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Storage stability of cauliflower soup powder: The effect of lipid oxidation and protein degradation reactions

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ABSTRACT

Soups based on cauliflower soup powders, prepared by dry mixing of ingredients and rapeseed oil, showed a decrease in quality, as evaluated by a sensory panel, during the storage of the soup powder in the dark for up to 12 weeks under mildly accelerated conditions of 40 °C and 75% relative humidity. Antioxidant, shown to be effective in protecting the rapeseed bulk oil, used for the powder preparation, had no effect on storage stability of the soup powder. The freshly prepared soup powder had a relatively high concentration of free radicals, as measured by electron spin resonance spectroscopy, which decreased during storage, and most remarkably during the first two weeks of storage, with only marginal increase in lipid hydroperoxides as primary lipid oxidation products, and without any increase in secondary lipid oxidation products. Analyses of volatiles by SPME-GC–MS revealed a significant increase in concentrations of 2-methyl- and 3-methyl butanals, related to Maillard reactions, together with an increase in 2-acetylpyrrole concentration. The soup powders became more brown during storage, as indicated by a decreasing Hunter *L*-value, in accord with non-enzymatic browning reactions. A significant increase in the concentrations of dimethyl disulfide in soup powder headspace indicated free radical-initiated protein oxidation. Protein degradation, including Maillard reactions and protein oxidation, is concluded to be more important than lipid oxidation in determining the shelf-life of dry cauliflower soup powder.

1. Introduction

A common method for preparing soup powders is based on batch operations, in which preproduced dry ingredients are mixed together with addition of oil or fat powder. These dry ingredients are usually powders made of dried vegetables, spices, flavours and yeast extracts. The microbial and enzymatic spoilage of dry products is prevented by a low water activity (Gibbs, 1986), thus leaving chemical and physical deterioration reactions as most important for shelf-life. Among the chemical reactions, lipid oxidation and non-enzymatic browning reactions are often linked and further depend on phase transitions in the product (Thomsen, Lauridsen, Skibsted, & Risbo, 2005a).

Lipid oxidation, one of the major causes of the degradation of food products during storage, leads to formation of off-flavours and furthermore affects the nutritional value and safety. Free radicals are formed in the early stage of lipid autoxidation (Frankel, 2005), and electron spin resonance (ESR) spectroscopy is a specific and sensitive technique for detection of such free radicals (Schaich, 2002). In dry systems, free radicals can be directly detected using ESR spectroscopy, since free radicals are stabilised by low molecular mobility and therefore are sufficiently long-lived for detection. Recent studies have indicated a correlation between free radical formation and lipid oxidation during the storage of dry food systems (Nissen, Huynh-Ba, Agerlin Petersen, Bertelsen, & Skibsted, 2002; Nissen, Månsson, Bertelsen, Huynh-Ba, & Skibsted, 2000; Stapelfeldt, Nielsen, & Skibsted, 1997; Thomsen et al., 2005a), thus allowing ESR spectroscopy to be used to study the initial stages of lipid oxidation in dry foods and for prediction of shelf-life of such products.

Non-enzymatic browning reactions, including Maillard reactions, occurring in foods during thermal processing and long storage, are complex and involve both carbohydrates and proteins. Ultimately, the Maillard reactions lead to the formation of high molecular weight coloured compounds known as melanoidins, resulting in a discolouration of pale food products. Besides discoloration, other negative effects related to the Maillard reactions in foods are formation of off-flavours, decrease in solubility and nutritional value, and formation of toxic compounds (Nursten, 2005). ESR spectroscopy may also be employed to study the Maillard reactions, as several studies have shown the appearance of free radicals

Abbreviations: AP, ascorbyl palmitate; a_w, water activity; CaA, carnosic acid; Cia, citric acid; DMDS, dimethyl disulfide; DUS, degree of unsaturation; ESR, electron spin resonance; IP, induction period; RE, rosemary extract; RH, relative humidity; TP, tocopherols extract.

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in the early stages of non-enzymatic browning reactions (Hayashi, Mase, & Namiki, 1985; Hoffman, Bors, & Stettmaier, 1999a; Namiki & Hayashi, 1975; Roberts & Lloyd, 1997), as well as in the Maillard reaction end-products, melanoidins (Hoffman, Bors, & Stettmaier, 1999b). Furthermore, Thomsen, Lauridsen, Skibsted, and Risbo (2005b) found a correlation between the formation of late-stage Maillard reaction products and change in the ESR line shape when studying milk powder.

In general, product water activity (a_w) is a major issue in relation to chemical stability of dry food products. Very low values of a_w are related to high lipid oxidation rates while between a_w values of 0.2 and 0.4, lipids have been suggested to have optimal stability and oxidation rates increase again with increasing a_w (Labuza, 1971). However, the oxidative stability of dry food products does not always follow this "general scheme", but is more product-related (Jensen & Risbo, 2007; Stapelfeldt et al., 1997). Non-enzymatic browning reactions are also strongly dependent on a_w, and the rate of Maillard reactions increases with increasing values of a_w to reach a maximum around an a_w of 0.7 (Labuza, 1971). Lipid oxidation and Maillard reactions may further be coupled through a_w, since water is produced in the Maillard reactions (Nursten, 1986), which increases the a_w value of the product and further enhances lipid oxidation. In turn, the volatiles (Elizalde, Dalla Rosa, & Lerici, 1991) and melanoidins (Borrelli, Visconti, Mennella, Anese, & Fogliano, 2002) formed in Maillard reactions may act as antioxidants, protecting against lipid peroxidation. Storage stability of dry food products may be enhanced by using antioxidants to delay the lipid oxidation (Nissen et al., 2000; Sarkardei & Howell, 2008). In the model systems, antioxidants have also been found to prevent the formation of mutagenic/carcinogenic compounds due to the Maillard reaction (Kato, Harashima, Moriya, Kikugawa, & Hiramoto, 1996). The overall chemical stability of dry food products accordingly depends on both composition and storage conditions of each particular dry food system.

The purpose of the present study was to study the mechanisms of quality deterioration in cauliflower soup powder, adapting methods, which also could be of use for similar sensitive dry food products. In addition, the effects of different antioxidants on storage stability of cauliflower soup powder during accelerated storage tests were studied. The antioxidants selected for the investigations differed by action mechanism and/or by solubility. The selected antioxidants were: lipophilic rosemary extract (containing radical-scavenging compounds), hydrophilic carnosic acid (radical-scavenger), hydrophilic citric acid (metal chelator), lipophilic tocopherol extract (radical-scavenger), and ampiphilic ascorbyl palmitate (e.g. regeneration of phenolic antioxidants) (Burton & Ingold, 1981; Frankel, 2005; Hall & Cuppett, 1997).

2. Materials and methods

2.1. Chemicals

$BaCl_2{\cdot}2H_2O$, hexane, absolute ethanol, 2-methylbutanal, pentanal, dimethyl disulfide, α-pinene, and carnosic acid were purchased from Sigma–Aldrich (Steinheim, Germany); hexanal was from Fluka (Steinheim, Germany), and HPLC grade chloroform was from Lab-Scan (Dublin, Ireland). HPLC grade isooctane, analytical grade methanol, dried methanol, NaCl, and $FeSO_4{\cdot}7H_2O$ were from Merck (Darmstadt, Germany). Analytical grade NH_4SCN was from Riedel-De-Haën (Seelze, Germany). Food grade refined rapeseed oil, rosemary extract, tocopherol extract, ascorbyl palmitate, and citric acid were used for preparing the soup powder. Rosemary extract contained 4.5% of carnosic acid and tocopherol extract a minimum of 50% of tocopherols according to the data provided by the manufacturer.

Fatty acid methyl esters used as standards for GC were obtained from Sigma–Aldrich (Steinheim, Germany).

2.2. DSC analysis

The induction periods for oxidation (IP) were determined for rapeseed oil with the following antioxidant additions: control (no antioxidant addition), rosemary extract (RE) 500 ppm and 1000 ppm, carnosic acid (CaA) 45 ppm, citric acid (CiA) 1000 ppm, tocopherol extract (TP) 1000 ppm, and ascorbyl palmitate (AP) 50 and 300 ppm. Rosemary and tocopherol extracts were lipid-soluble and were added directly to rapeseed oil. Citric acid, ascorbyl palmitate, and carnosic acid were dissolved in absolute ethanol and dispersed into the oil. The DSC experiments were performed with a DSC 1 Star^e system (Metler Toledo, Schwerzenbach, Switzerland) isothermally at 100 °C. The samples (5.00 mg ± 0.05 mg) were placed in 40 μl aluminium crucibles which were closed with lids with a hole (diameter ≈ 1 mm) to ensure the oxygen availability inside the crucible. A hermetically sealed empty crucible was used as a reference. The experimental curves were simulated with software Origin 7 (OriginLab Corporation, Northampton, MA, USA), and the induction periods (IP) for lipid oxidation were calculated as previously described (Velasco, Andersen, & Skibsted, 2004), but now from the data simulations. The analyses were made in duplicate.

2.3. Preparing soup powders

Cauliflower soup powders with different antioxidant additions were prepared by mixing preproduced dry ingredients and by adding 0.5% of rapeseed oil (RO). The ready soup powder contained approximately 20% of fat, calculated from the information given by raw material suppliers. The antioxidant additions to rapeseed oil before powder preparation were the same as used with the DSC analysis (see Section 2.2) and the concentrations of antioxidants were expressed in relation to rapeseed oil. The soup powders (70 g) were stored in closed, 110 ml polypropylene containers in a climate cupboard (Climacell, Planegg, Germany) at 40 °C and 75% relative humidity (RH) for up to 12 weeks, and one container was removed from the climate cupboard at each sampling time. The powders were stored frozen at −40 °C until analysed. Two separate batches of each soup powder were prepared. The cauliflower soup powder with carnosic acid after 4 weeks of storage and cauliflower soup powder with 300 ppm of ascorbyl palmitate after 12 weeks of storage from the one storage series were discarded from the analyses because the packaging had been slightly open during the storage.

2.4. Fatty acid composition

The fatty acid compositions of acyl glycerols of the soup powders were determined from fresh powders and after 12 weeks of storage and for rapeseed oil. The analyses were done for cauliflower soup powder only from other storage series which did not have any discarded samples. Fatty acid determinations were also done for rapeseed oil with addition of antioxidants (RE 1000 ppm, CaA 45 ppm and AP 300 ppm). The methylations were carried out directly on 40 mg of dry soup powder or on 5 mg of oil with 0.087 M sodium methylate solution at 60 °C for 40 min. The formed fatty acid methyl esters were extracted with 1.5 ml of hexane prior to chromatographic analysis (HP 6890 Series, Hewlet-Packard, Palo Alto, CA, USA; FFAP column (25 m × 0.20 mm × 0.33 μm) from Agilent Technologies, Waldbronn, Germany) with FID detection. The oven temperature programme was: 50 °C for 1 min; from 50 °C to 180 °C at 15 °C/min; from 180 °C to 195 °C at 2 °C/min, held for 15 min; from 195 °C to 240 °C at 4 °C/min, held for 10 min. Injected volume was 1 μl and split ratio was 1:25. Helium was used as carrier