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EFFECT OF ROSEMARY EXTRACT ON THERMAL STABILITY OF SUNFLOWER OIL

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Abstract: *The purpose of this study was to evaluate the effect of rosemary extract (Rosemarinus officinalis L.) on thermal stability of sunflower oil. Samples of sunflower oil and sunflower oil containing 0.1% rosemary extract were subjected to three successive cycles of thermal heating at burning point for 8 hours, followed by cooling at room temperaturefor16 hours. After each cycle, samples of oils were taken for analysis ofdensity, viscosity and FTIR spectroscopy measurements. Analyzed parameters were used as indicators of structural changes in analyzed samples of oils. According obtained results the addition of rosemary extract in sunflower oil effectively protect its triglyceride structure and level of unsaturation during thermal heating and increase its thermal stability. Performed FTIR spectroscopy has indicated the role of rosemary extract as a natural protective agent. Samples of sunflower oil with rosemary extract have shown improved thermal stability compared with pure sunflower oil.*

Keywords:*sunflower oil, thermal stability, rosemary extract, natural antioxidants,FTIR spectroscopy*

1. Introduction

Vegetable oils, especially cold pressed are an essential component of a healthy diet. Polyunsaturated fatty acids contained in vegetable oils are important substances from physiological and nutritional points of view. Despite their health benefits, they can also be considered as a reason of instability of oils during the technological processes of their production, thermal heating, during cooking or during the storage [1]. Double bounds present in chemical structure in edible oils make them prone to oxidative reactions, which are major cause of deterioration of oils during the period of heating. Thermal heating processes may compromise oil`s stability, causing modifications in the chemical structure and organoleptic properties. Moreover, these processes result in the formation of secondary, potentially toxic compounds [2-4].
Diets in developed countries contain substantial quantities of oils subjected to different processing and heating treatments [5]. High temperature treatment such as deep frying oil is one of the most common

food processing methods used worldwide. The quality parameters of the edible oils such as: taste, texture, shelf life and nutritional composition are affected as a result of complex chemical reactions i.e. oxidation, hydrolysis, and polymerization, which are occurred during the high temperature heating process [6].

Heating in the presence of air cause oxidative and thermal degradations in polyunsaturated triacylglycerolsin the oils, and induce the formation of polar compounds and polymers [5].

The changes linked to the process of heating itself, depends of: temperature, duration of heating, type of heating (continuous or discontinuous), type of used oil, its initial quality, unsaturation level, antioxidant content and presence of additives, etc. [7, 8].

Lipid oxidation occurring in food products is responsible for rancid odors and flavors of the products, and leads to consequent decrease in their nutritional value and safety, and is one of the major concerns in food technology. The problem of ensuring a high quality of lipids and lipid-containing products and prolonging their storage time is directly associated with their optimum stabilization by addition of suitable antioxidants. This is very important from aspect of human health protection, and also it is economically important [9, 10].

Due to their ability to protect foods containing oils and fats, antioxidants play an important role in food processing [2]. They are added to food in order to retard, reduce or prevent oxidative deterioration. In food industry it is not unusual the use of synthetic antioxidants. However, the utilization of some of them has been questioned because of their toxicity [11].

According to recent literature data there concerns about the safety and health risks associated with the use of some of synthetic antioxidants. For this reason, the use of herbs and spices to inhibit the development of oxidative reactions in food systems and improve the oxidative stability of food has recently become popular. Plants, including herbs and spices, are known to have many phytochemicals that could be potential sources of natural antioxidants, which can retard oxidative rancidity via the following pathways: capturing of free radicals, decomposing/deoxidizing peroxides, and scavenging oxygen [9,12, 13].

Many species of the *Lamiaceae* family have strong antioxidant capacity. Rosemary (*Rosmarinus officinalis L.*) extract has potentanti oxidant activity and it is widely used in the food industry. Its antioxidant activity has been associated with the presence of several phenolic compounds: diterpenes, triterpenes, carnosic acid, carnosol, rosmarinic acid, rosmanol,rosmariquinone, rosmaridiphenol and flavonoids [14-16].

The effects of high temperatures on vegetable oils with high contents of unsaturated fatty acids, especially polyunsaturated fatty acids are major concern both for product quality and for human health. In the diet, sunflower oil is widely used, and it is a valuable source of essential linoleic acid [17]. It is one of the most important vegetable oils employed for deep-frying. Because of higher content of unsaturated fatty acids, especially polyunsaturated fatty acids, sunflower oil is more susceptible to oxidation. The purpose of this study was to evaluate the effect of rosemary extract on thermal stability of sunflower oil.

2. Matherials and methods

2.1. Samples

Sunflower oil was purchased from local market in Kosovo. According to the manufacturer`s specifications, the oil was free from antioxidants. The samples were prepared as: sunflower oil (control) and sunflower oil with 0.1% rosemary extract.

The samples were subjected to three successive cycles of thermal heating at burning point for 8 hours, followed by cooling at room temperature for 16 hours. After each cycle, samples of oils were taken for analysis of density, viscosity and fourier transform infrared (FTIR) spectroscopy measurements. Analyzed parameters were used as indicators of structural changes in analyzed samples of oils.

2.2. Chemicals

Folin Ciocalteu reagent, DPPH (2, 2-diphenyl-1-picrylhydrazyl), gallic acid and sodium carbonate were purchased from Sigma – Aldrich. Gallic acid stock solution in ethanol (1 mg/ml) was prepared and used for the preparation of working standard solutions necessary for creation of calibration curve.

2.3. Characterisation of rosemary extract

Rosemary extract was obtained from rosemary (*Rosemarinus officinalis* L.) leaves by steam distillation.

Determination of total phenolic content of rosemary extract - The total phenolic content in the rosemary extract was determined using Folin–Ciocalteu reagent [16]. A volume of 1 ml of rosemary extract 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 was left 5 min at room temperature before mixing with 7.5 ml of 60 mg/ml of aqueous sodium bicarbonate (Na_2CO_3) solution. The prepared mixture was placed at room temperature at darkness for 2 h. The absorbance of the sample was measured at 725 nm using spectrophotometer (Jasco V-630). The concentration was determined using gallic acid as reference and the result is expressed as mg of gallic acid equivalents per gram extract (mg GAE/g).

Antioxidant activity of rosemary extract– The antioxidant activity of rosemary extract was determined using DPPH (2, 2-diphenyl-1-picrylhydrazyl). For this purpose, 0.3 mL aliquot of rosemary extract was mixed with freshly prepared 1.5 mL of DPPH solution in ethanol (0.1 mmol/L). The solution was stored at 25 °C for 30 min at dark and then the absorbance was measured at 517 nm by UV-VIS spectrophotometer. The control was conducted in the same manner, except that distilled water was used instead of sample (rosemary extract). The IC_{50} is the concentration of an antioxidant that is required to inhibit 50% of the initial DPPH radicals under given experimental conditions. The DPPH scavenging capacity assay value was calculated according to the formula (1):

$$IC_{50}\ \% = [1 - (A_{samples} / A_{control})] \times 100 \quad (1)$$

2.4. Density and Viscosity Measurements

After each cycle of thermal heating, samples of oils (with and without rosemary extract) were taken for analysis of viscosity and density. Density of oil samples was measured by pycnometer using 10 ml of sample at 25°C, and viscosity was measured using Ostwald viscometer (ASTM D445 England).

2.5. FTIR Measurements

An IRAfinity-1 Shimadzu Fourier transform infrared (FTIR) spectrophotometer equipped with a DLATGS (deuterated L-alanine triglycene sulfate) detector and calcium fluoride CaF_2 as transparent window, managed by the IR software was used to acquire FTIR spectra of analyzed samples of sunflower oil (with and without rosemary extract). Samples for analysis were taken after each cycle of thermal heating. Spectra were recorded in the spectral region from 4000 to 1000 cm^{-1}

with a resolution of 4 cm^{-1}. FTIR spectral bands were assigned to specific vibrations based on literature data and software spectral library.

3. Results and discussion

In recent years, natural antioxidants from plant origin have attracted considerable attention due to their beneficial functional and nutritional effects including antioxidant activity. Since ancient times, herbs have been used not just for food flavorings, but also for its medicinal antiseptical, and preservative properties. Preservative effects of herbal extracts suggest the presence of antimicrobial and antioxidant constituents in their composition [18, 19].

In this study, rosemary extract was obtained by steam distillation from *Rosemarinus officinalis* L. leaves. The physicochemical properties of the obtained extract are presented in Table 1. The density of the exract was 0.87 (g/cm^3), and viscosity 67±2 mP. The Folin-Ciocalteu assay was used for determination of the total phenolic content, which in the analysed rosemary extract was 21.6±0.5 mg GAE/g. The antioxidant activity is defined as capacity of antioxidants to protect a biological system against the harmful effects of oxidative processes. The antioxidant activity of analysed extract was 76±2.5%.

Physicochemical characterization of rosemary extract indicates high content of polyphenols compounds as well as high antioxidant activity of analyzed extract, and obtained results are in accordance with the literature data [20].

Table 1.

Physicochemical parameters of rosemary extract

Physicochemical parameters	Rosemary extract
Density ($g/cm^{3)}$	0.87
Viscosity (mP)	67±2
Polyphenols (mg GAE/g)	21.6±0.5
Antioxidant activity (%)	76±2.5

Effect of rosemary extract on thermal stability of sunflower oil was studied through analysis of density, viscosity, and FTIR measurements. Analyzed parameters were used as indicators of structural changes in analyzed samples of oils during their thermal heating. Comparative analysis of parameters between samples of two types of oil, sunflower oil (SFO) and sunflower oil with rosemary extract (SFO + RE) was done.

Density changes during the heating of sunflower oil samples with and without rosemary extract are presented in Figure 1. Differences are very clear between the samples. During the heating of oil several reactions are occurred. These reactions lead to decomposition of natural constituents into oxidative and non-oxidative degradation products that can polimerize, which later results with density increase [21].

The viscosity changes of analyzed samples of oil during the thermal heating are presented in Figure 2. According obtained results during the first heating cycle, decrease of viscosity was noted in both type of oil (SFO and SFO + RE). This should be due to the weakening of the intermolecular forces between oil components which lead to the oil degradation. In the second and third heating cycles an increase of viscosity values was noted.

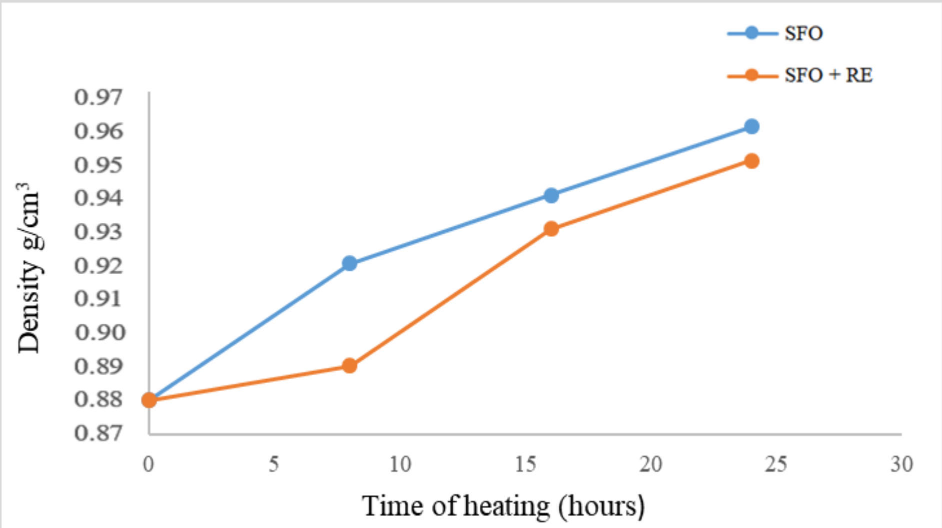

Fig. 1. Density changes in sunflower oil (SFO) and sunflower oil with 0.1% rosemary extract (SFO + RE) during the thermal heating

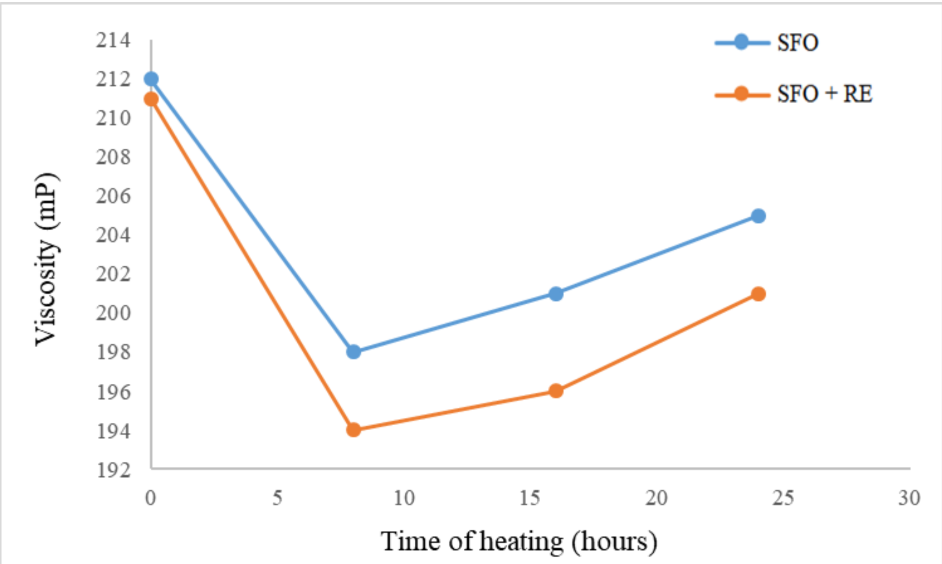

Fig.2. Viscosity changes in sunflower oil (SFO) and sunflower oil with 0.1% rosemary extract (SFO + RE) during the thermal heating

According literature data high temperature process such as frying produces compounds (polymers) with high molecular weight. Polymerization products decrease the stability of frying oils and can be used to measure oil fry life [22].

Results of this study indicate that the increase of oil viscosity is a consequence of increased amount of polymerization compounds. The changes in density and visosity values are more rapidly in the pure sunflower oil (SFO) compared with mixture (SFO + RE) (Figure 1 and Figure 2), this is probably due to the effect of

polyphenols content and antioxidative activity of rosemary extract on higher thermal stability of the mixture oil.
Another procedure used in this study for evaluation of chemical changes in analysed samples of oils (SFO and SFO+RE) during the thermal heating was FTIR spectroscopy. The characteristic functional group used in this research and their wavenumbers are presented in Table 2. FTIR spectral bands were assigned to specific vibrations based on software spectral library and literature data [23, 24].

Table 2.

FTIR absorbance bands and their characteristic functional groups

Wavenumbers cm^{-1}	**Characteristic group and mode of vibration**	
3008	=C–H	Stretching symmetric vibration of the cis double bonds
2925	−CH(CH_2)	Asymmetric stretching vibration of the aliphatic CH_2 group
2854	−CH(CH_2)	Symmetric stretching vibration of the aliphatic CH_2 group
1745	−C = O	Stretching vibration of ester carbonyl functional groups of triglycerides

FTIR characterization of analysed samples of oils during the first heating cycle is presented in Figure 3. Obtained FTIR spectra peaks are common for the majority of vegetable oils. Intesity of peak at $3007cm^{-1}$ can be interpreted by the unsaturation level. Analysis of FTIR spectra based on carbonyl group at $1745cm^{-1}$ indicate triglycerides as mayor compounds in anlysed oil`s samples.

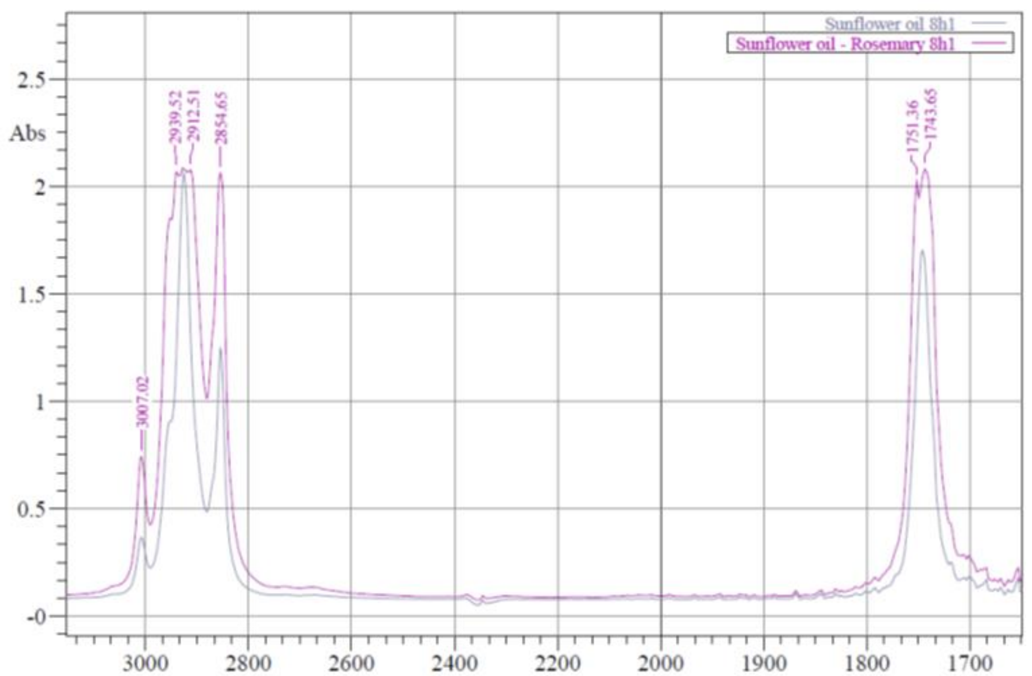

Fig. 3. FTIR Spectra of sunflower oil and sunflower oil with 0.1% rosemary extract after 8 hours of thermal heating

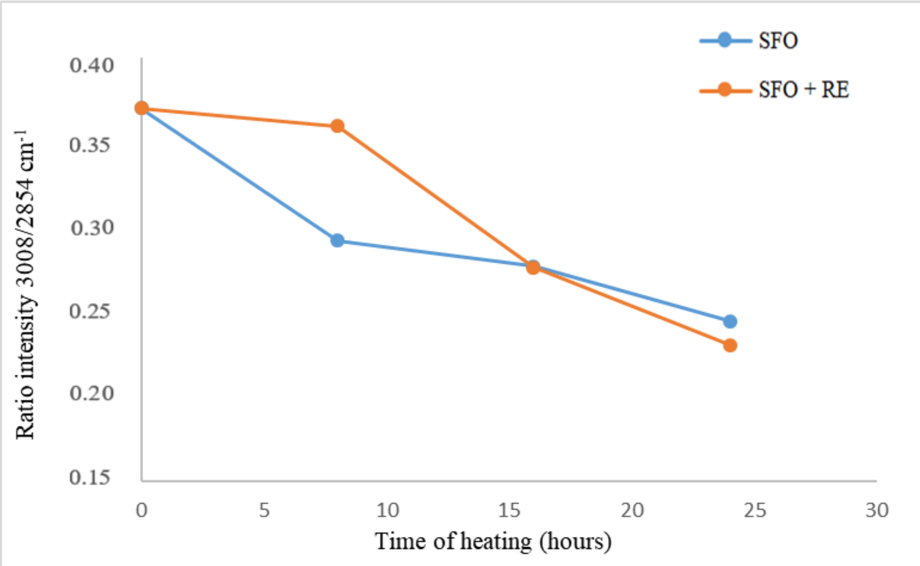

Fig. 4. Intesity ratio at 3008/2854 cm^{-1} during the thermal heating of sunflower oil (SFO) and sunflower oil with 0.1% rosemary extract (SFO + RE)

In this study as an indicator for the chemical changes in analysed samples of oil during thermal heating the intensity ratio of selected peaks is used (Figure 4). Oxidative reactions, are major cause of deterioration of vegetable oils during the period of heating. Usually as a result of oxidation, double bonds are converted in single. The decreasy of ratio intensity 3008/2854 cm^{-1} means conversion of double bonds in single. According obtained results rapid decrease of ratio 3008/2854 cm^{-1} was noted in sunflower oil, especially during the first heating cycle, which was not the case for sunflower oil with rosemary extract (the decrease was more slowly).

4. Conclusion

The results obtained in the present study showed that the rosemary extract is a promising source of natural antioxidants for vegetable oils. It can protect the oils against oxidative processes, even at high temperatures. According obtanied results rosemary extract was more effective in delaying the oxidation of sunflower oil.

Samples of sunflower oil with rosemary extract have shown improved thermal stability compared with pure sunflower oil. In general rosemary extract in sunflower oil effectively protect its triglyceride structure and level of unsaturation (with minor structural changes).

FTIR Spectroscopy used in this study was proved to be suitable method for the analysis of structural changes vegetable oil during heating. This methodology brings advantages over conventional laboratory procedures and allows rapid, specific, non-invasive analyses independent of number of chemicals and without requirement of special sample preparation.

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