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Antioxidant effect of *Majorana syriaca* extract in bulk corn oil and o/w emulsion after applying high hydrostatic pressure

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ABSTRACT

Bulk oils and oil-in-water emulsions were subjected to high hydrostatic pressure (HHP) (200, 650 MPa) treatment so as to estimate the effect of applied pressures on lipid oxidation. HHP-treated and non-treated samples were left to autoxidise under accelerated conditions (2 weeks, 70 °C) and their oxidative status was periodically estimated by measurement of conjugated dienes and peroxide value. Total changes of thiobarbituric acid-reactive substances were recorded as additional oxidative markers for emulsions. Results showed an increase in oxidation as pressure was increased especially at 650 MPa. Lipid oxidation rates that were more pronounced for HHP-treated samples can be correlated to measured dissolved oxygen that was also higher. HHP did not seem to have an effect on emulsion droplet size. The addition of *Majorana syriaca* (200 ppm) ethyl acetate extract led to protection against lipid oxidation under HHP and atmospheric conditions, 20.9–38.7% and 28.9–43.2%, respectively. It was observed that the antioxidant effect of *M. syriaca* extract under HHP was weaker.

1. Introduction

High hydrostatic pressure (HHP) processing has been introduced as an alternative non-thermal technology that causes inactivation of microorganisms and denaturation of several enzymes while minimally affecting quality and sensory characteristics (Rastogi, Raghavarao, Balasubramaniam, Niranjan, & Knorr, 2007). Over the last two decades, it has attracted considerable research attention related to the extension of shelf life of food products such as fruits, fruit juices, milk and milk products, meat and meat products (Farkas & Hoover, 2001). The application of HHP, instead of thermal processing, could be beneficial for the sensory characteristics of foods like salad dressings or fresh-cheese type products, which are susceptible to thermal deterioration. However, since these products have a high fat content, the effect of HHP treatment on their oxidative stability should be first examined. Few investigations have been conducted on the effect of HHP treatment on lipid oxidation and they concern mainly meat and fish products. According to different studies (Andrés, Møller, Adamsen, & Skibsted, 2004; Beltran, Pla, Yiste, & Mor-Mur, 2004; Orlien, Hansen, & Skibsted, 2000; Rivas-Cañedo, Fernández-García, & Nuñez, 2009; Wiggers, Kroger-Ohlsen, & Skibsted, 2004), HHP initiates oxidative processes and volatile formation, inducing flavour and colour changes. 500–600 MPa has been found to be critical as a working pressure for processing of certain meat products, while higher pressure has resulted in development of rancidity.

Lipid oxidation is usually the major deteriorative factor in high fat-containing foods. It starts with the formation of free radicals and hydroperoxides, which are unstable and decompose further to secondary products, like ketones, aldehydes that contribute to off flavours. Peroxide value (PV) and conjugated diene hyproperoxides (CD) are the main tools to estimate primary oxidation products, while the measurement of thiobarbituric acid-reactive substances (TBARs) is indicative of the formation of secondary products, more specifically aldehydes (Kiokias, Dimakou, & Oreopoulou, 2009).

Chemical additives are commonly used to retard oxidation. However, essential oils or plant extracts are regarded as natural alternatives to chemical preservatives and their use in foods meets consumer demand for mildly processed or natural products. Widely used culinary herbs of the Lamiaceae/Labiatae family such as rosemary, thyme, marjoram, and oregano have gained the interest of many research groups (Frankel, Huang, & Aeschbach, 1996; Kouri, Tsimogiannis, Bardouki, & Oreopoulou, 2007; Tsimogiannis, Stavrakaki, & Oreopoulou, 2006; Yanishlieva & Marinova, 2001).

Majorana syriaca (family *Labiatae,* genus *Origanum,* section *Majorana*) is an important food-flavouring ingredient in the Middle Eastern culture known commonly as Za'atar. Al-Bandak and Oreopoulou (2007) studied *M. syriaca* revealing the existence of thymol, carvacrol, rosmarinic acid, taxifolin, eriodictyol, apigenin and

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several non-identified flavonoids, compounds that possess antiradical and antioxidant activities. An extract of *M. syriaca* was efficiently used as an antioxidant in bulk oil and in chilled tuna fish (Al-Bandak & Oreopoulou, 2007; Al-Bandak, Tsironi, Taoukis, & Oreopoulou, 2009).

The present study examines the antioxidant effect of an ethyl acetate extract of *M. syriaca* in bulk corn oils and o/w emulsions after applying high hydrostatic pressure treatment. Lipid oxidation rates of samples treated with different pressures were correlated to dissolved oxygen concentration. To investigate the HHP effect on the structure of emulsions, oil droplet size was also measured.

M. syriaca extract was added to the samples subjected to HHP treatment to investigate its ability to retard oxidative deterioration of oils and emulsions under these conditions. The knowledge of the effect of high hydrostatic pressure treatment on lipid oxidation of emulsions and oils as model systems could be used to predict the behaviour of products such as salad dressings under HHP.

2. Materials and methods

2.1. Sample preparation

2.1.1. Oil samples

Refined corn oil (Minerva SA, Inofita, Greece) was used as bulk oil or to prepare emulsions.

2.1.2. Oil-in-water emulsion samples

The oil-in-water emulsions (20% w/w) were prepared by mixing the oil for 10 min in a blender (Waring Commercial, Torrington, CT, USA) with distilled water containing 2% Tween-20 as emulsifier. The pre-emulsion passed through a high-pressure valve, two-stage APV Lab 1000 homogenizer (Albertslund, Copenhagen Denmark) at 200 bars.

2.1.3. Oil and oil-in-water emulsion samples containing M. syriaca extract

Dried leaves of *M. syriaca* were purchased from the local market of Bethlehem and ground in a mill (Retch ZM 1, Haan, Germany) to pass 5 mm sieve. The ground material was subjected to extraction with ethyl acetate in a Soxhlet apparatus until the exhaustion of the colour. The obtained yield was 12.3% on dry basis. The extract was diluted in refined corn oil to obtain a concentration of 200 ppm as follows: the specific volume of the extract was added in the corresponding quantity of the oil, followed by continuous stirring and purging with nitrogen until total removal of the solvent. The resulting oil, free of solvent, was then used as bulk oil or in preparing 20% corn oil-in-water emulsion samples.

2.1.4. Packaging of oil and oil-in-water emulsion samples

Samples (oils or oil-in-water emulsions) of 5 g were packaged in polypropylene bags and sealed (BOSS NT42N, Bad Hamburg, Germany).

2.2. High hydrostatic pressure treatment

HHP experiments were conducted in triplicate at two different pressures, 200 and 650 MPa for time 6 min. The temperature was kept constant at 25 (±1.5) °C. Non-HHP-treated emulsions were used as control samples. Conditions (pressure–temperature–time) of HHP processing were selected in accordance with previous laboratory experiments as well as relative publications on emulsions (Puppo, Chapleau, Speroni, de Lamballerie, Anon & Anton, 2004; Puppo et al., 2008).

The high pressure unit (Food Pressure Unit FPU 1.01, Resato International BV, Roden, Holland), comprised a pressure intensifier and a high pressure vessel of 1.5 l in volume, with a maximum operating pressure and temperature of 1000 MPa and 90° C. The pressure transmitting fluid used was polyglycol ISO viscosity class VG 15 (Resato International BV, Roden, Holland). Process temperature in the vessels was achieved by liquid circulation in the outer jacket controlled by a heating cooling system. The desired value of pressure was set and after pressure build up (20 MPa/s), the pressure vessel was isolated. The pressure of the vessel was released after 6 min by opening the corresponding pressure valve. The initial adiabatic temperature increase during pressure build up (about 3 °C per 100 MPa) was taken into consideration in order to achieve the desired operating temperature during pressurisation. Pressure and temperature were constantly monitored and recorded (in 1 s intervals) during the process.

2.3. Oxidation tests

All samples were subjected to accelerated oxidation at 70 °C in a ventilated oven (Heraeus Instruments GmbH, Hanau, Germany) for approximately 2 weeks. The oxidative status of oil-in-water emulsion samples was periodically estimated by measurement of conjugated dienes hydroperoxides (CD) and thiobarbituric acid-reactive substances (TBARs). The oxidation of bulk oil samples was monitored by measuring conjugated dienes hydroperoxides (CD) and peroxide value (PV).

2.4. Analytical methods

2.4.1. Measurement of conjugated diene hydroperoxides

A modification of the method described by IUPAC 2.505 (1987) has been used for the determination of conjugated diene hydroperoxides in emulsions. More specifically, the emulsion sample (20 μl) was added to a mixture of 10 ml isooctane/2-propanol (2:1 v/v) and vortexed (1 min). For bulk oil samples, an amount of 0.1 g was diluted in 100 ml iso-oactane and mixed thoroughly. The absorbance was measured at 232 nm using a UV–VIS scanning spectrophotometer (Unicam Helios, Spectronic Unicam EMEA, Cambridge, United Kingdom). The amount of CD in the oxidising oils and emulsions was calculated by monitoring absorbance at 232 nm and using the relative molecular mass (280 g mol^{-1}) and the molar absorptivity of linoleic acid (e = 26,000) (Kiokias, Dimakou, Tsaprouni, & Oreopoulou, 2006).

2.4.2. Measurement of peroxide value

The oxidative process of bulk corn oil samples was also monitored by the determination of the peroxide value (PV) according to IUPAC official method 2.501 (1987). An amount of oil sample (1.0 g) was dissolved in 25 ml of a solution of acetic acid: chloroform (2:1), then 1 ml of saturated potassium iodide was added and the sample was kept in dark for 5 min. The sample was diluted by 50 ml distilled water and titrated with sodium thiosulfate (0.01 N). The PV was expressed in meq oxygen (O_2) kg^{-1} oil.

2.4.3. Measurement of thiobarbituric acid-reactive substances

Thiobarbituric acid-reactive substances (TBARs) were determined according to an adapted method of McDonald and Hultin (1987). A portion of the emulsion (0.6 ml) was combined with 1.4 ml of water and 2.0 ml TBA solution (prepared by mixing 15 g trichloroacetic acid, 0.375 g thiobarbituric acid, 1.76 ml 12 N HCl and 82.9 ml H_2O) in test tubes and placed in a boiling water bath for 15 min. The tubes were cooled to room temperature for 10 min and centrifuged (2000g) for 15 min. The absorbance of the supernatant was measured at 532 nm. The concentration of TBARs was calculated from a standard curve prepared by 1,1,3,3-tetraethoxypropane.