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Lipid oxidation induced oxidative degradation of cereal beta-glucan

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ABSTRACT

In food systems, lipid oxidation can cause oxidation of other molecules. This research for the first time investigated oxidative degradation of β-glucan induced by lipid oxidation using an oil-in-water emulsion system which simulated a multi-phased aqueous food system containing oil and β-glucan. Lipid oxidation was monitored using peroxide value and hexanal production while β-glucan degradation was evaluated by viscosity and molecular weight measurements. The study showed that while lipid oxidation proceeded, β-glucan degradation occurred. Emulsions containing β-glucan, oil and ferrous ion showed significant viscosity and molecular weight decrease after 1 week of oxidation at room temperature. Elevated temperature (40 °C) enhanced the oxidation reactions causing higher viscosity drop. In addition, the presence of β-glucan appeared to retard the hexanal production in lipid oxidation. The study revealed that lipid oxidation may induce the degradation of β-glucan in aqueous food systems where β-glucan and lipids co-exist.

1. Introduction

(1 → 3)(1 → 4)-β-D-Glucan (β-glucan) is a major non-starch polysaccharide in cereals, especially in oats and barley. β-Glucan is water soluble and can form viscous solutions and even gels, which are dependent on its structural properties. These properties are affected by concentration, molecular weight, conformation, ratio of (1 → 4)-β- to (1 → 3)-β-linkages and the length of the cellulose-like blocks of glucose units (Lazaridou & Biliaderis, 2007; Lazaridou, Biliaderis, & Izydorczyk, 2003). The health claims for β-glucans from oats and barley concerning the lowering of blood cholesterol and postprandial glucose response have been approved by European Food Safety Authority EFSA (2011a, 2011b). The health effects are suggested to result from the ability of β-glucan to enhance viscosity in the digestive track, thus, affecting the absorption and excretion of glucose, cholesterol and bile acids (EFSA, 2011a, 2011b; Wood, 2010). Thus, for functionality it may be essential that viscosity enhancement properties of β-glucan are maintained during processing and storage of the product.

During processing and storage, there are several factors that can lead to degradation of β-glucan in food products. In addition to the enzymatic and acid hydrolysis that are well-studied, depolymerisation by oxidative degradation has been recently shown (Kivelä, Gates, & Sontag-Strohm, 2009; Kivelä, Nyström, Salovaara, & Sontag-Strohm, 2009). Hydroxyl radical (OH·) is the most reactive of all reactive oxygen species (ROS), and thus, it can be an efficient initiator of chemical oxidation reactions. Hydroxyl radicals can be formed via several different pathways, for example as a decomposition product of hydrogen peroxide (H_2O_2) in the Fenton reaction, which is catalysed by the transition metals such as ferrous ions (Fe^{2+}) (Haber & Weiss, 1934). Kivelä et al. (2009) showed that oxidative degradation of β-glucan can also occur in aqueous solution containing ascorbic acid. In the presence of transition metal catalysts, ascorbic acid facilitates reduction of molecular oxygen to hydrogen peroxide, which can then decompose to hydroxyl radicals (Guo, Yuan, Wu, Xie, & Yao, 2002).

Current studies on oxidative degradation of β-glucan have focused on hydroxyl radicals mediated oxidation reaction (Faure, Andersen, & Nyström, 2012; Faure, Werder, & Nyström, 2013; Mäkelä, Sontag-Strohm, & Maina, 2015). As another common source of radicals in food systems, lipid oxidation should also be considered. In foods, lipid oxidation results in several kinds of

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radicals during the initiation and propagation reactions (Kamal-Eldin & Pokorny, 2005). The lipid alkyl radicals (L·) formed from unsaturated lipids (LH) can react with oxygen to form reactive hydroperoxides (LOOH). Even trace amounts of these hydroperoxides may lead to excessive oxidation in the presence of transition metals leading to formation of several radicals in the propagation stage (McClements & Decker, 2000). Recently alternative pathways for this traditional chain reaction have been proposed and the study indicated various oxidation products that may not be considered in routine analyses (Schaich, 2012). Radicals that are commonly produced in lipid oxidation are listed in Fig. 1. These radicals are able to abstract hydrogens from any molecules with labile hydrogens, leading to co-oxidation of these molecules (Schaich, Shahidi, Zhong, & Eskin, 2013). The co-oxidation of proteins (Schaich, 2008), DNA (Yang & Schaich, 1996), starch (Ishii, Shimada, Yoshimatsu, Kainuma, & Suzuki, 1976) and β-cyclodextrin (Kawakishi, Satake, Komiya, & Nagoya, 1983) during lipid oxidation has been documented. As a result, cross-linking, degradation and other changes in chemical and physical properties of these macromolecules have been shown.

In food products, oil is typically present in the form of oil-in-water emulsions (O/W) e.g. in milk, cream, fruit beverages, soups, salad dressings and sauces (McClements & Decker, 2000). β-Glucan can be a natural part of emulsion products, like in functional drinkable oat-based products (Angelov, Gotcheva, Kuncheva, & Hristozova, 2006). Additionally, β-glucan can be used as a stabiliser in emulsion containing products as shown by Burkus and Temelli (2000) who studied the stabilisation of canola oil O/W emulsions by barley β-glucan. The main mechanism of stabilisation was attributed to the increase in viscosity by the added β-glucan. Consequently maintaining the physical state of β-glucan is therefore essential for the long term stability of emulsions.

The role of lipid oxidation in polysaccharide oxidation chemistry is relevant in cereal products such as drinks which contain dispersed lipid phases. In this study, lipid radicals were hypothesised to be able to attack β-glucan molecules leading to their oxidative degradation. An oil-in-water emulsion model was used to simulate the multi-phased aqueous food system where lipid and β-glucan coexist. Lipid oxidation was evaluated by determining peroxide value and hexanal production while oxidative degradation of β-glucan was investigated by viscosity and molecular weight analysis.

2. Materials and methods

2.1. Production of lipid hydroperoxides and stock emulsions

Purified rapeseed oil (RO) and methyl linoleate (ML, Nu Check Prep. Inc., Elysian, MN, USA, purity > 99%) were used in this study. Rapeseed oil was purified as described by Lampi, Dimberg, and Kamal-Eldin (1999). The purified rapeseed oil was stored in heptane at a concentration of 0.29 g/ml. The final content of α- and γ-tocopherol in the purified rapeseed oil was less than 1 μg/g.

A 6% oil-in-water (o/w) emulsion (stock emulsion) was prepared using oil (RO or ML) and 0.6% Tween20 (polyoxyethylene sorbitan monolaurate, Merck-Schuchardt, Germany) as an emulsifier. The stock emulsion was prepared by homogenising the mixture for 5 min with an ultrasonicator (Labsonic U Braun, Allentown, PA). During sonication, the emulsion was kept in an ice bath. In addition to non-oxidised oil (nRO), RO and ML were oxidised at 55 °C for 6 days in an open container to produce lipid hydroperoxides (LOOH) before stock emulsion preparation. ML was also oxidised under limited oxygen supply to produce mildly oxidised ML in order to observe the effect of hydroperoxide concentration on the oxidation of β-glucan.

2.2. Preparation of β-glucan solutions

Barley β-glucan (BBG) solutions (0.7% (w/v)) were prepared by weighing β-glucan (High Viscosity Barley beta-glucan, purity above 94%, Megazyme, Ireland) into a volumetric flask and wetting it with 99.5% ethanol (8% of the final volume). MilliQ-water (Millipore system, Merck Millipore, Germany) was added up to 80% of the total volume and solution was stirred at 85 °C for 2 h. After cooling down, the flask was filled to the mark and stirring was continued for 1 h at room temperature.

2.3. Production of emulsions containing β-glucan

β-Glucan containing emulsions were prepared by adding the stock emulsion and iron (II) sulphate heptahydrate ($FeSO_4{\cdot}7\ H_2O$) (Merck, Germany) to the β-glucan solutions. The final emulsion (BBG + oil + Fe) contained 0.56% (w/v) β-glucan, 1.0% oil, 0.1% emulsifier and 1.0 mM ferrous sulphate heptahydrate. The final emulsions were mixed adequately by vortexing to obtain uniform emulsions.

2.4. Experimental set-up

Four different oils were used for oxidation of β-glucan: non-oxidised RO (nRO), oxidised RO, mildly oxidised ML (MML) and highly oxidised ML (HML) (Table 1). As shown in Table 1, all samples were oxidised at room temperature (T_r) except samples from set RO-40 °C which were oxidised at 40 °C. The effect of a metal catalyst on emulsions containing β-glucan and oil was evaluated by preparing emulsions with or without 1 mM iron (II) sulphate heptahydrate (BBG + oil + Fe and BBG + oil samples, respectively). Control samples included oil with and without metal catalyst (oil + Fe and oil samples, respectively) and β-glucan with and without metal catalyst (BBG + Fe and BBG samples, respectively). In addition, control samples with ethanol (oil + Fe (ethanol) and oil (ethanol)), prepared similarly to β-glucan solutions, were included to study the effect of ethanol on lipid oxidation. The samples and controls were oxidised for 1 week and they were analysed immediately (day 0) and after 3 and 7 days. All samples were prepared in triplicates.

2.5. Analysis of lipid oxidation

2.5.1. Peroxide value measurement

The peroxide value of samples was measured with the ferric thiocyanate method as described by Ueda, Hayashi, and Namiki (1986). 200 μl of 30% (w/v) aqueous solution of ammonium thiocyanate (NH_4SCN, Sigma–Aldrich, USA) was added into 10 ml 96% (v/v) ethanol (Altia Oyj, Finland) after which 200 μl sample solution (after appropriate dilution) was added. 200 μl of 20 mM $FeCl_2$ (Sigma–Aldrich, Germany) in 3.5% HCl (37%, Riedel–deHaen, Sigma–Aldrich, USA) was then added, and absorbance measured after 3-min mixing at 500 nm with spectrophotometer (UV-1800, Shimadzu, Japan). Samples containing β-glucan were filtered (Acrodisc 13 mm Syringe Filter with 0.45 μm GHP Membrane, Pall Corporation, USA) prior to measurement to remove β-glucan precipitated by the ethanol. A standard curve was prepared with $FeCl_3$ ($FeCl_3$, 1000 mg/l HCl, Merck KGaA, Germany) with amounts ranging from 0 μg to 40 μg.

Peroxide value (mequiv peroxide/kg of sample) was calculated according to the Eq. (1) where A_{sample} is the absorbance of the measured sample, A_{blank} is the absorbance of the blank sample, b is the y-axis intercept, k is the slope of the standard curve, 55.84 is the atomic weight of Fe and m_{sample} is the mass of the sample in grams.