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Thermal oxidative alteration of sunflower oil

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Sunflower oil is extensively used in frying in Algeria as an alternative to olive oil due to its low cost. However, the high level of unsaturated fatty acids (FA) contained in sunflower oil enhances its susceptibility to oxidation. In our study, the sunflower oil was heated at 99±2°C with incorporation of 9 L of oxygen/second for 52 h continuously in the absence of foodstuff. Heating polyunsaturated fatty acids (PUFAs) in the presence of air causes a greater degree of lipid peroxidation. The oil oxidation degree was monitored through several physicochemical analyses. The products of thermal oxidation were monitored using UV- spectrophotometric method and Fourier transform infrared spectroscopy (FT-IR). Compared to fresh oil, the free-fatty acid contents, peroxide value, density and moisture of the thermally oxidized sunflower oil increased. In addition, the iodine and saponification values decreased during thermal treatment. The treatment applied had a negative effect on FA composition; the most significant effects were on C18:2, C18:1 and C16:0 contents. Analysis of chromatographic profile of thermoxidized sunflower oil showed a reduction in linoleic acid (LA) and an increase in oleic and palmitic acids; decrease of linoleic acid content is used as an indicator of lipid oxidation. Moreover, during the early stages, conjugated dienes (CDs), absorbing at 233 nm, were formed upon decomposition of hydroperoxides. In our study, the early stages of lipid oxidation were measured by UV-spectrophotometric method. Hydroperoxides broke down into secondary products and were revealed by FT-IR; these scission products are generally odoriferous by nature. The C=O stretching band at 1739-1724 cm^{-1} of the aldehydes was much more intense. Formation of conjugated double bond systems and the isomerisation of *cis* to *trans* double bonds was observed in the C=C stretching region at 980 to 965 cm^{-1}. The results obtained reveal that even fresh oil contains products of peroxidation and isomerization of C18:2, n-6; indeed, CDs can be produced during the refining process of oil. The treatment applied increased the rate of these products and conferred a marked rancid taste and a thick texture to the thermoxidized sunflower oil.

Key words: Sunflower oil, Linoleic acid, thermally oxidative treatment, alteration level.

INTRODUCTION

Sunflower oil is a high-quality edible oil. It is used in cooking, frying, and in the manufacture of margarine and shortening and considered by some as desirable as olive oil. Sunflower oil was selected in this study due to its high use in food as it is a rich source of linoleic acid. Furthermore, it is light in taste and appearance and has a high vitamin E content compared to other vegetable oils (Shahidi et al. 1992).

At high temperature and in the presence of air, many chemical reactions can be observed in oil: hydrolysis, polymerization, oxidation and isomerization (Rossell, 2001). Thus, new and unstable compounds potentially

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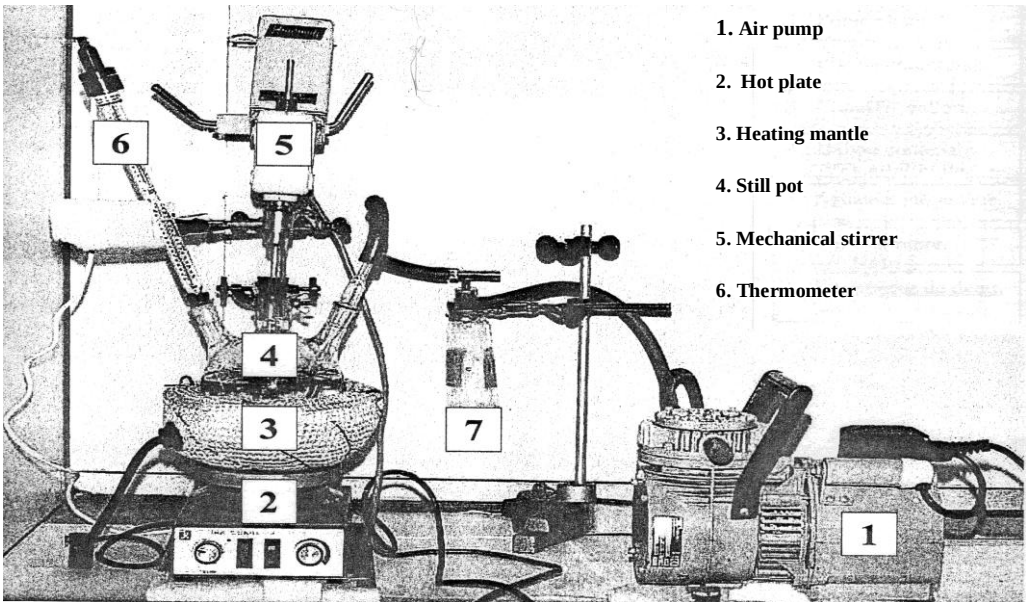

Figure 1. Mounting of thermal oxidation device.

toxic at low concentrations may be generated after destruction of the linoleic acid (Nawar, 1996; Min and Boff, 2001).

The objective of this study was to evaluate the deterioration levels of sunflower oil subjected to thermoxidative treatment (in the absence of foodstuff) according to the laboratory instrumental method developed by Drozdowski and Szukalska (1987) modified by Blanc-Gondardmary et al. (1989). There is no standard method to detect oxidetive changes during the entire process, and a combination of different analytical techniques is usually required (Gray, 1978; Frankel, 1993; Warner and Eskin, 1995). In our study, the primary oxidative products were monitored through peroxide value (PV), loss of unsaturated fatty acids, conjugated diene value, and others. Secondary changes are measured by Fourier transform infrared (FT-IR) spectroscopy, this latter gives information about the different functional groups present in the sample; thus, it is not limited to just one kind of compound like the indices mentioned above (Muik et al., 2005).

MATERIALS AND METHODS

Sunflower oil was purchased at a local market in Tizi-Ouzou, Algeria. This oil was obtained from the seeds of *Héliantalus annus linnaeus* containing 40% of oil. Sunflower oil-like most vegetable oils is composed mainly of triacylglycerols (98 to 99%), and a small fraction of phospholipids, tocopherols, sterols, and waxes (all of the latter are commonly referred to as the ‘‘unsaponifiable fraction’’). Sunflower oil is characterized by a high concentration of linoleic acid, followed by oleic acid and it has a low content of palmitic acid compared with other oils (Grompone, 2005). Decrease of linoleic acid content is used as an indicator of lipid oxidation. The mechanism of lipid oxidation changes significantly at elevated temperatures and depends strongly on oxygen availability. In our study, the sunflower oil (700 ml) was heated at 99±2°C with incorporation of 9 L of oxygen / s for 52 h continuously in dark. Figure 1 show the apparatus setup used in thermally oxidative treatment.

After treatment, thermoxidized sunflower oil was kept under nitrogen before sealing airtight in a glass bottle and stored at -20°C until further analysis. The degree of oxidation of the oil was monitored through several physicochemical analyses. The following parameters were studied: free-fatty acid (FFA) contents, peroxide value (PV), refractive index (RI), humidity (H%), iodine value (IV), saponification value (SV) and density (AOCS, 1989); fatty acid (FA) composition (AOAC, 1999); specific extinction at 232 nm (*K*232) and 270 nm (*K*270) related to the content of conjugated dienes (CDs) and trienes (CTs) of linoleic acid (18:2 n-6) respectively was determined using UV spectrophotometer (IUPAC, 1987); secondary lipid oxidation products were determined using FT-IR spectroscopy.

Statistical data analysis

The average comparison was realized by the analysis of variance (ANOVA) with Stat. Box. Edition 6.4. The significance level was selected at $p < 0.05$.

RESULTS

The study shows that compared to fresh oil, the FFA content, PV, RI, density and moisture of the oxidized sunflower oil increased from 0.093 to 1.25%, 5.83 to 152.5 meq/kg, 1.461 to 1.476, 0.910 to 0.985 and 0.100 to 2.006 respectively. The IV and SV decreased from 125.84 to 80.51 g I_2/100 g and 192.60 to 183.79 mg KOH/g respectively. In addition, a reduction in linoleic acid (from 58.14 to 40.59%) and an increase in oleic acid

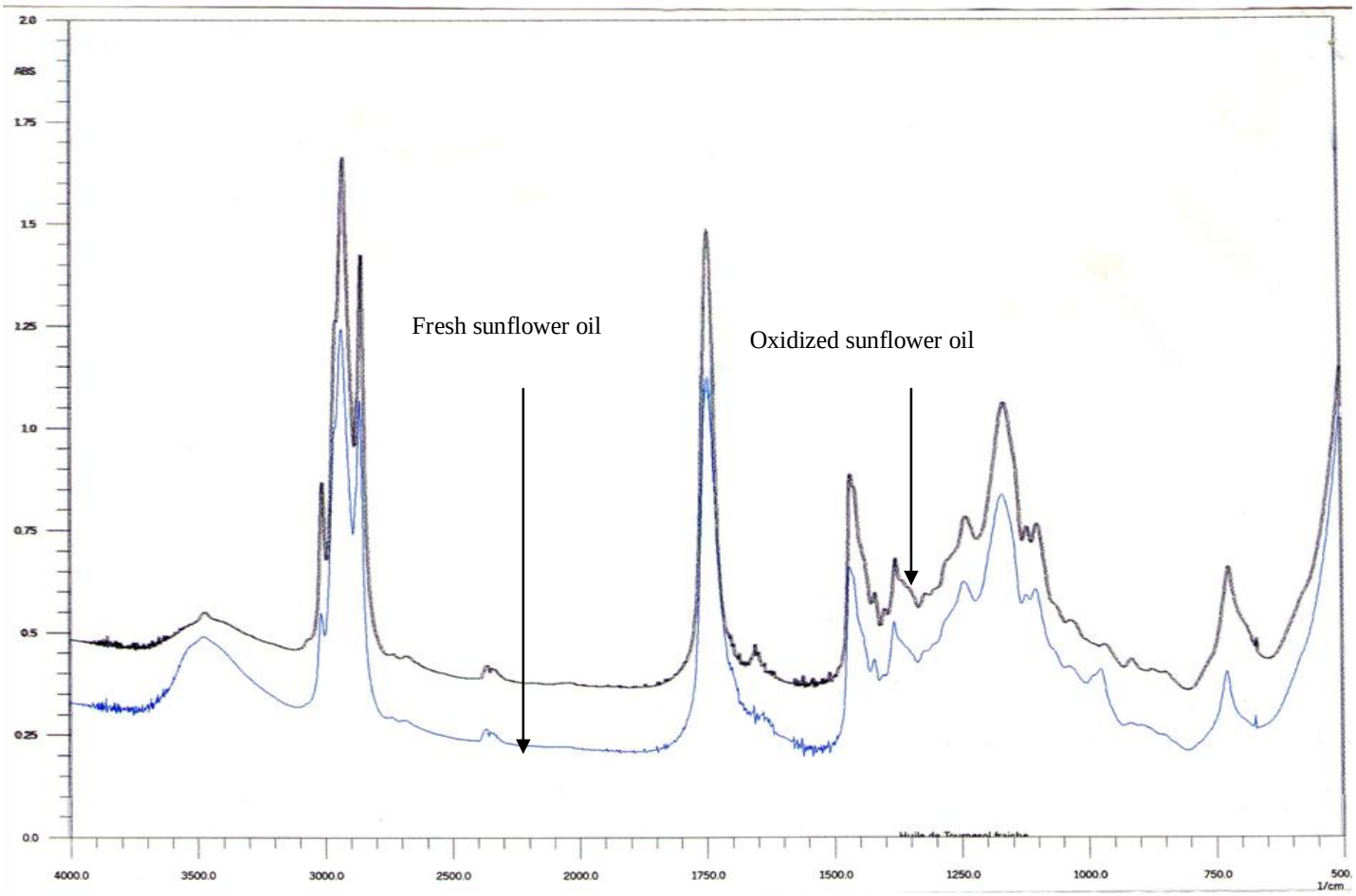

Figure 2. FT-IR spectra of fresh and thermoxidized sunflower oils (4000 - 500 cm^{-1}).

(from 33.500 to 46.04%) in relation to fresh sunflower oil were observed. Decrease of linoleic acid content was used as an indicator of lipid oxidation. Conjugated double bonds (C=C–C=C) values (expressed as extinction values at 232 nm), which are primary products, increased from 0.0002 to 0.033, whereas conjugated trienes values at 232 nm ranged from 0.423 to 0.655. Formation of aldehydes, ketones and other secondary oxidation products, revealed by FT-IR spectroscopy, in thermoxidized oil was accelerated by constantly bubbling air into the oil during heating (Figure 2). Then, flavour, aroma and taste of the oil were affected. Also, the formation of conjugated double bond systems and the isomerisation of *cis* to *trans* double bonds as observed in the C=C stretching region contributed to change of the density and viscosity of the thermoxidized sunflower oil.

Nevertheless, part of the double bonds of the linoleic acid remained at configuration *cis* (C=C–C–C=C); this essential FA was proportioned at 40.59% in oxidized oil. Our results show a strong increase of the band located at 1667 to 1639 cm^{-1} which can be assigned to *cis* double bonds in oxidized oil compared to fresh oil.

DISCUSSION

In order to document the thermally oxidative treatment influence on sunflower oil, an exhaustive examination was needed for both physical and chemical criteria of this oil (Table 1). The results of various investigated parameters led to the conclusion that the treatment applied in our study caused a high level of deterioration of this oil.

Compared to fresh oil, the thermoxidized oil contained approximately 13 times more total FFA than fresh oil (0.093 *vs*. 1.25%) and its acidity content was higher (P=0) than fresh oil (0.182 *vs*. 2.51 mg KOH/g). Formation of FFA might be an important measure of rancidity of foods. FFAs are formed due to hydrolysis of triglycerides and may get promoted by reaction of oil with moisture (Freja et al., 1999). The advanced deterioration of thermoxidized oil was due to its strong humidification. The treatment caused a very significant (P=0) rise in humidity (2% *vs.* 0.1%). Humidification of oxidized oil would be due to the formation of water and volatile compounds which constitute the final products of decomposition of hydroperoxides.

Table 1. Physico-chemical properties of fresh and thermoxidized sunflower oil.

Characteristic	Fresh oil	Thermoxidized oil
Physical state at room temperature	Fluid	Thick texture, flavor faded
Peroxide value (meq/Kg)	5.83 ± 0.76	152.5 ± 5.33
Acid value (mg KOH/g)	0.182 ± 0.04	2.51 ± 0.11
Free Fatty Acids (%)	0.093 ± 0.02	1.25 ± 0.07
Iodine value (g I_2/100g)	125.84 ± 1.59	80.51 ± 1.37
Saponification value (mg KOH/g)	192.60 ± 2.91	183.79 ± 1.32
Refraction index	1.461 ± 0.037	1.476 ± 0.023
Density at 20°C (g/ml)	0.910 ± 0.018	0.985 ± 0.010
Moisture (%)	0.100 ± 0.012	2.006 ± 0.221
C16 :0 content (%)	6.14 ± 0.451	9.48 ± 0.367
C18 :1, n-9 content (%)	33.500 ± 2.317	46.040 ± 3.939
C18 :2, n-6 content (%)	58.140 ± 2.475	40.590 ± 0.829

Values are mean±standard deviation of triplicate determinations.

Table 2. CDs and CTs extinctions values in both oils.

λ (nm)	Extinction values « K »	
	Fresh oil	Thermoxidized oil
200	-	0.112
232	-	0.036
250	0.0002	0.033
262	-	0.027
268	0.293	0.407
270	0.423	0.655

In addition, this treatment decreased the global unsaturation of thermoxidized oil. The IV is a measure of the total number of double bonds. During the oxidation process, a very significant decrease (P=0) in IV was observed (125.84 *vs.* 80.51). This reduction was more pronounced than those obtained by Blanc-Gondardmary et al. (1989). This variation was due to the more prolonged time of heating applied. Decrease in IV is an indicator of lipid oxidation (Naz et al., 2004). Our results obtained by gas chromatography (GC) showed a dramatically reduced level of unsaturated FA.

PV is a widely used measure of primary lipid oxidation indicating the amount of peroxides formed in fats and oils during oxidation (Ozkan et al., 2007). Our result show a considerable (P=0) increase (5.83 *vs.* 152.5 meq/Kg) in PV after subjecting the oil to oxidation conditions. Such increase in PV had been reported by Neff et al. (1994), Liu and White (1992).

Oxidation of polyunsaturated fatty acids (PUFA) leads to primary and secondary oxidation products. Compounds and amounts of these products vary, depending on the oxidative conditions. To evaluate the oxidation state of the oil, the following parameters have been measured in the two oils. The UV spectrophotometric absorption at 232 and 270 nm, expressed as *K*232 and *K*270, measures the formation of CD and CT, respectively. The *K*232 value increased strongly in oxidized oil reflecting that much CD was formed (Table 2). The spectrophotometric absorption at 270 nm showed for the thermoxidized oils a tendency that resembles very well that of the band located at 833 to 866 cm^{-1} for hydroperoxides, 1739 to 1724 cm^{-1} for aldehydes and 1724 to 1709 cm^{-1} for ketones.

In addition, our experimental conditions supported the peroxidation of linoleic acid and increased the polarity of oil revealed by measurement of PV and IR spectrophotometry at 3636 to 3571cm^{-1} respectively. In the frame of this study, we compared the FA composition of thermoxidized and fresh sunflower oil.

Thermal treatment led to dramatical differences in sunflower oil FA composition; the linoleic acid decreased upon heating, which explained the increase in oleic and palmitic acids. This has been previously reported in heated sunflower oil (Juaneda et al., 2003). The sensitivity of the double bounds of linoleic acid to the combined action of heat and oxygen would be responsible for this finding. Crapiste et al. (1999) demonstrated that as alteration advanced, there was a continuous decrease of

unsaturated fatty acids, particularly linoleic acid, being more pronounced at the highest temperature. It resulted in an increase in the oleic acid to linoleic acid ratio (o/l), indicating a preferential use of linoleic acid in oxidation reactions. Otherwise, Marmesat et al. (2009) observed, in high linoleic sunflower oil, that the oxidation took place mainly in the linoleyl group of the triacylglycerols, while the loss of oleyl group was minimum throughout the total oxidation period. However, in high oleic sunflower oil, due to the high relative content in oleic acid, the decrease of oleic acid was similar to that found for linoleic acid.

Different FA isomers were formed during heating and higher differences were found between their contents in the thermoxidized and fresh sunflower oils. The hydroperoxides and CD, relatively stable, absorbed at 232 nm. They are quantifiable by UV spectrophotometric method (Laguerre et al., 2007). These primary products of oxidetion were formed highly in oxidized oil; an extinction of 0.073 was noted. Hydroperoxides can be decomposed into secondary products. Aldehydes and ketones have been reported as major secondary oxidation products. For oxidized oil, the value of this parameter was much higher than for the fresh oil (1.122 *vs.* 0.716). Accumulation of these secondary products in oxidized oil caused deterioration of its flavor.

FT-IR spectroscopy has been used to investigate the chemical changes taking place during lipid oxidation in several edible oils. Differences among the spectra of the fresh and oxidized oils were located at all of the bands suggested by Mazliak (1968) (Figure 2). The intensities of these bands were higher in oxidized oil than in fresh oil which reflects the high level deterioration of oil. Thermoxidized oil contained more hydroperoxides than fresh oil; part of this primary product was converted into secondary products; the C=O stretching band of the aldehydes was much more intense. Thermal oxidation led to strong increases of the bands at 833 to 866 and at 1739 to 1724 cm^{-1} respectively.

Oxidative degradation of sunflower oil was accelerated by heating at 100°C combined to oxygen insufflated. The formation of conjugated double bond systems and the isomerisation of *cis* to *trans* double bonds was observed in the C=C stretching region (980 to 965 cm^{-1}). Thermal oxidation led to strong increases of the band at 980 to 965 cm^{-1} assigned to CD. Thick texture of thermoxidized oil can be attributed to high amounts of CD and CT produced, which is also reflected in *K*270 and *K*232 of this oil; this principal parameters reflect the isomerisation of *cis* double bonds to *trans* double bonds reflecting change of the density and texture of this oil.

In addition to ketones and aldehydes, oxidized oil exhibited a very strong band at 1761 cm^{-1} which corresponds to the C=O stretching (1761 cm^{-1}) of the formic acid (HCOOH). In fact, this compound contributed to the deterioration of the organoleptic quality of oil. This acid will be converted into CO_2 and H_2O, other final products of oxidation.

Conclusion

From the results of various investigated parameters, it can be concluded that the treatment applied to the sunflower oil, which is heating at 100°C with continuous air insufflations for 52 h, caused a high level deterioration with development of oxidative rancidity. Results obtained spectrophotometrically showed very strong band at 980 to 965 cm^{-1} which corresponds to the C=C stretching vibration in conjugated systems; the C=O stretching band of the aldehydes (1739 to 1724 cm^{-1}) was much more intense in oxidized oil regardless of treatment. Over-consumption of these components can be detrimental to health. Significant losses in the essential fatty acid (linoleic acid) were also evident in sunflower oil subjected to treatment.

In further work, we plan to apply this technique to the study of related oxidation processes in biological systems that are gaining increased attention with regard to possible connection between lipid oxidation and pathological events.

REFERENCES

AOCS (1989). Official and Recommended Practices of the American oil Chemists Society, 5th eds. Champaign, I.L. pp. 48-62.

Blanc-Gondardmary P, Revol A, Pacheco H (1989). Chronical ingestion of oxidized oil in young rat. Effect on lipid composition and cytidyl transferase activity. Biomembranes et nutrition, colloque INSERM., Paris, 12-14 juin.

Crapiste GH, Brevedan MIV, Carelli AA (1999). Oxidation of Sunflower Oil During Storage. JAOCS 76 : 1437-1443.

Drozdowski B, Szukalska E (1987). A rapid instrumental method for the evaluation of the stability of fats. J. Am. Oil. Chem. Soc. 64:1008–1011.

Frankel EN (1993). In Search of Better Methods to Evaluate Natural Antioxidants and Oxidative Stability in Food Lipids. Trends Food Sci. Technol. 4:220–225.

Freja N, Mozzon M, Lercker G (1999). Effect of free fatty acids on the oxidative stability of vegetable oil. J. Am. Oil Chem. Soc. 76 : 325-329.

Gray JI (1978). Measurement of Lipid Oxidation: A Review. J. Am. Oil Chem. Soc. 55:539–546.

Grompone MA (2005). Sunflower Oil. Bailey's Industrial Oil and Fat Products, Sixth Edition, Six Volume Set. Edited by Fereidoon Shahidi. Copyright © John Wiley & Sons, Inc.

International Union of Pure and Applied Chemistry (IUPAC) (1987). Standard method for the analysis of oils, fat and derivatives; 7th revised and enlarged edn., edited by C. Paquat and A. Hautfenne, Blackwell Scientific, London.

Juaneda PSB, De la Perriere JL, Sebedio, Gregoire S (2003). Influence of heat and refining on formation of CLA isomers in sunflower oil. J. Am. Oil Chem. Soc. 80:937–940.

Laguerre M, Lopez-Giraldo LJ, Lecomte J, Pina M, Villeneuve P (2007). Outils d'évaluation in vitro de la capacité antioxydante. Oléagineux, Corps Gras, Lipides. 14 : 278-292.

Liu RH, White RJ (1992). High temperature stability of soybean oils with altered fatty acid compositions. J. Am. Oil. Chem. Soc. 69:533-537.

Marmesat S, Morales A, Velasco J, Ruiz-Méndez MV, Dobarganes MC (2009). Relationship between changes in peroxide value and conjugated dienes during oxidation of sunflower oils with different degree of unsaturation. Grasas Y Aceites 60 : 155-160.

Mazliak P (1968). Le métabolisme des lipides dans les plantes supérieures. [Ed. Masson et Cie. pp. 224.

Min DB, Boff JF (2001). Lipid oxidation of edible oil. In C. Akoh & D. B . Min edn. Food lipids. New York, Marcel Dekker. pp. 335-363.

Muik B, Lend B, Molina A, Ayora MJ (2005). Direct monitoring of lipid oxidation in edible oils by Fourier transform Raman spectroscopy. Chem. Phys. Lipids. 134:173–182.
Nawar WW (1996). Lipids. In O.R. Fennema edn. Food chemistry 3rd edn. New York: Marcel Dekker. pp. 225-319.
Naz S, Sheikh, H, Saddiqi, Sayeed SA (2004). Oxidative stability of olive, corn and soybean oil under different conditions. Food Chem. 88:253-259.
Neff WE, Mounts TL, Rinsach WM, Konishi H, Elegamy MA (1994). Oxidative stability of purified canola oil triacylglycerols with altered fatty acid compositions. J. Am. Oil Chem. Soc. 71:215-221.
Official Methods of Analysis, AOAC (1999). 16th eds. AOAC International, Gaithersburg.
Ozkan, G, Simsek B, Kuleasan H (2007). Antioxidant activity of satureja cilicica essential oil in butter and in vitro. J. Food Eng. 79:1391-1396.
Rossell JB (2001). Frying. Improving quality. In J. B. Rossell edn. Cambridge England. Woodhead Publishing Limited.
Shahidi F, Janitha PK, Wanasundara PD (1992). Phenolic antioxidants. Crit. Rev. Food Sci. Nutr. 32:67–103.
Warner K, Eskin NAM (1995). Methods to Assess Quality and Stability of Oils and Fat-Containing Foods. AOCS Press, Champaign.