined using a particle electrophoresis instrument (ZEN3600, Nano-series, Zetasizer, Malvern Instruments, Worcestershire, UK). The particle size and -potential were observed during the course of the experiments.

2.2.3. Lipid oxidation measurements

Samples (1 ml) were placed in 10 ml glass vials, sealed with polytetrafluoroethylene (PTFE)/butyl rubber septa using a crimper and aluminium seals, and incubated at 37 °C in the dark. Oxidation was followed by measuring hydroperoxide (primary product) and headspace hexanal (secondary product) formation.

Lipid hydroperoxides were determined using a method adapted from Mancuso, McClements, & Decker (1999). Emulsion samples (0.3 ml) were added to 1.5 ml of isooctane/2-propanl (3:1 v/v). The mixture was then vortexed (10 s, 3 times) and the organic solvent phase was isolated by centrifugation at 1000g for 3 min. The organic solvent phase (0.2 ml) was added to 2.8 ml of methanol/1-butanol (2:1 v/v), followed by 15 μl of 3.9 M ammonium thiocyanate, and 15 μl of ferrous iron solution (prepared by adding equal amounts of 0.132 M $BaCl_2$ and 0.1444 M $FeSO_4$). After 20 min, the absorbance was measured at 510 nm using a spectrophotometer (Genesys 20, Thermo Spectronic, Waltham, MA). Lipid hydroperoxide concentrations were determined, using a standard curve made from cumene hydroperoxide.

Headspace hexanal was determined according to a method described by Panya et al., (2010) using a Shimadzu GC-2014A gas chromatograph (GC) equipped with an AOC-5000 auto-injector (Shimadzu, Tokyo, Japan). A 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/carboxen/PDMS) stable flex SPME fibre (Supelco, Bellefonte, PA) was inserted through the septum into the vial and exposed to the sample headspace for 15 min at 55 °C, extraction time 2 min. The SPME fibre was desorbed at 250 °C for 3 min in the GC detector, at a split ratio of 1:5. The chromatographic separation of volatile aldehydes was performed on a fused-silica capillary column (30 m × 0.32 mm i.d. × 1 μm) coated with 100% poly(dimethylsiloxane) (Equity-1, Supelco). The temperatures of the oven, injector, and flame ionization detector were 65, 250 and 250 °C, respectively. Sample run time was 10 min. Relative hexanal concentrations were determined using a standard curve made from dissolving different amounts of 3-hexanal in 10 ml of methanol and then dispersing them in buffer solution. In emulsions some of the hexanal may partition into the oil phase, and so the reported head-space hexanal concentrations should only be used to compare the relative formation of secondary products between different emulsion samples.