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Phosphatidylcholine and dihydrocaffeic acid amide mixture enhanced the thermo-oxidative stability of canola oil

Felix Aladedunye [a,*], Roman Przybylski [b]

[a] Max Rubner-Institut (MRI), Federal Research Institute for Nutrition and Food, Department for Safety and Quality of Cereals, Working Group for Lipid Research, Schützenberg 12, D-32756 Detmold, Germany
[b] Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, AB T1K 3M4, Canada

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ABSTRACT

Recently, we reported the synthesis of a series of dihydrocaffeic acid amides and evaluated their performance as antioxidants for frying applications using a model frying. In the present study, the possibility of a synergy between the amide, N-propyl-N-benzyl-3-(3,4 dihydroxyphenyl)propanamide (DCA) and phosphatidylcholine (PC) was explored in a 6-day actual frying operation. As measured by the amount of polar components (TPC), anisidine value (AnV), changes in fatty acid composition, residual tocopherol and hydroxynonenal (HNE), canola oil containing the formulated antioxidant was twice as stable compared to the regular unfortified oil. At the end of the frying period, the amount of HNE detected in regular canola oil and the fortified sample was at 5.7 and 2.5 μg/g, respectively. Thus, the mixture containing phosphatidylcholine and dihydrocaffeic acid amide is a promising antioxidant for frying application.

1. Introduction

Deep fat frying is the process of cooking foods by immersing them in edible fat or oil at a temperature above the boiling point of water, usually 150–200 °C. Although deep fat frying is a relatively simple way of food preparation, the complex chemical reactions involved are yet to be fully understood. The stringent conditions used during frying, coupled with the complex interaction between frying oil and food components often result in general failure of traditional antioxidants like tocopherols.

Although conventional synthetic antioxidants such as BHT and BHA are effective antioxidants at ambient and accelerated storage temperatures (Khan & Shahidi, 2000; Nenadis, Zafiropoulou, & Tsimidou, 2003), they offer little or no protection during frying of food (Augustin & Berry, 1983; Tsaknis, Lalas, & Protopapa, 2002). Aside from poor protection, the use of synthetic antioxidants has also been limited due to their perceived toxicity. Nevertheless, the formation of a host of potentially toxic degradation products during frying, coupled with an ever increasing demand for fried food necessitates the development of safe, yet potent antioxidants for frying applications.

Recently, we reported the syntheses, radical scavenging activity and performance under storage and frying conditions of a series of novel phenolic antioxidants composed from precursors naturally present in oilseeds (Aladedunye, Catel, & Przybylski, 2012; Catel, Aladedunye, & Przybylski, 2010). Using a reliable frying model (Aladedunye & Przybylski, 2011), preliminary investigations indicated that the dihydrocaffeic acid amides were better antioxidants for frying application compared to the trolox benzoates and cinnamates derivatives. Although model frying can offer a good prediction, actual frying still remains the most reliable method for assessing frying stability of oils and the performance of applied antioxidants. Performance assessment of antioxidative compounds in bulk edible oils is usually carried out using a stripped substrate devoid of all endogenous minor components (Khan & Shahidi, 2000; Romero et al., 2007; Aladedunye et al., 2012; Warner & Moser, 2009). While activity in purified oils can provide some information on the potential of an antioxidant, the model precludes possible interactions of applied antioxidants with oil's endogenous minor components. Such interactions, however, can exert significant influence on the effectiveness of an antioxidant, defining its overall performance (Aladedunye & Przybylski, 2012a, 2012b; Kortenska, Yanishlieva, & Roginskii, 1991). Thus, in the present study, the effectiveness of an antioxidant mixture of phosphatidylcholine and dihydrocaffeic acid amide was tested in refined, bleached and deodorized canola oil in a 6-day actual frying operation.

2. Materials and methods

2.1. Materials

Commercially refined, bleached and deodorized regular canola oil was donated by Richardson Oilseed Processing (Lethbridge,

* Corresponding author. Tel.: +49 (0) 5231 741 222; fax: +49 (0) 5231 741 200.
E-mail address: felix.aladedunye@mri.bund.de (F. Aladedunye).

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Canada). Frozen par-fried French fries in institutional pack were obtained from a local food store. Standards of tocopherols were obtained from Calbiochem–Novabiochem (San Diego, CA). Standards of fatty acid methyl esters were purchased from Nu-Check-Prep (Elysian, MN). Egg yolk phosphatidylcholine (type XVI, ⩾99%) was purchased from Sigma–Aldrich (St Louis, MO). Unless otherwise stated, other solvents and chemicals of analytical grade used in this study were purchased from Sigma–Aldrich (St Louis, MO).

2.2. Addition of antioxidants

A standard solution of N-propyl-N-benzyl-3-(3,4 dihydroxyphenyl)propanamide (DCA) and phosphatidylcholine (PC) in oil was prepared by dissolving appropriate amounts of DCA and PC in methanol, which was then added to a sample of canola oil. The solvent was evaporated at 40 °C using a rotary evaporator and traces of solvent were removed under gentle streams of nitrogen. The concentration of antioxidants in the oil was confirmed by HPLC (Aladedunye et al., 2012; Beare-Rogers, Bonekamp-Nasner, & Dieffenbacher, 1992). Then, aliquot of the antioxidants in oil was mixed with the proper amount of canola oil in the fryer at 60 °C to prepare 3.75 L of oil sample containing 350 and 1000 μg/g of DCA and PC, respectively.

For preliminary experiments using a frying test, five concentration levels of DCA (200, 350, 500, 1000, and 1500 μg/g) and three concentration levels of PC (500, 1000, and 2000 μg/g) were examined. Antioxidant mixtures containing different amounts of PC and DCA were also evaluated.

2.3. Frying procedure and oil sampling

The frying was conducted in 8 L capacity restaurant style stainless steel deep fryers (General Electric Company, New York, USA). The oil (3.75 L) was heated at 185 ± 5 °C for 5 h daily for 6 days. A batch of 200 g of frozen French fries was fried for 5 min for a total of 5 batches per frying day. At the end of each frying day, fryers were shut off and left to cool overnight. Two 5 mL samples of oil from each of the fryers were taken daily and kept frozen at −16 °C until analysed. Before commencing frying each day, oils were filtered to remove solid debris. The oil was not replenished throughout the entire frying period.

Preliminary frying test was as described by Aladedunye and Przybylski (2011). Briefly, vegetable oil (12.0 g) was weighed into a clean glass beaker (30 mL, Pyrex, USA). Clean octagonal stir bars (9.5 × 25 mm, Fischer Scientific, USA) was placed in the glass vessel. The oil sample in glass beaker was heated at 185 ± 5 °C for 10 min, and 1.2 g of gelatinized starch (potato starch, glucose, silica gel, 4:1:1; w/w/w) was added. The heating was continued for another 20 min without mixing and then was stirred at 500 rpm. Heating and stirring were continued for an additional 90 min. About 0.5 g of oil sample was withdrawn at the 60th, 80th, 100th, and 120th minutes for the analysis.

2.4. Fatty acid composition

Fatty acid methyl esters (FAMEs) were prepared following the AOCS Official Method Ce 1-62 (Firestone, 2009). The FAMEs were analysed on Trace GC Ultra gas chromatograph (Thermo Electron Corporation, Rodano, Italy) using a Trace TR-FAME capillary column (100 m × 0.25 mm × 0.25 μm; Thermo Scientific, Waltham, MA, USA). Hydrogen was used as carrier gas with flow rate of 1.5 mL/min. Column temperature was programmed from 70 °C to 160 °C at 25 °C/min and held for 30 min, then further programmed to 210 °C at 3 °C/min. Initial and final temperatures were held for 5 and 30 min, respectively. Splitless injection was used utilizing PTV injector. Detector temperature was set at 250 °C. FAME samples, 1 μL, were injected with AS 3000 autosampler (Thermo Electron Corporation, Rodano, Italy). Fatty acids were identified by comparison of retention data with authentic standards purchased from Nu-Chek-Prep (Elysian, MN).

2.5. Total polar components (TPC)

The total amount of polar components was determined by the gravimetric method after column chromatography separation of non-polar fraction according to the AOAC Method 982.27 (1990).

2.6. Tocopherols

Tocopherols were analysed following the AOCS Official Method Ce 8-89 (Firestone, 2009) using Finnigan Surveyor HPLC (Thermo Electron Corporation, Waltham, MA) with a Finnigan Surveyor Autosampler Plus and Finnigan Surveyor FL Plus fluorescence detector, set for excitation at 292 nm and emission 324 nm. The column was a normal-phase Microsorb 100 silica (250 × 4.60 mm; 3 μm; Varian, CA). Of each sample, 10 μL was injected and separated by mobile phase consisted of 7% methyl-*tert*-butyl-ether in hexane with a flow rate of 0.6 mL/min. The tocopherols were quantified using external calibration for each isomer separately.

2.7. Colour component

Colour of the frying oils was assessed according to AOCS Official method Cc 13c-50 (Firestone, 2009) using a DU®-65 spectrophotometer (Beckman, Fullerton, CA).

2.8. Anisidine value (AnV)

Anisidine value (AnV), a measure of secondary oxidation products, was determined according to ISO Method 6885 (2004).

2.9. Hydroxynonenal (HNE)

Amount of 4-hydroxynonenal (HNE) in the frying oil was analysed as previously described (Aladedunye, Matthäus, Przybylski, Zhao, & Curtis, 2011).

2.10. Synthesis of DCA

The synthesis of DCA is as described elsewhere (Aladedunye et al., 2012).

2.11. Statistical analysis

Data are presented as means ± standard deviation (SD). Data were analysed by single factor analyses of variance (ANOVA) using SPSS package (version 10.0). Statistically significant differences between means were determined by Duncan's multiple range tests for $P < 0.05$.

3. Results and discussion

3.1. Preliminary study

Although the use of purified oils (stripped of interfering endogenous minor components) as lipid substrates for antioxidant study can provide useful information on the potential of an antioxidant, the model precludes possible interactions of applied antioxidants with oil's endogenous minor components. Such interactions, however, can exert significant influence on the ultimate performance of the applied antioxidants, informing the use of