LWT - Food Science and Technology 59 (2014) 467–478

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Properties of model systems of sunflower oil and green coffee extract after heat treatment and storage

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A R T I C L E   I N F O

Article history:
Received 8 August 2012
Received in revised form
13 May 2014
Accepted 26 May 2014
Available online 9 June 2014

Keywords:
Sunflower oil
Green coffee
Antioxidant activity
Oxidative stability
Fatty acids

A B S T R A C T

Model systems of sunflower oil and green coffee extract (GCE) were examined. GCE was added to the oil at 3 g/100 g. Complex systems of the oil with saccharose, starch and egg white protein were studied. Samples were heated at 110 °C or 180 °C for 60 min and stored for 3 months. The research was aimed at determining the effects of high concentrations of green coffee antioxidants on the oxidative status of fatty acids and antioxidant activity of the systems depending on their composition. The fatty acid profile using the GC-FID method and peroxide value of sunflower oil as well as potentiometric determination of redox potential and the DPPH$^{\bullet}$ radical scavenging ability of model systems were analyzed. The obtained results showed a limiting of oxidation of sunflower oil heated with 3 g/100 g of GCE alone and in more complex systems. The average inhibition degree was 65% when compared to analogical non-enriched systems. The research also concluded that, despite prolonged heating and storage, these systems exhibited a significantly higher ($P < 0.05$) antioxidant activity in a test with DPPH$^{\bullet}$ when compared to those without GCE.

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1. Introduction

Lipids are an important component of human diet. They provide essential fatty acids (EFA) that are precursors to hormones, as well as control many physiological indicators. Oils rich in EFA are often used as supplements of food. Their quality and stability depends mainly on the progress of autooxidation reactions – the complex process in which a strange flavor is formed and the nutritional value is reduced (Giuffrida et al., 2007). Polyphenols can act as lipid antioxidants in complex food systems and in dietary supplements containing unsaturated fatty acids (Nissen, Byrne, Bertelsen, & Skibsted, 2004), additionally demonstrating an inhibitory effect on protein oxidation (Estévez, Kylli, Puolanne, Kivikari, & Heinonen, 2008). Sunflower oil, rich in polyunsaturated fatty acids is one of the major edible vegetable oils. It is added to a number of food products, contributing to the increase of EFA content in their composition. The addition of natural antioxidants can effectively maintain high quality of the oil in foods during processing and storage (Valencia, O'Grady, Ansorena, Astiasarán, & Kerry, 2008). Previous studies confirm the possibility of reducing the oxidation of sunflower oil by plant extracts including ones obtained from coffee (Budryn, Nebesny, & Żyżelewicz, 2011).

Coffee extracts have extremely strong antioxidant properties against lipid oxidation, higher than many other food products or common antioxidants (Pellegrini et al, 2003). This applies to both roasted and green coffee (Vanzani, Rosetto, Marco, Rigo, & Scarpa, 2011). The antioxidant properties are mainly caused by chlorogenic acids and caffeine (Davicino, Alonoso, & Anesini, 2011; Marinova, Toneva, & Yenishliewa, 2009). Additionally the beneficial effect of inhibiting the activity of food enzymes, chelation of transition metals and an increase of the microbiological safety of products enriched with coffee extracts can be achieved (Raghavendra, Ramesh Kumar, & Prakash, 2007; Sikwase & Duodu, 2007). In such applications relatively low concentrations of coffee extract or isolated coffee antioxidants were analyzed, such as 0.1–0.2 g/100 g, thus emphasizing their high antioxidative efficiency for lipids (Anwar, Jamil, Iqbal, & Sheikh, 2006).

However, current trends in food production focus on health promoting effects of antioxidants added to foods (Viljanen, Kivikari, & Heinonen, 2004). Both chlorogenic acids and caffeine exhibit *in vivo* antioxidant properties that may counteract the development of degenerative diseases (Cheng, Dai, Zhou, Yang, & Liu, 2007; Yamaguchi et al., 2008). Plant extracts with proven health effects must be added to food in much greater concentrations than those

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http://dx.doi.org/10.1016/j.lwt.2014.05.048
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required for the inhibition of lipid oxidation if they have to act as bioactive components. The relatively high concentration of bioactive compounds must at the same time provide the desired physiological effect as well as the toxicological safety of such products (Henekamp & Bast, 2007). Enrichment of functional foods with polyphenols generally aims to deliver an amount of about 1 g of polyphenols along with a daily serving dose of the product (mostly about 100 g) (Glei, Kirmse, Habermann, Persin, & Pool-Zobel, 2006; Williamson & Holst, 2008). Previous studies showed that in some systems the concentration of polyphenols, including coffee chlorogenic acids, even at a level of 0.1 g/100 g might give a pro-oxidant effect on lipids (Luzia et al., 1997). In light of that fact the oxidative stability of products with a relatively high level of plant extracts must be verified.

The aim of this study was to determine the effect of addition of green coffee extract in quantities having a potentially significant nutritional importance to sunflower oil model systems and verification whether such supplementation will have an antioxidative effect on the fatty acids. Another important aspect of this study was to answer the question to what extent the antioxidant activity of green coffee extract is preserved after thermal treatment and storage in oil alone and in more complex model systems (Lindley, 1998).

2. Materials and methods

2.1. Materials

Green Robusta coffee beans *(Coffea canephora)* originating from Brazil, dehulled by dry method, purchased from Bero Polska (Gdynia, Poland) were used. Chemically refined sunflower oil was provided by ZPT Kruszwica S.A. (Kruszwica, Poland), spray-dried egg white protein by PPHU Japart (Opatów, Poland), saccharose by Nordzucker S.A. (Opalenica, Poland), and starch by Pepees S.A. (Łomża, Poland).

2.2. Chemicals and reagents

2,2-Diphenyl-1-picrylhydrazyl (DPPH$^{\bullet}$), boron trifluoride, methanol solution (14 g/100 g), heptane, Supelco 37 Comp. FAME Mix, *cis/trans* isomer of linoleic acid methyl ester and *cis*-10-heptadecenoic acid were purchased from Sigma–Aldrich (St. Louis, MO, USA), ethanol, sodium chloride and chloroform from Chempur (Piekary Śląskie, Poland), methanol from JT Baker (NJ, USA), iron (II) chloride, sodium hydroxide, acetic acid, potassium iodide, petroleum ether and sodium thiosulfate from Poch (Gliwice, Poland).

2.3. Methods

2.3.1. Preparation of green coffee extract (GCE)

An aqueous extract of green coffee was prepared. Ground beans were sieved to a particle size 480–680 μm. The extract was obtained using the 1:5.75 ratio of coffee to water by boiling in a PS-5682 First pressure pot (Vienna, Austria) at 110 °C for 10 min, rapidly cooled and filtered under vacuum using a KNF Neuberger AT.18 035.3 N pump (NJ, USA). The extract was then freeze-dried in a DELTA 1-24LSC Christ freeze drier (Osterode am Harz, Germany). The resulting preparation had the following composition determined according to Budryn et al. (2009): chlorogenic acids 37.6 g 100 g^{-1}, protein 14.5 g 100 g^{-1}, fat 0.7 g 100 g^{-1}, ash 11.9 g 100 g^{-1}, caffeine 6.3 g 100 g^{-1}, soluble fiber 6.8 g 100 g^{-1}, carbohydrates 19.9 g 100 g^{-1}. Ochratoxin A content was less than 0.4 μg kg^{-1}.

2.3.2. Preparation and storage of model systems

GCE was added at 1.5 and 3 g·100 g^{-1} to sunflower oil and at 3 g 100 g^{-1} to model systems. In addition to sunflower oil and GCE, also saccharose, potato starch, egg white protein, water and ferrous ions at a concentration typical for low food fortification were also used (Suliburska, Krejpcio, & Kołaczyk, 2011). Components of the model system were chosen according to the bakery products recipes, including confectionery. Their mutual proportions were determined at equilibrium in order to analyze the equal influence of each of the components on the properties of the oil in heated systems. The lyophilized GCE was introduced into the oil or model system according to the experimental assumptions as a solid of about 15 μm particle size obtained through freeze drying. The components of coffee extract, being polar substances, formed a mixture with the oil, which was maintained in a homogenous state thanks to the proper construction of the retort, namely sloping, at an angle of 30° to level, rotating at 48 rpm with an U-shaped baffle along the cylinder wall and the bottom (retort diameter 11 cm, length 30 cm, baffle height 1.5 cm), ensuring intensive mixing of the material. The retort was constructed at the Technical University of Lodz, equipped with indirect electric heated and precise linear temperature control. The retort was open during the experiment, and the stirred system temperature was measured continuously using a thermocouple. The cylindrical vessel of the retort was made of stainless steel. The resulting samples were heated at 180° C for up to 1 h. Heating of systems containing saccharose was performed at a temperature of 110 °C because of its caramelization. The complete mixing of the components in the retort was reached after 1 min , and the system achieved the desired experimental temperature of 110 °C after about 3 min, and 180 °C after 4 min. The samples which were not heated were subject to analogous mixing as in case of heating. The model systems were stored in open beakers in a closed cabinet in an air conditioned room without access to light for a period of 3 months at 25 °C and relative humidity of 50%. The storage conditions corresponded to storage of food products not protected by packaging, in order to observe the influence of antioxidants on the quality of stored products (Bhanger et al., 2008). In order to facilitate the description of the results schematic abbreviations were applied, according to Table 1 The systems were analyzed to estimate changes in fatty acid composition and peroxide value of sunflower oil and their antioxidant activity, depending on composition, heating conditions and storage time.

2.3.3. Analysis of fatty acid composition

Oil was continuously extracted from model systems in a Soxtec Avanti 2000 extractor (Foss, Hoeganaes, Sweden) during 1 h, using petroleum ether with a boiling point of 40–60 °C. The oil extraction was performed according to the apparatus application note. The 15 g sample was put into a standard filter paper thimble, and then the extraction vessel was filled with 120 mL of the solvent. The heating phase of the sample immersed in the solvent took 15 min, the second phase of continuous extraction of the samples placed over the solvent with a condensate of pure ether took 45 min, and the additional phase of distilling away the solvent took 25 min.

Fatty acid composition was determined by gas chromatography with flame ionization detection (GC-FID) according to the standard methodology (AOAC, 2000). The oil samples (about 0.05 g) were hydrolyzed with 1 mL of methanolic sodium hydroxide solution (20 g L^{-1}) in a Reacti-therm 188821 derivatizer (Thermo Scientific, Waltham, Massachusetts, USA) at 60 °C with magnetic stirring. After 20 min 1 mL of boron trifluoride methanolic solution was added and next after 3 min 1 mL of heptane. After cooling to 25 °C the saturated sodium chloride solution was added and phase

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