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Influence of Tunisian aromatic plants on the prevention of oxidation in soybean oil under heating and frying conditions

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p-Cymene (PubChem CID: 7463)
1.8-Cineole (PubChem CID: 2758)
Camphor (PubChem CID: 2537)
Thymol (PubChem CID: 6989)

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A B S T R A C T

The aim of this study was to improve the oxidative stability of soybean oil by using aromatic plants. Soybean oil flavored with rosemary (ROS) and soybean oil flavored with thyme (THY) were subjected to heating for 24 h at 180 °C. The samples were analyzed every 6 h for their total polar compounds, anisidine values, oxidative stability and polyphenols content. The tocopherols content was determined and volatile compounds were also analyzed. After 24 h of heating, the incorporation of these plants using a maceration process reduced the polar compounds by 69% and 71% respectively, in ROS and THY compared to the control. Until 6 h of heating, the ROS kept the greatest oxidative stability. The use of the two extracts preserves approximately 50% of the total tocopherols content until 18 h for the rosemary and 24 h for the thyme flavored oils. Volatile compounds known for their antioxidant activity were also detected in the formulated oils. Aromatic plants added to the soybean oil improved the overall acceptability of potato crisps ($p < 0.05$) until the fifteenth frying.

1. Introduction

Soybean oils one of the most consumed polyunsaturated vegetable oil worldwide (Malheiro et al., 2013; Rodrigues et al., 2012). This oil is known for its wide availability on the local Tunisian market mainly because of its low cost. Alone or in mixture, soybean oil is commonly used for frying as well as for cooking. This oil presents a good nutritional profile due to its composition rich in polyunsaturated fatty acids. However, this makes it unstable under heating conditions resulting in a rapid quality deterioration following the oxidation process (Malheiro et al., 2013).

Soybean oil, like the majority of crude vegetable oils, contains a variety of minor components such as tocopherols which are beneficial to oil stability (Rossi, Alamprese, & Ratti, 2007). Tocopherols, naturally present in soybean oil, are considered to be primary or chainbreaking antioxidants involved in the radical chain reactions. They effectively convert lipid radicals to more stable products, extending therefore the shelf life of food (Fang & Wada, 1993; Nogala-Kalucka et al., 2005). While protecting the oil, tocopherols are generally themselves first oxidized and are quickly decomposed by oxidation reactions or during the refining process and will therefore be present in a small proportion (Rossi et al., 2007).

The treatment of oil with antioxidants seems to be a solution opposing to the problems of oxidation and instability that can occur throughout its use. A number of works discussed the effects

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of the use of natural antioxidants in vegetable oils (CheMan and Jaswir, 2000; Karoui, Dhifi, Ben Jemia, & Marzouk, 2011; Lalas & Dourtoglou, 2003; Malheiro et al., 2013). Studies have shown that the majority of natural extracts from herbs possess strong antioxidant activity. However, a significant difference is observed in their antioxidant effect when added to vegetable oils that are used, especially for frying. Other works showed that plants, in general, display a higher antioxidant activity than different solvent extracts obtained from these herbs (Adams, Kruma, Verhe, De Kimpe, & Kreicbergs, 2011).

Rosemary (*Rosmarinus officinalis*) and thyme (*Thymus capitatus*) are typical plants of the Mediterranean region known by their interesting antioxidant activities. These two plants are currently used in Tunisia since ancient time to improve the taste and the flavor of various foods and products. Their activities are related to their richness on flavonoids, phenolic acids, diterpenes and triterpenes. The main volatile compounds responsible for the strong aroma of rosemary are mainly the 1,8-cineole, camphor, α-pinene, and camphene (Zaouali, Bouzaine, & Boussaid, 2010). Other compounds like carnosol and carnosic acid were recognized as the main compounds responsible for the antioxidant activity of rosemary plant. These compounds are present at high proportions in the extracts prepared from leaves extraction using organic polar solvents (Nogala-Kalucka et al., 2005). In the thyme plant and depending on the species, thymol and carvacrol have been described as the major compounds responsible for a marked antioxidant activity (Bitar, Ghaddar, Malek, Haddad, & Toufeili, 2008; Nieto, Huvaere, & Skibsted, 2011; Sarikurkcu et al., 2010).

The antioxidant compounds from plants and herbs can be added to oil by different ways, as crude extracts, essential oils or simply by maceration of herbs in oil. This technique is currently used for the aromatization of olive oil. As different active compounds naturally present in herbs are oil-soluble, the use of this methodology will enable their extraction. These compounds with antioxidant properties can contribute to modify the sensory characteristics of the product, giving a specific taste and aroma, but can also contribute to the stability of oil during its use and may increase the antimicrobial and the antioxidant activity (Adams et al., 2011; Ayadi, Grati-Kamoun, & Attia, 2009).

Considering the modifications occurring on soybean oil in frying conditions, this work has a purpose to discuss the capacity of rosemary (*Rosmarinus officinalis*) and thyme (*Thymus capitatus*) components to counteract the oxidative process, using a maceration technique. The changes occurring during the heating process concerning the phenolic content, the tocopherols composition, the oxidative stability, the total polar compounds and the anisidine values were evaluated. The present work was an opportunity to study the resistance of different volatile and aromatic compounds in soybean oil in the heating conditions. The ability of natural antioxidants on preserving tocopherols content during the heating process was discussed. The differences in sensory characteristics of fried chips were assessed to show the capacity of plant maceration in retarding heating degradation of soybean oil. Therefore, this work aims the valorization of two Tunisian aromatic plants as active sources of natural antioxidants added to the promotion of their use as natural food additives.

2. Materials and methods

2.1. Materials

The rosemary (*Rosmarinus officinalis*) and thyme (*Thymus capitatus*) leaves used in this study were collected in September from the region of *Zaghouan* in the north-east of *Tunisia*. Soybean oil was given by a local industry specialize in vegetable oils refining (Nejma oils, Slama Frère, *Tunisia*). Fresh potatoes for sensorial analysis were purchased from a local market. All chemicals reagents were of analytical grade.

2.2. Maceration protocol

Thyme and rosemary leaves were first dried and then introduced at a rate of 6% (w/w) separately in glass bottles containing soybean oil. The mixture was kept in the darkness for 7 days. After maceration, two flavored oils were obtained: soybean oil flavored with rosemary (ROS) and soybean oil flavored with thyme (THY). The oils were filtered and stored at 4 °C until analysis. All results obtained in the analysis of the flavored oils were compared to results obtained for the original soybean oil (control oil).

2.3. Heating test

The flavored oils and the control oil (2 L) were submitted to heating at 180 °C (±2 °C) during 24 h (6 h per day) for 4 consecutive days, separately in an electric fryer (Ufesa, EEC) with a maximum oil capacity of 7.5 L, surface/volume ratio of 0.07 cm^{-1}. Samples were collected at the end of each assay and stored at 4 °C until analysis (Chammem et al., 2015).

2.4. Anisidine value

Anisidine value (AV) was determined according to the AOCS official methods Cd 18-90 (1997). In the presence of acetic acid, *p*-anisidine reacts with aldehydic compounds in oils, giving yellowish reaction products. The absorbance of the colored solution was measured at 350 nm using a spectrophotometer (Varian, Inc., CA, USA).

2.5. Total polar compounds

Total polar compounds were measured directly in the oil with a Testo 265 deep-frying oil tester (Testo, Germany). The estimation of polar compounds (PC) was based on the detection of dielectric constant of oil and the results were given in percentage (%) (Casal, Malheiro, Sendas, Oliveira, & Pereira, 2010). Two experiments were set up for each oil and samples from each repetition were analyzed in duplicate (n = 4). The total polar compounds were also measured with the AOCS Official Method Cd 20-91 (1997) and the results were compared with those obtained with the Testo 265 tester.

2.6. Preparation of phenolic extracts from oils

Polyphenols were extracted from frying oils according to Capannesi, Palchetti, Mascini, and Parenti (2000). Briefly, about 2.5 g of oil sample was mixed with 2.5 mL of hexane. The resulting mixture was extracted three times with 2.5 mL of methanol/water (80:20, v/v), vortexed vigorously for 2 min and then centrifuged for 5 min at 5000 rpm. The resulting phenolic fractions were collected each time and stored at −20 °C until analysis.

2.7. Determination of total phenolic content

Total phenolic content was determined by the Folin-Ciocalteu method (Gutfinger, 1981). Briefly, 0.5 mL of the Folin-Ciocalteu reagent and 4.8 mL of distilled water were added to the phenolic fraction. The mixture was left for 3 min at room temperature before adding 1 mL of saturated sodium bicarbonate solution and water was added to bring the final volume to 10 mL. The mixture was placed in the dark for 1 h at room temperature. Absorbance was then measured at 725 nm with spectrophotometer (Varian, Inc.,