GRASAS Y ACEITES, 62 (4),
OCTUBRE-DICIEMBRE, 389-398, 2011,
ISSN: 0017-3495
DOI: 10.3989/gya.126010

Effects of storage and industrial oilseed extraction methods on the quality and stability characteristics of crude sunflower oil (*Helianthus annuus* L.)

By **M. Tasan*, U. Gecgel** and **M. Demirci**

Department of Food Engineering, Agricultural Faculty, Namik Kemal University, Tekirdag, Turkey
* Corresponding author: mtasan@nku.edu.tr

RESUMEN

Efecto del almacenamiento y de los métodos industriales de extracción de semillas oleaginosas sobre ciertas características de calidad y estabilidad de aceites crudos de girasol (Helianthus annuus L.).

La influencia de los métodos industriales de extracción de semillas oleaginosas sobre la calidad y la estabilidad de aceites crudos de girasol (pre-prensado, extraídos con disolventes, prensado completo y mezclas de aceites) se ha estudiado mediante la determinación de los ácidos grasos libres, índice de peróxidos, valor del color, hierro, fósforo, contenido de tocoferoles totales e individuales, así como su estabilidad frente a la oxidación (tiempo de inducción mediante Rancimat), y composición en ácidos grasos, con especial énfasis en los ácidos grasos trans. Además, estos aceites crudos fueron almacenados durante un período de cuatro meses a 40 ± 2°C y se analizaró mensualmente la acidez, índice de peróxidos, y el tiempo de inducción Rancimat para evaluar su estabilidad durante el almacenamiento. Los resultados revelaron que los aceites de girasol sin refinar y obtenidos mediante extracción completa tenían peor calidad y peores parámetros de estabilidad que los aceites crudos obtenidos por otros métodos de extracción. El contenido de tocoferoles mostró una disminución drástica con la extracción completa mediante presión. Además, los aceites de girasol sin refinar obtenidos mediante extracción completa presentaron un mayor contenido total de ácidos grasos trans que los otros. Por el contrario, el método de extracción mediante solvente influyó más que el resto sobre los contenidos de fósforo e hierro. Los resultados indican, sin embargo, que el aceite de pre-prensado resultó ser mejor que los demás. Este estudio sugiere que en la industria de aceites vegetales se hace absolutamente necesario reevaluar las condiciones de una extracción completa mediante presión y también la extracción con disolvente para la obtención de los aceites de girasol, tanto para conservar el valor nutritivo como la estabilidad oxidativa.

PALABRAS CLAVE: Aceite de girasol crudo – Ácidos grasos trans – Almacenamiento – Estabilidad – Extracción – Tocoferoles.

SUMMARY

Effects of storage and industrial oilseed extraction methods on the quality and stability characteristics of crude sunflower oil (*Helianthus annuus* L.)

The influence of industrial oilseed extraction methods on the quality and stability of crude sunflower oil (pre-pressed, solvent-extracted, full-pressed and mixed oils) was studied by means of the determination of free fatty acids, peroxide value, color value, iron, phosphorus, total and individual tocopherol contents, their stability against oxidation (Rancimat induction time) and the fatty acid composition with special emphasis on *trans* fatty acids. In addition, these crude oils were stored for a period of four months at 40 ± 2°C and analyzed at monthly intervals for free fatty acids, peroxide value, and Rancimat induction time to evaluate their storage stability. The results revealed that the crude sunflower oils obtained by the full-pressed extraction method had worse quality and stability parameters than the crude oils obtained by other extraction methods. Tocopherol content showed a drastic decrease with full-pressed extraction. Also, the crude sunflower oils obtained by the full-pressed extraction presented a higher total *trans* fatty acid content than the others. On the contrary, the solvent extraction method influenced the phosphorus and iron contents more than the others. The results indicated, however, that pre-pressing the oil appeared to be better than other methods. This study suggests that it is absolutely necessary for the vegetable oil industry to reevaluate the full pressing method as well as the solvent extraction conditions used for sunflowerseeds in order to retain both nutritive value and oxidative stability.

KEY-WORDS: Crude sunflower oil – Extraction – Stability – Storage – Tocopherols – Trans fatty acid.

1. INTRODUCTION

Crude vegetable oils are traditionally refined by physical or chemical processes. The objective of refining is to eliminate impurities with the least possible effect on desirable components present in the crude vegetable oils in order to obtain an odorless, bland and oxidatively stable refined vegetable oil that is acceptable to consumers (Ferrari *et al*., 1996; Medina-Juarez *et al*., 2000). Acceptable quality characteristics of crude vegetable oils processed by refining methods are of crucial importance in order to obtain such refined vegetable oils. Most crude vegetable oils conventionally have been obtained from oilseeds by either mechanical pressing or solvent extraction methods. Solvent oil extraction is usually applied to seeds with low oil content (<20%), such as soybeans (Azadmard-Damirchi *et al*., 2010). There are three major steps in solvent extraction *i.e.*, oilseed preparation, oilseed extraction and desolventizing of the oil and meal (Wang, 2002). The quality characteristics of crude vegetable oils obtained by

solvent extraction methods are primarily dependent on extraction solvents, extraction temperature, pretreatment of oilseeds, *etc.* (Yoon and Min, 1986; Jung *et al*., 1989). The solvent extraction most commonly used today is percolation extraction using hexane as a solvent. However, flammability, toxicological risks, health and environmental concerns have motivated interest in replacing hexane (Kartika *et al*., 2010). In the mechanical pressing method, the preconditioned oilseed is passed through a screw press (expelling) where a combination of high temperature and shears is used to crush the oilseed to release the crude oil. This method is relatively less efficient as it recovers only 70-80% of the available oil depending on the oilseed and pressure employed (Bargale, 2000). Oil extraction by mechanical pressing is simpler, safer and contains fewer steps, compared with oil extraction by solvent (Oyinlola *et al*., 2004). Many of the higher oil content oilseeds, such as sunflowerseeds, are extracted by pre-pressing with a screw press followed by extensive extraction of the oilseeds with hexane as solvent. The solvent must then be eliminated from meal and crude oil (Lajara *et al*., 1990). This method is most widely used for oilseed extraction in the vegetable oil industries to proceed efficiently and trouble-free. The pre-pressed and solvent extracted oils are generally blended before storage. Also, both are usually mixed before refining. Pressed oils are sometimes commercialized separately from solvent extracted oils (O'Brien, 2004). In the vegetable oil industries, some plants may employ only mechanical extraction while other mills not having expellers may employ direct solvent extraction (Campbell, 1983).

The oilseed extraction methods have a direct effect on quality and stability characteristics of crude vegetable oils obtained from the oilseeds (Bargale, 2000). As a corollary, the critical point for the production of good quality crude vegetable oils is the selection of an optimized oilseed extraction method. If optimum oilseed extraction conditions are not met, a drastic loss in quality will result. This loss in quality is noticeable by different analytical determinations which describe the quality and stability characteristics of the crude vegetable oils such as free fatty acids, peroxide value, trace metals, tocopherols, color value, *etc*. In addition to using various traditional analytical evaluations, *trans* fatty acid levels are a powerful tool for determining good oilseed extraction processes and also for assessment from a nutritional viewpoint because of their adverse effects on health.

The aim of this paper was to evaluate oilseed extraction methods through some quality and stability characteristics of the crude sunflower oil produced under industrial processing conditions. In addition, some stability changes were determined during accelerated storage. Such data may provide useful information about the starting quality characteristics of the crude sunflower oils used for the application of refining processes and can also be used to produce refined oils with or without the possible minimum level of *trans* fatty acids. Since at the present time one of the most widely cultivated oilseeds in the world is sunflower (*Helianthus annuus* L.), this oilseed was chosen as appropriate for the present study. Furthermore, the bulk of vegetable oil production in Turkey is mainly derived from sunflowerseeds. Hence, nearly two-thirds of the total production capacity of oilseed crushing is used by the sunflowerseed crushing plants.

2. MATERIALS AND METHODS

2.1. Materials

Standards and Reagents:

Both *trans* and *cis* fatty acid methyl ester (FAME) standards (99% purity) were provided by Nu-Check-Prep Inc. (Elysian, MN). Tocopherol standards (α-, β-, γ-, and δ-tocopherols) were obtained from Merck Chemical Company (Darmstadt, Germany). All reagents, chemicals and solvents employed in this study were analytical and chromatographic grades that were purchased from Merck Chemical Company (Darmstadt, Germany).

Crude sunflower oil sample collection:

Fresh, crude sunflower oil samples produced under industrial oilseed extraction conditions were used for the study. All crude sunflower oil samples were obtained directly from eight selected vegetable oil plants that are all major producers with integrated processing systems (mechanical pressing, solvent extraction and refining) and located in the Trakya region (Turkey). These different vegetable oil plants employ different parameters (pretreatment of oilseeds, pressure, extraction temperature and time, *etc.*) for the extraction methods. The sunflowerseeds employed in the selected vegetable oil plants were of the traditional type and grown in same harvest season with similar environmental conditions (moisture, temperature, location, *etc*.). In addition, the same lot of sunflowerseeds for each extraction method in each processing plant was used. The crude oil samples obtained from the oilseed extraction processing lines were classified into four groups: pre-pressed oils, which were produced by pre-pressing in screw presses; solvent-extracted oils, which were produced by the solvent extraction of oilcakes with hexane in continuous extractors. Since the pre-pressed and solvent extracted oils are usually blended before the refining process, an equal amount of pre-pressed and solvent extracted oils taken from the processing lines were mixed to prepare the third group, called mixed oil. As for the fourth group, full-pressed oils from the same lot of sunflowerseeds in each processing plant were prepared by screw and subjected to high pressure to extract the crude oil. Since the direct

solvent extraction method for sunflowerseeds in the industrial applications was not employed, this oil group oil was not examined.

The samples were taken from eight different vegetable oil plants. From three different production periods, approximately 1000 ml each, of three samples for each of the four crude sunflower oil groups from the processing line of each plant were collected for homogeneous sampling and properly labeled. Each of the analyses was done three times for each sample in triplicate. The data obtained were given as arithmetic means ($n = 8 \times 3 \times 3 \pm$ standard deviation) for each group of crude sunflower oil unless otherwise indicated. The sampling was carried out regularly by using an appropriate device with a cooling system. Immediately after collection, dark brown-colored glass bottles were purged with nitrogen gas after filling to prevent oxidation and kept at −20°C until analyzed. The sample bottles were shaken well and the crude oil samples, drawn from each bottle with the help of disposable syringes, were analyzed.

Storage experiment:

In order to predict the long term stability of the fresh crude sunflower oils, an accelerated storage experiment was carried out. The crude oil samples were stored for a period of four months in 100 mL dark brown-colored glass bottles, without headspace, tightly covered with plastic caps, and heated at 40 ± 2°C in a standard laboratory oven. The crude oil samples were withdrawn periodically at monthly intervals and immediately analyzed.

2.2. Methods

Chemical and physical tests, *viz.* free fatty acids, peroxide value, color, iron, phosphorus, total and individual tocopherol contents were carried out on the crude sunflower oil samples along with their stability against oxidation (Rancimat induction time) and fatty acid composition with special emphasis on *trans* fatty acids. Free fatty acids, peroxide value and Rancimat induction time were determined for the crude oil samples during storage. The analyses were performed using the official methods of the American Oil Chemists Society (AOCS) or International Union of Pure and Applied Chemistry (IUPAC) unless otherwise stated.

Free fatty acids, expressed in % (w/w) of oleic acid and *peroxide value*, expressed as meqO_2/kg of the oil, using titration methods, according to IUPAC (1992) official method no. 2.201 and 2.501, respectively. *Stability to oxidation*, expressed as induction time (hours), determined by the Rancimat method (Laubli *et al*., 1988). All experiments were carried out with the model 679 Rancimat apparatus (Metrohm AG, Herisau, Switzerland). In brief, 2.5 g of the crude oil samples were heated for 10 min at 120°C in the Rancimat heating block. Air flow rates were set at 20 L/h for all determinations. The dry air feed and the collection vessel were then connected. The measurement of the conductivity curve then started. The breaking point was equal to the induction time (hours). The evaluation of the resulting curves was carried out automatically by the Metrohm program. *Lovibond color* of the crude oil samples was read in a Lovibond Tintometer model AF 900 (model E) using a 5 ¼ inch cell and was expressed in units of yellow (Y) and red (R), according to AOCS (1998) official method no. Cc 13b-45. The determination of *phosphorus* was carried out according to IUPAC (1992) official method no. 2.421. *Iron* was measured using a Varian SpectrAA-280 atomic absorption spectrophotometer according to NMKL (1998) followed by a microwave digestion procedure using a MARS–5 microwave digestion system (Microwave accelerated reaction system, CEM Inc., Matthews).

Tocopherols were determined by high-performance liquid chromatography using a Hewlett-Packard 1100 HPLC system according to IUPAC (1998) official method no. 2.432. The crude oil samples were dissolved in *n*-hexane. Tocopherols were separated by a LiChrosorb Si-60 (250x4 mm, 5 µm particle size) column (Merck, Darmstadt, Germany) held at 37°C. The column was eluted with *n*-hexane containing 0.5% isopropanol at a flow rate of 0.8 mL/min. Tocopherols were identified by comparing their retention times with those of pure standards of α, β, γ, and δ isomers of tocopherol, and were quantified on the basis of peak areas of the unknowns with those of pure standards (Merck, Darmstadt, Germany). The amount of tocopherols was calculated using external calibration curves obtained for each tocopherol standard. A standard addition technique was also employed in order to determine if the oil matrix significantly affected tocopherol quantification. Therefore, crude sunflower oil was spiked with known amounts of α-, β-, γ- and δ-tocopherols. The amounts of individual tocopherols were determined after spiking in the same experimental conditions as in the unspiked crude sunflower oil sample. The recovery of individual tocopherols was calculated (Chun *et al*., 2006) by the following equation: R (%) = [(Cs-Cp)/Ca]100, where R (%) is the percent recovery of added standard; Cs the tocopherol content in the spiked sample; Cp the tocopherol content in the sample; and Ca the tocopherol standard added. The results of the standard addition experiment on the crude sunflower oil, that is; the recoveries of individual tocopherol were acceptable.

Preparation of FAMEs

FAMEs were prepared according to the AOCS (1998) official method Ce 2-66. The FAMEs were obtained from the lipid fractions after alkaline hydrolysis, followed by methylation in methanol with a 12.5% boron trifluoride catalyst. The final

concentration of the FAMEs was approximately 7 mg/mL in heptane.

Capillary Gas-Liquid Chromatography (GLC) Analyses of FAMEs

Analyses of the FAMEs by capillary GLC were carried out on a Hewlett-Packard 6890 chromatograph (Hewlett-Packard, Wilmington, DE) equipped with a Chrompack Autosampler-M911 (Chrompack, Middelburg, the Netherlands) for split-type injection and a flame-ionization detector. A fused-silica capillary column (Chrompack) was used for the FAME analysis; CP-Sil 88, 100 m $\times$ 0.25 mm i.d., 0.20 µm film thickness. GLC operating conditions were: a temperature program of 130°C for 5 min increasing at a rate of 2°C/min to 177°C; injector temperature, 200°C; detector temperature, 250°C. The carrier gas was helium at a flow rate of 1 mL/min; the split ratio was 1:100; the volume of the injected sample was 1µL. The peaks were tentatively identified by comparing the retention times and area percentages with those of authentic standards of FAMEs obtained from Nu-Chek-Prep Inc. (Elysian, MN) and on the basis of literature data (Wolff, 1992; Duchateau *et al.,* 1996). Total *trans* fatty acid was calculated as the sum of *trans* isomers (except conjugated fatty acid) of the relevant fatty acid. The final results were expressed as relative percentage of individual fatty acid.

Statistical Data Analysis

For statistical evaluations, all analytical data generated from each group of crude sunflower oil were subjected to analyses of variance using SPSS software program (SPSS Inc., Chicago, IL). Differences among the means were compared using the Duncan's multiple range tests. Statistical significance was expressed at $P<0.01$ unless otherwise indicated.

3. RESULTS AND DISCUSSION

The change in the quality and stability characteristics of the crude oils obtained from the sunflowerseeds at the end of industrial oilseed extraction processes ae presented in Table 1. As indicated, the crude sunflower oil groups varied in their phosphorus contents from 62.13-92.88 ppm, depending on the extraction methods. The iron contents of these oil groups varied from 0.61 to 0.80 ppm at the end of the extraction process. The major differences between solvent-extracted oil and pre-pressed or full-pressed oils were determined by their phosphorus and iron contents ($P<0.01$). Slightly higher values, although not significantly different, were found for the full-pressed oil with respect to the mixed oil. The solvent-extracted oil as a group had both high phosphorus (92.88 ppm) and high iron (0.80 ppm) contents. Previous studies conducted by Dimic *et al.* (1994), Crapiste *et al.* (1999) and Brevedan *et al.* (2000) support these results. Similarly, Carelli *et al.* (2002) found that solvent extracted sunflower oils had higher total phospholipid contents than these obtained by pressing. Kartika *et al*. (2005) found that total phosphorus content was low, below 100 mg/kg, in the crude oils obtained with oil extraction from sunflower seeds using a twin-screw extruder. On the other hand, we found a relationship between two element contents in the crude sunflower oil groups. As is well known, the phosphorus and iron contents of crude oils have always been a significant factor in vegetable oil refining. The poor quality of soybean oil by Evans *et al.* (1974) was attributed to both high iron and high phosphorus contents. Similarly, Leibovitz and Ruckenstein (1981) reported that the stability of the oil was affected by traces of metals and phosphorus. Cleenerwerck and Dijkstra (1992) also revealed that darkening of the oil during physical refining was related to its phosphorus and iron contents. On the other hand, Calvo *et al.* (1994) indicated that poor oxidative stability of supercritical carbon dioxide-extracted oil could be explained by the low content of phosphorus as compared to crude hexane-extracted oil. In addition, List and Friedrich (1985) reported that poor oxidative stability was attributed to low phospholipid contents. According to Calvo *et al.* (1994), this hypothesis is supported by the fact that phospholipids may act as an oxygen barrier at the oil/air interface. Good quality refined vegetable oils, regardless of the various processing techniques employed by the oil industry, must have only a slight (less than 5 ppm) phosphorus content (Dimic *et al*., 1994; Wesdorp, 1996) and iron content of less than 0.2 ppm (Cleenerwerck and Dijkstra, 1992). First things first, the proper crushing and extraction techniques should be selected to reduce the initial levels of two elements in the initial crude oils.

The group of minor components of vegetable oils is composed of tocol-related compounds, tocopherols and tocotrienols, which are important lipid oxidation inhibitors in food and biological systems. These natural antioxidants are found in oilseeds in four different forms: α-, β-, γ-, and δ-tocopherols (Kamal-Eldin and Appelqvist, 1996). These components are also important as potent natural antioxidants that prevent the rancidity of oils during storage and, thus, increase the shelf life of edible oils (Aluyor and Ori-Jesu, 2008). α-tocopherol is the precursor of vitamin E and an excellent in vivo antioxidant; however, it is not as good an antioxidant in vitro as γ- and δ-tocopherol. Sunflower oil, which has approximately 95% of its tocopherols in the α configuration, could possibly have improved the oxidative stability if its tocopherol profile had more γ- and δ- tocopherols (Warner *et al*., 2008). The tocopherol content and pattern of oils are characteristic and depend on plant genotype, the climatic conditions of growth and harvest, polyunsaturated fatty acid contents

Table 1
Some quality and stability characteristics of crude sunflower oils[1]

Characteristics	Crude sunflower oil groups			
	Pre-pressed	Solvent-extracted[8]	Mixed[9]	Full-pressed
Iron (Fe, ppm)	0.61 ± 0.22^{a}	0.80 ± 0.20^{c}	0.70 ± 0.14^{b}	0.71 ± 0.12^{b}
Phosphorus (P, ppm)	62.13 ± 20.82^{a}	92.88 ± 22.80^{c}	78.00 ± 23.29^{b}	76.50 ± 2.12^{b}
Free fatty acids (% oleic acid)	0.71 ± 0.19^{a}	0.86 ± 0.12^{a}	0.79 ± 0.13^{a}	1.05 ± 0.10^{b}
Peroxide value (meqO_2/kg)	8.96 ± 1.31^{a}	9.20 ± 2.21^{a}	9.18 ± 1.15^{a}	12.10 ± 0.85^{b}
Rancimat IT[2] (h, at 120°C)	2.49 ± 0.25^{c}	2.05 ± 0.26^{b}	2.29 ± 0.17^{bc}	1.83 ± 0.18^{a}
Lovibond color[3] red	4.09 ± 0.63^{a}	4.71 ± 1.02^{b}	4.59 ± 0.63^{ab}	5.10 ± 0.14^{c}
Lovibond color[3] yellow	38.00 ± 12.28^{a}	41.63 ± 10.72^{a}	39.75 ± 8.22^{a}	50.00 ± 0.35^{b}
α-tocopherol (ppm)	641.8 ± 68.4^{c}	603.5 ± 42.9^{b}	611.3 ± 53.5^{b}	484.1 ± 63.7^{a}
β-tocopherol (ppm)	26.7 ± 5.3^{c}	17.0 ± 2.8^{b}	21.6 ± 5.1^{b}	13.8 ± 2.7^{a}
γ-tocopherol (ppm)	20.9 ± 3.9^{c}	13.6 ± 4.2^{b}	18.4 ± 4.0^{c}	9.3 ± 2.4^{a}
δ-tocopherol (ppm)	n.d.[10]	n.d.	n.d.	n.d.
Total tocopherol (ppm)	689.4 ± 56.8^{c}	634.1 ± 46.2^{b}	651.3 ± 59.7^{b}	507.2 ± 61.5^{a}
Fatty acid composition (%)[4]				
$C_{16:0}$	5.98 ± 0.35^{a}	6.00 ± 0.39^{a}	5.99 ± 0.37^{a}	5.90 ± 0.37^{a}
$C_{18:0}$	3.89 ± 0.17^{a}	3.89 ± 0.17^{a}	3.89 ± 0.17^{a}	3.90 ± 0.24^{a}
Σ $C_{18:1}$ *trans*[5]	0.01 ± 0.01^{a}	0.01 ± 0.01^{a}	0.01 ± 0.01^{a}	0.04 ± 0.02^{b}
$C_{18:1}$ *cis*	25.86 ± 1.40^{a}	25.85 ± 1.39^{a}	25.86 ± 1.39^{a}	27.15 ± 2.05^{b}
Σ $C_{18:2}$ *trans*[6]	0.03 ± 0.02^{a}	0.03 ± 0.02^{a}	0.03 ± 0.02^{a}	0.08 ± 0.01^{b}
$C_{18:2}$ *cis*	62.65 ± 1.43^{b}	62.63 ± 1.43^{b}	62.63 ± 1.42^{b}	61.37 ± 2.19^{a}
$C_{18:3}$ *cis*	0.07 ± 0.01^{a}	0.07 ± 0.01^{a}	0.07 ± 0.01^{a}	0.07 ± 0.02^{a}
Σ other fatty acids[7]	1.51 ± 0.02^{a}	1.52 ± 0.02^{a}	1.52 ± 0.03^{a}	1.49 ± 0.01^{a}
Σ *trans* fatty acids	0.04 ± 0.03^{a}	0.04 ± 0.03^{a}	0.04 ± 0.03^{a}	0.12 ± 0.02^{b}

[1]Data are the mean ± standard deviation (SD), and fatty acid ratios are expressed as a weight percentage of total fatty acid methyl esters. The means in thesame row with different letters (a-c) show statistically significant differences ($P<0.01$, LSD multiple range test, except for color values and $C_{18:1}$ *cis*, at thelevel $P<0.05$).
[2] induction time, [3]5 ¼ inch cell, [4]fatty acids are designated by number of carbon atoms: number of double bonds, [5]constituents of the 18:1 Δ9 *trans*, [6] the sum of only Δ9*cis*, Δ12 *trans* and Δ9 *trans*, Δ12 *cis* isomers for the C18:2, [7] the other fatty acids include C14:0, C16:1, C20:0, C20:1, C22:0 and C24:0 acids, [8]with hexane, [9] mixed equal amounts of the pre-pressed and solvent-extracted oils, taken from processing lines, [10]not detected.

in the oil as well as the processing and storage conditions (Rabascall and Riera, 1987). It is clear from Table 1 that total and individual tocopherol contents seem to be partially affected by different extraction methods. As indicated, total tocopherol content in the pre-pressed oil wsd on average equal to 689.4 ppm while in the solvent-extracted and full-pressed oils, it was 634.1 and 507.2 ppm, respectively ($P<0.01$). The pre-pressed oil samples were quite satisfactory. Slightly higher values, although not significantly different, were found for solvent-extracted oil with respect to the mixed oil. According to pre-pressed method, the reduction of approximately 26.4% in total tocopherol content was observed after full-pressed process. In our finding, there was statistically significant decline in α-, β- and γ-tocopherol levels for solvent-extracted and full-pressed oils with respect to the pre-pressed oil ($P < 0.01$). Full-pressed oils contained the lowest α-, β- and γ-tocopherol levels. In comparison with pre-pressed oil, the other oil groups had different relative proportions of individual tocopherol. Namely, the relative proportions of β- and γ-tocopherols decreased, whereas the α-tocopherol proportion increased for the solvent-extracted and full-pressed oils with respect to the pre-pressed oil. All crude oil samples studied contained no measurable amounts of δ-tocopherol. From the results obtained it can be assumed that full-extracted oils with relatively low total and individual tocopherol contents exposed to improper conditions during the extraction of the crude oil from the oilseeds. Generally, the loss during the oilseed extraction process was attributed to the longer contact time of the crude oil with air and to exposure to overheating or overpressure. In addition, even though the oilseeds were carefully

extracted, previous hot drying or even roasting of the oilseeds may affect the crude oil. Also, the storage conditions of oilseeds before industrial extraction might influence the tocopherol contents of the crude oil. Previous studies (Kellens, 1997; Alpaslan *et al*., 2001; Tasan and Demirci, 2005) revealed that tocopherols were sensitive to light, temperature, heating time, pressure, alkali, air, and metal contaminants, primarily iron and copper. Controls of temperature and contact time during the oil extraction from sunflower seeds in a batch extractor with hexane as solvent are essential to obtain good quality oil, and reduce refining costs *i.e*., significant tocopherol and reduced phospholipid extraction (Baumler *et al*., 2010). Optimal processing conditions are important to retain these compounds in their active form (Ortega-Garcia *et al*., 2006). It is essential to avoid the reduction of natural antioxidants, i.e., vitamin E, by improving processing practices to enhance the nutritive value and shelf life of the oil (Naz *et al*., 2010).

Crude vegetable oils contain various natural color substances. Color is divided into several aspects: red, yellow, green-blue (chlorophyll), and β-carotene. The Lovibond Tintometer is the most widely used in the vegetable oil industry. In our findings, the Lovibond colors (red value) varied from 4.09 to 5.10 (5 ¼ inch cell) in all crude oil groups ($P<0.05$). On the other hand, we found a small variation (from 38.00 to 41.63) of the Lovibond colors (yellow value) among the crude oil groups ($P>0.05$), except in the full-pressed oil (50.00). Darkening of the crude sunflower oils could be due to the oxidation of colorless compounds and the existing color pigments becoming fixed by overheating, depending on the extraction methods. In relation to the initial raw material preparation, the thermal treatments (drying, roasting *etc*.) of the sunflowerseeds before extraction might also be employed at high temperatures. Besides, it is generally accepted that the color of crude oils can be directly affected by oilseed/crude oil storage conditions (time, temperature, oxygen availability, air-to-oil ratio *etc*.). Removing the color components is one of the critical aspects of refining.

As illustrated in Table 1, all obtained fatty acid profiles were within the ranges found in the literature. Also, the fatty acid profile in all crude oil samples corresponded to the traditional sunflowerseed type. The C16:0 and C18:0 acids were the principal saturated fatty acid for all crude samples analyzed. These fatty acid contents obtained for the crude oils were not significantly different ($P>0.01$). The main monounsaturated fatty acid, the C18:1 *cis* acid, ranged from 25.85 to 27.15% in all groups of the crude oils and the value obtained for the full-pressed oil was significantly higher ($P<0.01$) than those obtained for the others. Among the polyunsaturated fatty acids, the C18:2 *cis* acid level ranged from 61.37 to 62.65% in all groups of the crude oils, with a significantly lower value ($P<0.05$) observed for the full-pressed oil in comparison with the others. As for the C18:3 *cis* acids, their low levels (0.07%) in all crude oil samples were statistically similar ($P>0.01$). The sum of six minor fatty acids (C14:0, C16:1, C20:0, C20:1, C22:0, C24:0), expressed as other fatty acids in Table 1, varied from 1.49 to 1.52% of total fatty acids ($P>0.01$). Carelli *et al.* (2002) state that only small differences in the fatty acid compositions were observed between pressed and extracted sunflower oils.

All crude oil samples studied contained geometrical isomers of fatty acids. In other words, all samples studied contained the C18:1 *trans* acid and the C18:2 *trans* acid. No C18:3 *trans* acid was detected in all crude oil groups, as expected. Thus, the total *trans* fatty acid comprised isomers of the C18:1 and C18:2 acids. The full-pressed oils had higher total *trans* fatty acid contents (0.12%) than did the others (0.04%). The results were observed for the total C18:1 *trans* acid and total C18:2 *trans* acid, which varied from 0.01 to 0.04% and 0.03 to 0.08% of the total fatty acid in all crude oil groups ($P<0.01$), respectively. The total C18:2 *trans* polyunsaturated fatty acid was the predominant *trans* fatty acid found in all samples studied. Only two main isomers for C18:2 (9*c,* 12*t*) and (9*t,* 12*c*) were identified in the crude oil samples. Generally, the amounts of 18:2 (9*c,* 12*t*) were higher than in 18:2 (9*t,* 12*c*). The 18:2 (9*t,* 12*t*) isomer was a minor isomer and not detected. Finally, the fatty acid compositions of the crude oil samples were not notably different, depending on the extraction methods, except for the full-pressed method. From the results obtained it can be assumed that the full-pressed crude oils with higher amounts of total *trans* fatty acid in comparison with the others were exposed to improper conditions during extraction of the oils from the oilseed. Similarly, Matthaus and Bruhl (2003) reported that evidence for an improper extraction of the oils, especially cold-pressed oils, may be the presence of *trans* fatty acids. Crude oils may contain very small amounts of *trans* fatty acids (Yılmam and Tasan, 2008). Similar observations were made by several research studies (Ferrari *et al*., 1996; Schwarz, 2000; Tasan and Demirci, 2003; Ortega-García *et al*., 2006). Cmolik *et al.* (2000) revealed that *trans* isomers of C18:1, C18:2 and C18:3 acids were detected in crude rapeseed oils produced by prepressing in screw presses, followed by hexane-extraction, 0.01-0.06, 0.01-0.04 and 0.04-0.06%, respectively. On the other hand, Van Hoed *et al.* (2006) revealed that *trans* fatty acids were not detected in the crude rice bran oil, produced by using a hexane-extraction process. Perretti *et al.* (2004) announced that no C18:1 *trans* acid was found in the sunflower seed oils that were extracted either mechanicaly or by and conventional solvent extraction. But, only the latter contained C18:2 *trans* acid at 0.4-0.5%. Tasan*trans* fatty acids are probably formed by heat treatment of oilseeds before or during extraction process. Even though the oilseed or nuts is carefully pressed or solvent extracted processes, previous hot drying or even the roasting of seeds will increase the *trans*

fatty acid content in the crude oils. Besides, heating the oilseed or nuts may considerably increase the *trans* fatty acid content of the refining oils (Bruhl, 1996). In addition, the distribution of the C18:1, C18:2, and C18:3 acids in vegetable oils show rather different?. Thus, the quantity of measurable *trans* fatty acid formed during relevant processes may be diverse.

As indicated in Table 1, free fatty acid contents ranged from 0.71 and 1.05% (expressed as oleic acid) in the crude oil samples at the end of these extraction processes. Free acidity was statistically significant and greater in the full-pressed oil in comparison to the other oil groups ($P<0.01$), indicating hydrolytic alteration as well as further decomposition of hydroperoxides. However, pre-pressed oil had the lowest free acidity. Slightly higher values, although not significantly different, were found for the solvent-extracted and mixed oils with respect to the pre-pressed oil. The results revealed that released fatty acids were evidently due to the partial hydrolysis of the triglycerides, which may occur at the different conditions of the oilseed extraction processes. Previous studies conducted by Dimic *et al.* (1994) and Crapiste *et al.* (1999) support these results. Leonardis *et al.* (2001) reported free fatty acid content to be 0.2% for industrial pressed crude sunflower oil, although this content in crude oils, which were mechanically extracted in the laboratory, ranged from 0.5 to 0.8%. Abitogun and Oshodi (2010) found that free fatty acid content was 1.4% in the crude sunflower oil obtained by hexane extraction. Kartika *et al.* (2005) stated that the acid value was below 2 mg of KOH/g of oil in crude oils obtained with oil extraction using a twin-screw extruder. Frega *et al.* (1999) stated that one of the important alterations in lipids is lipid hydrolysis, with consequent free fatty acid generation, by chemical or enzymic action. The initial content of free fatty acids in crude oils is one of the most significant controlling parameters for successful application of the refining procedure and quality during storage.

Peroxide values ranged from 8.96 to 12.10 meqO_2/kg in the oil samples, depending on the extraction method. Peroxide value reached 9.20 meqO_2/kg at the end of the solvent extraction application. Similarly, the peroxide value in the mixed oil was 9.18 meqO_2/kg. By comparison, no significant oxidation, as measured peroxide value, was observed. However, peroxide value in the full-pressed oil was higher presumably due to oxidation and statistically different from the other oil groups ($P<0.01$). Peroxide values followed the same trend as the free fatty acid contents. This indicates that deterioration occurs in the extraction process, not only owing to oxidation but also due to hydrolysis, as evidenced by increased free fatty acids. Peroxide formation is a major concern from the point of view of industrial applications and nutritional properties. The high peroxide value of the crude oils indicates that they were extracted and stored in improper conditions. Leonardis *et al.* (2001) stated that industrial pressed crude sunflower oil had higher peroxide values (8.9 meqO_2/kg) than crude oils obtained by mechanical extraction in a laboratory (from 1 to 3 meqO_2/kg). Abitogun and Oshodi (2010) found that the peroxide value was 12.6 meqO_2/kg in the crude sunflower oil obtained by hexane extraction. Crapiste *et al.* (1999) revealed that these values were found between 2.45-3.92 meqO_2/kg in industrial crude sunflower oils obtained by pressing and hexane extraction, respectively. Similarly, Dimic *et al.* (1994) reported that low peroxide values of 0.81 and 2.02 mmol/kg were found in pressed and hexane-extracted crude sunflower oils, produced under usual industrial conditions. It is well know that hydroperoxides are the primary products formed during oxidation, but they are labile intermediate compounds that decompose into several secondary oxidation products. Thus, even though peroxide value is a common indicator of lipid oxidation, its use is limited to the earlier stage of oxidation (Crapiste *et al.*, 1999).

Induction times for oxidative stability of the crude oil groups, measured by the Rancimat method at 120°C, varied from 1.83 h to 2.49 h. The statistically significant differences are apparantly to due to the extraction method ($P<0.01$). The Rancimat induction time of full-pressed oil was lower than in the other oil groups. Surprisingly, significant differences were found comparing the Rancimat induction time in the crude oils after the pre-pressing and solvent extraction applications. The literature (Gordon and Mursi, 1994; Perretti *et al.*, 2004) supports a high correlation between peroxide value and induction time. The Rancimat method can show any oxidative damage of the oil during processing (Matthaus and Bruhl, 2003); for instance, it gives an indication of the application of improper extraction conditions. In our findings, induction times of the pre-pressed oil groups indicated good preservation with respect to oxidative damage compared to the other oil groups. According to the literature (Dimic *et al.*, 1994; Crapiste *et al.*, 1999), oxidative stabilities in hexane-extracted crude sunflower oils, measured by Rancimat induction times, were higher than in pressed crude sunflower oils produced under normal industrial conditions. Brevedan *et al.* (2000) revealed that sunflower oils obtained by hexane extraction presented a higher initial deterioration but also a higher oxidative stability than oils obtained by pressing. Leonardis *et al.* (2001) reported that industrial pressed crude sunflower oil had a low induction time (1.7 h) by Rancimat at 120°C and 20L/h air flow. In this study, crude sunflower oil with high oleic acid content (86.6%) obtained by mechanical extraction in a laboratory a showed high Rancimat induction time (12.6 h). Many factors contribute to the oxidative stability of vegetable oils. Oxidative stability is influenced by factors such as peroxidase activity, fatty acids,

fatty acid composition, tocopherol, carotenoids, and sterols (List and Friedrich, 1989; Arranz *et al*., 2008). Also, a low level of oxidative stability is attributed to the phospholipids and trace metals present in vegetable oils (Alpaslan *et al*., 2001).

The changes in peroxide value, free fatty acids, and Rancimat induction time of the crude sunflower oils obtained by different industrial oilseed extraction processes during accelerated storage are presented in Table 2. In recent years, the storage stability and shelf life of fats and oils have received special attention from nutritionists, food processors and consumers because of their influence on food quality (Stefanoudaki *et al*., 2010). Most crude oils are exposed to changing temperatures during the relatively long times before refining, in storage tanks, and/or in ships' holds during transportation (Crapiste *et al*., 1999). Also, storage conditions of oilseeds before industrial extraction might influence the quality of crude oil. Ghasemnezhad and Honermeier (2009) stated that the storage life of sunflower seeds can be decreased by longer storage time and higher storage temperature. Their results showed that the oleic acid ratio was reduced and free fatty acid content increased as the storage time progressed. As a result, it is necessary to evaluate quality changes during the storage of crude oils, obtained by different extraction methods. By comparison of the crude oil groups obtained by different extraction methods, statistically significant oxidation, as measured by peroxide value and by Rancimat induction time, was observed during accelerated storage ($P<0.01$). All crude oil samples, except for the full-pressed oil, showed a very similar rate of increase in peroxide values. With respect to the combined effect of the storage temperature and time, this value in the full-pressed oil reached 27.50 $meqO_2$/kg after 120 days of accelerated storage, while it was below 20 $meqO_2$/kg for the other oil groups. The Rancimat induction time decreased with storage time for all crude oil samples ($P<0.01$). Apparently, in comparison with the other oil groups, the full-pressed oil showed relatively low oxidative stability during accelerated storage. It seems that the crude oil samples with high levels of hydroperoxides were less stable against oxidative degradation. Furthermore, differences in oxidative stability can be attributed to total and individual tocopherol contents because they were found in higher amounts in pre-pressed oil as compared to the other oil groups. At this time, it is necessary to evaluate the iron and phosphorous contents in the crude oil samples. On the other hand, Calvo *et al.* (1994) stated that because differences in stability cannot be fully explained by differences in chemical composition, it appears that there is something intrinsic to the extraction procedure itself. As shown in Table 2, free fatty acid contents increased progressively during accelerated storage in all crude oil samples ($P<0.01$). With respect to the combined effect of the storage temperature and time, free fatty acid contents of the full-pressed oil, which give indications to the application of improper pressing conditions, increased from 1.05 to 2.42%, where it was below 2% for the other oil groups at the end of storage. Frega *et al.* (1999) stated that they seem to interact with each other

Table 2
Changes in peroxide value, free fatty acids and Rancimat induction time of the crude sunflower oilduring storage (at 40°C ± 2)[1]

Stability indexes	Storage time (d)	Crude sunflower oil groups			
		Pre-pressed	Solvent-extracted[3]	Mixed[4]	Full-pressed
Free fatty acids (% oleic acid)	Fresh	0.71 ± 0.19^{a}	0.86 ± 0.12^{a}	0.79 ± 0.13^{a}	1.05 ± 0.10^{a}
	30	0.89 ± 0.19^{b}	0.98 ± 0.13^{a}	0.98 ± 0.30^{b}	1.24 ± 0.26^{b}
	60	1.08 ± 0.25^{c}	1.28 ± 0.29^{b}	1.23 ± 0.21^{b}	1.69 ± 0.09^{c}
	90	1.35 ± 0.27^{d}	1.48 ± 0.19^{c}	1.49 ± 0.26^{c}	1.91 ± 0.12^{d}
	120	1.69 ± 0.32^{e}	1.79 ± 0.45^{d}	1.86 ± 0.35^{d}	2.42 ± 0.09^{e}
Peroxide value ($meqO_2$/kg)	Fresh	8.96 ± 1.31^{a}	9.20 ± 2.21^{a}	9.18 ± 1.15^{a}	12.10 ± 0.85^{a}
	30	10.63 ± 1.22^{a}	10.43 ± 1.83^{a}	11.13 ± 1.33^{b}	13.60 ± 2.26^{a}
	60	12.46 ± 1.90^{b}	11.88 ± 1.99^{b}	12.94 ± 1.36^{c}	17.60 ± 0.99^{b}
	90	13.84 ± 2.51^{b}	13.46 ± 1.34^{b}	14.24 ± 1.31^{c}	21.30 ± 2.55^{c}
	120	18.25 ± 3.81^{c}	19.66 ± 2.29^{c}	18.29 ± 2.44^{d}	27.50 ± 2.41^{d}
Rancimat IT[2] (h, at 120°C)	Fresh	2.49 ± 0.25^{c}	2.05 ± 0.26^{c}	2.29 ± 0.17^{c}	1.83 ± 0.18^{c}
	60	2.14 ± 0.17^{b}	1.87 ± 0.27^{b}	2.05 ± 0.23^{b}	1.54 ± 0.11^{b}
	120	1.78 ± 0.21^{a}	1.55 ± 0.35^{a}	1.60 ± 0.19^{a}	1.22 ± 0.23^{a}

Data are the mean 6 standard deviation (SD). The means in the same column with different letters (a-e) show statistically significant differences (P,0.01, LSD multiple range test).
[2] induction time, [3] with hexane, [4] mixed equal amounts of the pre-pressed and solvent-extracted oils, taken from processing lines.

and contribute to the reduction of the oil shelf life, although the original causes and the consequences of oxidative and hydrolytic degradation processes are quite different.

4. CONCLUSIONS

The results demonstrated an important difference in the some quality and stability characteristics among the studied crude sunflower oils due to different industrial oilseed extraction methods employed. Apparently, the effect of the full pressing method exceeded that of the others with respect to influence on the fatty acid composition, tocopherols, free fatty acid, peroxide value, Rancimat stability and color value. In other words, the full-pressed oils had worse quality and stability parameters than the others. On the contrary, the solvent extraction method had a greater influence than the others on phosphorus and iron contents. The results indicated the best protection in the examined quality and stability parameters of crude sunflower oil obtained by the prepressing method. The present data, with respect to the initial quality of crude oils can play a significant role as an aid in the optimization of the refining process optimization, particularly to produce refined oils with the lowest possible level of *trans* fatty acids and to reduce the loss of tocopherols. As a corollary, this study suggests that it is absolutely necessary for the vegetable oil industry to reevaluate the full pressing process and solvent extraction conditions used for the sunflower seeds in order to retain both the nutritive value and oxidative stability. Additionally, the results obtained clearly show that greater attention has to be given to the storage of full-pressed oil in comparison with the crude oils obtained by other methods.

ACKNOWLEDGEMENTS

This work was supported by the Trakya University Scientific Research Projects Fund (Project no. TUBAP–465).

REFERENCES

Abitogun AS, Oshodi AA. 2010. Effects of degumming and bleaching on physicochemical properties of crude sunflower oil. *E. J. Envir. Agr. Food Chem*. **9**, 1145–1151.

Alpaslan M, Tepe S, Simsek O. 2001. Effect of refining processes on the total and individual tocopherol content in sunflower oil. *Int. J. Food Sci. Technol.* **36,** 737–739.

Aluyor EO, Ori-Jesu M. 2008. The use of antioxidants in vegetable oils–a review. *Af. J. Biotechnol.* **7**, 4836–4842.

AOCS. 1998. *Official Methods and Recommended Practices of the American Oil Chemists'Society*. 5th edn., Firestone D (Ed.), AOCS Press, Champaign, Methods Cc 13b–45, Ce 2–66.

Arranz S, Cert R, Perez-Jimenez J, Cert A, Saura-Calixto F. 2008. Comparison between free radical scavenging capacity and oxidative stability of nut oils. *Food Chem.* **110,** 985–990.

Azadmard-Damirchi S, Habibi-Nodeh F, Hesari J, Nemati M, Achachlouei BF. 2010. Effect of pretreatment with microwaves on oxidative stability and nutraceuticals content of oil from rapeseed. *Food Chem*. **121**, 1211–1215.

Bargale PC. 2000. Prediction of oil expression by uniaxial compression using time-varying oil seed properties. *J. Agr. Eng. Res.* **77,** 171–181.

Baumler ER, Crapiste GH, Carelli AA. 2010. Solvent extraction: Kinetic study of major and minor compounds. *J. Am. Oil Chem. Soc.* **87**, 1489–1495.

Brevedan MIV, Carelli AA, Crapiste GH. 2000. Changes in composition and quality of sunflower oils during extraction and degumming. *Grasas y Aceites* **51,** 417–423.

Bruhl L. 1996. Determination of *trans* fatty acids in cold pressed oils and in dried seed. *Fett/Lipid* **98,** 380–383.

Calvo L, Cocero MJ, Diez JM. 1994. Oxidative stability of sunflower oil extracted with supercritical carbon-dioxide. *J. Am. Oil Chem. Soc.* **71,** 1251–1254.

Campbell EJ. 1983. Sunflower oil. *J. Am. Oil Chem. Soc.* **60,** 387–392.

Carelli AA, Ceci LN, Crapiste GH. 2002. Phosphorus to phospholipid conversion factors for crude and degummed sunflower oils. *J. Am. Oil Chem. Soc.* **79,** 1177–1180.

Cleenerwerck B, Dijkstra AJ. 1992. The total degumming process - theory and industrial application in refining and hydrogenation. *Fat Sci. Technol.* **94,** 317–322.

Cmolik J, Schwarz W, Svoboda Z, Pokorny J, Reblova Z, Dolezal M, Valentova H. 2000.Effect of plant-scale alkali refining and physical refining on the quality of rapeseed oil. *Eur. J. Lipid Sci. Technol.* **102,** 15–22.

Crapiste GH, Brevedan MIV, Carelli AA. 1999. Oxidation of sunflower oil during storage. *J. Am. Oil Chem. Soc.* **76,** 1437–1443.

Chun J, Lee J, Ye L, Exler J, Eitenmiller RR. 2006. Tocopherol and tocotrienol contents of raw and processed fruits and vegetables in the United States diet. *J. Food Comp. Anal.* **19**, 196–204.

Dimic E, Karlovic DJ, Turkulov J. 1994. Pretreatment efficiency for physical refining of sunflowerseed oil. *J. Am. Oil Chem. Soc*. **71,** 1357–1361.

Duchateau, GSMJE, van Oosten HJ, Vasconcellos MA. 1996. Analysis of *cis* and *trans* fatty acid isomers in hydrogenated and refined vegetable oils by capillary gas–liquid chromatography. *J. Am. Oil Chem. Soc.* **73,** 275–282.

Evans CD, List GR, Beal RE, Black LT. 1974. Iron and phosphorus contents of soybean oil from normal and damaged beans. *J. Am. Oil Chem. Soc*. **51,** 444–448.

Ferrari RAp, Schulte E, Esteves W, Brühl L, Mukherjee KD. 1996. Minor constituents of vegetable oils during industrial processing. *J. Am. Oil Chem. Soc.* **73,** 587–592.

Frega N, Mozzon M, Lercker G. 1999. Effects of free fatty acids on oxidative stability of vegetable oil. *J. Am. Oil Chem. Soc.* **76,** 325–329.

Ghasemnezhad A, Honermeier B. 2009. Influence of storage conditions on quality and viability of high and low oleic sunflower seeds. Int. J. Plant Product. **3**, 39–47.

Gordon MH, Mursi E. 1994. A comparison of oil stability based on the Metrohm Rancimat with storage at 20°C. *J. Am. Oil Chem. Soc.* **71,** 649–651.

Jung MY, Yoon SH, Min DB. 1989. Effects of processing steps on the content of minor compounds and oxidation of soybean oil. *J. Am. Oil Chem. Soc.* **66,** 118–120.

IUPAC. 1992. *Standard methods for the analysis of oils, fats and derivatives.* 7th edn., Paquot C and Hautfenne A (Ed.), International Union of Pure and Applied Chemistry, Blackwell Scientific Publications Inc., Oxford, UK. Methods 2.201, 2.421, 2.501.

IUPAC. 1998. *Standard methods for the analysis of oils, fats and derivatives*, determination of tocopherol and tocotrienols in vegetable oils and fats by high performance liquid chromatography. Method 2.432, **60,** 887–892.

Kamal-Eldin A, Appelqvist LA. 1996. The chemistry and antioxidant properties of tocophero and tocotrienols. *Lipids* **31,** 671–701.

Kartika IA, Pontalier PY, Rigal L. 2005. Extraction of sunflower oil by twin screw extruder: Screw configuration and operating condition effects. *Bioresource Tech.* **97**, 2302–2310.

Kartika IA, Pontalier PY, Rigal L. 2010. Twin-screw extruder for oil processing of sunflower seeds: Thermo-mechanical pressing and solvent extraction in a single step. *Ind. Crop. Prod.* **32**, 297–304.

Kellens M. 1997. *Current Developments in Oil Refining Technology*. Technical Report, De Smet-Belgium. Antwerp, Belgium, pp.35–48.

Lajara JR, Diaz U, Diaz Quidiello R. 1990. Definite influence of localization and climatic conditions on fatty acid composition of sunflower seed oil. *J. Am. Oil Chem. Soc.* **67,** 618–623.

Laubli MW, Bruttel PA, Schalch E. 1988. Determination of the oxidative stability of fats and oils comparison between active oxygen method (AOM) and Rancimat method. *Fat Sci. Technol.* **90,** 56–58.

Leibovitz Z, Ruckenstein C. 1981. New process in degumming, bleaching, deacidification–deodorization and winterizing of edible oils. *Rev. Franç. Corps Gras.* **28,** 303–308.

Leonardis A, Macciola V, Felice M. 2001. Chemical and commercial characteristics of pressed sunflower seed oils. *Italian Food Bev. Technol.* **25,** 46–52.

List GR, Friedrich JP. 1985. Processing and properties of seed oils obtained by supercritical CO_2 extraction at high temperatures and pressures. *J. Am. Oil Chem. Soc.* **62,** 640–645.

List GR, Friedrich JP. 1989. Oxidative stability of seed oils extracted with supercritical carbon dioxide. *J. Am. Oil Chem. Soc.* **66,** 98–101.

Matthaus B, Bruhl L. 2003. Quality of cold-pressed edible rapeseed oil in Germany. *Nahrung/Food* **47,** 413–419.

Medina-Juarez LA, Gamez MN, Ortega GJ, Noriega RJA, Angulo GO.2000. *Trans* fatty acid composition and tocopherol content in vegetable oils produced in Mexico. *J. Am. Oil Chem. Soc.* **77,** 721–724.

Naz S, Sherazi STH, Talpur FN. 2010. Changes of total tocopherol and tocopherol species during sunflower oil processing. *J. Am. Oil Chem. Soc.*, **88**, 127–132.

NMKL. 1998. *Determination by Atomic Absorption Spectrophotometer after Wet Digestion in a Microwave Oven.* Metals. Nordic Committee on Food Analysis, Nordisk Metodikkomité for Næringsmidler, National Veterinary Institute-Oslo, Norwegian, Method no. 161.

Ortega-Garcia J, Gamez-Meza N, Noriega-Rodriguez JA, Dennis-Quinonez O, Garcia-Galindo HS, Angulo-Guerrero JO, Medina-Juarez LA. 2006. Refining of high oleic safflower oil: effect on the sterols and tocopherols content. *Eur. Food Res. Technol.* **223**, 775–779.

O'Brien RD. 2004. *Fats and Oils: formulating and processing for applications.* 2nd ed., CRC Press, New York.

Oyinlola A, Ojo A, Adekoya LO. 2004. Development of a laboratory model screw pres for peanut oil expression. *J. Food Eng.* **64,** 221–227.

Perretti G, Finotti E, Adamuccio S, Della Sera R, Montanari L. 2004. Composition of organic and conventionally produced sunflower seed oil. *J. Am. Oil Chem. Soc.* **81,** 1119–1123.

Rabascall NH, Riera JB. 1987. Variations of the tocopherols and tocotrienols content in the obtention, refining and hydrogenation processes of edible oils. *Grasas Aceites* **38,**145–148.

Schwarz W. 2000. Formation of *trans* polyalkenoic fatty acids during vegetable oil refining.*Eur. J. Lipid Sci. Technol.* **102,** 648–649.

Stefanoudaki E, Williams M, Harwood J. 2010. Changes in virgin olive oil characteristics during different storage conditions. *Eur. J. Lipid Sci. Technol.* **112**, 906–914.

Tasan M, Demirci M. 2003. *Trans* fatty acids in sunflower oil at different steps of refining.*J. Am. Oil Chem. Soc.* **80,** 825–828.

Tasan M, Demirci M. 2005. Total and individual tocopherol contents of sunflower oil at different steps of refining. *Eur. Food Res. Technol.* **220,** 251–254.

Wang T. 2002. Soybean oil. In: Gunstone FD (Ed.), *Vegetable Oils in Food Technology: Composition, Properties and Uses*, Blackwell Scientific Publications Inc., Oxford, UK., pp. 24–25.

Warner K, Miller J, Demurin Y. 2008. Oxidative stability of crude mid-oleic sunflower oils from seeds with high γ- and δ-tocopherol levels. *J. Am. Oil Chem. Soc.* **85,** 529–533.

Wesdorp L. 1996. Current trends in oil processing. *Lipid Technol.* **8,** 129–135.

Wolff RL. 1992. *Trans*-polyunsaturated fatty acid in French edible rapeseed and soybean oils. *J. Am. Oil Chem. Soc.* **69,** 106–110.

Van Hoed V, Depaemelaere G, Vila Ayala JV, Santiwattana P, Verhe R, De Greyt W. 2006. Influence of chemical refining on the major and minor components of rice bran oil. *J. Am. Oil Chem. Soc.* **83**, 315–321.

Yılmam L, Tasan M. 2008. *Trans* fatty acid contents of crude soybean oils industrially obtained by solvent extraction with hexane. *Asian J. Chem.* **20**, 3741–3749.

Yoon SH, Min DB. 1986. Effect of thermally oxidized compounds on the flavor stability of soybean oil. *J. Am. Oil Chem. Soc.* **63**, 425–426.

Recibido: 14/12/10
Aceptado: 7/3/11