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Characterization of tocopherols, tocotrienols and total carotenoids in deep-fat fried French fries

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ABSTRACT

French fries were deep-fat fried in crude palm oil (CPO), refined canola oil (RCO) and a blend of CPO/RCO (1:1 *w/w*) at 170 °C for different durations. The fries were analyzed for the presence of certain bioactive nutrients originating from the frying oils. The French fries absorbed over 50% of total carotenoids, 40% of tocotrienols and < 20% of tocopherols from the oils. The order of enrichment based on the frying oil was CPO/RCO blend > CPO > RCO. The moisture ratio, oil uptake, and browning index were modeled with a first order kinetic model, while the changes in the concentration of nutrients in the fries were modeled using the biphasic first order model. In all cases, the coefficients of determination, R^2, calculated were above 0.92. The French fries produced using CPO and the blend of CPO/RCO absorbed less oil and were significantly enriched with carotenoids and vitamin E.

1. Introduction

Consumers' escalating interest in healthy eating has revived attention to the potential health benefits of bioactive phytonutrients. Careful choice of raw materials, process controls, and optimizations have led to the creation of functional ingredients and food products that serve as carriers for bioactive compounds (Boon et al., 2010). It has been reported that vegetable oils are a rich source of bioactive compounds, such as vitamin E, phenolic compounds, and carotenoids (Azlan et al., 2010). These phytonutrients contribute to the rich organoleptic values, antioxidant properties, and thermostability of vegetable oils (Choo et al., 2004).

The carotenoids and all the isomers of vitamin E, namely, α-, β-, γ-, δ-tocopherols and α-, β-, γ-, δ-tocotrienols, have demonstrated a high biological activity and are considered as natural antioxidants (Pinheiro-Sant'Ana et al., 2011). They are essential phytonutrients that must be obtained from the diet. Crude palm oil (CPO) is rich in tocotrienols, tocopherols, and carotenoids (Mba et al., 2015b). Recent studies have shown that palm-derived tocotrienols lower plasma triacylglycerol levels and have cardiovascular benefits (Daud et al., 2013; Zaiden et al., 2010). Carotenoids contribute to the color of media and foods. They are antioxidants that can modulate other cellular antioxidants (Flakelar et al., 2015; Luzia and Jorge, 2013). It has also been reported that carotenoids and tocopherols act synergistically to provide enhanced antioxidant activity (Sampaio et al., 2013; Zhang et al., 2014). Beta-carotene (a carotenoid homolog), has been reported to possess pro-vitamin A activity. Vitamin A is required for epithelial maintenance, reproduction and vision (Fernández-García et al., 2012).

A vast variety of fried foods is available worldwide. Nowadays, fried foods are regularly associated with "junk food" that aggravates the risk of obesity (Li et al., 2009). Fried foods can also contain various thermo-oxidized compounds with significant health concerns (Ghidurus et al., 2010; Wang et al., 2008). However, the benefits offered by frying foods, such as faster cooking time, characteristic flavor, crispy texture, crunchy mouthfeel, distinctive color, and feeling of satiety, still make fried foods popular (Bou et al., 2012; Vauvre et al., 2014). In addition, the nutritive value of fried foods increases due to the absorption of frying oils and phytonutrients. For instance, the total lipid content of fresh raw potato is 0.10 g/100 g (USDA, 2016). Thus, much of the oil present in French fries is mainly the oil absorbed during frying (Chiou et al., 2012). Also, the chemical and phytonutrients composition of the absorbed oil does not significantly differ from those of the oils used in the frying process (Chiou et al., 2012; Chiou et al., 2009; Dobarganes et al., 2000). However, these same useful bioactive phytonutrients are susceptible to thermal degradation. For instance, the degradation rates of vitamin E and carotenoids depend on the type of fats and oil and are

Abbreviations: BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; BLFF, blend oil fried French fries; CPO, crude palm oil; CPOFF, crude palm oil fried French fries; ΔE, overall color change; DMPS, dimethylpolysiloxane; HPLC, high performance liquid chromatography; LOD, limits of detection; LOQ, limits of quantification; MR, moisture ratio; NEB, non-enzymatic browning; OU, oil uptake; PDA, photodiode array; PTFE, polytetrafluoroethylene; RCO, refined canola oil; RCOFF, refined canola oil fried French fries; RMSE, root mean square error

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modulated by the processing techniques applied especially in oil refining and the oil's end use. Our previous work showed that the vitamin E isomers and carotenoids are stable in CPO and blends after 15 h of repeated deep-fat frying at 170 and 180 °C (Mba et al., 2017). Thus, there is a need to monitor the extent of absorption of these phytonutrients in fried foods, their retention, and stability. The changes in the phytonutrient concentrations were quantified based on the temperature dependent rate constants (Ling et al., 2014). Generally, the changes in food quality are described by zero-, first- or second-order reaction kinetics. Other kinetic models such as the biphasic first-order and the fractional conversion models have been used to explain the thermal degradation trend of phytonutrients (Hiwilepo-van Hal et al., 2012; Ling et al., 2014; Vieira et al., 2000). The objectives of this study were to monitor the enrichment of French fries that can provide additional nutritional benefits besides energy and macronutrients, and to determine the presence and level of vitamin E isomers and total carotenoids in French fries after deep-fat frying in CPO, RCO, and CPO/RCO blend. The application of the modified biphasic model to predict the changes in the concentration of the phytonutrients in the French fries' samples was also evaluated. As reported by Ghidurus et al. (2010), increasing the phytonutrient concentrations in snack foods such as French fries implies increasing the phytonutrients available in the diet. Phytonutrients with antioxidant activities also have the potential of increasing the shelf stability of par-fried and frozen fries on supermarket shelves.

2. Materials and method

2.1. Materials and reagents

Crude palm oil (CPO) was supplied by a palm oil mill in Nigeria. Commercially refined canola oil (RCO) (labeled as containing butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and dimethylpolysiloxane (DMPS)) was obtained from Titan Oils Inc., Montréal, Canada. Binary blends, containing CPO and RCO only, were prepared in the laboratory at room temperature by mixing, using a digital lab stirrer/electric mixer (model no. WDQY96; Shanghai Loikaw Instrument, Shanghai China) at 500 rpm (360*g* relative centrifugal force (rcf)). White-fleshed Russet potato (*Solanum tuberosum L.*) variety was purchased from a local grocery shop. HPLC-grade *n*-hexane, methanol, ethyl acetate, acetic acid and ascorbic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Stock standard solutions of α-, β-, γ-, δ-tocopherols purchased as Tocopherol Set – Calbiochem and carotenes (purity ≥ 95% by HPLC for each component) were obtained from Sigma-Aldrich, St Louis, MO. The internal standard and standard α-, β-, γ-, δ-tocotrienols samples were gifts from ExcelVite Perak, Malaysia, with purity greater than 97% by HPLC.

2.2. Frying protocol

Each of the oil samples (CPO, RCO, and blend) was preheated at 170 °C for 2 h, in a temperature-controlled bench-top deep-fryer (model D24527DZ; Dēlonghi Appliances, Treviso, Italy) of 5-L capacity. Batonnet cuts (≈ 10 cm long and 1.6 cm thick) of peeled potatoes were washed to remove surface starch and then quickly dried with a light stream of warm air. About 100 g of potato slices were deep-fat fried for 1, 3, 5, 7, 9 and 11 min. The potato to frying oil ratio was 1:10. K-type thermocouple interfaced with HotMux data logger was used to monitor the set temperature of the oil during the frying process. The oil temperature dropped to approximately 165 °C as fresh potatoes were introduced. The oil bath regained the set temperature of 170 °C within 60 s. At the end of each frying time, adhering surface oil on the French fries was quickly drained and wiped off using paper towels and allowed to cool. A set of unfried potato cuts was used as the reference sample and termed '0 min fries'. The frying experiment was performed in triplicate. The cooled French fries samples were weighed and packaged in non-transparent self-sealing polyethylene pouches. The unfried and fried French fries samples were kept frozen at −80 °C until freeze-drying.

2.3. Samples preparation

The lyophilized French fries samples were freeze-dried using a ThermoSavant freeze dryer (model no: VLP200; Savant Instruments Inc. Holbrook, NY). Freeze-drying was performed to avoid further degradation and loss of the phytonutrients. After the freeze-drying step, the moisture loss was calculated. The oil extraction method described by AOAC (1990) and Manirakiza et al. (2001) was followed for extracting oil from the French fries samples. Briefly, the samples were ground using a pestle and mortar. Oil extraction was done using a solvent extractor (SER 148-6; Velp Scientifica, Usmate, Italy). Thimbles containing 5.0 g of ground sample were refluxed for 75 min. The extraction solvent was petroleum ether containing 0.05% ascorbic acid to prevent oxidation. Any residual solvent in the extracted oil was evaporated using nitrogen gas in a fume hood for 30 min. The oil in the flask was weighed and siphoned into amber-colored vials. The oil extraction was done in triplicate and the oil uptake by the French fries samples at different times was calculated from this step. All the oil samples were analyzed for their vitamin E and carotenoid content.

2.4. Analysis of vitamin E isomers

One percent stock solutions of α-, β-, γ-, δ-tocopherol, and α-, β-, γ-, δ-tocotrienol standards were prepared using hexane. The internal standard was also diluted to obtain 1% stock solution using hexane. All the stock standard solutions were kept in amber-colored bottles and stored at −20 °C. Working standard solutions for each isomer were prepared by diluting the stock standard solutions in hexane containing 1% isopropanol. The concentrations used are shown in Table 1. After this step, 10 μL of each concentration were injected in triplicate. The calibration curves were obtained through linear correlation between peak areas and concentrations of the injected external standards. The linear regression equation obtained for each isomer was the basis for the quantification of the bioactive phytonutrients in the French fries and to calculate the limits of detection (LOD) and the limits of quantification (LOQ). The weighted linear regressions were performed using SAS® Analytics (Version 9.4; SAS Institute Inc., Cary, NC).

The method described by Chen and Bergman (2005) was used to extract the vitamin E isomers from the fresh oil and the French fries samples. In brief, 0.1 g of the oil samples, 0.5 g of ground French fries and 0.5 g ground unfried potato samples were measured into centrifuge tubes and 7 mL of methanol containing 0.05% ascorbic acid were added. The tubes with samples immersed in the solvent were continuously shaken in a horizontal shaker at 200 oscillations/min for 30 min. The samples were centrifuged at 3500 rpm (2560*g* relative centrifugal force (rcf)) for 8 min. The solvent layers were collected in another set of clean tubes. Another 7 mL of the extraction solvent were added to the residual oil samples in the first set of tubes. The shaking

Table 1
Different concentrations (μg mL^{-1}) of vitamin E homologs used for the calibration curves.

sample #	α-TP	β-TP	γ-TP	δ-TP	α-T3	β-T3	γ-T3	δ-T3
1	0.77	0.08	3.83	1.27	0.58	0.11	0.87	0.33
2	1.54	0.17	7.66	2.54	1.17	0.23	1.75	0.65
3	2.30	0.25	11.5	3.80	1.75	0.34	2.62	0.98
4	3.07	0.33	15.3	5.07	2.33	0.46	3.49	1.31
5	3.84	0.42	19.2	6.34	2.91	0.57	4.37	1.63
6	4.61	0.50	23.0	7.61	3.50	0.70	5.24	1.96

α-TP = alpha-tocopherol; β-TP = beta-tocopherol; γ-TP = gamma-tocopherol; δ-TP = delta-tocopherol; α-T3 = alpha-tocotrienol; β-T3 = beta-tocotrienol; γ-T3 = gamma-tocotrienol; δ-T3 = delta-tocotrienol.