EFFECT OF SOME NATURAL HERBS INCORPORATION IN SUNFLOWER OILS ON ITS RESISTANCE AT FRYING TEMPERATURES

Bianca FURDUI[1], Rodica-Mihaela DINICĂ[1], Mariana LUPOAE [2]*, Romică CREŢU[1]

[1]Dunărea de Jos University of Galati, Faculty of Sciences, Chemistry Department, Domnească 111, Galati, 800201, Romania, rodinica@ugal.ro, bfurdui@ugal.ro
[2]Ovidius University Constanta, Faculty of Natural and Agricultural Sciences, Street Mamaia no. 124, 900527, Constanţa, Romania, mariana_lupoaie@yahoo.com

Abstract: *Sunflower oil is an excellent source of essential fatty acids necessary for human body. Extending the frying life of oil is of commercial and economic importance. Therefore, improving the thermal stability of cooking oils could provide considerable savings to the food processors. The present work aims at evaluating thermal resistance of sunflower oil after the incorporation of three species of natural herbs, from Salvia genus and Allium ursinum, used in food as condiments or under other forms. By this treatment, we seek to preserve almost unchanged the oil quality during thermal treatment, by increasing the level of antioxidants from oil.*
For this study, four different frying temperatures i.e. 110, 150, 180 and 200ºC were applied for 30 minutes to sunflower oil before and after the addition of plants. At 110 ºC we have also made a kinetic study on samples stability in time. Official AOAC methods were used to determine free fatty acids content (FFA) and peroxide value (PV) of all samples during heating.
The quality parameters of sunflower seed oil were improved by treatment with either Salvia officinalis., Salvia sclarea or Allium ursinum (wild garlic). Salvia and wild garlic exhibited a comparable high ability in reducing peroxide value (PV), probably due to their high content of polyphenols and flavonoids.
In conclusion, the incorporation of Salvia and wild garlic into sunflower oil helped improve its thermal resistance and stability, which sustains their use in order to extend frying life of oils during food processing.

Keywords: *sunflower oil; Salvia; wild garlic; heat treatment; PV; FFA.*

Introduction

Oils used in the home and oils used commercially require significantly different properties. Perhaps most importantly, commercial oils need to withstand intense heat and frying for longer periods of time.
During the frying process, a number of changes take place in fats and oils, depending on the type of oil used and the food fried [1,2]. So complex thermolytic and oxidative reactions occur, leading to the formation of new compounds such as diacylglycerols, monoacylglycerols, free fatty acids (FFAs), monomers, polymers, and so on, which are harmful to the human body [3,4]. However, the most interesting transformations are FFA content, viscosity and colour change of the vegetable cooking oil as well as formation and decomposition of hydro-peroxides and polymerization via complex free radical processes at elevated temperatures above 160ºC [5].
Extending the frying life of oil is of commercial and economic importance. Therefore, improving the thermal stability of cooking oils could provide considerable savings to the food processors. In order to

increase stability, many healthy oils must be hydrogenated for commercial use, a process that adds unhealthy transfats. Therefore, the present work aims at evaluating the thermal resistance of sunflower seed oil before and after treatment with three kinds of aromatic plants, from *Salvia* and *Allium* families, used in alimentation as condiments or under other forms. By this treatment, we believed that the quality of frying oils can be kept almost constant throughout heat treatment, by increasing of oil's antioxidants content.

The choice of the sunflower oil has been determined by its very frequent use in home and food industry. Sunflower (*Helianthus annuus*) is one of the four major annual oilseed crops produced in the world [6]. Being an excellent source of the essential fatty acids required by the human body, sunflower oil is among the healthiest vegetable oils available. The linoleic acid is one of its essential unsaturated fatty acids [7]. Also, sunflower oil is an important source of vitamin E (45 mg □-tocoferol/100g).

Aromatic plants have been used since ancient times in food flavorings, pharmaceuticals, cosmetics and perfumery. Essential oils or some of their constituents such as polyphenols, flavonoids and carotenoids present biological activities, including antimicrobial and antioxidant properties [8,9].

Since antiquity, *Salvia* species have been well known plants and widely used as folk medicines with antibacterial, antituberculosis, antiviral, cytotoxic, cardiovascular, liver protective and other properties [10-15]. Sage is also used to preserve foods, especially meat and cheese, due to its antioxidant properties, as well as being employed as a spice for flavoring.

Phytochemical investigations have shown that *Salvia* species are mainly rich in diterpenoids and triterpenoids (ursolic acid, oleanic acid) as well as in flavonoids and other phenolic compounds (tannins, cholorogenic, p-cumaric, cafeic and nicotinic acids) [16-20].

Allium is the largest and most important representative genus of the *Alliaceae* family and comprises 450 species, widely distributed in the northern hemisphere. Besides the well known garlic (*Allium sativum* L.) and onion (*Allium cepa* L.), several other species are widely grown for culinary use, such as leek (*Allium porrum* L.), scallion (*Allium fistulosum* L.), shallot (*Allium ascalonicum* Hort.), wild garlic (*Allium ursinum* L.), chive (*Allium schoenoprasum* L.) etc.. *Allium* species are a rich source of phytonutrients, useful for the treatment or prevention of a number of diseases, including cancer, coronary heart disease, obesity, hypercholesterolemia, diabetes type 2, hypertension, cataract and disturbances of the gastrointestinal tract (e.g. colic pain, flatulent colic and dyspepsia)[21]. Due to its composition rich in volatile oils, minerals and oligoelements, flavonoids, polyphenols, vitamins (C and B complex), sulfur compounds, the wild garlic (*Allium ursinum*) has garlic's properties but stronger curative power.

Experimental

Considering their interesting properties, we wanted in particular to test the effect of *Salvia officinalis*, *Salvia sclarea* and *Allium ursinum* plants, which are widely used as condiments in salads in most of the countries of the Balkan Peninsula.

In order to test the contribution of natural herbs to the thermal resistance of sunflower seed oil, the evolution of peroxide value (PV) and free fatty acids content (FFA) during heat treatments, was investigated before and after oil aromatization with the three species of plants. We studied the evolution in time of those parameters at a determined frying temperature, and the evolution at different

frying temperatures for a constant period of time, too.

We used sunflower oil directly from a technological flow, without added antioxidants. Plants were bought from local market (*Salvia off.* and *Allium ursinum*) or harvested from the Botanical Garden of Galati (*Salvia sc.*). All chemicals used were of analytical grade.

Oil treatment with natural herbs

The aerial part of plants dried in air, mortar and sieved to 630 □m, was incorporated into sunflower oil at 2% (w/v). After ultrasonic stirring for 30 minutes, samples were kept in refrigerator for 7 days. After this treatment, the undesirable colour observed in the mixture was removed by an additional decolorizing step, using Cameroun clay (50□m).

Thermal stability evaluation

In order to evaluate the effect of sunflower oil treatment with an aromatic herb on its thermal resistance, both untreated oil and treated oils were heated for 30 min at 110, 150, 180, and 200° C, respectively. Also, a kinetic evaluation of samples was made at 110°C.

Peroxide value determination

The peroxide value (PV) was determined by using the ***AOAC method*** (AOAC, 1999). About 1 g of oil was weighed into a 250 mL iodometric flask. Previously prepared acetic acid–chloroform (1:2) solution (6 mL) and saturated potassium iodide (1 mL) were added. After 3 min. stirring and 5 min. rest, the mixture was titrated with 0.01 N $Na_2S_2O_3$ until yellow colour is almost gone. Approximately, 5 drops of 1% starch solution was added, and titration was continued with shaking vigorously to release all iodine from $CHCl_3$ layer, until the blue colour just disappeared. In parallel, a blank sample is similarly treated. PV was calculated by using the following equation:

$$\mathbf{PV = S \cdot N \cdot 1000 / m_p \ (meq\ Na_2S_2O_3/Kg\ oil)}$$

where, S is the ml $Na_2S_2O_3$ (blank corrected), N is the normality of $Na_2S_2O_3$ solution and m_p is the mass of oil sample (g).

FFA determination

FFA content was determined in triplicate, by the titration method of AOAC (AOAC, 1999). About 1 g of oil was weighed into a 250 ml flask. 10 mL benzene: alcohol (1:1) mixture and 3-4 drops of 1% phenolphthalein, as indicator, were added. The mixture was titrated with 0.1 N NaOH with vigorous shaking until permanent faint pink colour appeared and persisted at least for 1 min. The FFA value was calculated according to the following equation:

$$I.A = 3.9998\, V/m_p \ [\text{mg NaOH/g sample}]$$

where m_p is the mass of the oil test portion (g), and V the volume of NaOH consumed (mL).

Results and Discussion

Peroxide formation is a major concern from the point of view of rancidity and toxicology in fried oils. Food lipid oxidation products such as peroxides, malonaldehyde, and several cholesterol oxidation products are reported to cause atherosclerosis and coronary heart disease [22].

The evolution in time of PV (meq. of peroxide per kg of sample) of the sunflower oil samples during heat treatment at the 110°C is shown in Fig. 1.

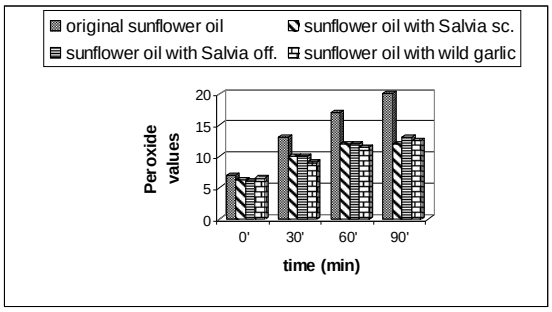

Fig.1. Effect of Salvia and wild garlic addition to sunflower oil on time evolution of peroxides (PV) formed after exposure at 110°C temperature

The change in PV of the untreated and treated sunflower oil during heat treatment, at different frying temperatures is shown in Fig. 2.

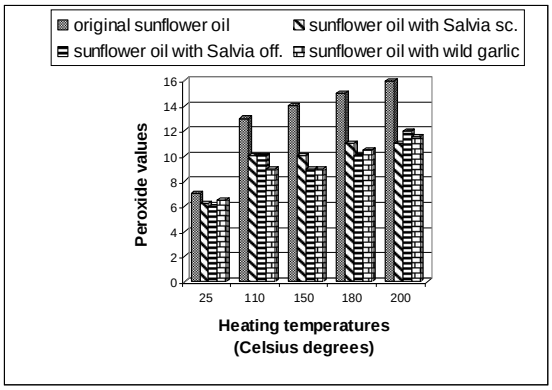

Fig.2. Effect of Salvia and wild garlic addition to sunflower seed oil on peroxides (PV) formed after exposure to different frying temperatures.

The obtained results showed a significant difference between PV of treated (sunflower oil with *Salvia sc*., *Salvia off*. and with *Allium ursinum*) and PV of untreated (original sunflower oil) samples during heating. Although the same temperatures were applied to all samples, the amount of peroxides found in untreated sample was higher than that of peroxides contained in treated samples. However, no big differences were observed between PV of treated oil samples. The peroxides values increased in 90 minutes from 7 to 20 meq/kg for original sunflower oil, from 6.25 to 12 meq/kg for sunflower with *Salvia sc*., from 6 to 13 meq/kg for sunflower with *Salvia off*. and from 6.5 to 12.5 meq/kg for sample with *Allium ursinum*, after heating at 110°C. As the temperature was raised from 25 to 200°C respectively, PV for original sunflower oil increased from 7 to 16 meq/kg and for treated oils the increase was smaller, about from 6 to 12 meq/kg.

Another important indicator of oil deterioration during heating is the FFA content. During frying, at elevated temperatures (160–180°C), in the presence of air and moisture, free fatty acids resulted from the hydrolysis of triacylglycerols as well as from further decomposition of hydroperoxides. The released fatty acids are more susceptible to thermal oxidation at frying temperatures. The oxidized products of fatty acids give the off-flavors and odors (hydrolytic rancidity) to the frying medium and fried foods. Therefore, controlling the level of FFA within a reasonable range would prevent the breakdown of fats.

In the present study, the FFA content increased from 1.2 to 2.6 (mgNaOH/g sample) in the original sunflower oil, from 1.2 to 1.5 (mgNaOH/g sample) sunflower with *Salvia sc*. and *Salvia off*. and from 1.2 to 1.45 (mgNaOH/g sample) in the sunflower oil with wild garlic, by heating from 25 to 200 °C, respectively, as shown in Fig. 3.

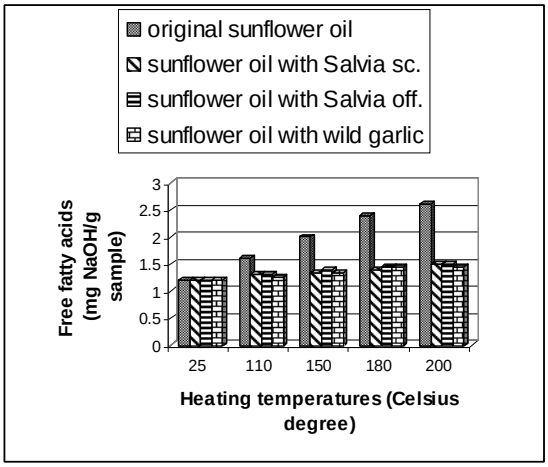

Fig.3. Effect of Salvia and wild garlic addition to sunflower seed oil on free fatty acids (FFA) formed after exposure to frying temperatures.

The analysis of results shown in Fig. 1 revealed the existence of a significant difference between treated and untreated samples during heating. However, it did not show any difference between sunflower oil with *Salvia* species and sunflower oil with wild garlic samples.

Conclusions

In the present work we have studied the stabilizing effect of aromatizing plants from *Salvia* and *Allium ursinum* (wild garlic) species added to sunflower oil, during heat treatments.

The obtained results showed that the quality parameters of sunflower oil following exposure to frying temperatures were improved by the addition of natural herbs. In fact, though the PV and FFA increased with temperature for all samples, however, the evolution of studied parameters in treated oil was found to be slower than the one observed in untreated oil. So, sunflower oil with salvia and wild garlic samples exhibited relatively reduced peroxides values and FFA contents, following heat treatment, comparatively with the original sunflower oil.

In conclusion, our studies have proved that these plants (*Salvia officinalis*, *Salvia sclarea* and *Allium ursinum*) used in alimentation for their aromatizing and curative properties, exhibit also good properties as antioxidants and/or free radical scavengers.

Thus, their incorporation into sunflower oil helped improve its thermal resistance and stability, which support their use to control lipid oxidation during food processing.

This may be due to the abundance of natural antioxidants (such as polyphenols and flavonoids) present both in salvia and wild garlic which were transferred into sunflower seed oil following its treatment with natural herbs. In fact, these natural components can react with free radicals of the frying oil, acting synergistically as free radical scavengers and/or contributed to the protection of tocopherols, susceptible of heat-induced loss, particularly to the protection of □-tocopherols, the main antioxidant contained in original sunflower seed.

The obtained results comply with other studies regarding the effect of natural herbs on oil stabilization [23]. Further studies will be carried out to understand better the factors influencing antioxidant activity of those aromatizing plants.

References

1. R. DEMIR, M. BAS-HAN, A study on the investigation of fatty acids in pulps and seeds of Olea Europae L. (Hırhali) and Olea Europae L. (Zoncuk), Biochemical Archives, 14, 1998, 187–191;
2. R. DEMIR, B. OTLUDIL, Investigation of the saturated and unsaturated fatty-acids in the internodes and leaves of Vitis-Vinifera L. (Mazruma), Biochemical Archives, 13(4), 1997, 223–228;
3. W. L Clark, G. W. SERBIA, Safety aspects of frying fats and oils, Food Technology, 45(2), 1991, 84–86, 88–89, 94;
4. P. J. WHITE, An overview of methods for measuring changes in deep-fat frying oils, Food Technology, 45(8), 1991, 75–80;
5. M. M. BLUMENTHAL, A new look at the chemistry and physics of deep fat frying, Food Technology, 45(2), 1991, 68–71;
6. K. M SCHMIDT, Sunflower oil processing manual. Bismarck, North Dakota: National Sunflower Association, 1991;
7. J. M. BOURRE, M. DUMONT, M. PICIOTTI, G. PASCAL, G. DURAND, Les acides gras du cerveau; nature, role, origine, leur importance alimentaire, In Congres International CHEVREUL pour lţetude des corps gras, Proceeding, Angers, 1989, 49–81;
8. A. LOO, H. RICHARD, Nature, Origine et Proprietes des Epices et des Aromates Bruts, In H. Richard (Ed.), Epices et Aromates, Paris, TEC. & DOC. Lavoisier, 1992, 18–22;
9. V. PRAKASH, Leafy spices, Boca Raton, FL: CRC Press Inc, 1990;
10. A. ULUBELEN, S. ÖKSÜZ, G. TOPÇU, A. C. GÖREN, W. VOELTER, Antibacterial diterpenes from the roots of Salvia blepharochlaena, Journal of Natural Products, 64, 2001, 549–551;

11. A. ULUBELEN, G. TOPÇU, H. LOTTER, H. WAGNER, C. ERIS, Triterpenoids from the aerial parts of Salvia montbretii, Phytochemistry, 36, 1994, 413–416;
12. G. TOPÇU, E. A. ALTINER, Ş. GOZCU, B. HALFON, J. M. PEZZUTO, D. G. I. KINGSTON, Studies on di- and triterpenoids from *Salvia staminea* with cytotoxic activity, Planta Medica, 69, 2003, 464–467;
13. A. ULUBELEN, Cardioactive and antibacterial terpenoids from some Salvia species, Phytochemistry, 64, 2003, 395–399;
14. A. ULUBELEN, H. BIRMAN, S. OKSÜZ, G. TOPÇU, U. KOLAK, A. BARLA, Cardioactive Diterpenes from Salvia eriophora, Planta Medica, 68, 2002, 818–821;
15. L. ZHOU, Z. ZUO, M. S. S. CHOW, Danshen: An overview of its chemistry, pharmacology, pharmacokinetics, and clinical use. Therapeutic reviews/herbal medicine, The Journal of Clinical Pharmacology 45, 2005, 1345–1359;
16. G. TOPÇU, A. ULUBELEN, Structure elucidation of organic compounds from natural sources using 1D and 2D NMR techniques, Journal of Molecular Structure, 834–836, 2007, 57–73;
17. G. TOPÇU, Z. TÜRKMEN, J. K. SCHILLING, D. G. I. KINGSTON, Highly hydroxylated triterpenes from Salvia kronenburgii., Journal of Natural Products, 67, 2004, 118–121;
18. G. TOPÇU, N. TAN, A. ULUBELEN, D. SUN, W. H. WATSON, Terpenoids and flavonoids from the aerial parts of Salvia candidissima, Phytochemistry, 40, 1995, 501–504;
19. Y. LU, L. Y. FOO, Polyphenolics of Salvia – a review, Phytochemistry, 59, 2002, 117–140;
20. Volkan YEŞILYURT, Belkıs HALFON, Mehmet ÖZTÜRK, Gülaçtı TOPÇU, Antioxidant potential and phenolic constituents of *Salvia cedronella*, Food Chemistry 108, 2008, 31–39;
21. Virginia LANZOTTI, Review. The analysis of onion and garlic, J. Chromatogr. A, 1112, 2006, 3–22;
22. R. SUBRAMANIAN, K. E. NANDINI, P. M. SHEILA, A. G. GOPALAKRISHNA, K. S. M. S. RAGHAVARAO, M. NAKAJIMA et al., Membrane processing of used frying oils, Journal of the American Oil ChemistsSociety., 77(3), 2000, 323–328;
23. Meriem BENSMIRA, Bo JIANG, Consolate NSABIMANA, Tang JIAN, Effect of Lavender and Thyme incorporation in sunflower seed oil on its resistance to frying temperatures, Food Research International 40, 2007, 341–346.