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Anti-polymerization activity of tea and fruits extracts during rapeseed oil heating

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ABSTRACT

The aim of the study was to analyze the influence of natural antioxidants on polymerization of partially hydrogenated rapeseed oil heated in 170 °C for 40 h. In the research ethanolic extracts of green tea leaves (China Lung Ching), yellow tea leaves (China Kakecha), cranberry, blackberry, and lime were used. The yellow and green tea extracts were characterized by the highest content of total polyphenol and antioxidant activity. Polymers of triacylglycerols were found only in the polar fraction of heated oil. During heating, the increase of dimers, trimers, and oligomers was observed. However, it was dependent on the used additives and not directly related to the content of phenolic compounds and their antioxidant activity. The final content of polymers in oil samples increased in the fallowing order: green tea < yellow tea < blackberry < BHT < cranberry < lemon < oil without additives.

1. Introduction

Frying is one of the most popular processes of food preparation all over the word. During frying the food is immersed in hot oil, and heated in temperature from 150 to 190 °C, for a short period of time. Frying is also one of the most effective ways to obtain food with high sensory properties that are highly desired by consumers. These properties are connected with golden color, crispy texture and characteristic flavors typical for frying food (Aladedunye, 2014). The most important role during frying plays oil used as a heat transfer medium. The oil is also responsible for the uniform heating of the entire surface of the frying food. Multiple uses of oil in the deep-fat frying process leads to formation desirable, but also undesirable components that influence the flavor, color, texture and nutritional quality of frying food (Choe & Min, 2007). The composition of fatty acids, the content of native antioxidants, time, temperature and type of process, the air access, type of frying food are the main factors affecting the thermal stability of used oil (Gertz, Klostermann, & Kochhar, 2000; Kmiecik, Korczak, Rudzińska, Gramza-Michałowska, & Hęś, 2009; Marinova et al., 2012). The oxygen (from air), the moisture (from food) and the high temperature of the process led to oxidation, hydrolysis, and polymerization of oil, three basic reactions that we can observe in oil during frying. The hydrolysis and oxidation are the first reactions which can be observed and which start at the same time as the frying process. The polymerization requires higher temperatures. Because of the fact that frying is the process running in elevated temperature and oxygen supply is limited by a stream from frying food, the main reaction in oil leads to polymerization (Gertz et al., 2000). Improved stability of frying fats includes two groups of methods. The first one is related to optimization the best conditions of frying and using the most stable oil. The second one is related to the use of antioxidants (Aladedunye, 2015). Antioxidants used for protecting oil during frying can be divided into natural and synthetic. The synthetic antioxidants such as BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), TBHQ (*tert*-butylhydroquinone) or gallates are the most often added substances to the frying oil. However, the synthetic antioxidants are less effective compared to natural ones under frying conditions and are less appealing to consumers (Márquez-Ruiz, Ruiz-Méndez, & Velasco, 2014). Natural antioxidants such as tocopherols, phytosterols, squalene, phenolic compounds, carotenoids or phospholipids can naturally be present in oil or can be added (Aladedunye, 2014; Marmesat, Morales, Velasco, & Dobarganes, 2010). The phenolic compounds are the biggest group of substances which have a protective effect in relation to fats. Extracts of herbs and plants such as rosemary, sage, thyme, oregano and olive, mulberry or tea leaves added to oil or fat products show a positive action of these substances against oxidation process of fat and other oils components such as tocopherols or phytosterols. The positive effects were observed in storage and in elevated

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temperature from 60 to 180 °C (Chiou, Kalogeropoulos, Salta, Efstathiou, & Andrikopoulos, 2009; Gramza-Michałowska, Kobus-Cisowska, et al., 2016; Kmiecik et al., 2015; Kobus-Cisowska, Flaczyk, Rudzińska, & Kmiecik, 2014; Roy, Arabshahi-Delouee, & Urooj, 2010).

The aim of the study was to analyze the influence of addition of natural antioxidants – extracts from plants and fruits on thermal decomposition, especially the composition of the polymer of partially hydrogenated rapeseed oil heated in elevated temperature.

2. Materials and methods

2.1. Materials

In the study, partially hydrogenated rapeseed oil, and ethanolic extract of green China Lung Ching and yellow China Kakecha tea, cranberry, blackberry, and lime were used. Partially hydrogenated rapeseed oil, green and yellow tea leaves (dry) were purchased on the local market. The ethanolic extracts were prepared in the laboratory according to Gramza et al. (2006). Briefly, 100 g of freeze-dried fruit pulp (cranberry, blackberry, and lime) or 100 g of tea leaves were homogenized in 250 ml of 80% ethanol. Extracts were obtained after 24 h of maceration process which was repeated three times. Extracts after maceration were collected, filtered and centrifuged (3000 rpm, 6 min, Heraeus Megafuge 40R, Thermo Scientific, Waltham, MA, USA). In the end, ethanol was evaporated in the rotary evaporator (Rotavapor R-215, Buchi, Switzerland) and the residue was lyophilized and shortly stored until further analysis (−18 °C). BHT (butylated hydroxytoluene) was purchased from Sigma-Aldrich (Sigma-Aldrich, Poland).

2.2. Heating process

Heating process was done at 170 °C ± 5 °C in 3.5 litre electric fryers (Caterina, Poland) in two parallel frying bath (fryer A and B). Rapeseed oil was heated without addition of additives – RO, and with addition of ethanolic extracts of green tea leaves – GTE (0.2%), yellow tea leaves – YTE (0.2%), cranberry – CE (0.2%), blackberry – BE (0.2%), lime – LE (0.2%) and BHT (0.02%). Each sample of oil was heated 40 h (5 days for 8 h per day). Between next days of heating oil was cooled and stored at 5 °C. After every 8 h of the heating 200 ml of oil was collected, sealed under nitrogen and stored at a −24 °C until analysis. Before the start of each day of heating, 200 ml of fresh oil was added to the fryers.

2.3. Total polar compounds (TPC) analysis

Total polar compounds of oil were analyzed according to by the AOCS Official Method 982.27 (2009a). Briefly, a sample of oil was dissolved in toluene and applied to a silica gel column (Sigma-Aldrich, silica gel 60, 63–200 μm). A nonpolar fraction was eluted with a mixture of hexane and diisopropyl ether (82:18, v:v), and was collected. After evaporation of solvent the nonpolar fraction was weighted and from weight difference of the sample and nonpolar fraction, the polar fraction was calculated. The results were expressed as% of total content of oil sample.

2.4. Iodine value calculation

The iodine value of oil used for frying calculated according to the AOCS Official method Cd 1c-85 (2009b).

2.5. Fatty acid composition analysis

Fatty acid composition was determined according to AOCS Official method Ce 1h-05, (2009c). Oil samples (10 mg) were dissolved in hexane and transesterified with sodium methylate (0.1 M). Fatty acid methyl esters (FAME) were analyzed using an Agilent 7820 A GC (Agilent Technologies) equipped with SLB-IL111 capillary columns (Supelco, Bellefonte, PA, USA) (100 m, 0.25 mm, 0.20 μm) and a FID (flame ionization detector). The oven temperature was initially 150 °C and increased to 200 °C at 1.5 °C/min. The injector and detector temperature was 250 °C and split 1:10. The carrier gas was helium at 1 mL/min. The fatty acids methyl esters (FAME) were identified by comparison with commercially available standards – grain fatty acid methyl ester mix (Supelco, Bellefonte, PA, USA). Results were expressed as a percentage of the total fatty acids.

2.6. Total polyphenols content analysis

Total polyphenols content was determined according to Folin-Ciocalteu reagent assay by Gramza-Michałowska, Kulczyński, Xindi, and Gumienna, 2016. The results were expressed as GAE gallic acid equivalents in mg/1 g of the extract.

2.7. DPPH radical scavenging assays analysis

The antioxidative potential of plant extracts was estimated using DPPH radical scavenging assays. The DPPH procedure described by Sanchez-Moreno, Larrauri, and Saura-Calixto (1998) is based on the DPPH (2,2-diphenyl-1-picrylhydrazyl) solution absorbance decrease at λ = 515 nm in the presence of antioxidants. The radical scavenging activity is presented as mg of Trolox equivalent (TE) in 1 g of the extract.

2.8. Trolox equivalent antioxidant capacity (TEAC) analysis

TEAC assay (Trolox Equivalent Antioxidant Capacity) by Re et al. (1999) is based on the extracts ability to scavenge blue-green colored ABTS cation radical, formed from ABTS (2,2-azinobis-(3-ethyl benzothiazoline-6-sulfonic acid)), measured spectrophotometrically at λ = 734 nm. The ABTS radical cation scavenging percentage is presented as mg of Trolox equivalent (TE) in 1 g of the extract.

2.9. The division of polar and nonpolar fraction

A sample of the oil was a separation into a polar and nonpolar fraction using silica gel (Sigma-Aldrich, silica gel 60, 63–200 μm). Briefly, oil sample was weighed, dissolved in toluene and applied to a top of silica gel column. First, a nonpolar fraction was eluted with a mixture of hexane and diisopropyl ether (82:18, v:v), then a polar fraction was eluted with pure diisopropyl ether. The purity of both fractions and separation accuracy was verified using the thin layer chromatography method. Silica gel TLC plate was developed with hexane – diisopropyl ether (82:18, v:v), sprayed with cooper sulphate-phosphoric acid-methanol solution and heated at 120 °C.

2.10. Polymer composition analysis

The polymers composition was determined in the polar and nonpolar fraction of the oil. The polymer composition was analyzed using an Infinity 1290 HPLC (Agilent Technologies, Santa Clara, CA, USA) equipped with ELSD (Evaporative Light Scattering Detector) and two connected together Phenogel columns (100 Å i 500 Å, 5 μ, 300 × 7.8 mm) (Phenomenex, Torrance, CA, USA). Separation of the polymer was carried out under the following condi-