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Effects of solubility characteristics of sensitiser and pH on the photooxidation of oil in tuna oil-added acidic O/W emulsions

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ABSTRACT

The effects of sensitisers and pH on the oil oxidation of acidic O/W emulsions were studied under light by measuring hydroperoxide content and headspace oxygen consumption in the emulsions. The emulsions consisted of canola and tuna oil (2:1 w/w, 32%), diluted acetic acid (64%), egg yolk powder (4%), chlorophyll b or erythrosine (5 μM), and/or diazabicyclooctane (DABCO) or sodium azide (0.5 M). The emulsion pH values were 2.67, 3.68, and 6.27. Chlorophyll increased oil oxidation in the emulsion under light via singlet oxygen production while erythrosine did not. DABCO significantly decreased photooxidation of the oil containing chlorophyll, suggesting singlet oxygen involvement. However, sodium azide increased photooxidation of the oil containing chlorophyll possibly via azide radical production under acidic conditions. The oil photooxidation was higher in the emulsion containing chlorophyll at pH 6.27 than at pH 2.67 or 3.68, primarily by singlet oxygen and secondarily by free radicals produced from hydroperoxide decomposition.

1. Introduction

Oxidation is one of the most frequently encountered reactions that deteriorates the quality of foods, and is especially critical in oil-containing foods. The oxidation of edible oils has been studied with greater emphasis on autoxidation and thermal oxidation than on photooxidation because most edible oils are refined, free from sensitisers, and used mostly in deep-fat frying. Photooxidation, however, is more important in oils used for salad dressing, which are in clear or semi-clear bottles, which allow light to pass during shelf display and marketing and are usually consumed at relatively low temperatures. Salad dressing contains oil as a main ingredient, and fruits and vegetables are added for color and flavor to increase consumer attraction and acceptability. Some of these materials can provide sensitisers to produce singlet oxygen from atmospheric triplet oxygen under light (Choe & Min, 2005). Oil oxidation by singlet oxygen proceeds very fast compared to oxidation by triplet oxygen (Min & Boff, 2002), and more unsaturated oil is more susceptible to oxidation by both singlet and triplet oxygen than less unsaturated oil (Min & Boff, 2002).

Fish oil is regarded as an excellent oil since it contains high amounts of beneficial eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), known to prevent coronary heart disease (Rissanen, Voutilainen, Nyyssönen, Lakka, & Salonen, 2000). Fish oil is still limited to the capsule form of functional foods due to its high content of highly polyunsaturated fatty acids, although it can be used as an auxiliary oil in salad dressing to give physiological functionality. Salad dressing is an emulsion consisting of oil and acidic water occasionally with pigments, and is stabilized by an emulsifier. It has been shown that oil autoxidation in an emulsion system occurs differently from that in a bulk oil system since an interface is present (McClements & Decker, 2000), and thus mass transfer is an important key in the oil oxidation of emulsions (Liu, Fu, Yin, & Liao, 2005; McClements & Decker, 2000). Pigments, such as chlorophyll or riboflavin can cause fast singlet oxygen-related oxidation in emulsions under light (Huang, Choe, & Min, 2004; Lee & Choe, 2008). Depending on the composition of an emulsion, pH varies, which might have different effects on the photooxidation of oil in an emulsion containing sensitisers. Also, the solubility nature of sensitisers may result in different behavior in the photooxidation of oils in emulsions.

Most studies on oil oxidation in emulsions have examined autoxidation in the dark (Hu, McClements, & Decker, 2003; McClements & Decker, 2000), and there are few reports on photooxidation. To our knowledge, singlet oxygen-related photooxidation of oil in emulsion systems has not been reported. To extend the use

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of fish oil in emulsion foods, such as salad dressing, it is necessary to study the photooxidation of emulsions supplemented with fish oil under various pH conditions as well as the use of pigments as sensitisers with different solubility characteristics, prior to industrial application. Therefore, this study was performed: (1) to investigate the oxidation of tuna oil-added acidic O/W emulsions containing water- or oil-soluble sensitisers under light, (2) to show the involvement of singlet oxygen in the oxidation of emulsions containing sensitisers under light by using singlet oxygen quenchers, and (3) to show the effects of pH on singlet oxygen-related photooxidation of tuna oil-added acidic O/W emulsions.

2. Materials and methods

2.1. Materials and chemicals

The RBD (refined, bleached, and deodorized) canola and tuna oil were products of CJ Co. (Seoul, Korea) and Neomega Co. (Daejeon, Korea), respectively. Tocopherols were completely removed from these oils by passing the oil with n-hexane through a glass column (30 mm i.d. × 300 mm) packed with alumina (Type WN-3; Sigma–Aldrich Co., St. Louis, Mo., USA) according to the method of Lee and Choe (2009). The n-hexane in the eluent was completely removed by a rotary evaporator (N,N series; Eyela, Tokyo, Japan) at 40 °C to achieve tocopherol-stripped canola (TSCO) and tuna oil (TSTO). The fatty acid compositions, peroxide and conjugated dienoic acid contents, and tocopherol contents of the TSCO and TSTO were analyzed by gas chromatography (Lee & Choe, 2009), AOCS Cd 8-83 and Ti 1a-64 methods (1990), and HPLC (Lee, Lee, & Choe, 2007), respectively. Chlorophyll b, diazabicyclooctane (DABCO), and cumene hydroperoxide (CuOOH) were products of Sigma–Aldrich Co. (St. Louis, Mo., USA), and egg yolk powder was purchased from Into Food Co. (Incheon, Korea). Erythrosine and sodium azide were purchased from Junsei Chemical Co. (Tokyo, Japan) and Shinyo Pure Chemical Co. (Osaka, Japan), respectively. All other chemicals were of analytical grade.

2.2. Preparation of tuna oil-added acidic O/W emulsion and its photooxidation

The tuna oil-added acidic W/O emulsion (100 g) consisted of TSCO (21.4 g), TSTO (10.6 g), 5% acetic acid solution (0, 6.4, or 48 g) with additional distilled water to make 64 g of solution (64, 57.6, or 16 g, respectively), and egg yolk powder (4 g). The final pH of the emulsion was 6.27, 3.68, or 2.67. Water-soluble erythrosine or oil-soluble chlorophyll b as sensitisers at 5 μM, and/or DABCO or sodium azide as singlet oxygen quenchers at 0.5 M were also added. A sample that did not contain any sensitiser or singlet oxygen quencher was considered the control. All ingredients were mixed for 30 s and homogenized in a Ultra-Turrax T25 homogenizer equipped with an S25N-25F dispersing tool (IKA Instruments, Staufen, Germany) at 10,000 rpm for 6 min. Light was excluded during sample preparation as much as possible. The viscosity of the final emulsion was 0.07 dPa.

Ten grams of the emulsion were transferred into 20 ml glass serum vials, which were then tightly capped with rubber septa and aluminum caps. The vials were placed in an incubator (LBI-250; Daihan Labtech Co., Seoul, Korea) with fluorescent light of 1700 lux at 25 °C for 48 h for oxidation. The lipid oxidation mechanism by short-lived singlet oxygen is different from free radical autoxidation only at the initiation, and free radical formation after initiation is a common result in both kinds of oxidation (Choe & Min, 2005). Therefore, 48 h was taken as maximum time to consider singlet oxygen oxidation as much as possible. Samples for the dark system were prepared by covering the vials with aluminum foil. All samples were prepared in duplicate.

2.3. Evaluation of oil oxidation in tuna oil-added acidic O/W emulsion

Oil oxidation in the tuna oil-added acidic O/W emulsion was determined by measuring the hydroperoxide content in the oil and oxygen content in the headspace of sample vials. The hydroperoxide content of the oil in the emulsion was determined by the ferric thiocyanate method (Shantha & Decker, 1994). The emulsion (0.3 ml) was mixed with a 1.5 ml mixture of isooctane and 2-propanol (3:1, v/v) for 10 s followed by centrifugation (MIKRO 200; Hettich, Tuttlingen, Germany) at 1000*g* for 2 min, with three repetitions. A solution (2.8 ml) of methanol and chloroform (2;1, v/v), 3.94 M ammonium thiocyanate solution (15 μl), and 15 μl of 0.132 M $BaCl_2$ and 0.144 M $FeSO_4$ solution were added to the organic layer (200 μl), in the respective order. After 20 min of standing at room temperature, the absorbance of the solution was read at 510 nm with a UV–Visible spectrophotometer (HP8453; Hewlett Packard, Wilmington, Del., USA). The hydroperoxide content of the oil was expressed with CuOOH where the calibration curve was 'Absorbance = 0.9429 × (mmol CuOOH eq/kg of oil) − 0.0265, r^2 = 0.9924.'

The headspace oxygen content was determined by gas chromatography (Lee & Choe, 2009). The headspace gas (0.5 ml) of the sample vial was injected into a Younglin M600D gas chromatograph (Younglin Co., Ltd.) with a 2.5 ml gas-tight syringe (Hamilton Co., Reno, NV, USA). The detector was a thermal conductivity detector and a stainless steel column packed with a 80/100 mesh molecular sieve 13X (1.83 m × 0.32 cm; Altech, Deerfield, Ill., USA) was used. Helium (99.995%) was the carrier and auxiliary gas. The oven, injector, and detector temperatures were 35, 100, and 140 °C, respectively. Areas of the oxygen peak in the chromatograms were converted to μmole of oxygen in 1 ml of headspace gas under the assumption that atmospheric air contains 20.946% oxygen, which gives the result that 1 ml of air is equivalent to 9.35 μmole oxygen (Parker, 1982). The amount of oxygen consumed by the oil in the emulsion for oxidation was calculated by subtracting the headspace oxygen content of the oxidized samples from the oxygen content in the headspace of the samples before oxidation (blank) which was 8.62 μmole/ml.

2.4. Data analyses

SAS (Version 8.2; SAS Inst. Inc., Cary, Nc., USA) and Microsoft Excel 2003 (Microsoft Corporation, Seoul, Korea) were used for the statistical treatment of the data. Statistical treatment included Duncan's multiple range test at 5% significance level as well as determination of means and standard deviations.

3. Results and discussion

3.1. Chemical characteristics of canola and tuna oil

Table 1 shows the chemical characteristics of TSCO and TSTO. TSCO contained palmitic (4.55%), stearic (2.02%), oleic (66.00%), linoleic (20.41%), and linolenic (7.02%) acid, providing 27.43% of polyunsaturated fatty acids. This composition was similar to that in another study with canola oil (Lee & Choe, 2009). TSTO contained myristic (4.30%), palmitic (21.62%), palmitoleic (6.68%), stearic (4.33%), oleic (20.75%), linoleic (2.20%), linolenic (0.35%), eicosenoic (6.93%), eicosapentaenoic (12.08%), and docosahexaenoic (20.76%) acid, providing 35.39% of polyunsaturated fatty acids, which was similar to the report of Klinkesorn, H-Kittikun, Chinachoti, and Sophanodora (2004).

The TSCO did not have any peroxides, but it contained conjugated dienoic acids (CDA) at 0.56%. The peroxide value (POV) and CDA content of TSTO were 1.34 meq/kg oil and 1.09%, respectively.