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Effects of sodium caseinate concentration and storage conditions on the oxidative stability of oil-in-water emulsions

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ABSTRACT

The oxidative stability of various oils (sunflower, camelina and fish) and 20% oil-in-water (O/W) emulsions, were examined. The mean particle size decreased from 1179 to 325 nm as sodium caseinate (emulsifier) concentration was increased from 0.25% to 3% in O/W emulsions ($P < 0.05$). Increasing the microfluidisation pressure from 21 to 138 MPa, resulted in a particle size decrease from 289 to 194 nm ($P < 0.05$). Emulsified oils had lower detectable lipid hydroperoxide and p-Anisidine values than their corresponding bulk oils ($P < 0.05$). The lipid hydroperoxide and p-Anisidine values of emulsions generally decreased as sodium caseinate concentration increased, and similarly decreased as microfluidisation pressure increased ($P < 0.05$). Increasing storage temperature of the emulsions from 5 to 60 °C, resulted in lower detectable lipid oxidation products during storage ($P < 0.05$).

1. Introduction

Essential polyunsaturated fatty acids (PUFAs) of importance in human nutrition include omega (ω)-6 PUFAs; linoleic (C18:2) and arachidonic (C20:4) acids, and ω-3 PUFAs; α-linolenic acid (ALA, C18:3), obtained from plant oils, and eicosapentaenoic acid (EPA, C20:5) and docasahexenoic acid (DHA, C22:6), obtained from fish oils. Omega-3 fatty acids bestow several health benefits, protecting against: heart disease, inflammatory disease, asthma, mood disorders and retinal diseases, along with aiding brain function (Arterburn, Hall, & Oken, 2006; Dyerberg, Bang, & Hjorne, 1975; Ruxton, Reed, Simpson, & Millington, 2004).

Lipid oxidation can lower the nutritional value and quality of foods, together with the formation of toxic compounds, off-flavours and off-odours (Chaiyasit, Elias, McClements, & Decker, 2007). Fatty acids, especially PUFAs are subject to rapid and/or extensive oxidation and other chemical changes upon exposure to air, light, transition metals, or heat during food processing. Primary oxidation is a free radical process, resulting in the formation of hydroperoxides (Osborn & Akoh, 2004). These odourless and flavourless transitionary intermediates are unstable, and decompose during lipid oxidation, to form secondary oxidation products, such as aldehydes, ketones, hydrocarbons and alcohols. Secondary oxidation products are small, volatile molecules, associated with oxidative rancidity (Chaiyasit et al., 2007). To meet the recommended intake levels of 0.8–1.1 g ALA/day, and 0.3–0.5 g EPA and DHA/day, ω-3 rich oils can be incorporated into various food systems (Kris-Etherton, Harris, & Appel, 2002). However, the successful manufacture of ω-3 enriched food products can be impeded by their high susceptibility to lipid oxidation. This problem may be overcome or delayed by incorporating them into emulsion systems. Emulsions are dispersed, multiphase systems consisting of at least two immiscible liquids, often water and oil (oil-in-water: O/W emulsion, or water-in-oil: W/O emulsion). Emulsifiers are surface active molecules that absorb to the surface of freshly formed droplets during homogenisation, forming a protective membrane, which prevents droplets from coming close enough together to aggregate (Ogawa, Decker, & McClements, 2003). A stable emulsion has no noticeable change in the size distribution of the droplets, their state of aggregation, or their spatial arrangement within the sample during storage. Physical properties such as droplet size, surface charge and viscosity, affect the creaming and oxidative stability of emulsions (Sun & Gunasekaran, 2009). A previous study reported that decreased particle size in soybean O/W emulsions lowered levels of lipid oxidation products (Nakaya, Ushio, Matsukawa, Shimizu, & Ohshima, 2005). However, another study reported that particle size had no effect on lipid oxidation in caprylic acid/canola O/W emulsions (Osborn & Akoh, 2004). A

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study reported lipid oxidation levels in food emulsions are generally accelerated as storage temperature is increased (Klinkesorn, Sophanodora, Chinachoti, McClements, & Decker, 2005). Yet, other studies reported that increased storage temperatures increased the antioxidant activity of whey and casein proteins, thereby improving the oxidative stability of such emulsions (Taylor & Richardson, 1980; Tong, Sasaki, McClements, & Decker, 2000). Negative temperature coefficients have also been reported in spray dried fish oil emulsions (Hogan, O' Riordan, & O' Sullivan, 2003).

The oxidation of emulsified oils differs to that of bulk oils, due to the presence of a droplet membrane, interactions between ingredients, and partitioning of ingredients between the oil, aqueous and interfacial regions (Coupland & McClements, 1996). Controlling the emulsifier type, location, and concentration at the oil–water interface may increase the oxidative stability of emulsions. Certain surface active proteins are used as emulsifiers due to their ability to absorb to an interface, aid formation, lower surface tension, provide a viscoelastic layer, improve stability, repulse transition metals from lipid droplets, and produce desirable physiochemical properties throughout emulsion processing, storage and utilisation (Dickinson, 2006). Following preliminary trials using various emulsifiers (whey protein isolate, calcium caseinate, phosphocasein, β-lactoglobulin and sodium caseinate; results not shown), sodium caseinate was selected, due to improved stabilisation and oxidative stability, and lower cost. As lipids are introduced into many food systems in the form of O/W emulsions, it is also important to examine their oxidative state in this form. The objectives of this study were to determine the effects of oil type (various fatty acid compositions), sodium caseinate concentration, oil droplet size and storage temperature on the oxidative stability of O/W emulsions. The formation and stabilisation of O/W emulsions were also of particular interest in this study, as these emulsions were subsequently used in the production of O/W/O spreads. Production and oxidative analysis of omega-3 enriched fat spreads were then carried out in another study (results not shown here).

2. Materials and methods

2.1. Materials

All chemical reagents and solvents were purchased from Sigma–Aldrich (Dublin, Ireland) except *n*-hexane which was purchased from Fisher Scientific (Dublin, Ireland). Sodium caseinate (NaCas) was supplied by Dairygold (Mallow, Co. Cork, Ireland) and contained 91.9% protein. Refined camelina oil and refined sunflower oil were sourced from Statfold Seed Oil Ltd (Staffordshire, UK). The camelina oil contained 0.006% tocopherols, and fatty acid analysis determined it contained 34.1% ALA (C18:3, ω-3), 17.2% linoleic acid (C18:2, ω-6), 15.5% eicosenoic acid and 14.6% oleic acid (C18:1 c-9). Its lipid hydroperoxide value was 6.15 μmol hydroperoxides/g oil and p-Anisidine value was 6.18. According to manufacturer's specifications, the oil had a peroxide value of <5 and an iodine value of 140–180. Fatty acid analysis of the sunflower oil determined it contained 60.9% linoleic acid, 25.4% oleic acid, 6.21% palmitic acid (C16:0) and 4.1% stearic acid (C18:0). Its lipid hydroperoxide value was 0.42 μmol hydroperoxides/g oil and p-Anisidine value was 3.25. According to manufacturer's specifications, the oil had a peroxide value of ⩽5, and an iodine value of 120–140. Refined, bleached, dried, cold-filtered and deodorised omega fish oil (a blend of fish oils processed from fish species containing high levels of omega-3 fatty acids), without added antioxidants, was supplied by Lysi (Reykjavik, Iceland). Fatty acid analysis of the omega fish oil determined it contained 20.3% EPA (C20:5, ω-3), 13.2% DHA (C22:6, ω-3), 15.4% palmitic acid and 10.4% oleic acid. The lipid hydroperoxide value of the oil blend camelina: omega fish oil (72:28) was 3.75 μmol hydroperoxide/g oil and the p-Anisidine value was 8.39. According to manufacturer's specifications, the oil had a peroxide value of 0.8 meq. O2/kg, a p-Anisidine value of 13.2 and contained no added antioxidants. Distilled water was used in all experiments.

2.2. Methods

2.2.1. Fatty acid analysis of the oil

Methylation of the oil samples was first achieved by dissolving 20 mg of the respective samples in 5 ml *n*-hexane. Subsequently, 200 μl of 2 M KOH in methanol were added to the samples, which were then vortexed vigorously to facilitate the methylation. After 5–7 min, the methylation reaction was terminated via the addition of 0.5 g sodium hydrogen sulphate monohydrate. Following centrifugation, a representative sample was removed and diluted appropriately. The fatty acid methyl esters (FAME) were separated using a CP Sil 88 column (100 m × 30.25 mm i.d., 0.20 mm film thickness) (Chrompack, Middelburg, The Netherlands) and quantified using a gas liquid chromatograph (3400) (Varian, Harbor City, CA, USA). The GLC instrument was calibrated using a range of commercial fatty acid methyl ester standards. FAMEs were analysed by gas liquid chromatography (GLC) using the parameters described by Childs et al. (2008). The GLC instrument was fitted with a flame ionisation detector (FID) and helium (37 psi) was used as the carrier gas. The injector temperature was held isothermally at 225 °C for 10 min, and the detector temperature was 250 °C. The column oven was held at an initial temperature of 140 °C for 8 min, and was then increased at a rate of 8.5 °C per minute, to reach a final temperature of 200 °C, which was held for 50 min. The data were recorded and analysed on a Varian Datastar system (Harbor City, CA, USA).

2.2.2. Preparation of emulsions

A series of emulsions were prepared using an M-110EH Microfluidiser (Microfluidics, Neon, Massachusetts, USA) at various pressures (21–138 MPa). The aqueous phase was prepared by heating distilled water to 50 °C, then slowly adding sodium caseinate powder, while stirring for 2 h. The solution was stored overnight at 5 °C, and the pH was subsequently adjusted to 7.0, by adding 1 M sodium hydroxide (NaOH) at 20 °C. The oil phase (20%) was added to the aqueous phase and mixed using a Silverson L4RT mixer (Silverson Machines Ltd, Waterside, Chesham, Bucks, England) for 5 min, followed by microfluidisation, using a M-110EH Microfluidiser (at various pressures), fitted with a Butech pressure system, and a Y shaped ceramic interaction chamber. Sodium azide (0.02%) was added to the emulsions to decrease microbial activity during storage. The composition, production and storage conditions can be seen in Table 1.

2.2.3. Röse Gottlieb fat analysis

Determination of fat content was carried out gravimetrically using the Röse Gottlieb extraction method (IDF, 2003). Ammonia and ethanol were used to separate the protein from the oil. Extraction solvents diethyl ether and petroleum spirit were used to extract the oil.

2.2.4. Storage of oils and emulsions

Bulk oils and O/W emulsions were stored in 30 ml screw cap glass tubes at refrigeration temperature (5 °C), room temperature (22 °C) and oven temperature (60 °C), and the oxidation state was determined regularly during storage. An unopened glass tube containing the emulsion/oil was used each week for oxidative analysis. Tests were carried out in triplicate.