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Stabilisation of sunflower oil and reduction of acrylamide formation of potato with rosemary extract during deep-fat frying

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ABSTRACT

The aim of this study was to evaluate the effects of rosemary extract on the stabilisation of sunflower oil and the reduction of acrylamide formation in potato during deep-fat frying. The synthetic antioxidants butylated hydroxyanisole, tertiary butylhydroquinone, and tocopherols served as positive controls. Thermo-oxidative alterations were measured according to various physical and chemical parameters. Total polar compounds, free fatty acids, conjugated dienes, conjugated trienes, and colour (L^*, b^*) were evaluated for effectiveness of the antioxidants to stabilise the sunflower oil. The acrylamide concentration was evaluated for effectiveness of the antioxidants to reduce the acrylamide content in the deep-fried potato. Except for the decreased L^* value (darkness of oil colour), these parameters all increased with the number of frying cycles. The order of effectiveness for inhibition of sunflower oil degradation and reduction of acrylamide formation in deep-fried potato was: rosemary extract > tocopherols > tertiary butylhydroquinone > butylated hydroxyanisole > control ($P < 0.05$). Total polar compounds, free fatty acid and acrylamide levels were significantly correlated with frying time ($P < 0.05$). The acrylamide formation in fried potatoes was significantly correlated with the formation of total polar compounds ($P < 0.05$) in the frying oil during the frying process.

1. Introduction

Deep-fat frying is one of the most commonly used procedures for the preparation and production of foods. However, deep-fat frying produces both desirable and undesirable flavour compounds, and it can change the flavour stability and quality, the colour and texture, and the nutritional quality of the fried foods. Hydrolysis, oxidation and polymerisation are common chemical reactions during the use of frying oil, with the production of volatile and non-volatile compounds, some of which are potentially toxic (Choe & Min, 2007). Volatile compounds are lost from hot frying oil, while non-volatile compounds steadily increase in concentration. The non-volatile compounds are often of high molecular weight and/or polarity, and their presence has been used in several studies to indicate the quality of used or reprocessed oil (Lumley, 1988). From the nutritional point of view, the non-volatile degradation products of used frying fats and oils are of particular relevance, as these can remain in the oil, and they can be retained in the food, and subsequently ingested. Such non-volatile products include polymeric triglycerides and monomeric triglycerides that contain cyclic fatty acyls and various breakdown products. The greatest concern for the nutritional effects of used frying fats relates to intermittent, or discontinuous, frying, because the highest degradation levels have been demonstrated under these conditions (Márquez-Ruiz & Dobarganes, 2006).

Potatoes and other foods that have a high content of the amino acid asparagine and a high accumulation of reducing sugars are subject to the formation of acrylamide upon frying. Acrylamide has the potential to cause a spectrum of toxic effects (IARC, 1994), including neurotoxic effects that have been observed in humans. Acrylamide has also been classified as a "probable human carcinogen" (IARC, 1994).

It is widely accepted that acrylamide is mainly formed through the Maillard reaction from free asparagine and a carbonyl source (Mottram, Wedzicha, & Dodson, 2002; Stadler et al., 2002). In most foods, reducing sugars are the main carbonyl compounds that react with free asparagine, as their levels are usually very high. Nevertheless, carbonyl compounds in foods can also arise from lipid oxidation, and particularly during heating (Frankel, 2005). Lipid oxidation has been proposed as a minor pathway of acrylamide formation, with acrylic acid as a direct precursor that can be formed by way of acrolein, by oxidative degradation of lipids (Gertz &

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Klostermann, 2002). Proposals for lowering acrylamide levels include reducing heating time and temperature, lowering the pH, and using raw materials with low sugar or asparagine content. As for exogenous additives, many substances have been reported to be effective for the mitigation of acrylamide, including some organic acids (e.g., citric acid), some amino acids (e.g., glycine) and some monovalent and divalent cations (e.g., Na^+ or Ca^{2+}) (Taeymans et al., 2004). Natural antioxidants are another important way to reduce the acrlyamide content in foods.

Low-cost synthetic antioxidants are often used to slow down lipid oxidation, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and tertiary butylhydroquinone (TBHQ). However, BHT and BHA have been reported to have toxic and carcinogenic effects (Deshpande, Deshpande, & Salunkhe, 1996), and these are allowed as additives in the food industry only within the legal limits. They are very effective during the storage and transport of oils and fats, but they are less effective at frying temperatures, due to their volatility.

With the growing concern over the potential hazards of synthetic antioxidants and a worldwide trend to avoid, or at least minimise, the use of artificial food additives, there is renewed interest in the use of naturally occurring antioxidants. As these occur in nature and are in many cases derived from plant sources, natural antioxidants are believed to be safe (Yanishlieva-Maslarova, 2003). The advantages of natural antioxidants include their relatively unquestioned safety, according to their 'generally accepted as safe' (GRAS) status, the higher concentrations allowed, their worldwide acceptance, and their lower volatility in heated foods (Frankel, 2005). Indeed, in October 2010, rosemary extract was classified as a food additive (as an antioxidant) by European Commission Directive 2010/69/EU, and it is allowed for use in frying oils at concentrations of up to 50 mg/kg (expressed as the sum of the carnosol and carnosic acid contents).

Extracts of rosemary, *Rosmarinus officinalis* L., are natural antioxidants, and in several comparison tests, they have been demonstrated to be as effective as other antioxidants that are commonly used for food preservation (Etter, 2004). Rosemary extracts are particularly active as antioxidants at the high temperatures of frying fats. They can protect the oils during frying, and their antioxidant activity is carried over into the fried foods. The active components of rosemary extract, carnosic acid and carnosol, are readily decomposed during thermal oxidation into products that remain active as antioxidants in heated fats (Frankel, 2005).

The loss of natural antioxidants during their use in frying oils are relatively small, as their volatility is much lower than that of the common synthetic antioxidants. Frying oils must contain nonvolatile antioxidants, otherwise the antioxidants will be gradually lost by evaporation at the high frying temperatures, and into the stream of water vapour that is formed from the water present in the frying material (Pokorný, Trojáková, & Takácsová, 2003). Rosemary extract has been reported to be effective for protection against oil deterioration during frying (Che Man & Jaswir, 2000; Che Man & Tan, 1999; Filip, Hribar, & Vidrih, 2011; Lalas & Dourtoglou, 2003; Réblová, Kudrnová, Trojáková, & Pokorný, 1999). There is still little known about the effectiveness of rosemary extract as an acrylamide inhibitor.

Refined sunflower oil belongs to the edible oils that have high sensory and nutritional value, although it is relatively unstable due to its high content of linoleic acid.

The present study was designed to follow a real-life approach to what happens in frying oil (and to the food) when foods are fried in it. The aim was thus to investigate the benefits of the addition of rosemary extract and other antioxidants in terms of the extent of deterioration of sunflower oil. The protocol used 20 discontinuous cycles of deep-fat frying of frozen, pre-fried potato, without any oil replenishment. The consequent deterioration of the sunflower oil was monitored by measuring the contents of free fatty acids (FFAs), total polar compounds (TPCs), and conjugated dienes and trienes, and the oil colour parameters (L^*, brightness/darkness; b^*, yellowness/blueness). Furthermore, carry-over effects of the antioxidants in the frying oil on the quality of the resultant deep-fried potato were evaluated according to acrylamide concentrations. The correlation between lipid degradation products and acrylamide content was also determined.

2. Materials and methods

2.1. Materials

The rosemary extract was produced by the Vitiva d.d. company (Markovci, Slovenia). The contents of the two major rosemary antioxidative components, carnosic acid and carnosol, were given as 4.0% and 0.9% (w/w), respectively. All of the chemicals for the analysis and the synthetic antioxidants BHA and TBHQ were of analytical grade, and were purchased from Merck (Darmstadt, Germany). The mixed tocopherols (90%) were purchased from Xinguang Technology Co. Ltd. (China). The frozen pre-fried potato was purchased from the Tuš d.d. company (Celje, Slovenia), and the sunflower oil was purchased from the Gea d.d. company (Slovenska Bistrica, Slovenia).

2.2. Frying experiments

A domestic deep-fat fryer with a 3-L-volume vessel was used for the deep-fat frying. The rosemary extract was added to the sunflower oil at 1000 mg/kg, which included 49 mg/kg carnosol and carnosic acid, as the active ingredients, as defined according to present legislation (EU Commission Regulation No 1129/2011, 2011) and various studies (Filip et al., 2011; Ramalho & Jorge, 2008). The maximum allowed concentration of the sum of the active ingredients of rosemary extract (carnosol and carnosic acid) that can be added to frying oil is 50 mg/kg and at this concentration the rosemary extract does not contribute to the sensory quality of the oil or the fried product. The tocopherols were added to the sunflower oil at 1000 mg/kg (900 mg/kg active ingredient) according to industrial practice and previous studies, which were mainly focused on the addition of single tocopherols (α, δ or γ) at different concentrations, rather than addition of a commercially available tocopherol mixture (Braunrath, Isnardy, Solar, & Elmadfa, 2009; Tabee, Azadmard-Damirchi, Jägerstad, & Dutta, 2008; Warner & Moser, 2009). According to European legislation, tocopherols can be added *quantum satis* ("as needed"), as related to good manufacturing practice (EU Commission Regulation No 1129/2011, 2011). The synthetic antioxidants BHA and TBHQ were added to the sunflower oil at their legal limits of 200 mg/kg each (200 mg/kg active ingredient). For each deep-frying cycle, after heating the oil to 180 °C, pre-fried potato (250 g per batch) was added and deep-fried for 5 min, and the oil was then allowed to cool to room temperature. Twenty batches of the pre-fried potato were deep-fried over a 10-day period (two batches per day, over a total of 20 frying cycles), and samples were removed for analysis after each frying operation. The use of 20 frying cycles was chosen as the endpoint because the best performing oil reached approximately 25% polar compounds at this stage, which is close to that of the standard for spoiled oils in Europe (Bastida & Sánchez-Muniz, 2002; Wai, 2007). Fresh oil was not added between the batches. Two batches were fried per day (one in the morning, the other in the afternoon), as intermittent heating of unsaturated fats is generally believed to be more destructive than continuous heating (Frankel, 2005). The deep-fat fryer was left uncovered during the frying operations. The