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Oxidative stabilization of mixed mayonnaises made with linseed oil and saturated medium-chain triglyceride oil

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ABSTRACT

Mayonnaises, made with either saturated medium chain triglyceride (MCT) oil or unsaturated purified linseed oil (LSO), were mixed. Raman confocal microspectrometry demonstrated that lipid droplets in mixed mayonnaise remained intact containing either MCT oil or LSO. Peroxide formation during storage was lower in mixed mayonnaise compared to LSO mayonnaise, while in mixed oil mayonnaise the level of peroxides was constantly low. Mixed oil mayonnaise had a lower rate of oxygen consumption than mixed mayonnaise, LSO mayonnaise having the highest rate. The decay of water-soluble nitroxyl radicals showed radicals are formed in the aqueous phase with the same rate independent of the lipids. This was also reflected in decay of α-tocopherol during storage being similar in MCT and LSO mayonnaises, but being stable in mixed oil mayonnaise and mixed mayonnaise. Results suggest that other effects than simply diluting unsaturated triglycerides with saturated triglycerides is causing the oxidative stabilization observed for mixed mayonnaise and mixed oil mayonnaise.

1. Introduction

Many processed foods contain emulsified fat, and understanding the physical and chemical instability of emulsions has accordingly received a great deal of attention in food science. Oxidation of unsaturated fatty acids, and more recently oxidation of proteins, have been the main focus of chemical instability of emulsions, whereas the change of droplet size and the eventual separation of bulk lipid and water phases has been the focus of understanding the physical instability. Lipid oxidation in emulsified systems has been studied extensively on a macroscopic scale, but there is less knowledge of the physical and chemical processes on the microscopic scale contributing to the overall oxidative reactions.

The effect on oxidative stability of mixing emulsions with different lipid composition is unknown. One proposition is that due to coalescence, the contents of the oil droplets would mix with two or more droplets merging into one, which would cause an increment in the droplet size (McClements, 2005) and lead to physical instability of the emulsion. Another proposition is that the contents of the oil droplets mix, but the sizes of the droplets remain the same; and therefore the emulsion would be physically stable. This could happen due to reversible coalescence, which could include fusion and fission, or permeation of fatty acids from the pores of the interface of one droplet to another in very close proximity (Malassagne-Bulgarelli & McGrath, 2009). On the other hand, fatty acid exchange between two oil droplets with different fatty acid compositions might occur via transportation mechanisms by surfactant micelles. These are able to incorporate fatty acids from one droplet and carry them through the aqueous phase to another droplet, causing mixed contents with characteristics of the two oils and retaining the droplet size (McClements, Dungan, German, & Kinsella, 1992). In addition, a study conducted on oil-in-water emulsion crystallization showed there was intermixing of the contents of oil droplets in the emulsion due to transportation mechanisms supplied by micelles of emulsifier in the aqueous phase (Dickinson, Goller, McClements, & Povey, 1991).

The objective of this study was to investigate the oxidative stability of a food related oil-in-water emulsion containing two different types of oil droplets. This has been carried out by making mayonnaises either with saturated medium-chain triglyceride (MCT) oil or with purified unsaturated linseed oil (LSO). Mixed mayonnaises were made from these two mayonnaises. Also a mayonnaise was made with a mixed MCT and linseed oil. Raman confocal microspectrometry was applied to investigate the composition and spatial distribution of the lipid droplets in the mayonnaises, as well as to determine the physical stability of the emulsions. The oxidative stability has been studied by following the formation of peroxides and the loss of α-tocopherol during storage, as well as oxygen consumption measurements and radical

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trapping with electron spin resonance (ESR) spectroscopy for characterization of oxidation events on a shorter time scale.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical grade. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 4[-N,N-dimethyl-*N*-(2-hydroxyethyl)]ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl chloride (TEMPO choline) were obtained from Molecular Probes Inc., Eugene, Oregon, USA. Nonpolar fluorescent stain BODIPY$^{493/503}$ (D-3922) was purchased from Life Technologies Corporation, Oregon, USA. (±)-α-tocopherol was purchased from Fluka Chemie GmbH, Steinheim, Switzerland. MCT (medium-chain triglyceride) oil was from Cognis GmbH, Ludwigshafen, Germany. Linseed oil (LSO) was purchased from a local supermarket and purified before use by alumina column chromatography according to method by Yoshida, Kondo, and Kajimoto (1992) with some small changes: LSO was mixed with hexane 1:1 and purification was done once. The purification process ensured that the oil was cleaned from naturally occurring tocopherols, peroxides and trace metals (Fuster, Lampi, Hopia, & Kamal-Eldin, 1998). After evaporation process the oil was extracted from hexane by rotational evaporator (Büchi Rotavapor R-144, Labortechnik AG, Flawil, Switzerland). Vinegar, Dijon mustard, lemon juice and pasteurized egg yolk were purchased from a local supermarket.

2.2. Mayonnaise

Mayonnaise was produced in small batches and were made of egg yolk (12 wt%), mustard (2 wt%), oil (82 wt%), vinegar (2 wt%) and lemon juice (2 wt%). 83% of the mayonnaise was composed of oil phase and the rest was the aqueous phase. There were two different mixing methods used – either the mayonnaise was made using Ultra-Turrax T25 (IKA Works GmbH & Co. KG, Staufen, Germany) with dispersion element of 8 mm in diameter at a speed of 8000 rpm or mixed manually; and three different mayonnaise systems – either MCT oil or LSO mayonnaise, mixed oils (MO) mayonnaise, which consisted of one part of LSO and four parts of MCT oil mixed before mayonnaise was emulsified, or mixed mayonnaises (MM), which contained one part of LSO mayonnaise and four parts of MCT mayonnaise mixed together. For the ESR experiments mayonnaise samples were made without lemon juice but with 4 wt% vinegar.

2.3. Composition of oils by FAME analysis

MCT oil and LSO were analyzed by gas chromatography for fatty acid methyl esters (FAMEs) according to the method by Jart (1997) with some alterations: 1 ml of 0.025 M sodium methylate was added to the pure oil sample and hexane was added to the clear solution with 4 ml of saturated sodium chloride. Settings for gas chromatography were as follows: GC-chromatograph (5890 A-II; Hewlett–Packard Co., San Fernando, CA) with a 50 m × 0.25 mm × 0.20 μm CP-Sil 88 column (Chrompack, Middelburg, The Netherlands) under the following oven temperature program and conditions: 1 μl was injected to 1:25 split-flow with a constant flow of 1 ml/min, injector temperature was 250 °C and the detector temperature was 300 °C. The oven program was 50 °C for 1 min, and then increased by 15 °C/min to 180 °C. From that point on the rate was changed to 3 °C/min to 240 °C. This temperature was kept for 10 min. The fatty acid composition was calculated from the chromatograms as percentage of total fatty acid content.

2.4. Crystallization and melting temperatures of MCT oil, LSO, MCT mayonnaise, and LSO mayonnaise with differential scanning calorimetry (DSC)

The crystallization and melting temperatures of MCT oil, LSO, MCT mayonnaise, and LSO mayonnaise were investigated with a DSC instrument equipped with STAR^e SW 9.20 system (DSC 1, Mettler Toledo, Columbus, Ohio, USA) according to the following method: Starting temperature 25 °C was kept for 5 min, and then the temperature was increased up to 40 °C and kept for 5 min. After 5 min the temperature was lowered to −30 °C and kept for 5 min. The program finished at 25 °C. The samples were scanned with a scanning rate of 10 °C/min. Samples of 7.26–10.19 mg were weighed into 40 μm aluminium pans (ME-27331 Al-crucibles with pin), sealed hermetically with aluminium covers and measured with an empty aluminium hermetically sealed pan as a reference.

2.5. Confocal laser scanning microscopy (CLSM)

CLSM imaging was done on a typical mayonnaise sample using non-polar fluorescent stain BODIPY$^{493/503}$ (D-3922) at a concentration of 1 μM. Objective HCX PL APO lambda blue 20.0×, NA 0.70 oil immersion, argon laser 488 nm, image resolution 1024 × 1024, pinhole 1 AU, zoom 6.3×, line averaging were used.

2.6. Droplet size distribution

Size distribution of the droplets in the mayonnaises was determined by Laser Diffraction Mastersizer Micro Pro (Malvern Instruments Ltd., Malvern, UK), and calculated using the software based on Mie theory of laser light scattering. It was assumed that the sample was polydisperse. Volume mean diameter D[4,3] and surface mean diameter D[3,2] of the droplets were calculated for each of the mayonnaises.

2.7. The spatial distribution from the variation in chemical composition of the mayonnaises by Raman confocal microspectrometer

Three different emulsion systems were analyzed – MCT oil mayonnaise, LSO mayonnaise and the mixture of MCT oil and LSO mayonnaise (1:1). Raman measurements were performed using a home-built Raman confocal microspectrometer (Pully, Lenferink, & Otto, 2010; Sijtsema, Wouters, de Grauw, Otto, & Greve, 1998; van Manen, Lenferink, & Otto, 2008). A krypton ion laser (Coherent, Innova 90 K, Santa Clara, CA, USA) with excitation wavelength 647.1 nm, and a dry objective Plan Neofluar 40×, NA 0.95 (Carl Zeiss, Thornwood, NY, USA) were used to illuminate and collect the Raman-scattered signal (photons) from the sample. The scattered light was filtered by a razor-edge filter (Semrock Inc., Rochester, New York, USA) to reduce reflected laser and Rayleigh-scattered light, and focused onto a 15 μm diameter pinhole. The Raman images were obtained from three-dimensional hyperspectral (spatial × spatial × spectral) datasets with a spectral resolution of 1.85 cm^{-1}/pixel to 2.85 cm^{-1}/pixel over the wavenumber range from 20 cm^{-1} to 3670 cm^{-1}. The Raman spectra were acquired by raster scanning with a laser output power of 130 mW. The acquired data was converted to real Raman data by using software that removes cosmic rays, subtracts the camera off-set, and converts the wavenumbers axis from pixels to wavenumbers using the bands of toluene as calibration and the emission of a tungsten lamp of known temperature as a pixel-to-pixel transmission correction. The output of the software was organized in a matrix format, where each column represented the position the spectra was