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Improvement of vegetable oils quality in frying conditions by adding rosemary extract

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ABSTRACT

The effect of rosemary extract (*Rosemarinus officinalis* L.), a natural antioxidant, on stability of frying oil during heat treatment and on sensorial quality of fried potato was studied. A mixture of soybean and sunflower oils in an equal proportions and containing 0.08% of rosemary extract was evaluated for thermo-oxidation at 180 °C for 30 h. This evaluation was carried out comparatively to an oil mixture without antioxidant. Results showed a significant difference ($p < 0.05$) between oils according to the measured parameters especially at the end of treatment. The addition of the rosemary extract in the mixture of soybean and sunflower oil reduce the peroxide value by 38% after 30 h of heating. This oil resists to oxidation and conserves the higher amount of unsaturated fatty acids even after 30 h of heating. The evolution of saturated fatty acid composition is estimated at 5.5% and 25% in the oil with and without extract, respectively, at the end of the heating treatment. Sensorial analysis carried out showed that the fried potato prepared in oil with rosemary extract had the best crispiness and taste until the fifteenth frying. The oil with rosemary extract showed an enhanced stability and therefore a best quality compared to the oil without rosemary extract.

1. Introduction

Deep fat frying is one of the most procedures used for preparing food (Rababah et al., 2012). It leads to obtain products with appreciated sensorial properties. However, the limit of this technique lies into the rapid deterioration of the quality and the stability of the oil during its use in frying. This deterioration takes place following a series of reactions leading to a qualitative and a nutritional change (rancidity, discoloration and loss of essential fatty acids). These may also be responsible for the production of toxic compounds such as peroxides, aldehydes, and epoxides (Zhang et al., 2012).

Oxidation is one of the most significant chemical reactions occurring during the frying process. This reaction is influenced by several factors such as high temperatures, presence of oxygen and presence of unsaturated fatty acids in a high rate, targets of this reaction (Gupta, 2005). To improve the quality of the oil, increase its stability and subsequently its duration of use, different approaches have been implemented by several companies in the world such as the mixture of different oils, research and use of new plant species producing better stable oils and the use of synthetic or natural antioxidants.

Several studies are interested in finding new sources of natural antioxidants could be more efficient than synthetic ones. For instance, it is known that plant extracts are a mixture of different phenolic compounds known for their antioxidant activity (Michalowska and Korezak, 2007). Several plants were therefore tested for this activity and even how do their extract act in oils.

Nowadays, the most studied extracts are sage extract (*Salvia officinalis* L.) and rosemary extract (*Rosemarinus officinalis* L.), coffee beans, tea leaves, vegetables especially onions and peppers (Jaswir et al., 2000a; Lalas and Dourtoglou, 2003) and olive leaves (Chiou et al., 2009).

Among these natural extracts that are likely to be used industrially, the rosemary ones have a significant antioxidant effect even at high temperatures. Their effectiveness was tested in soybean oils (Lalas and Dourtoglou, 2003; Ramalho and Jorge 2008) and Palm oil (Jaswir et al., 2000a) used for frying. Several studies in this context have shown that the rosemary extracts added to the frying oil

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can inhibit the decomposition of polyunsaturated triacylglycerols, inducing the formation of polar compounds and polymers. It seems that, these extracts are more effective in the inhibition of oil oxidation than synthetic antioxidants such as Butylated hydroxyanisole (BHA) and Butylated hydroxytoluen (BHT) (Jaswir et al., 2000b).

On one side, many compounds have been isolated from rosemary, including flavones, diterpenes, and triterpenes. The antioxidant activity of rosemary extract has been attributed primarily to the presence of carnosic acid and carnosol (Frankel et al., 1996; Nogala-Kalucka et al., 2005). On the other side, it was confirmed that this activity may also be related to the existence of other phenolic diterpenes like Rosmanol, isorosmanol, epirosmanol, and phenolic acids such as rosmarinic acid. These compounds are present at low proportions in the rosemary extract (Nogala-Kalucka et al., 2005).

It has been observed that in fresh rosemary, carnosic acid is the major phenolic diterpene. During the extraction process, this compound can be converted, in part, into carnosol or into other diterpenes which can be degraded further to produce other phenolic diterpenes such as rosmanol or isorosmanol (Huang et al., 1996; Richheimer et al., 1996; Nogala-Kalucka et al., 2005). These compounds act as antioxidants. However, they are more lipophilic and their antioxidant activities are relatively lower than that of carnosic acid (Huang et al., 1996). However, their activity is more important if they are subjected to high temperatures such as at frying (Nogala-Kalucka et al., 2005). Several degradation products are likely to be created once the temperature exceeds 100 °C. Some of these products are active as antioxidants.

When applying antioxidants in oils for frying, their activity depends largely on their composition and type of compounds involved. Thus, as the "polar paradox", and in oil phase, polar antioxidants are more active than non polar. This is explained by the fact that hydrophilic antioxidants are oriented towards the air–oil interface where they are more effective in protecting fatty acids against oxidation than lipophilic antioxidants which remain in solution in the oil phase (Frankel et al., 1996).

The purpose of this study was to formulate stable frying oil based on the antioxidant effects provided by an ethanolic rosemary extract. To improve the stability of frying oil, it was proposed to study the effectiveness of rosemary extract in retarding oxidation of the formulated oil.

2. Materials and methods

2.1. Materials

In the present work, two oils are selected for the formulation of the frying oil: sunflower oil and soybean oil. These oils and fresh potatoes for sensorial analysis were purchased from a local market. The Rosemary leaves (*Rosemarinus Officinalis* L.) used in this study were collected in October from the region of Zaghouan in the north-east of Tunisia. Vouchers specimens are kept in the herbarium of the National Institute of Applied Science and Technology (Tunis, Tunisia). All chemical reagents used were of analytical grade. HPLC-grade acetonitrile and methanol were both from Carlo-Erba (Rodano, Italy), and formic acid was from Interchim (Montluçon, France). All of them were used without any further purification.

2.2. Preparation of the rosemary extract

Rosemary leaves were dried in the open air and then blended. The resulting powder was extracted using a Soxhlet apparatus for 2 h with ethanol as solvent at a 1/10 ratio (powder/solvent).

Table 1
Characteristics of individual oil before mixture.

Oils[a]	PV (meq O_2/kg)	Acidity (%)	UFA (%)	SFA(%)
Soybean oil	2.8 ± 0.03	0.05 ± 0.01	85.73 ± 0.12	15.12 ± 0.10
Sunflower oil	2.1 ± 0.06	0.03 ± 0.01	87.32 ± 0.18	12.74 ± 0.12

PV: peroxide value; UFA: unsaturated fatty acids; SFA: saturated fatty acids.
[a] Mean ± standard deviation (n = 2).

The solvent containing the plant extract is then filtered. It is recovered by using a rotary evaporator (Heidolph, Germany). The final extract was stored at −18 °C until use (Erkan et al., 2008).

2.3. Mixture preparation

In the present work, the choice of oils mixture was based on a preliminary study that was aiming a new frying oil formulation for a Tunisian industry. During this preliminary study, different mixtures of oils (corn oil, sunflower oil, soybean oil, and palm olein oil) were prepared and studied (data no shown). The mixture that was characterized by an interesting fatty acid composition, specifically unsaturated fatty acid one, was chosen to be used for formulation. Other parameters were also taken into account, especially those related to food security, physico-chemical properties, respective stability and costs of the oils considered. As a result, the mixture used in this study was formulated with sunflower oil and a soybean one in equal proportions. Characteristics of both oils before mixture are described in Table 1. An amount of rosemary extract (RE) was added to this mixture. A control was prepared with the same amounts of oils and obviously without any extract.

2.4. Characterization of the rosemary extract

2.4.1. Polyphenols content of rosemary extract

The polyphenols content in the RE was determined using Folin–Ciocalteu reagent (Erkan et al., 2008). A volume of 1 ml of RE solution, prepared in ethanol at a concentration of 0.1 mg/ml, was mixed with 7.5 ml Folin–Ciocalteu reagent diluted 10 times.

The mixture is left 5 min at room temperature before mixing with 7.5 ml of 60 mg/ml of aqueous sodium bicarbonate solution Na_2CO_3. The prepared mixture is placed at room temperature and darkness for 2 h.

The absorbance of the sample was measured at 725 nm using spectrophotometer (Varian, Inc., CA, USA). The concentration was determined using gallic acid as reference and the result is expressed in gallic acid equivalents per gram extract (GAE/g).

2.4.2. HPLC-DAD and HPLC–MS analysis.

HPLC–MS experiments were performed on a U-3000 system (Dionex, Voisins-Le Bretonneux, France) coupled to an Exactive mass spectrometer equipped with an H-ESI ion source (Thermo Scientific, Courtaboeuf, France).

The mass spectrometer was operated in positive ion mode. Spray voltage was set at 4.5 kV. The capillary temperature was set at 250 °C. Tube lens and skimmer voltages were set at 50 and 20 V, respectively. Nitrogen was used as sheath, auxiliary and sweep cone gas at flow rate of 15, 2 and 1 (arbitrary units), respectively. Heater temperature was set at 200 °C.

Separations were carried out on a 50 × 2.1 mm Atlantis T3C18 (3 μm), column (Waters, St-Quentin-en Yvelines, France) protected with a 10 × 2.1 mm pre-column filled with the same stationary phase. All experiments were carried out at 25 °C at a flow-rate of 0.3 mL/min. The mobile phase consisted of 1% formic acid in a mixture of water/acetonitrile (30/70, v/v). 84 mg of the dry residue of the extract are dissolved in 10 ml of methanol. After dilution in water (1/1, v/v) and centrifugation (15 min at 2000 × g), the super-