

Chemical Characteristics and Antioxidant Capacity of Egyptian and Chinese Sunflower Seeds: A Case Study

S.F. Hamed*, Suzanne M. Wagdy, and M.G. Megahed

Fats and Oils Dept., National Research Centre, 33 Tahrir St., 12622 Dokki,
saidfatouh123@yahoo.com

Abstract: In the last few years Chinese sunflower seed has invaded our Egyptian market increasingly. We took it and the Egyptian sunflower seed as a comparable case study to characterize and investigate them as a source of effective natural antioxidants, oil and protein. Chemical characteristics of the two seeds revealed that protein, oil, ash, moisture and total phenolic contents (TPC) increased significantly ($P < 0.05$) after dehulling with pronounced larger amount of these parameters in the Egyptian sunflower seed compared to the Chinese one. Fatty acid analysis showed that Egyptian sunflower oil contains more than 86% and Chinese sunflower oil contains more than 80% unsaturated fatty acids which give these oils a relative advantage. Chlorogenic acid was the major phenolic compound present in TPC as measured by HPLC. Antioxidant activity (AA %) of the phenolic extracts was followed up by measuring radical scavenging activity (RSA %) of the stable DPPH• radical, the degradation rate of β -carotene-linoleic acid o/w emulsion, and the oxidation stability measured by the fully automated active oxygen method (Rancimat). Egyptian sunflower seed have more AA % than Chinese seed as revealed by the higher RSA%, less degradation rate of β -carotene-linoleic acid color and higher induction period measured by Rancimat. Results also demonstrated the suitability of Egyptian and Chinese sunflower seed to be an effective source of protein, with some good functional properties such as solubility, dispersibility water absorption capacity, and emulsifying capacity. Contrary, it showed poor foaming and gelling abilities. Egyptian sunflower oil can also be used as an effective source of unsaturated fats and natural antioxidants (TPC). Hence, can be supplemented in many foods and can replace the synthetic antioxidant with their remarkable hazards.

[S.F. Hamed, Suzanne M. Wagdy, and M.G. Megahed. **Chemical Characteristics and Antioxidant Capacity of Egyptian and Chinese Sunflower Seeds: A Case Study.** Life Sci J 2012;9(2):727-735] (ISSN:1097-8135). <http://www.lifesciencesite.com>. 108

Key words: sunflower seed, chlorogenic acid, total phenolic content, antioxidant activity.

1. Introduction

Sunflower is one of the major oilseed crops ranking fourth with a worldwide production of about 10.6 million metric tons in 2006⁽¹⁾. Sunflower is an annual plant native to the Americas belonging to the family Asteraceae. Per 100 g the seed enclose protein up to 20.78 g, total lipid (fat) up to 51.46 g, ash up to 3.02 g, fiber up to 8.6 g with total energy of 2445 kJ. The oil accounts for 80% of the value of the sunflower crop, as contrasted with soybean which derives most of its value from the meal. Sunflower oil is generally considered a premium oil because of its light color, high level of unsaturated fatty acids and lack of linolenic acid, bland flavor and high smoke points. The primary fatty acids in the oil are oleic and linoleic (typically 90% unsaturated fatty acids), with the remainder consisting of palmitic and stearic saturated fatty acids. The primary use is as a salad and cooking oil or in margarine. In the USA, sunflower oils account for 8% or less of the market, but in many sunflower-producing countries, sunflower is the preferred and the most commonly used oil⁽²⁾.

Egypt's production of edible vegetable oils suffers several problems nowadays. During the early sixties, Egypt used to be self-sufficient in edible

vegetable oils, where self-sufficiency ratio reached 95%. Such ratio followed a declining trend until reaching as low as 31.6% in 2007, which led to increasing volume of oil imports that reached 5.6 thousand tons worth L.E 1.992 billion in 2007⁽³⁾. The problem is further complicated by the reliance of the edible oils industry in Egypt on imported raw materials, where private sector's dependency ratio is estimated at 85%⁽³⁾ and according to Egyptian-British Chamber of Commerce Egypt imported 92% of edible oil consumed in 2010⁽⁴⁾. As a result of such a gap between consumption and production Chinese sunflower seed has increasingly invaded the Egyptian market during the last few years.

Lipid oxidation is well known to cause deterioration of fats or fat-containing foods. Also, reactive oxygen species (ROS) produced during natural biological activity in the human body tends to accumulate therein. Antioxidants are needed to retard or delay lipid oxidation and to scavenge ROS. Antioxidants can act by the following mechanisms in lipid peroxidation: (1) decreasing localized oxygen concentrations, (2) preventing chain initiation by scavenging initiating radicals, (3) binding catalysts, such as metal ions, to prevent initiating radical generation, (4) decomposing peroxides so they

cannot be reconverted to initiating radicals, and (5) chain-breaking, to prevent continued hydrogen abstraction by active radicals⁽⁵⁾. Commonly utilized chain-breaking antioxidants include butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), tert-butylhydroquinone (TBHQ), propyl gallate (PG) and the naturally occurring tocopherols. There are some serious problems concerning the safety and toxicity of BHA, BHT and TBHQ related to their metabolism and possible absorption and accumulation in body organs and tissues⁽⁶⁾. Therefore, the search for natural antioxidants is highly desirable. The phenolic components and tocopherols are the most important antioxidants for storage stability, as well as, nutritional quality of food made from sunflower seeds. Cells contain a complex system of antioxidant defenses to protect against the harmful consequences of activated oxygen species. When such a complex mechanism inside the cell fail to get rid of ROS it may cause many dangerous diseases such as inflammation, cardiovascular-diseases, cancer and aging^(7, 8). Numerous scientific articles refer to several natural phenols delaying the in vitro oxidation of simple or complex lipid matrices⁽⁹⁾.

So, the aim of this work was to take Egyptian and Chinese sunflower seeds as a comparable case study for investigating their suitability as effective sources for natural antioxidants, oil and protein.

2. Materials and Methods

Materials

Two samples of sunflower seed, an Egyptian and a Chinese, were purchased from the local market, Dokki district, Cairo, Egypt. Chlorogenic acid (CGA) and TBHQ were purchased from Sigma. All reagents were BDH or of analytical grade.

Methods

Proximate composition of sunflower seeds

Sunflower seeds were divided into two parts. Half of the seeds were used as such with hull and designated whole seed (WS) while the rest half was dehulled manually and designated (DS). Hulls were separated by aspiration. WS and DS were ground and sieved to pass an 80 mesh screen and then analyzed for their proximate composition that is moisture, crude protein, oil content, crude ash, and crude fiber as recommended by A.O.A.C.⁽¹⁰⁾. Oil content was measured using a Soxhlet extractor and n-hexane as a solvent. Hexane was evaporated using a rotary evaporator (Buchi Rotavapor Switzerland) at 40°C. The oil was dried over anhydrous sodium sulphate then placed in a vacuum oven until constant weight. The oil was kept at -20°C until analyses.

The defatted meal resulting from WS and DS was spread to dry at room temperature and designated defatted meal of whole seeds (DMWS) and defatted meal of dehulled seeds (DMDS). The meal was kept in closed containers at -20°C until further work.

Phenolic extract preparation

Preparation of phenolic extracts was carried out following scientific literature regarding this subject⁽¹¹⁻¹³⁾. Briefly, ground samples of whole (WS) or dehulled (DS) sunflower seeds (20 g) were extracted with 200 ml of solvent consisting of methanol, 0.16 M hydrochloric acid and water, mixed in proportion 8:1:1, respectively, for 2 h. The above mentioned procedure was repeated on the residue and extracts were combined and washed three times with 15 ml hexane to remove escaped oil using separatory funnel. The combined methanol layer was dried using rotary evaporator at 40°C and stored in darkness at -20°C.

Total phenolic content (TPC)

Total phenolics were determined colorimetrically using Folin-Ciocalteu reagent according to Hung et al.⁽¹⁴⁾. The absorbance was measured at 725 nm using a UV – 1601 PC UV-visible spectrophotometer (Shimadzu, Japan). Total phenolics were quantified by calibration curve obtained from measuring the absorbance of a known concentration of chlorogenic acid and the results were expressed as milligrams chlorogenic acid equivalent (CAE) per 100 g extract.

Chemical characteristics and fatty acid composition

The chemical characteristics of the oils used for the experiment have been determined according to A.O.A.C.⁽¹⁰⁾

For determination of fatty acid composition sunflower oil methyl esters were prepared according to A.O.A.C. method⁽¹⁰⁾. Determination of fatty acids composition was performed using a Hewlett Packard HP 6890 gas chromatograph, operated under the following conditions: Detector, flame ionisation (FID); column, capillary, 30.0 m X 530 µm, 1.0 µm thickness, polyethylene glycol phase (INNO Wax); N₂ with flow rate, 15 ml/min with average velocity 89 cm/s (8.2 psi); H₂ flow rate, 30 ml/min; air flow rate, 300 ml/min; split ratio, 8:1, split flow, 120 ml/min; gas saver, 20 ml/min. Detector temperature, 280°C; column temperature, 240°C; injection temperature, 280°C. Programmed temperature starting from 100°C to reach a maximum of 240°C was used for eluting the fatty acid methyl esters. The identification of the peaks was made as compared

with chromatograms of standard fatty acids methyl esters (Sigma, USA).

Antioxidant Activity (AA%)

Antioxidant activity was determined by three methods: Radical scavenging activity⁽¹⁵⁾, by the β -carotene/ linoleic acid method described by Al-Shaikhan et al.⁽¹⁶⁾ and the fully automated active oxygen (i.e. Rancimat) method. The later method was carried out using the Rancimat 679[®] (Metrohm AG, Herisau, Switzerland) instrument at 110°C with the air flow rate of 20 L/hr⁽¹⁷⁾. The oxidative stability was expressed as induction time (hr).

All antioxidant activity experiments were performed using 500 ppm of phenolic extracts in purified (stripped) sunflower oil.

Sunflower oil stripping (purification)

Sunflower oils were stripped from antioxidants and from trace metals and other prooxidants according to Fuster et al., 1998⁽¹⁸⁾ via adsorption chromatography to yield purified sunflower triacylglycerols fraction. A glass column (40 × 2.5 cm i.d.), plugged with glass wool, was packed with 250 g of alumina (activated at 100°C for 8 h and then at 200°C for 12 h) suspended in n-hexane, capped with sea sand, and conditioned by prewashing with 200 mL of n-hexane. The oil (100 mL) was dissolved in an equal volume of hexane and passed through the column, which was then washed with 200 mL of n-hexane. The chromatographic column was wrapped with aluminium foil to prevent light-induced oxidations during the purification process, and triacylglycerols were collected in an aluminum foil wrapped flask. Analysis of the purified oils by thin-layer chromatography (Merck precoated silica gel 60 thin-layer chromatographic plates, 0.25 mm layer thickness and chloroform diethyl ether; 90:10, vol/vol) showed that they are composed mainly of triacylglycerols (data not shown).

Functional properties of sunflower defatted meals

Nitrogen solubility index (NSI), protein dispersibility index (PDI) were determined as described by Smith and Circle⁽¹⁹⁾. Water absorption capacity (WAC) was estimated according to Huber⁽²⁰⁾. Oil holding capacity (OHC) according to Childs and Forte⁽²¹⁾. Emulsifying Capacity (EC) as indicated by Shahidi *et al.*⁽²²⁾. Foam Stability (FS) as described by A.A.C.C.⁽²³⁾. Gelation according to Circle et al.⁽²⁴⁾.

HPLC Analysis

Methanolic extracts (5 μ L) were injected in an Agilent 1100 Series HPLC system with a quaternary solvent delivery system, an online degasser, an autosampler, a DAD detector was used for the analysis. The column was a Phenomenex Luna C18 (5 μ m, 250 mm X 4.6 mm) and column temperature

was maintained at 30 °C. Two mobile phases, A 0.1% phosphoric acid and B acetonitrile were used in a gradient elution at a flow of 1 ml/min with the following gradient profile: 20 min from 10-22% B, 20 min with a linear rise to 40% B, 5 min reverse to 10% B, and additional 5 min equilibration time⁽³⁴⁾. The system was controlled and data analysis was performed by Agilent Chemstation Software. All the calculations concerning the quantitative analysis were performed with external standardization by the measurement of peak areas.

Statistical analysis

All chemical analyses were performed in three replicates and the results were statistically analysed. Statistical analysis was performed using the GLM procedure with SAS (25) software. Duncan's multiple comparison procedure was used to compare the means. A probability to $p \leq 0.05$ was used to establish the statistical significance.

3. Results and Discussion

Proximate composition of sunflower seeds

Results in Table 1. Revealed that Moisture content in WS (9.2±0.85%) and in DS (8.9±0.24%) of Chinese seeds was higher than that of the Egyptian ones (7.02± 0.66% and 7.45±0.35 in whole and dehulled seeds, respectively). Protein content in WS (22.96±1%) and DS (28.46±0.5%) of Egyptian sunflower were higher compared to the Chinese ones (21.22±0.99% and 26.69±1.99%, for WS and DS, respectively). The same trend was recorded for oil content where Egyptian sunflower seeds had higher oil content both in WS and DS than the Chinese seeds. The former recorded oil content of 22.11 ±1.01% and 29.09 ±0.99% while the latter recorded oil content of 16.33 ±0.96% and 20.36 ±0.89% in WS and DS, respectively. Whereas, the ash content of Chinese seeds recorded higher percentages both in whole (7.36±0.14%) and dehulled (8.3±0.33%) seeds than whole (3.95±0.22%) and dehulled (5.53±0.62%) seeds of the Egyptian type. Chinese sunflower seeds showed lower crude fiber content (31.51±2.1%) in WS than that of Egyptian WS (34.91±2.1%) but, higher crude fiber (18.81±0.36%) in Chinese DS than Egyptian DS (16.36±0.34%) were recorded. Nitrogen free extract (calculated) was higher in DS than WS, also higher in Chinese seeds than the Egyptian ones.

From the results we notice that after dehulling there is a significant increase in all constituents except crude fiber which is high in the seed hulls. Similar finding were also found by some other scientists^(26, 27). Bhagya and Sastry⁽²⁸⁾ also reported similar effects of dehulling on Niger seeds.

Table 1. Proximate composition of Egyptian and Chinese sunflower seeds

Parameter	Egyptian		Chinese	
	WS*	DS*	WS	DS
Moisture (%)	7.02±0.66 ^a	7.45±0.35 ^b	9.2±0.85 ^d	8.9±0.24 ^c
Protein (%)	22.96±1.2 ^b	28.46±0.5 ^d	21.22±0.99 ^a	26.69±1.99 ^c
Oil Content (%)	22.11 ±1.01 ^c	29.09 ±0.99 ^d	16.33 ±0.96 ^a	20.36 ±0.89 ^b
Ash (%)	3.95±0.22 ^a	5.53±0.62 ^b	7.36±0.14 ^c	8.3±0.33 ^d
Crude Fiber (%)	34.91±2.1 ^d	16.36±0.34 ^a	31.51±2.1 ^c	18.81±0.36 ^b
Nitrogen Free Extract	9.05±0.86 ^a	13.11±0.59 ^b	14.38±0.75 ^c	16.94±0.98 ^d

Means followed by the same letter within the same row are not significantly different ($P < 0.05$) *WS: Whole seed; DS: Dehulled seeds. Values are mean ± SD.

Total phenolic content (TPC)

According to the results (Table 2.) the total phenolic content (TPC), expressed as chlorogenic acid equivalent (mg/100g), was significantly higher ($P < 0.05$) in dehulled seeds (DS) than in whole seeds (WS) of both Egyptian and Chinese sunflowers. The TPC was lower by about 35% in WS than DS. The highest TPC in WS (772 ±3.3 mg CAE/100 g) and in the DS (1088 ±3.95 mg CAE/100 g) was in Egyptian seeds. Chinese seeds showed less phenolics content both in WS (625 ± 2.1 mg CAE /100 g) and in the DS

(886 ±3.5 mg CAE /100g). Various scientists have investigated the content of phenolic compounds in sunflower seeds⁽²⁹⁻³²⁾. De Leonardis and coworkers⁽³⁰⁾ reported that TPC in sunflower was in the range of 1.11 to 1.15 mg/mL chlorogenic acid equivalent which is in good agreement with our findings, while Fisk et al.⁽³¹⁾ determined the TPC in sunflower seeds and found it to be 2700 mg/100 g. Comparison is hardly possible because of differing analytical methodologies, and differences in the sample material and origin.

Table 2. Total phenolic compounds (mg/100g CAE*) in Egyptian and Chinese sunflower seeds

Parameter	Egyptian		Chinese	
	WS*	DS*	WS	DS
Total Phenolics (mg CAE*/100g, spectrophotometric)	772±3.3 ^b	1088±3.95 ^d	625±2.1 ^a	886±3.5 ^c
Chlorogenic acid (mg/100gm, HPLC)	501.8 ^b	728.96 ^d	400.2 ^a	602.3 ^c

Means followed by the same letter within the same row are not significantly different ($P < 0.05$), CAE *: chlorogenic acid equivalent *WS: whole seed; DS: dehulled seeds. Values are mean ± SD.

In the two (Egyptian and Chinese sunflower oils) samples, chlorogenic acid was the most abundant phenolic compound, 602.3-728.96mg/100gm for DS and 400.2- 501.8 for WS, respectively constituting ≈ 65% of total phenolics (Table 2.) as measured by HPLC. Other phenolic constituents were present in too small amounts to be detected by HPLC. Results of Žilić et al.⁽³³⁾ were comparable to our results where they found that TPC of sunflower oil comprised principally of chlorogenic acid, while caffeic acid, ferulic acid, rosmarinic acid, myricetin, and rutin were found in very small percentages. De Leonardis et al.⁽³⁰⁾ showed that phenolic spectrum of sunflower seeds included seven components (chlorogenic acid, protocatechuic, caffeic acid, o-cinnamic acid, ferulic acid, syringic acid and an unidentified phenolic compound). These authors also reported that the chlorogenic acid was the most abundant phenolic compound (≈79.4% of total phenols). Phenolic compounds in seeds and kernels of sunflower deserve much more attention

because the total phenolic content, strongly correlate ($r=0.93$, $P < 0.05$) with total antioxidant activity^(30,33).

Chemical characteristics and fatty acid composition

The chemical characteristics of the Egyptian and Chinese sunflower oil samples are shown in Table 3. Results revealed that acid and peroxide values of the two samples were moderate and comparable to each other and were not significantly different ($P < 0.05$). Iodine value (IV) which represents the degree of unsaturation indicated that Egyptian sunflower oil has higher IV (129.41) compared to IV of the Chinese oil (115.18), hence Egyptian sunflower oil had significantly ($P < 0.05$) higher total unsaturation than the Chinese one. Regarding the ester value, saponification value, and unsaponifiable matters, results showed that the Egyptian sunflower oil had higher values than the Chinese one ($P < 0.05$).

Table 3. Chemical characteristics of Egyptian and Chinese sunflower oils

Parameter	Egyptian	Chinese
Acid value (mg KOH /g oil)	3.23±0.22 ^a	3.8±0.31 ^a
Peroxide value (meq.O ₂ /kg oil)	0.71±0.33 ^b	0.88±0.23 ^b
Iodine value	129.41±1.44 ^d	105.18±1.54 ^c
Saponification value (mg KOH / g oil)	189.4±2.1 ^b	187.6±2.3 ^a
Unsaponifiable matter (%)	1.85±0.15 ^b	1.74±0.13 ^a
Ester value	186.17±1.53 ^b	183.8±0.99 ^a

Means followed by the same letter within the same row are not significantly different (P<0.05), Values are mean ± SD.

Regarding fatty acid profile, Table 4 shows that palmitic acid contents ranged from 6.50 to 9.53%, palmitoleic acid contents from 1 to 1.3%, stearic acid contents from 7.25 to 9.78%, oleic acid contents from 32.95 to 27.8% and linoleic acid contents seeds ranged from 52.3 to 51.56% for Egyptian and Chinese sunflower oils, respectively. As seen from Table 4, almost 86% of Egyptian sunflower oil and 80% of Chinese sunflower oil are of good unsaturated type. Clinical studies show that higher unsaturated fat diets may be preferable even to low-fat diets because they lower total cholesterol, low density lipoprotein (LDL) or bad cholesterol and triglycerides, while maintaining beneficial high density lipoprotein (HDL) cholesterol, which is needed to carry the “bad” cholesterol away⁽²¹⁾.

Table 4. Fatty acid composition of Egyptian and Chinese sunflower oils

Fatty Acid	Egyptian	Chinese
Palmitic acid	6.5±0.77 ^a	9.53±0.98 ^b
Palmitoleic	1±0.39 ^a	1.33±0.64 ^a
Stearic	7.25±0.44 ^a	9.78±0.86 ^b
Oleic	32.95±0.79 ^b	27.8±0.69 ^a
Linoleic	52.3±0.85 ^b	51.56±0.8 ^a
Total Saturation (SFA)	13.75 ^a	19.31 ^b
Total unsaturation (UFA)	86.25 ^b	80.69 ^a
SAT/USAT	0.16 ^a	0.24 ^b

Means followed by the same letter within the same row are not significantly different (P<0.05), Values are mean ± SD

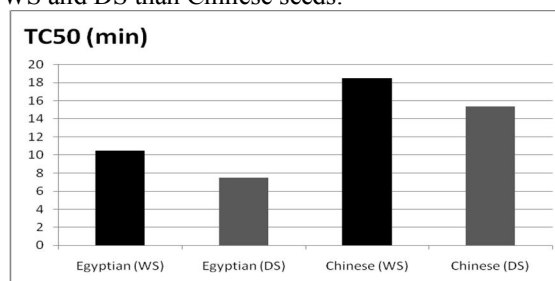
Antioxidant activity (AA%)

The antioxidant property of sunflower seed extracts influenced by the presence of phenolic compounds was followed up by measuring the capacity of scavenging DPPH• (RSA %), the oxidation of β-carotene- linoleic acid o/w emulsion and as well as measuring oxidation stability by the automated active oxygen method (Rancimat).

Radical scavenging activity (RSA%)

The stable DPPH• is scavenged by accepting a hydrogen atom or an electron from the antioxidant

and DPPH• transforms into its reduced form, DPPH-H⁽³⁴⁻³⁶⁾. DPPH• has a maximum UV-Vis absorbance at 516 nm. Decreasing the absorbance of DPPH solution indicates an increase in DPPH radical scavenging in terms of hydrogen-donating ability. The solution of the purple-colored DPPH radical changed to yellow-colored DPPH-H after reduction. The time taken for the initial DPPH• concentration to reach 50% is called TC₅₀. Decrease of TC₅₀ indicates high RSA% and vice versa. TC₅₀ of Egyptian and Chinese were shown in Fig. 1. As shown in Fig.1 the RSA% of dehulled seed extracts were higher (TC₅₀ ranged 7.5-15.33 min) than whole seed extracts (TC₅₀ ranged 10.5-18.5 min) for Egyptian and Chinese sunflower, respectively. Egyptian sunflower seeds revealed significantly (P<0.05) higher RSA% both in WS and DS than Chinese seeds.

**Figure 1.** DPPH radical-scavenging activity in Egyptian and Chinese sunflower seed extracts expressed as TC₅₀; WS: whole seed; DS: dehulled seeds.

β-Carotene – linoleic acid assay

The oxidation stability of WS and DS of Egyptian and Chinese sunflower TPC extracts in emulsions, was assessed by the coupled oxidation of β-carotene and linoleic acid in o/w emulsion. The test is based on the fact that β-carotene undergoes rapid discoloration in the absence of antioxidant and during oxidation an atom of hydrogen is abstracted from the active methylene group of linoleic acid located on carbon-11 between the two double bonds^(37, 38). The pentadienyl free radical so formed then attacks highly unsaturated β-carotene molecules to reacquire an hydrogen atom. As the β-carotene molecules lose their conjugation, they lose their characteristic orange color. This process can be monitored spectrophotometrically⁽³⁹⁾. The presence of phenolic antioxidant can hinder the extent of β-carotene degradation by neutralizing the linoleate free radical and any other radicals formed within the system. The rate of β-carotene bleaching by Egyptian (WS and DS), Chinese (WS and DS) sunflower seeds, TBHQ and α-tocopherol was shown in Fig.2. Among the six tested samples the least β-carotene bleaching (i.e. highest antioxidant activity) was recorded for TBHQ while highest β-carotene bleaching (i.e. least

antioxidant activity) was that of Chinese WS. The order of decreasing antioxidant as shown in Fig.2 was TBHQ>Egyptian DS> Egyptian WS > α -tocopherol >Chinese DS > Chinese WS.

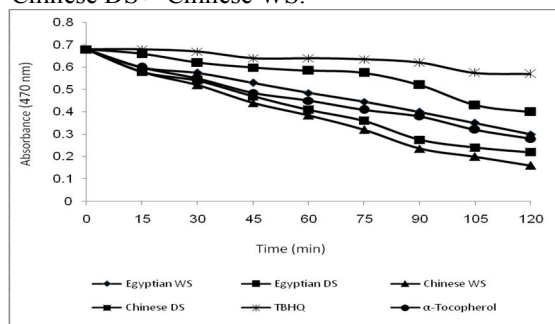


Figure 2. Effect of Egyptian and Chinese sunflower seed extracts on bleaching of β -carotene/linoleic acid w/o emulsion bleaching β -carotene/linoleic acid, WS: whole seed; DS: dehulled seeds.

Active oxygen method (Rancimat)

The measurement of fat and oil oxidation stability is commonly assessed by the fully automated version of active oxygen method available in Rancimat apparatus (Metrohm Ltd, Herisau, Switzerland) and is accepted as a standard method by American Oil Chemists' Society (AOCS Cd 12b-92) (10, 40-42).

Rancimat method determines the induction period by measuring the increase in volatile acidic by-products released from the oxidizing fat at 100-110 °C. The concentration of degradation products which are transferred into distilled water is monitored by measuring the conductivity. Longer induction periods suggest stronger activity of the added antioxidants.

It is clear that TBHQ revealed the highest protection as indicated by its longest induction period (12.3 hr) among all the tested samples, whereas the control (stripped sunflower oil without any addition) showed the least induction period (3.28 hr). The descending order of antioxidant capacity was TBHQ>Egyptian DS> Egyptian WS \geq Chinese DS >Chinese WS >control.

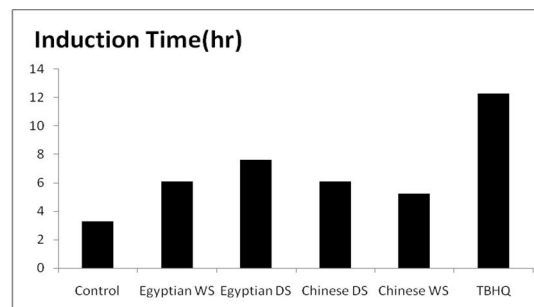


Figure 3. Effect of Egyptian and Chinese sunflower seed extracts on oxidation stability of stripped sunflower oil measured by Rancimat, WS: whole seed; DS: dehulled seeds.

Functional properties of defatted sunflower meals.

Proximate composition of the defatted meal of whole seed (DMWS) and defatted meal of dehulled seeds (DMDS) for both Egyptian and Chinese seeds are represented in Table 5.

Removal of the oil from WS meal and DS meal resulted in concentration of almost all other constituents specially protein.

Protein content was raised from 22.96 and 28.46% (Table 1) for Egyptian WS, and DS, respectively, to 45.36 and 51.43% protein for DMWS and DMDS (Table 5), respectively. While the Chinese WS and DS contained 21.22 and 26.69% protein respectively (Table 1), which increased upon defatting to 43.89 and 49.72% protein for DMWS and DMDS, respectively (Table 5). Other values in table 5 are self explanatory.

Apart from their nutritional properties, the functional properties of protein and protein products must be taken into account as stated by Finch⁽⁴³⁾. Pour -El⁽⁴⁴⁾ had broadly defined functionality as any property of a food or food ingredient except its nutritional ones that affected its utilization. The range of desirable and attractive functional properties that should be looked for is almost as broad as the range of foods themselves. Some of the important functional properties were chosen and investigated for DMWS and DMDS protein, and their results are illustrated in Table 6.

Table 5. Proximate composition of defatted meal of whole seed (DMWS) and defatted meal of dehulled seed (DMDS) of both Egyptian and Chinese sunflower seeds

Parameters (%)	Egyptian		Chinese	
	DMWS*	DMDS*	DMWS	DMDS
Moisture	8.23±0.56	7.69±0.66	7.99±0.85	9.01±0.23
Protein	45.36±0.62	51.43±0.55	43.89±0.98	49.72±0.42
Oil	0.5±0.16	0.4±0.35	0.2±0.57	0.4±0.62
Ash	6.7±0.52	8.04±0.43	9.01±0.72	10.12±0.29
Crude fiber	35.91±0.64	18.23±0.86	34.69±0.39	20.12±0.65
Nitrogen free extract	3.3±0.01	14.21±0.34	4.22±0.41	10.63±0.33

*DMWS= defatted meal of whole seeds; DMDS= defatted meal of dehulled seeds

Table 6: Functional properties of defatted meal of whole seed (DMWS) and defatted meal of dehulled seed (DMDS) proteins of both Egyptian and Chinese sunflower seeds, as well as soybean meal for comparison.

Functional Properties	Egyptian		Chinese		Soya bean* meal
	DMWS	DMDS	DMWS	DMDS	
NSI (%)	5.5±.23	7.9 ±.11	5.6 ±.35	6.9 ±.27	15.48 ±.66
PDI (%)	6.0 ±.44	9.4 ±.45	4.0 ±.36	15.5 ±.55	16.25 ±.51
WAC (%)	480 ±.35	450 ±.26	480 ±.16	460 ±.36	300 ±.32
OHC (%)	5.4 ±.72	6.3 ±.56	6.3 ±.32	7.14 ±.14	1.875 ±.71
EC (%)	20.0 ±.	20.8 ±.31	20.0 ±.55	20.8 ±.46	20.8 ±.42
GE (%)	1.0 ±.42	1.0 ±.37	1.0 ±.53	1.0 ±.12	3. ±.41
Foam Stability After					
40 Second	18.3 ±.34	12.85 ±.51	19.76 ±.31	10.86 ±.43	32.5 ±.33
50 Second	18.4 ±.25	15.67 ±.17	21.7 ±.11	14.13 ±.44	130.5 ±.54
60 Second	20.03 ±.55	20.03 ±.55	21.35 ±.53	8.7 ±.62	160.3 ±.66

*Taha and Ibrahim ⁽⁴⁶⁾. N.S.I: Nitrogen Solubility Index E.C.: Emulsifying Capacity
P.D.I.: Protein Dispersibility index O.H.C : Oil Holding Capacity ml oil to mg sample
W.A.C: Water absorption Capacity G.E: Gelation

Nitrogen Solubility Index (NSI)

NSI is a very important measure of the functionality of the proteins in different food systems, especially in fortifying nutritious beverages, instant foods, bakery products, salad dressings, soups and others. The American Dairy Products Institute emphasized that a high value of the NSI indicates that the product is less soluble. NSI of sunflower protein products indicate very good solubility of protein compared to soybean meal protein. NSI values for DMWS(Egyptian), DMWS (Chinese), DMDS (Chinese), DMDS (Egyptian), and soybean meal were 5.5, 5.6, 6.9, 7.9, and 15.48%, respectively.

Protein Dispersibility Index (PDI):

PDI is another criterion similar to NSI. It confirms the good solubility of sunflower protein. Soybean meal possessed 16.25% PDI, while DMDS (Chinese) had a close PDI 15.5% to soybean. On the other hand sunflower products, namely DMDS (Egyptian), DMWS (Egyptian), DMWS (Chinese) had 9.4, 6.0, and 4.0 % PDI, respectively, showing superiority to soybean protein.

Water absorption capacity (WAC):

It is the ability of a product to absorb water or swell. This property is important in the manufacture of bakery products, pastas, doughnuts and others. Sunflower protein products show better WAC than soybean meal protein thus is even more suitable to fortify the above mentioned products. DMDS (Chinese), DMWS (Egyptian), DMWS (Chinese), DMDS (Egyptian) showed 480, 480, 460, and 450% WAC, respectively, compared to 300 % WAC of soybean meal.

Oil Holding Capacity (OHC)

OHC is the ability of a protein to bind with oil. It is an important criterion in the meat industry (sausages, hamburgers etc.) OHC % for DMDS (Egyptian), DMDS (Chinese), DMWS (Egyptian), DMWS (Chinese), and soybean meal were 6.3, 7.14, 5.4, 6.3, and 1.875, respectively.

Emulsifying capacity (EC)

Emulsifying and film forming ability of plant proteins is essential for those proteins to perform well in meat systems. Also a protein's ability to form emulsion is critical to their application in mayonnaise, salad dressing, milks, and frozen desserts. EC of whole seed proteins is 20ml oil/100g sample which means less than soybean meal. EC of defatted meals is comparable to that of soybean meal (20.8ml oil/100g) sample. González –Pérez and Vereijken ⁽⁴⁶⁾ reported that the emulsifying properties of sunflower protein, show very interesting perspectives to enhance their usage, as they seem at least comparable to those of soy protein.

Gelling Ability or Gelation (GE)

It is an important criterion as a protein's EC in comminuted meat systems. It is reported as the lowest concentration of protein that remained as a stable gel after 30 min at room temperature. Soybean meal gelled at 3% protein concentration while sunflower protein products gelled at 1% protein concentration which indicates better gelling properties. On the other hand González –Pérez and Vereijken ⁽⁴⁶⁾ reported that gelling properties of sunflower were not as promising as the EC.

Foam Stability (FS)

FS is the capacity to form stiff, stable foam and is a requirement of proteins to be incorporated into gel cakes, whipped toppings, desserts and soufflé like products. Results in Table 6. reveal low foam stability of all sunflower protein products compared to soybean meal. Poor foaming properties of sunflower protein was in agreement with González – Pérez and Vereijken ⁽⁴⁶⁾ concluded poor foaming properties for sunflower protein.

In conclusion Egyptian and Chinese sunflower seed and meals did not show much difference between the functional properties of their meal proteins.

Conclusion

This work assessed that dehulling of sunflower seeds either Egyptian or Chinese increase significantly total proteins, total fats (of which the majority is unsaturated), and total phenolics. Egyptian seed and oil was found to be superior to the Chinese ones in most chemical characteristics and in its content of protein, fat and antioxidant activity. Although, its production is insufficient to meet the consumption of edible oils Egyptian sunflower seed can be used efficiently in supplementation of many foods due to its superior protein, unsaturated fat, and natural antioxidants contents. On the other hand, Egyptian and Chinese sunflower seeds and meals did not show much difference between the functional properties of their meal proteins.

Corresponding author

S.F. Hamed

Fats and Oils Dept. National Research Centre, 33 Tahrir St., 12622 Dokki, Cairo, Egypt.
E-mail: saidfatouh123@yahoo.com

References

- 1-FAO-STAT (2008). Food Bulletin. Website: <http://faostat.fao.org/site/567/default.aspx>.
- 2- USDA (2008). Accessed on, 2009/07/25, http://www.nal.usda.gov/fnic/foodcomp/cgi-bin/list_nut_edit.pl
- 3- Hassan M. B., Sahfique F. A. (2010). Current situation of edible vegetable oils and some propositions to curb the oil gap in Egypt. *Nature and Science*, 8: 1-7
- 4- Egyptian-British Chamber of Commerce Report (2010). Food Industry in Egypt – Spotlight on Egypt , 18 May 2010.
- 5- Shahidi, F. and R. Wanasundaras (1992). Phenolic antioxidants. *Critical Reviews in Food Science and Nutrition*, 32: 67–103.
- 6- Linderschmidt, R.; A. Trylka; M. Goad and H. Witschi (1986). The effects of dietary butylated

- hydroxytoluene on liver and colon tumor development in mice. *Toxicology*, 38: 151-160.
- 7- Kregel KC, Zhang HJ (2006). An integrated view of oxidative stress in aging: basic mechanisms, functional effects, and pathological considerations. *Am. J. Physiol.*, 292: 18-36.
- 8- Wang JS, Maldonado MA (2006). The ubiquitin-proteasome system and its role in inflammatory and autoimmune diseases. *Cell Molecular Immunol.*, 3: 255-261.
- 9- Fukumoto, L.R. and Mazza, G., 2000. Assessing antioxidant and prooxidant activities of phenolic compounds. *J. Agric. Food Chem.* 48: 3597–3604.
- 10- A.O.A.C. (2000). The Official Methods and Recommended Practices of the American Oil Chemists Society, 5th ed., AOCS Press, Champaign, Illinois.
- 11- Leung J, Fenton TW, Clandinin DR (1981). Phenolic components of sunflower flour. *J Food Sci.* 46: 1386-93.
- 12- Pedrosa MM, Muzquiz M, Garcia-Vallejo C, Burbano C, Cuadrado C, Ayet G, Robredo LM. (2000). Determination of caffeic and chlorogenic acids and their derivatives in different sunflower seeds. *J Sci Food Agric* 80: 459-64.
- 13- Paško P , Bartoń, Zagrodzki P, Gorinstein S, Fořta M, Zachwieja Z. (2009) Anthocyanins, total polyphenols and antioxidant activity in amaranth and quinoa seeds and sprouts during their growth. *J Food Sci* 115: 994-98.
- 14- Hung Y; Sava VM; Makan SY and Chen THJ. 2002. Antioxidant activity of melanins derived from tea: Comparison of different oxidative states. *Food Chem.*, 78, 233-240.
- 15- Blois MS. (1958). Antioxidant determinations by the use of a stable free radical. *Nature*;26:1199–1200.
- 16- Al-Shaikhan MS; Howard LR and Miller JC Jr. 1995. Antioxidant activity and total phenolics in different genotypes of potato. *J. Food Science*, 60, 341-343.
- 17- Läubli M.W., and P.A. Bruttel (1986). Determination of the oxidative stability of fats and oils: comparison between the active oxygen method and the Rancimat method. *Journal of the American Oil Chemists' Society*, 63: 792–795.
- 18- Fuster M. D, A-M. Lampi, A. Hopia, and A. Kamal-Eldin (1998). Effects of α - and γ -tocopherols on the autooxidation of purified sunflower triacylglycerols, *Lipid*, 33(7): 715- 722.
- 19- Smith A.K. and Circle S.J. Editors (1997). Nitrogen solubility index and protein dispersibility index. In "Soybean: Chemistry and Technology" Volume 1. Proteins, Appendix pp415-454 AVI Publishing Company.
- 20- Huber H. (1982). Water binding of rye flour during its processing. *Proceedings of the World Cereal Bread Congress (WCB 82)*, Prague, Czechoslovakia, p.765.

- 21- Childs E.A. and Forte J.F.(1976). Enzymatic and ultrasonic techniques for solubilization of protein from heat-treated cottonseed products.FJ.Food Science 41:652-655.
- 22- Shahidi, F., Xiao-Qing, H., Synowieck J., (1995) Production and Characteristics of protein hydrolysates from capelin (*Mallotus villosus*) Food Chem., 53, 285-293.
- 23- A.A. C. C. (1990). American Association of Cereal Chemists. Approved methods 12th ed. Pup. Univ. of Fam. St., Paul, Minn, USA
- 24- Circle S.J., Meyer E.W., and Whitney RW(1964)Rheology of soybean dispersions: effects of heat and other factors on gelation Cereal Chem. 41: 157.
- 25- SAS (2004). Statistical Analysis System. SAS User's Statistics SAS Institute Inc. Editors, Cary, NC.
- 26- Srilatha K, Krishnakumari K (2003). Proximate composition and protein quality evaluation of recipes containing sunflower cake. Plant foods for Human Nutri., 58: 1-11.
- 27- Nadeem M., Anjum F. M., Arshad M. U. and S. Hussain (2010). Chemical characteristics and antioxidant activity of different sunflower hybrids and their utilization in bread, African Journal of Food Science Vol. 4(10): 618-626.
- 28- Bhagya S., Sastry MCS (2003). Chemical, functional and nutritional properties of wet dehulled niger (*Guizotia abyssinica* Cass.) seed flour. Lebensm.-Wiss. u.-Technol., 36: 703-708.
- 29- Pedrosa, M.M., Muzquiz, M., Garcia-Vallejo, C., Burbano, C., Cuadrado, C., Ayet, G. and Robredo, L.M., 2000. Determination of caffeic and chlorogenic acids and their derivatives in different sunflower seeds. J. Sci. Food Agric. 80: 459-464.
- 30- De Leonardis, A., Macciola, V. and Di Domenico, N., 2005. A first pilot study to produce a food antioxidant from sunflower seed shells (*Helianthus annuus* L.). Eur. J. Lipid Sci. Technol. 107: 220-227.
- 31- Fisk LD, White DA, Carvalho A, Gray DA (2006). Tocopherol – An Intrinsic Component of Sunflower Seed Oil Bodies. J. Am. Oil Chem., Soc., 83: 341-344.
- 32- Hamed S.F., H.S.A. Hassan (2005).Fruit and oil quality of three olive cultivars grown under different climatic regions. J. Agric. Sci. Mansoura Univ., 30 (3): 1617-1630.
- 33- Žilić, S., Maksimović Dragišić, J., Maksimović, V., Maksimović, M., Basić, Z., Crevar, M., Stanković, G. (2010). The content of antioxidants in sunflower seed and kernel. *HELIA*, 33 (52): 75-84.
- 34- Kim S., Nga W. K., Shena S., Donga Y., Tan R. B.H. (2009). Phase behavior, microstructure transition, and antiradical activity of sucrose laurate/propylene glycol/the essential oil of *Melaleuca alternifolia*/water microemulsions Colloids and Surfaces A: Physicochem. Eng. Aspects 348: 289-297
- 35- Huang, D., Ou, B., & Prior, R. L. (2005). The chemistry behind antioxidant capacity assays. Journal of Agricultural and Food Chemistry, 53, 1841-1856.
- 36- Prior, R. L., Wu, X., Schaich, K. (2005). Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. Journal of Agricultural and Food Chemistry, 53, 4290-4302
- 37- miller, H.E. (1971). A simplified method for the evaluation of antioxidants. JAOCS, 48: 91.
- 38- Frankel, E.N. (1998). Hydroperoxide formation. In *Lipid oxidation* (pp. 23-41). Dundee: The Oily Press.
- 39- Hamed, S.F. (2006). Edible oil as an alternate solvent of antioxidant components from natural herbs. Journal of Applied Sciences Research, 2 (9): 567-571.
- 40- Antolovich M., P. D. Prenzler, E. Patsalides, S. McDonald, and K. Robards, (2002) Analyst, 127, 183.
- 41- Pratt D. E., 1995. in Y. H. Hui, ed., *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products, Products and Application Technology*, 5th ed., Wiley, New York, p. 523.
- 42- Dziedzic S. Z. and B. J. F. Hudson(1984), J. Am. Oil Chem. Soc., 61, 1042.
- 43- Finch R. (1970) Fish protein for human foods. CRC Reviews in Food Technology 1(4): 519
- 44- Pour- El A. (1981). Protein functionality: Classification, definition and Methodology. Chapter 1 in "Protein Functionality in Foods" Ed., J.P. Cherry, pp1-9, ACS Series 147, Washington DC.
- 45- Taha FS and Ibrahim M.A.(2002), Effect of degree of hydrolysis on the functional properties of some oilseed proteins. *Grasa y Aceites* 53: 273-281.
- 46- González-Pérez S. and Vereijken J.M. (2007) Review. Sunflower proteins: physicochemical, structural and functional properties. J. of the Science of Food and Agriculture 87: 2173-2191.

4/29/2012