## Physicochemical studies on sunflower oil blended with cold pressed tiger nut oil during the deep frying process

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#### RESUMEN

# Estudios fisicoquímicos sobre mezclas de aceite de girasol con aceite de chufa prensado en frío durante el proceso de fritura

Aceites de girasol se mezclaron con diferentes niveles de aceite de chufa prensado en frío. Se obtuvieron mezclas de aceite de chufa con girasol en las proporciones: 0:100, 10: 90, 20: 80, 30: 70, 40: 60, 50:50 y 100: 0. Se ha evaluado el efecto del proceso sobre los parámetros físico-químicos (ácidos grasos libres (FFA), índice de peróxido (PV), índice de ácido tiobarbitúrico (TBÁ), índice de yodo, compuestos polares totales (TPC), color y viscosidad) tras 30 horas de fritura. Se determinó también el contenido fenólico total de los aceites originales. Mediante GLC se determinó la composición de ácidos grasos de los aceites de girasol, de chufa y las mezclas binarias de ellos, y se calculó el tipo de alteración. Los aceites originales y sus mezclas se calentaron a 180 °C ± 5°C, a continuación, se frieron patatas pre-fritas congeladas cada 30 min. Se tomaron muestras de aceite cada 5 horas y el período completo de fritura continua fue de 30 h. Los resultados mostraron que el aceite de girasol original tenía un valor significativamente más alto de COX (7,25), mientras que el aceite de chufa presentó el valor más bajo significativamente (2,24). Las mezclas de aceite de girasol con crecientes niveles de aceite chufa lleva a aumentar la estabilidad frente a la oxidación. El contenido fenólico del aceite de chufa prensado en frío fue 3,3 veces superior que el del aceite de girasol. Los datos analíticos mostraron que el menor deterioro durante el proceso de fritura se produjo en el aceite de chufa y el más alto en el de girasol. Los cambios de los parámetros fisicoquímicos controlados fueron disminuyendo significativamente (P < 0.05) cuando las proporciones chufa / aceite de girasol variaron entre 20/80 y 50/50 (W/W). Los resultados obtenidos indican que el aceite de girasol mezclado con aceite de chufa prensado en frío aumenta la estabilidad y por lo tanto mejora la calidad del aceite de girasol durante el proceso de fritura.

PALABRAS CLAVE: Ácidos Grasos – Aceite de chufa – Aceite de girasol – Antioxidantes – Estabilidad – Mezcla – Oxidación – Valor COX

#### SUMMARY

#### Physicochemical studies on sunflower oil blended with cold pressed tiger nut oil during deep frying process

Sunflower oils were blended with different levels of cold pressed tiger nut oil. Blended oils were obtained by mixing tiger nut oil with sunflower oil at the volume ratios of 0:100, 10: 90, 20: 80, 30: 70, 40: 60, 50:50 and 100: 0. The effects of deep frying on physico-chemical parameters (Free Fatty Acid (FFA), Peroxide Value (PV), thiobarbituric acid value (TBA), iodine value, Total Polar Compounds (TPC), color and viscosity) were evaluated over 30 hours of the frying process. The total phenolic content of native oils was determined. GLC analysis was performed to illustrate the fatty acid composition of sunflower oil, tiger nut oil and binary mixtures of them as well as their oxidation rates. The pure and blended oils were heated at  $180^{\circ}C \pm 5^{\circ}C$ , then frozen French fried potatoes were fried every 30 min. Oil samples were taken every 5 h and the entire continuous frying period was 30 h. The results showed that fresh sunflower oil had significantly the highest value of COX (7.25); while tiger nut oil had significantly the lowest (2.24). Mixing sunflower oil with different levels of tiger nut oil led to an increase in its stability against oxidation. The phenolic content of cold pressed tiger nut oil was about 3.3 times as high as that of sunflower oil. The analytical data showed that the lowest deterioration during the frying process occurred in tiger nut oil and the highest in sunflower. The changes in the physico-chemical parameters were controlled and significantly (P < 0.05) decreased when tiger nut /sunflower oil (W/W) proportions were varied between 20/80 to 50/50. The obtained results indicate that mixing sunflower oil with cold pressed tiger nut oil increased the stability and hence improved the quality of sunflower oil during the frying process.

KEY-WORDS: Antioxidants – Blending – COX value – Fatty acids – Oxidation – Tiger nut oil – Sunflower oil – Stability.

## 1. INTRODUCTION

Deep-fat frying is one of the oldest and most popular food preparation methods (Garayo and Moreira, 2002). Deep-fat frying is a process of immersing food in hot oil with a contact among oil, air and food at a high temperature of 150 to 190 °C (Yamsaengsung and Moreira, 2002). In the presence of oxygen, moisture, trace elements and free radicals, physiochemical reactions such as thermoxidation, hydrolysis, polymerization, isomerization or cyclization take place at the high temperatures of the frying process, thus leading to the decomposition of the frying oil and the formation of monomeric, polymeric, primary and secondary oxidative compounds, thereby affecting the quality of the oil and the fried product (Andrikopoulos *et al.*, 2002).

These reactions in the deep-fat frving process depend on factors such as replacement with fresh oil, frying conditions, original quality of the frying oil, food materials, type of fryer, type and concentration of antioxidants and oxygen concentration (Sánchez-Muniz et al., 1992). Other factors such as frying temperature, quantity of frying, initial content of free fatty acids, polyvalent metals, type of food material, design and maintenance of fryer, light, use of filters and unsaturated fatty acid content of the oil also affect the oxidative stability and overall quality of the oil during the frying process (Melton et al., 1994; Paul and Mittal, 1996; Farag and El-Anany, 2006; El-Anany and Ali, 2008). Various methods to improve the oxidative stability of soybean oil have been developed and studied, for example, partial hydrogenation, fatty acid modification and blending with more saturated or monosaturated oils to reduce the amount of polyunsaturated fatty acids (Cuesta et al., 1993; Hunter and Applewhite, 1991; Su and White, 2004). Partial hydrogenation decreases polyunsaturated fatty acid but increases saturated fatty acid and trans-fatty acid to produce more stable frying oil. However, trans fatty acid may have adverse effects on cardiac health (Ascherio et al., 1994). Blending has long been used to modify oils and fats to improve the fat functionalities and thus optimize their application in food products. It modifies the physicochemical properties of oils without changing their chemical composition (Chu and Kung, 1997). The oils can be blended even to derive a protective advantage due to the presence of specific ingredients that offer protection against oxidation to improve frying recyclability (Toliwal et al., 2005).

Normal sunflower oil is characterized by a high concentration of linoleic acid (48-74%), followed by oleic acid (14-40%). Saturated fatty acids (mainly palmitic acid and stearic acid) do not amount to more than 15% of the fatty acid content (Nagao and Yamazaki, 1983; Firestone, 1997). Sunflower oil has a good nutritional profile, with poor oxidative stability and is, accordingly, prone to flavor deterioration because of the high proportion of unsaturated fatty acids (White, 2000). The oxidation of unsaturated fatty acids is one of the major causes of the development of off-flavor compounds and in the reduction in the nutritional value of food products (Hemalatha, 2007). Tiger nut (Cyperus esculentus L.) is an underutilized crop which belongs to the division-Magnoliophyta, classliliopsida, order - cyperales and family-Cyperaceae and was found to be a cosmopolitan perennial crop of the same genus as the papyrus plant. Tiger nut is not really a nut but a small tuber, first discovered some 4000 years ago in ancient Egypt and is cultivated today in China, Spain and West Africa for its small tuberous rhizomes which are eaten raw or roasted, used as hog feed or pressed for its juice to make a beverage. Non-drying oil (usually called chufa) is equally obtained from the rhizome. (Belewu and Belewu, 2007). The tubers contain 20-36% oil, Cyperus esculentus has been suggested as a potential oil crop for the production of biodiesel, (Zhang et al., 1996). The nut was found to be rich in myristic acid (15.58%), oleic acid (66.22%) and linoleic acid (13.10%) (Zhang et al., 1996; Eteshola and Oraedu, 1996; El-Anany and Ali, 2012). The effects of feeding blended oils consisting of coconut oil (CNO) with different proportions of Tiger nut oil (TNO) on serum lipid levels of Albino rats were studied by El-Anany and Ali, (2012). Their results showed that coconut oil had 86% saturated fatty acids. TNO on the other hand contain 66% oleic acid. Therefore, blending coconut oil with tiger nut oil can reduce proportions of saturated to unsaturated fatty acids in CNO. They showed also that the rats fed on diets rich in tiger nut oil resulted in significant decreases in total cholesterol, LDL cholesterol and triglyceride levels as compared to those fed on diets rich in coconut oil.

Although the quality of pure vegetable oils before and after frying has been evaluated by many researchers, the physicochemical properties for binary oil blends have not been studied extensively. Actually, the stability of unsaturated vegetable oils can be increased by blending with stable oil that has high saturation (Chu and Kung, 1998; Siddique et al., 2010). The main objective of the present study was to evaluate the effects of the fatty acid compositions of tiger nut oil, sunflower oil and binary mixtures of them on the changes in physicochemical parameters during the deep frying process by assessing the Free Fatty Acids (FFA), Peroxide Value (PV), thiobarbituric acid value (TBA value), iodine value, Total Polar Compounds (TPC), as well as the color and viscosity of the oils. In addition, the fatty acid compositions of tiger nut oil, sunflower oil and binary mixtures of them were quantified by GLC to indicate their oxidative stability effect by assessing their COX values.

## 2. MATERIALS AND METHODS

## 2.1. Materials

Tiger nut tubers (*Cyperus esulentus*) were obtained from Harraz Spices and Herbs Co. Cairo, Egypt. Refined sunflower oil was purchased from the local market (Giza, Egypt).

All reagents and chemicals that were used in this work were of analytical grade.

## 2.2. Methods

*Tiger nut oil (TNO) extraction.* Fifty Kg of dried Tiger nut tubers (*Cyperus esulentus*) were crushed and pressed using a hydraulics laboratory press model C S/N 37000-156 Freds from Carver (WI, USA). Anhydrous sodium sulphate was added to the extracted oil and it was allowed to stand for 30 min to remove excessive residual moisture. The resulting dry oil was centrifuged at 3500 rpm for 15 min and filtered through Whitman filter paper No.1 and kept in a brown glass bottle at  $4 \pm 0.5$  °C. *Preparation of Blends.* Cold pressed tiger nut oil (TNO) was blended with sunflower oil (SO) in varying proportions. The following TO: SO (% v/v) blends were prepared; 0:100, 10: 90, 20: 80, 30: 70, 40: 60, 50:50 and 100: 0. The oil blends were mixed at 60°C in an oven prior to initial analysis.

*Frying process.* A known amount (1250 mL) of each of the refined sunflower oil, tiger nut oil and binary mixtures of them were placed separately in a stainless steel pan fryer (40 cm diameter  $\times$  10 cm height). Each oil was separately heated at 180 °C  $\pm$  $\pm$  5 °C, then 50 g of frozen French fried potatoes were fried every 30 min. The fryer temperature decreased by approximately 10 °C within 1.5 min of the addition of the frozen potatoes and then increased until the end of frying time of 4 min. Oil samples were taken every 5 hrs and the entire continuous frying period was 30 h. The oil samples were left to cool then stored at -18 °C for the physico-chemical analysis.

## 2.3. Chemical analyses

Fatty acid compositions of tiger nut oil, Sunflower oil and the binary admixtures. Capillary gas chromatography (HP 6890) was used for the qualitative and quantitative determinations of the fatty acids of the oil samples and reported in relative area percentages. Fatty acids were transesterified into their corresponding fatty acid methyl esters (FAMEs) by shaking a solution of oil (ca. 0.1 g) in heptane (2 mL) with a solution of methanolic potassium hydroxide (0.2 mL, 2N). The FAMEs were identified using a gas chromatograph equipped with a DB-23 capillary column (60 m 3 0.32 mm 3 0.25 µm film thickness) and a flame ionization detector. The nitrogen flow rate was 3 mL/min; hydrogen and airflow rates were 40 and 450 mL min<sup>-1</sup>, respectively. The oven temperature was programmed from 150 °C to 170 °C at a rate of 10 min, then raised to 192 °C at a rate of 5 °C minand kept at this temperature for 5 min and then raised again to 220 °C at a rate of 10 °C min<sup>-1</sup> and kept at this temperature for 3 min. The injector and the detector temperatures were 230 °C and 250 °C. respectively. MEFAs were identified by comparing their retention times with a known fatty acid standard mixture. Peak areas were automatically computed by an integrator.

*Oxididation value (Cox).* The calculated oxididation stability value (Cox) of the oils was calculated by applying the formula proposed by Fatemi and Hammond (1980).

*Total phenolic content.* The phenolic content of oil was extracted according to the method described by Rotondi *et al.*, (2004); Henna Lu and Tan (2009). Approximately 15 g of oil was weighed into a 50 mL Falcon tube. Ten milliliters of n-hexane were mixed with the oil. The mixture was extracted with 10 mL of methanol: water (60:40). The mixtures were shaken for 5 min and then centrifuged at 5500 rpm for 5 min. The hydroalcoholic phase was collected and the hexane phase was re-extracted twice with 10 mL of methanol: water (60:40) each time. The

combined hydroalcoholic fractions from three extractions were subjected to final washing with 10 mL of n-hexane to remove residual oil in a separatory funnel. The excess solvent was evaporated under vacuum at 40 °C until dryness in a rotary evaporator. The residue was reconstituted in 20 mL methanol: water (60:40). The total phenolic content was determined by the Folin-Ciocalteu reagent assay (Lim et al., 2007). First, 0.5 mL of the extract obtained were mixed with 1.5 mL of Folin-Ciocalteu reagent previously diluted with distilled water (1:10). After standing at room temperature for 3 min, 1.2 mL of 15% sodium carbonate solution was added. The mixture was placed in dark room for 60 min. After that, the absorbance was measured at 765 nm against the blank using a spectrophotometer (Secomam UVi ligh XTD). The calibration curve was obtained by repeating the above procedures with known concentrations of gallic acid solutions. The results were expressed as milligrams of gallic acid equivalents (GAE) per 100 g of oil (mg GAE per 100 g of oil). Since the assay quantifies all phenolic compounds, the selection of gallic acid as a standard is based on the availability of a stable and pure compound. In addition, gallic acid is cheaper than other options. Analyses were performed in triplicate for each of the extracts.

Acid value. Acid value was determined according the A.O.A.C. (2000) as follows: a known weight (2 g) of the oil was dissolved in a neutral ethyl alcohol (30 mL); the mixture was boiled in a water bath for 2 min and then titrated with a potassium hydroxide solution (0.1N) in the presence of phenolphthalein as an indicator. Acid value is expressed as mg KOH required neutralizing the acidity in one gram of oil.

*Peroxide value.* The peroxide values were determined according to A.O.A.C (2000). A known weight of the oil sample (2.5 g) was dissolved in a mixture consisting of glacial acetic acid:cholroform (30 mL, 3:2, v/v), then freshly prepared saturated potassium iodide solution (1 mL) was added. Distilled water (30 ml) was added then titrated slowly with a sodium thiosulphate solution (0.1 N) in the presence of a starch solution (1%) as an indicator. Peroxide value is expressed as milliequivalent of  $O_2 \text{ kg}^{-1}$  oil.

*Thiobarbituric acid value (TBA).* The method of Sidwell *et al.*, (1954) was conducted to determine the thiobarbituric acid value (TBA value) as follows: a known weight of oil (3g) was dissolved in a carbon tetrachloride (10 mL) followed by the addition of the TBA reagent (10ml, 0.67% TBA in 50% acetic acid). The mixture was transferred to a separatory funnel and the aqueous layer was drawn into a test tube and immersed in a boiling water bath for 30 min. The absorbance of the developed pink color was then recorded at 532nm against a blank reagent.

*lodine value*. The iodine value was determined using the Hanus method as described in A.O.A.C. (2000). A known weight of oil (0.2 g) was dissolved in chloroform (20 ml), then Hanus iodine ( $I_2 + Br /$ ACOH) solution (25 mL) was added and left in the dark for 30 min. A potassium iodide solution (10 mL, 15%) was added followed by freshly distilled water (100 mL) and the excess iodine was titrated with sodium thiosulphate (0.1N) until the yellow color of solution had almost disappeared. Titration was continued after adding a few drops of starch as an indicator until the blue color had entirely disappeared. A blank was conducted where the total halogen content of the Hanus solution (25 mL) was determined by a sodium thiosulphate solution without the addition of oil. Iodine value is expressed as grams of  $I_2$ absorbed by 100g oil.

Total polar compounds (TPC) content. The TPC contents of the oil samples were measured by column chromatography according to the method described by Waltking and Wessels (1981). A slurry of (25 g) silica gel in 80 mL light petroleum-ethyl ether (90:10, v/v) was poured above a wad of cotton wool which was placed in the bottom of the column (2.1 cm  $\times$  54 cm) filled with 30 ml of light petroleum-ethyl ether (90:10, v/v). An aliquat of the oil sample (2.5 g) in 20 ml light petroleum-ethyl ether (90:10, v/v) was poured into the top of the column. The non-Total polar compounds of the oils were eluted with 150 ml light petroleum-ethyl ether (90:10, v/v) within 60-70 min by adjusting the eluent flow rate. The solvent was evaporated using a rotary evaporator at 60 °C until constant weight was obtained. Total polar compounds were calculated by difference as follows:

Total polar compounds,  $\% = ((E - A) / E) \times 100$ Where: A = weight of non – Total polar compounds fraction – E = weight of sample.

#### 2.4. Physical analysis

*Color.* **A** Lovibond tintometer (Tintometer Limited Solstice Park, Amesbury, UK) was used to measure the color of the oil samples under investigation, the yellow glass filter was fixed at 30 and the intensity of red glass color was measured according to the A.O.A.C. (2000).

**Viscosity. A** Brookfield LV viscometer Model TC-500 (Brookfield Engineering Laboratories Stoughton, MA, USA) was used to measure the viscosity of the oil samples at 30°C., according to the method described by Saguy *et al.* (1996).

2.5. Statistical analysis

Data are expressed as mean  $\pm$  SD. Data were statistically analyzed in a completely randomized design in factorial arrangement according to the procedures outlined by Gómez and Gómez (1984) and the treatment means were compared by least significant differences (L.S.D) and the Duncan multiple range using the SPSS program package. Data are presented in the text and tables as means of three determinations.

#### 3. RESULTS AND DISCUSSION

#### 3.1. Fatty acid compositions and (Cox) values.

The results in Table 1 show the fatty acid compositions of sunflower oil, tiger nut oil and binary mixtures of them. Fresh sunflower oil contained trace amounts of 16:1 and 18:3 fatty acids. A moderate amount of oleic acid was shown for sunflower oil (19.50%). Sunflower oil had significantly (P < 0.05) the highest level of linoleic acid, 18:2 (67.48%). Tiger nut oil was characterized by the presence of high levels of monounsaturated fatty acids. The most prominent fatty acid in tiger nut oil was oleic acid (66.22%). Mixing sunflower oil with different portions of tiger nut oil caused a significant (P < 0.05) increase in the content of monounsaturated fatty acids, in parallel with a significant decrease in the levels of polyunsaturated fatty acids. The calculated oxidation (cox) value which is based on unsaturated fatty acid percentages present in the oils, is a beneficial element usually taken as an evaluation of the oil's tendency to undergo autoxidation (Fatemi and Hammond, 1980). The results of the calculated

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Fatty	Sunflower	Tiger nut oil	Tiger nut oil + Sunflower oil (v/v)							
acid	oil (SO)	(TNO)	(10/90)	(20/80)	(30/70)	(40/60)	(50/50)	at 0.05		
C16:0	$7.60^{f} \pm 0.41$	$15.58^{a} \pm 0.11$	$8.41^{ef} \pm 0.65$	$9.19^{de} \pm 0.35$	$10.00^{\text{cd}}\pm0.65$	$10.80^{bc} \pm 0.15$	$11.60^{b} \pm 0.70$	0.852		
C18:0	$4.92^{a}\pm0.09$	$4.00^{\text{b}}\pm0.05$	$4.83^{a} \pm 0.15$	$4.74^{a} \pm 0.04$	$4.66^{a} \pm 0.20$	$4.55^{a} \pm 0.35$	$4.45^{a} \pm 0.25$	0.338		
C18:1	$19.50^{g} \pm 0.31$	$66.22^{a} \pm 0.82$	$23.70^{f} \pm 1.40$	$28.85^{\circ} \pm 0.69$	$33.55^{d} \pm 0.71$	$38.20^{\circ} \pm 0.45$	$42.85^{b} \pm 0.85$	1.424		
C18:2	$67.48^{a} \pm 1.22$	$13.10^{g} \pm 0.04$	$62.00^{b} \pm 0.85$	$56.60^{\circ} \pm 1.45$	$51.15^{d} \pm 2.05$	45.70 <sup>e</sup> ± 1.82	$40.30^{f} \pm 1.05$	2.361		
C18:3	$0.50^{d} \pm 0.02$	$1.10^{a} \pm 0.01$	$1.06^{a} \pm 0.04$	$0.62^{\circ} \pm 0.03$	$0.64^{\circ} \pm 0.09$	$0.75^{b} \pm 0.01$	$0.80^{b} \pm 0.10$	0.096		
SAFA	$12.52^{f} \pm 0.50$	$19.58^{a} \pm 0.16$	$13.24^{ef} \pm 0.80$	$13.93^{de} \pm 0.39$	$14.66^{cd} \pm 0.85$	$15.35^{bc} \pm 0.50$	$16.05^{b} \pm 0.95$	1.135		
MUFA	$19.50^{g} \pm 0.31$	$66.22^{a} \pm 0.82$	$23.70^{f} \pm 1.40$	$28.85^{\circ} \pm 0.69$	$33.55^{d} \pm 0.71$	$38.20^{\circ} \pm 0.45$	$42.85^{b} \pm 0.85$	1.424		
PUFA	67.98 <sup>a</sup> ± 1.24	$14.20^{g} \pm 0.05$	$63.06^{\text{b}} \pm 0.89$	57.22 <sup>c</sup> ± 1.45	$51.79^{d} \pm 2.14$	46.45 <sup>e</sup> ± 1.83	$41.10^{f} \pm 1.15$	2.322		
Cox	7.25	2.24	6.8	6.25	5.73	5.25	4.75	-		

 Table 1

 Fatty acid composition of Sunflower oil, tiger nut oil and binary mixtures of them

Means within the same row with different letters are significantly different (P < 0.05);  $\pm$  S.D; SAFA, Saturated Fatty Acids; MUFA, Monounsaturated Fatty Acids; PUFA, Polyunsaturated Fatty Acids.

Cox refers to calculated oxidisability value

oxidation index (COX) values for the oils under study are shown in Table 1. Fresh sunflower oil had significantly the highest value of COX (7.25); while tiger nut oil had significantly the lowest value (2.24). These values reveal that tiger nut oil is more resistant to oxidation than sunflower oil. Mixing sunflower oil with different levels of tiger nut oil led to an increase in its stability against oxidation and the extent of this phenomenon was basically dependent on the mixing ratios. The increase in oxidative stability is correlated with the increase in tiger nut oil levels.

## 3.2. Total polyphenol contents

The level of phenols in seed oils is an important factor when assessing the quality of oil because these compounds have been correlated with the color and the shelf-life of oil, and particularly its resistance to oxidation (Cheikh-Rouhou et al., 2006). These compounds are the main factor rendering nutritional importance to cold-pressed oil (Henna Lu and Tan. 2009). Tiger nut oil showed higher level of total poly phenols -16.5 mg GAE per 100 g of oil compared to sunflower oil- 5.0 mg GAE per 100 g of oil. This means that the phenolic content of Tiger nut oil was about 3.3 times higher than that of sunflower oil. Tiger nut oil (TNO) has been shown to be rich in polyphenols. (Okafor et al., 2003; Belewu and Abodunrin, 2006; Oladele et al., 2009; El-Anany and Rehab Ali, 2012).

#### 3.3. Changes in Acid value (AV)

Acid value was used to assess frying oil degradation and is related to fried food quality (Fritch, 1981; Melton *et al.*, 1994). The changes in the acid values of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at  $(180^{\circ}C \pm 5^{\circ}C)$  are given in Table 2. The initial acid values of the fresh oils under investigation were seen to range from 0.13 for sunflower oil to 0.31 for

tiger nut oil, these low values reflect the quality of these oils .The maximum level of acid value of the refined and cold pressed oils were 0.6 and 4.0 mg KOH g<sup>-1</sup> oil, respectively (Codex, 1999). Generally, frying at 180 °C ± 5 °C for 30 h led to a gradual and significant (P < 0.05) increases in the acid values for the all oils under study. The formation of free fatty acids was found to increase with an increased frying time. The increase in FFA could be attributed to oxidation and hydrolysis, which produces FFAs (Peeled et al., 1975; Abdel-Aal and Karara, 1986). Moreover, the FFA content is a dynamic value because at the same time that the acids are being produced, they have sufficient vapor pressure at frying temperatures to evaporate from the surface (Peeled et al., 1975). The highest change in acid value at the end of the frying period was shown for sunflower oil (AV increased from  $0.13 \pm 0.04$  at the beginning of the frying experiment to  $0.69 \pm 0.06$  at the end of frying period 30 h), whereas the lowest change was observed for tiger nut oil. The AV of tiger nut oil increased from of 0.31  $\pm$  0.03 to 0.73  $\pm$  0.02 during 30 h of frying. Blending sunflower oil with different levels of tiger nut oil led to a significant (P < 0.05) decrease in acid values during the frving periods. This decrement increased by increasing the blending ratio of tiger nut oil. The higher oxidative stability of tiger nut oil, compared to sunflower oil is due to the high oleic acid (monounsaturated) and low polyunsaturated fatty acid contents of the triacylglycerols. Hydrolysis is more preferable in oil with short and unsaturated fatty acids than in oil with long and saturated fatty acids because short and unsaturated fatty acids are more soluble in water than long and saturated fatty acids. Water from foods is easily accessible to short-chain fats and oils for hydrolysis (Nawar, 1969). On the other hand, tiger nut oil contains high levels of phenolic compounds; these compounds have antioxidative effects and possess antihydrolytic effects during the frying process.

Table 2 Changes in acid values (mg KOH g<sup>-1</sup> Oil) of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C ± 5 °C).

Frying	Tiger nut oil	Sunflower oil (SO)	TNO + SO (v/v)						
period (hr)	(TNO)		10:90	20:80	30:70	40:60	50:50		
0	$0.31^{op} \pm 0.03$	$0.13^{w} \pm 0.04$	$0.15^{vw} \pm 0.03$	$0.16^{uvw} \pm 0.03$	$0.16^{uvw} \pm 0.01$	$0.18^{uvw} \pm 0.02$	$0.20^{\text{uvw}} \pm 0.03$		
5	$0.40^{\text{hij}}\pm0.04$	$0.25^{\text{rst}} \pm 0.03$	$0.21^{\text{uvw}}\pm0.07$	$0.19^{uvw} \pm 0.03$	$0.19^{\text{uvw}} \pm 0.04$	$0.20^{\text{uvw}}\pm0.06$	$0.22^{\text{tuv}}\pm0.02$		
10	$0.54^{\text{de}} \pm 0.03$	$0.30^{\text{opq}} \pm 0.03$	$0.26^{\text{rst}} \pm 0.04$	$0.24^{\text{stu}} \pm 0.01$	$0.23^{\text{tuv}}\pm0.06$	$0.24^{stu} \pm 0.03$	$0.23^{\text{tuv}}\pm0.05$		
15	$0.62^{bc} \pm 0.06$	$0.35^{lmn} \pm 0.05$	$0.34^{\text{mno}} \pm 0.01$	$0.29^{\text{pqr}} \pm 0.03$	$0.27^{\text{qrs}} \pm 0.04$	$0.29^{pqr} \pm 0.01$	$0.27^{\text{qrs}} \pm 0.02$		
20	$0.69^{ab}\pm0.02$	$0.42^{hij} \pm 0.07$	$0.38^{jkl} \pm 0.06$	$0.37^{\text{klm}} \pm 0.04$	$0.36^{\text{klm}} \pm 0.03$	$0.34^{\text{mno}} \pm 0.08$	$0.31^{\text{opq}} \pm 0.04$		
25	$0.70^{a} \pm 0.03$	$0.53^{def} \pm 0.03$	$0.45^{\text{ghi}} \pm 0.03$	$0.42^{\text{hij}}\pm0.03$	$0.40^{\text{hij}} \pm 0.03$	$0.39^{ijk} \pm 0.03$	$0.37^{jkl}\pm0.03$		
30	$0.73^{a} \pm 0.03$	$0.69^{ab} \pm 0.03$	$0.58^{cd} \pm 0.03$	$0.56^{\text{cde}} \pm 0.03$	$0.52^{\text{def}} \pm 0.03$	$0.49^{\text{efg}} \pm 0.03$	$0.48^{\text{fgh}} \pm 0.03$		
LSD at 0.05 = 0.07246									

#### 3.4. Changes in peroxide value (PV)

Determination of peroxide value can give an idea about the early stages of oil oxidation. Table 3 presents the peroxide values of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at  $(180 \degree C \pm 5 \degree C)$ . Peroxide values for the fresh oils were very low which indicates the high quality of the oils used in this work. The range of peroxide values for the fresh oils was 0.96-1.32  $meqO_2$  kg<sup>-1</sup> oil, which is less than 10 meqO\_2 kg<sup>-1</sup>, and therefore within the acceptable value range for fresh oil (Codex, 1999). The peroxide values for the frying oil were progressively and significantly increased during the frying process, but not as sharply as the free acidity. Peroxides are unstable compounds particularly under high temperature conditions; therefore the peroxides decompose to form carbonyl and aldehydic compounds causing a decrease in peroxide value (Perkins, 1967; Shahidi and Wanasundara, 2002). Sunflower oil had significantly (P < 0.05) the highest value of peroxide 9.64 megO<sub>2</sub>/kg oil at the end of the frying period (30) h). Unsaturated fatty acids easily react with oxygen to form peroxides (Marina et al., 2009). Whereas the lowest values (6.51 and 6.76 megO<sub>2</sub>/kg oil) were recorded for tiger nut oil and its mixture with sunflower at level 50%, respectively, the rates of formation of hydroperoxides seem to be higher in sunflower oil than in case of tiger nut oil and their blends. These findings are in line with the degree of oil unsaturation; the increase in the amount of monounsaturated fatty acids helps to increase the oxidative stability of oil blends. At the same time , these findings were expected due to the faster oxidation (Chan et al., 1982) of the polyunsaturated fatty acids of sunflower oil and to the presence of the high levels of natural antioxidants, vitamins E and C (Belewu and Belewu, 2007) in tiger nut oil, which act as potent antioxidants during the frying process.

#### 3.5. Changes in Thiobarbituric acid value (TBA)

The changes in the TBA values (absorbance at 532 nm) of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C ± ± 5°C) are shown in Table 4. An increase in the TBA values for all oil samples under study was observed with prolonging frying time. This finding could be explained by the fact that the less stable primary oxidative compounds (i.e., hydroperoxides) decompose further to form aldehydic compounds. These carbonyl compounds react with TBA reagent to produce colored compounds which usual absorb at 532nm. (Przybylski and Eskin, 1995; Farag and El-Anany, 2006). The highest (P < 0.05) TBA value was recorded for sunflower oil (0.97 as absorbance at 532 nm) at the end of the frying period. On the other hand, Tiger nut oil and its mixture with sunflower oil at a level of 50% (v/v) had significantly (P < 0.05) the lowest values at the end of frying period at 0.55 and 0.61 as absorbance at 532nm, respectively. This means that the TBA value of tiger nut oil at the end of the frying period was about 1.76 times as low as that for sunflower oil at the end of the frying period. It is well known that linoleate hydroperoxides decompose faster than oleate hydroperoxides. The oleate: linoleate: linolenate oxidation ratio has been reported to be in the order of 1:12:25, based on peroxide formation (Aparicio et al., 1999). These facts support the results of the present study. At the same time, the presence of natural antioxidants in tiger nut oil had inhibitory effects on the formation of these secondary oxidation products during the frying process.

### 3.6. Changes in iodine value (IV)

lodine value is a measure of the unsaturation of the oils. It is one of the parameters used to measure

Table 3 Changes in Peroxide values (meq  $O_2 \text{ kg}^{-1}$ ) of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C ± 5 °C).

Frying	Tiger nut oil	Sunflower	TNO + SO (v/v)						
period (h)	(TNO)	oil (SO)	10:90	20:80	30:70	40:60	50:50		
0	$0.96^{t} \pm 0.20$	$1.32^{t} \pm 0.15$	$1.29^{t} \pm 0.16$	$1.23^{t} \pm 0.05$	$1.18^{t} \pm 0.10$	$1.16^{t} \pm 0.18$	$1.15^{t} \pm 0.10$		
5	$2.35^{\text{pqr}} \pm 0.17$	$2.33^{pqr} \pm 0.21$	$2.15^{pqr} \pm 0.16$	$2.14^{pqr} \pm 0.13$	$0.94^{qr} \pm 0.22$	$1.88^{pqr} \pm 0.17$	$1.86^{pqr} \pm 0.14$		
10	$2.00^{pqr}\pm0.09$	$2.00^{pqr}\pm0.33$	$3.86^{\text{lmn}} \pm 0.76$	$3.75^{Imn} \pm 0.11$	$3.52^{mn}\pm0.09$	$1.44^{st} \pm 0.32$	$2.67^{\circ} \pm 0.30$		
15	$3.45^{n} \pm 0.44$	$4.82^{\text{fgh}}\pm0.22$	$4.73^{\text{ghi}} \pm 0.33$	$2.64^{\circ} \pm 0.20$	$4.43^{hij} \pm 0.22$	$4.35^{ijk} \pm 0.30$	$2.42^{\text{opq}} \pm 0.04$		
20	$2.47^{op} \pm 0.22$	$5.21^{f} \pm 0.41$	$4.00^{\text{kIm}} \pm 0.50$	$4.86^{fg} \pm 0.12$	$4.20^{jkl} \pm 0.60$	$4.65^{\text{ghi}} \pm 0.05$	$4.31^{ijk} \pm 0.06$		
25	$4.89^{\text{fg}} \pm 0.66$	$8.46^{\circ} \pm 0.18$	$7.82^{d} \pm 0.10$	$7.65^{d} \pm 0.40$	$6.81^{e} \pm 0.15$	$4.50^{\text{hij}}\pm0.02$	$4.64^{\text{ghi}} \pm 0.22$		
30	$6.51^{\circ} \pm 0.08$	$9.64^{a} \pm 0.13$	$8.98^{b} \pm 0.012$	$8.41^{\circ} \pm 0.06$	$7.63^{d} \pm 0.11$	$7.44^{d} \pm 0.14$	$6.76^{e} \pm 0.71$		
LSD at 0.05 = 0.4668									

Table 4Changes in Thiobarbituric acid value (Absorbance at 532 nm) of sunflower oil, tiger nut oil and binary<br/>mixtures of them during deep fat frying at (180°C ± 5°C).

Frying	Tiger nut oil	Sunflower oil (SO)	TNO + SO (v/v)						
period (h)	(TNO)		10:90	20:80	30:70	40:60	50:50		
0	$0.04^{x} \pm 0.01$	$0.07^{\text{vwx}} \pm 0.01$	$0.04^{wx} \pm 0.02$	$0.05^{wx} \pm 0.01$	$0.05^{\text{wx}} \pm 0.01$	$0.06^{\text{wx}} \pm 0.01$	$0.06 \pm 0.00$		
5	$0.11^{\text{uv}}\pm0.05$	$0.16^{\text{tu}}\pm0.04$	$0.15^{tu} \pm 0.04$	$0.15^{tu} \pm 0.03$	$0.14^{tu}\pm0.02$	$0.14^{tu} \pm 0.01$	$0.10^{\text{vw}} \pm 0.00$		
10	$0.15^{tu} \pm 0.06$	$0.32^{\circ} \pm 0.04$	$0.25^{\text{pqr}} \pm 0.03$	$0.20^{\text{rst}} \pm 0.05$	$0.20^{\text{rst}} \pm 0.02$	$0.19^{\text{st}} \pm 0.03$	$0.15^{\text{tu}}\pm0.02$		
15	$0.21^{\text{qrs}} \pm 0.06$	$0.53^{ij} \pm 0.03$	$0.52^{ij} \pm 0.02$	$0.49^{jkl}\pm0.04$	$0.46^{\text{kIm}} \pm 0.00$	$0.42^{mn}\pm0.02$	$0.26^{pq} \pm 0.03$		
20	$0.27^{op} \pm 0.01$	$0.79^{\text{b}}\pm0.02$	$0.59^{\text{gh}} \pm 0.03$	$0.55^{\text{hi}}\pm0.04$	$0.50^{ijk} \pm 0.05$	$0.49^{jkl} \pm 0.05$	$0.40^{n} \pm 0.06$		
25	$0.30^{\text{op}} \pm 0.00$	$0.92^{a} \pm 0.01$	$0.72^{\circ} \pm 0.03$	$0.71^{\text{cd}} \pm 0.02$	$0.66^{\text{def}} \pm 0.04$	$0.60^{\text{fg}} \pm 0.02$	$0.44^{\text{lmn}} \pm 0.00$		
30	$0.55^{\text{hi}}\pm0.04$	$0.97^{a} \pm 0.02$	$0.81^{b} \pm 0.01$	$0.73^{\circ} \pm 0.03$	$0.70^{\text{cde}} \pm 0.01$	$0.65^{\text{ef}} \pm 0.09$	$0.61^{\text{fg}} \pm 0.01$		
LSD at 0.05 = 0.05124									

Data are expressed as mean  $\pm$  SD. Values given represent means of three determinations. Values followed by the same letter are not significantly different (p < 0.05).

the oil quality (Haryati et al., 1998). Table 5 demonstrates the IV of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180°C ± 5°C). The initial iodine values of tiger nut and sunflower oil were 105.80 and 123.00 g l<sub>2</sub> 100  $g^{-1}$  oil, respectively . Bending sunflower oil with various levels of tiger nut oil caused a significant (P<0.05) decrease in iodine values (degree of oil unsaturation), this decrease was due to the increase in the predominance of monounsaturated fatty acids in the tiger nut oil in the blended oils. The frying process induced significant (P < 0.05) decreases in the IV of the all oil under study. This observation could be attributed to the destruction of double bonds by oxidation and/or polymerization. As stated by Naz et al., 2005, oxidation, which consists of a complex series of chemical reactions, is characterized by a decrease in the total unsaturated content of the oil due to the abstraction of hydrogen adjacent to a double bond. It is well known that during frying some of the non-conjugated double bonds are converted to conjugated ones. The conjugated system, in general,

precludes the complete addition of iodine. This fact indicates the decrease of IV for the oils under study during frying at  $180^{\circ}C \pm 5^{\circ}C$  for 30 h frying time. The decrease in iodine value denotes a decrease in the degree of unsaturation of the oil caused by the extent of oxidation (Kirk and Sawyer, 1991). The highest decreases in IV was recorded for sunflower oil, the reduction percentage in the iodine value was 8.95% at the end of the frying period. On the other hand, tiger nut oil and its mixtures with sunflower oil at levels 30, 40 and 50% (v/v) had significantly the lowest reduction in iodine values 5.6, 7.2, 6.4 and 6.1%, at the end of the frying period respectively. The autoxidation of sunflower oils affected their fatty acids composition, as polyunsaturated fatty acids were oxidized faster than saturated and mono unsaturated fatty acids (Semwal et al., 1996). The addition of tiger nut oil, which contains high levels of oleic acid and natural antioxidants, to sunflower oil during the frying process effectively reduced the oxidation rate in sunflower oil, as detected by relatively low reduction in iodine values (Table 5).

Table 5 Changes in iodine value (g  $I_2$  100 g<sup>-1</sup> oil) of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C ± 5 °C).

Frying	Tiger nut oil	Sunflower oil	TNO + SO (v/v)						
period (h)	(TNO)	(SO)	10:90	20:80	30:70	40:60	50:50		
0	$105.80^{wx} \pm 0.26$	$123.00^{a} \pm 0.29$	$120.70^{\text{b}}\pm0.34$	$119.10^{cd} \pm 0.09$	116.50 <sup>fg</sup> ± 1.12	$113.5^{kl} \pm 0.31$	$112.00^{mn} \pm 0.63$		
5	$105.00^{xy} \pm 0.10$	121.50 <sup>b</sup> ± 1.05	$119.45^{\circ} \pm 0.18$	$118.00^{e} \pm 0.51$	$115.10^{hi} \pm 0.38$	$112.10^{mn} \pm 0.38$	$111.50^{n} \pm 0.52$		
10	$104.73^{yz} \pm 0.08$	119.55°± 0.21	$117.30^{\text{ef}} \pm 0.05$	116.85 <sup>f</sup> ± 1.10	$113.65^{kl} \pm 0.43$	$111.00^{no} \pm 0.25$	$109.44^{pqr} \pm 0.12$		
15	103.44 <sup>z</sup> ± 1.21	$118.10^{de} \pm 0.31$	$115.60^{gh} \pm 0.23$	$115.40^{jkl} \pm 0.08$	$112.00^{mn} \pm 1.36$	$110.21^{op} \pm 0.03$	$108.00^{stu} \pm 0.92$		
20	$102.65^{z} \pm 0.05$	117.22 <sup>ef</sup> ± 0.35	114.22 <sup>ijk</sup> ±1.19	$113.95^{\text{jkl}} \pm 0.97$	$110.12^{opq} \pm 0.90$	$109.00^{qs} \pm 0.05$	$107.15^{uv} \pm 1.14$		
25	101.23/ ± 0.38	$114.85^{\text{hij}} \pm 0.90$	$113.10^{\text{klm}}\pm0.07$	$113.00^{\text{Im}} \pm 0.75$	$109.25^{pqr} \pm 0.75$	$107.90^{tu} \pm 1.11$	106.00 <sup>vwx</sup> ± 1.12		
30	99.90// ± 0.13	$111.10^{no} \pm 0.38$	$112.75^{\text{Im}} \pm 0.43$	112.10 <sup>mn</sup> ± 1.10	108.33 <sup>rst</sup> ± 0.21	106.30 <sup>vw</sup> ± 0.20	105.26 <sup>wxy</sup> ± 0.30		
LSD at 0.05 =1	.039								

## 3.7. Changes in total polar compounds (TPC)

The level of polar compounds is a good indicator of the overall quality of frying oils, providing critical information about the total amount of newly formed compounds which have higher polarity than triacylglycerols. Many European countries have established regulatory limits for TPC in frying oils (Blumenthal, 1996). Most of these countries have considered a limit of 25% TPC. Table 6 shows the TPC of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C  $\pm$  5 °C). The fresh oils under study had low levels of total polar compounds ranging from 2.4 to 2.8%, which reflects the good quality of these oils. Total polar compound contents of unused oils normally ranges between 0.4% and 6.4% (Lumley, 1988). The frying process caused a significant (P < 0.05) and gradual increase in total polar compounds, this increase was linearly with frying time. Frying time increases the contents of polar compounds such as triacylglycerol dimers and oxidized triacylglycerols (Romero et al., 1998; Xu et al., 1999), dimers (Gordon and Kourimski 1995), polymers (Tompkins and Perkins 2000) and free fatty acids (Mazza and Qi 1992). Sunflower oil had significantly (P < 0.05) the highest value of total polar compounds at 19.40% at the end of the frying period 30 h. This value was about 8.08 times as high as that of fresh sunflower oil. However, tiger nut oil had significantly the lowest value of total polar compounds at 13.6% at the end of the frying period of 30 h. The levels of total polar compounds for tiger nut oil and its mixtures at levels of 40 and 50 were about 1.42, 1.34 and 1.35 time as low as that for sunflower oil at the end of frying period, respectively. This is probably due to the fact that that tiger nut oil contains high amounts of C18:1. These results agree with those of Warner and Knowlton, 1997 who detected significantly lower TPC in high-oleic corn oil compared to regular and hydrogenated corn oils after 20 h of frying. Decreasing the linolenic acid and increasing the oleic acid of canola oil produced good frying stability as measured by total polar compounds (Warner *et al.*, 1994). The low levels of total polar compounds for tiger nut oil and its blends may be due to the presence of poly phenolic compounds which had inhibitory effects during the frying process.

## 3.8. Changes in viscosity value

In the deep-fat frying process, the viscosity of the oil changes considerably with frying time and oil temperature (Moreira et al, 1999). The viscosity values of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at  $(180 \degree C \pm 5 \degree C)$  are shown in Table 7. The fresh oils under study had native viscosity values ranging from 45.40 to 46.10 mPa.s. The viscosity values of all the oils under investigation increased (P < 0.05) gradually and significantly over the 30 hours of the frving process. This increase has been attributed to the polymerization and the concomitant formation of high-molecularweight compounds via carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges between fatty acids (Blumenthal et al., 1991) The tendency of viscosity to increase during the frying of the oil has been found to correlate well with the formation of polymers (Gloria and Aguilera, 1998). The frying oils can be arranged according to their viscosity values at the end of the frying period in the following decreasing order: sunflower oil > 10%TNO +90%SFO > 20%TNO +80%SFO > 30%TNO +70%SFO > 40%TNO +60%SFO > 50%TNO +50%SFO > tiger nut oil. There is a relationship between the viscosity and the degree of oil unsaturation. One would report that mixing sunflower oil with different levels of tiger nut oil led to a decrease in the changes of viscosity values during the frying process. This means that the highest level of tiger nut blended with oil induced the lowest change on oil viscosity. These results could be explained by the fact that poly-unsaturated fatty acids tended to be rapidly oxidized and form polymer compounds (Bracco et al., 1981). At the same time, the addition of tiger nut oil with polyphenolic compounds significantly lowered the viscosity of sunflower oil by retarding polymerization reactions the during frying process.

Table 6
Changes in total polar compounds (TPC) content (% w/w) of sunflower oil, tiger nut oil
and binary mixtures of them during deep fat frying at (180 $^{\circ}$ C ± 5 $^{\circ}$ C).

Frying	Tiger nut oil	Sunflower oil (SO)	TNO + SO (v/v)						
period (h)	(TNO)		10:90	20:80	30:70	40:60	50:50		
0	$2.80^{x} \pm 0.13$	$2.40^{x} \pm 0.15$	$2.40^{x} \pm 0.55$	$2.40^{x} \pm 0.35$	$2.50^{x} \pm 0.15$	$2.50^{x} \pm 0.35$	$2.50^{x} \pm 0.48$		
5	$4.12^{w} \pm 0.21$	$5.55^{\circ} \pm 0.09$	5.11 <sup>vw</sup> ± 1.01	$5.10^{vw} \pm 0.35$	$5.00^{vw} \pm 0.52$	$4.60^{vw} \pm 0.34$	$4.44^{vw} \pm 0.33$		
10	$6.32^{u} \pm 0.34$	$9.34^{\text{opq}} \pm 0.20$	$9.20^{pq} \pm 1.05$	$8.63^{pqr} \pm 0.73$	$8.00^{\text{rst}} \pm 0.18$	$7.50^{st} \pm 0.36$	$7.31^{t} \pm 0.08$		
15	$8.45^{\text{qrs}} \pm 0.32$	$12.13^{kl} \pm 0.22$	$11.00^{mn} \pm 0.28$	$10.22^{no} \pm 0.76$	$9.53^{op} \pm 0.81$	$9.20^{pq} \pm 0.63$	$9.00^{pqr} \pm 0.55$		
20	$12.60^{ijk} \pm 0.59$	$14.65^{\text{ef}} \pm 0.39$	$13.96^{\text{fgh}} \pm 0.69$	$13.55^{\text{ghi}} \pm 0.45$	$12.81^{ijk} \pm 0.11$	$12.23^{jkl} \pm 0.33$	$11.53^{\text{Im}} \pm 0.47$		
25	$13.25^{hij} \pm 0.62$	$16.54^{\circ} \pm 0.59$	$15.45^{de} \pm 1.04$	$1435^{fg} \pm 0.18$	$14.00^{\text{fgh}} \pm 0.47$	$13.41^{\text{ghi}}\pm0.64$	$13.21^{hij} \pm 0.34$		
30	$13.61^{ghi} \pm 0.72$	$19.40^{a} \pm 0.15$	$18.00^{b} \pm 0.76$	16.92 <sup>c</sup> ±1.16	15.95 <sup>cd</sup> ± 1.02	$14.46^{fg} \pm 0.20$	$14.32^{fg} \pm 0.22$		
LSD at 0.05 =0.9350									

Table 7Changes in Viscosity (mPa·s at 30 °C) of sunflower oil, tiger nut oil and binary mixtures of them<br/>during deep fat frying at (180 °C ± 5 °C).

Frying	Tiger nut oil	Sunflower oil (SO)	TNO + SO (v/v)						
period (h)	(TNO)		10:90	20:80	30:70	40:60	50:50		
0	$46.10^{t} \pm 0.13$	$45.40^{t} \pm 0.43$	$45.45^{t} \pm 1.13$	$45.70^{t} \pm 0.20$	$45.90^{t} \pm 0.35$	$46.00^{t} \pm 0.19$	$46.00^{t} \pm 0.10$		
5	$48.00^{t} \pm 0.12$	48.70 <sup>s</sup> ± 1.27	48.50 <sup>s</sup> ± 1.10	$48.50^{s} \pm 0.67$	48.50 <sup>s</sup> ± 1.28	$48.00^{s} \pm 0.76$	$48.00^{\circ} \pm 0.13$		
10	$50.00^{r} \pm 0.22$	$52.30^{\text{nop}} \pm 0.46$	$52.00^{\text{opq}} \pm 0.28$	$52.00^{\text{opq}} \pm 0.36$	51.00 <sup>qr</sup> ± 1.25	$51.00^{qr} \pm 0.72$	$51.10^{\text{pqr}} \pm 0.12$		
15	$52.00^{\text{opq}} \pm 0.32$	$53.50^{n} \pm 0.28$	$53.50^{n} \pm 0.25$	$53.00^{\text{no}} \pm 0.38$	$53.00^{\text{no}} \pm 0.13$	$52.70^{\text{no}} \pm 0.80$	$52.50^{\text{no}}\pm0.22$		
20	$56.60^{\text{lm}} \pm 1.10$	$57.70^{jkl}\pm0.30$	$56.20^{m} \pm 0.25$	$57.00^{\text{kIm}} \pm 0.26$	$57.00^{\text{klm}} \pm 0.66$	$58.00^{ijk} \pm 0.57$	$57.00^{\text{kIm}} \pm 0.33$		
25	$58.75^{\text{hij}}\pm0.94$	$65.35^{\text{b}} \pm 0.18$	$62.60^{d} \pm 0.36$	$62.00^{\text{de}} \pm 0.24$	$61.00^{\text{ef}} \pm 0.21$	$59.50^{\text{gh}} \pm 0.34$	$59.00^{\text{ghi}} \pm 1.10$		
30	$59.00^{\text{ghi}} \pm 1.13$	$70.50^{a} \pm 1.16$	$65.00^{bc} \pm 0.36$	$64.00^{\circ} \pm 0.23$	$62.50^{d} \pm 1.10$	61.00 <sup>ef</sup> ± 1.41	$60.10^{\text{fg}} \pm 0.90$		
LSD at 0.05 =1.091									

Data are expressed as mean  $\pm$  SD. Values given represent means of three determinations. Values followed by the same letter are not significantly different (p < 0.05).

## 3.9. Changes in Color

The color of oil is one of the most eminent physical properties which attracts consumer acceptance. In general this property affects the color of fried food. The instrument used for the measurement of color in oils is the Lovibond tintometer. Color was measured on fixed yellow glass slides (35) and variable red glass slides. Table 8 shows the changes in color values for sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C ± 5 °C). Fresh sunflower oil had a lighter color at 2.50. However, tiger nut oil had a significantly t darker value at 4.00. The dark color of tiger nut oil was attributed to its high levels of pigments, polyphenolic compounds and carotenoids that were extracted into the oil. Blending sunflower oil with tiger nut oil caused a significant decrease in the darkening value of the blended oils due to the dilution effect. Frying caused a gradual and significant  $(P \le 0.05)$  increase in the color value of all the oils under investigation. The intensity of red glasses increased with prolonging the frying period. Darkening of the oil during deep-fat frying is due to the polymer formation of unsaturated carbonyl compounds and non-polar compounds of foodstuff solubilized in the oil. (Gutiérrez *et al.*, 1988 ; Irwandi *et al.*, 2000; Farag and El-Anany, 2006). Although tiger nut oil had significantly ( $P \le 0.05$ ) the highest color (red slide) value at the beginning of the frying experiment, the lowest values for color ( red slide) were observed for tiger nut oil and its blends with sunflower oil at levels 40 and 50%. These values were about 1.21, 1.17 and 1.13 times as low as that for sunflower oil at the end of the frying period, respectively.

These findings may attribute to the positive effect of oleic (66.22%) as monounsaturated fatty acid in tiger nut oil and its stability against oxidation and to the presence of high levels of polyphenolic compounds in tiger nut oil. Cold pressed oils have been reported to contain antioxidants and possess a remarkable radical scavenging activity and oxygen

Table 8 Changes in colour (Red slide) value of sunflower oil, tiger nut oil and binary mixtures of them during deep fat frying at (180 °C ± 5 °C).

Frying	Tiger nut oil	Sunflower	TNO + SO (v/v)						
period (h)	(TNO)	oil (SO)	10:90	20:80	30:70	40:60	50:50		
0	$4.00^{q} \pm 0.38$	$2.50^{r} \pm 0.25$	$2.50^{r} \pm 0.50$	$2.60^{r} \pm 0.30$	$2.80^{r} \pm 0.40$	$2.90^{r} \pm 0.35$	$3.00^{r} \pm 0.25$		
5	$7.01^{\circ} \pm 0.42$	$6.50^{op} \pm 0.50$	$6.50^{op} \pm 0.25$	$6.00^{p} \pm 0.35$	$6.50^{\text{op}} \pm 0.20$	$6.50^{op} \pm 0.50$	$6.00^{\text{p}} \pm 0.00$		
10	$8.50^{n} \pm 0.50$	$10.00^{I} \pm 0.80$	$10.00^{I} \pm 0.35$	$10.52^{kl} \pm 0.25$	$10.00^{I} \pm 0.25$	$9.33^{m} \pm 0.40$	$9.00^{mn}\pm0.25$		
15	$10.50^{kl} \pm 0.50$	$13.00^{\text{hi}}\pm0.45$	$13.00^{\text{hi}}\pm0.30$	$12.50^{i} \pm 0.50$	$11.50^{j} \pm 0.50$	$11.00^{jk}\pm0.00$	$10.50^{kl} \pm 0.50$		
20	$12.50^{i} \pm 0.36$	$16.00^{\text{bc}}\pm0.40$	$14.00^{\text{fg}}\pm0.30$	$13.50^{\text{gh}} \pm 0.50$	$14.00^{\text{fg}}\pm0.50$	$13.00^{hi} \pm 0.25$	$12.50^{i} \pm 0.40$		
25	$13.00^{hi} \pm 0.59$	$16.50^{ab} \pm 0.60$	$15.50^{\text{cd}}\pm0.40$	$15.50^{\text{cd}} \pm 0.40$	$15.00^{\text{de}} \pm 0.25$	$14.50^{ef} \pm 0.50$	$14.00^{\text{ef}} \pm 0.30$		
30	$14.50^{\text{ef}} \pm 0.40$	$17.00^{a} \pm 0.35$	$16.50^{ab} \pm 0.00$	$16.00^{bc} \pm 0.50$	$15.50^{cd} \pm 0.10$	$15.00^{de} \pm 0.50$	$14.50^{ef} \pm 0.45$		
LSD at 0.05 = 0.6149									

radical absorption capacity, when tested with the DPPH (1,1-diphenyl-2-picrylhydrazyl) and ABTS cation {2,20-azino-bis (3-ethylbenzo-thiazoline-6-sulfonic acid) diammonium salt} radical-scavenging assays or the oxygen radical absorption capacity (ORAC) assay (Yu *et al.*, 2005; Parry *et al.*, 2005). Phenolics compounds have a great influence on the stability, sensory and nutritional characteristics of the product and may prevent deterioration through the quenching of radical reactions responsible for lipid oxidation (Koski *et al.*, 2003).

## 4. CONCLUSIONS

The present results show that Tiger nut oil presents higher a content in oleic acid (C18:1) and lower content in linoleic acid (C18:2) than sunflower oil. Tiger nut oil had higher level of total poly phenols 16.5 mg gallic acid equivalents (GAE) per 100 g of oil as compared to 5.0 mg GAE per 100 g of sunflower oil. At the same time, blending sunflower oil with various levels of tiger nut oil as a source of phenolic compounds and monounsaturated fatty acids (MUFA) was suggested for improving the quality and the oxidative stability of sunflower oil during the frying process. Our findings indicate that the changes in physicochemical parameters were controlled and significantly (P < 0.05) decreased when tiger nut /Sunflower oil (W/W) proportions were varied between 20/80 to 50/50. These blended oils had better stability against oxidation during the deep fat frying process.

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