

## Influence of Grape Seed Phenolic Compounds on Thermal Stability of Frying Oils

Amany M. M. Basuny

*Fats & Oils Res. Dept., Food Tech. Res. Inst., Agric. Res. Center, Giza, Egypt.*

The effects of grape seed phenolic compounds on quality characteristics of a blend of sunflower: cottonseed oil during deep-fat frying (at 180 °C) of potato chips for 4h/day for 5 days in five systems were determined in this study. The systems used were a blend of sunflower: cotton seed oils (1:1 v/v) without antioxidant (control), with 200 ppm butylated hydroxytoluene (BHT), and 200, 400 and 800 ppm grape seed polyphenols. Analysis was carried out daily after frying to follow up the deterioration the occurred in the oil. Oil samples were analyzed for peroxide value, thiobarbituric acid (TBA) acidity, iodine value, polar content, polymer content, viscosity, ultraviolet absorption ( $E_{1cm}^{1\%}$  at 232 and 268 nm.), color and oxidized fatty acid content. Generally, the blends with 800 ppm grape seed polyphenols gave the least increase in these attributes compared to other three concentrations. Phenolic compounds were found at concentrations 950 ppm (as caffeic acid) in grape seed. Polyphenols of grape seed were fractionated by high performance liquid chromatography (HPLC). Five compounds were separated and were identified as gallic acid, catechin, epicatechin, tannic acid and procyanidin.

**Keywords:** Grape seed phenolic compounds (GSPC); Antioxidant activity ; Lipid oxidation; Deep- fat frying.

Frying of food is a very popular way of cooking at home and in fast food restaurants. However, factors such as price, stability, and nutritive value must be considered (Bastida and Sanchez-Muniz, 2002). The debate on deep-fat frying on commercial establishments is primarily focused on the point at which any oil used for frying should be discarded ( Bastida and Sanchez-Muniz, 2002).

Frying oil, used continuously or repeatedly at high temperatures, is subjected to a series of degradation reactions, thermal oxidation and hydrolysis due to the presence of moisture in the foods, and formation of a variety of decomposition compounds ( XU *et al.*, 2000; Gertz and Kochhar 2001 a). This decomposition results in poor performance of frying oil and off-flavor formation and may influence nutritional quality and food safety ( Gertz and Kochhar 2001 b). Some of these compounds may also be harmful to human health (Abdel Rahman 2001). The breakdown products from oxidation of fat may play a role in various diseases, such as initiating events of the coronary heart disease ( Eder and Stangl, 2000).

Lipid oxidation is one of the major deteriorative reactions in frying oils and fried foods, and often results in a significant loss of quality. It is well established that lipid oxidation leads to changes in functional, sensory, and nutritive values as well as in the safety of fried foods (Jaswir *et al.*, 2000). For these reasons, antioxidants are added to fats, oils, and foods containing fats. With the awareness concerning the use of commercial synthetic antioxidants in the food system such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert- butylhydroquinone (TBHQ) and their negative health effects as implicated in the promotion of carcinogenesis (Ito *et al.*, 1986). Considerable attention has been given to the application of natural antioxidants in foods, because of their potential nutritional and therapeutic effects (Halliwell *et al.*, 1995). Currently fruits, vegetables, spices, nuts, seeds, leaves, roots, and barks are being investigated as potential sources of natural antioxidants (Amarowicz; *et al.*, 2000). Many food manufacturers have shown considerable interest in the use of natural sources of antioxidants during the last few years (Irwandi *et al.*, 2000).

Grape (*Vitis vinifera*) is one of the world's largest fruit crops, which approximates an annual production of 58 million metric tons (FAO, 1997). Phenolics in grapes and red wines have been reported to inhibit human low density lipoprotein (LDL) oxidation in vitro (Jayaprakasha *et al.*, 2001).

Grape seeds are rich source of monomeric phenolic compounds, such as catechins, epicatechin and epicatechin gallate and these compounds act as antimutagenic and antiviral agents (Kaga *et al.*, 1999 and Saito *et al.*, 1998). There are reports of the possible use of the grape phenolics in preventing atherosclerosis (Kovac and Pekic, 1999). Recognition of such health benefits of catechins and procyanidins has led to the use of grape seed extract as a dietary supplement (Jayaprakasha *et al.*, 2001). Phenolic compounds extracted from twelve different varieties of grapes, showed antioxidant activity toward LDL oxidation in vitro (Mayer *et al.*, 1997).

Grapes are a major source of phenolic compounds among different fruits and vegetables (Macheix *et al.*, 1990). Phenolic compounds have been found at concentrations as high as 260 - 920 mg/kg in grapes and 1.800-3.200 mg / L in wines (Gamez -meza *et al.*, 1999). The present study was performed to optimize the use of grape seed phenolic compounds as antioxidant in stabilizing sunflower and cotton seed oils during deep-fat frying of potato chips.

## Material and Methods

### 1-Source of oils

Sunflower and cottonseed oils were obtained from Cairo Oils and Soap Company, El - Badrachin, Giza, Egypt.

### 2- Source of Potatoes

The potatoes were obtained from the local market in Egypt.

### 3- Source of red grape

Red grape El-fuomi- variety (*Vitis vinifera*) was obtained from the local market, season 2001.

### 4- Solvents

All solvent in this study were of analytical grade (Merck).

### 5- Commercial antioxidant

Butylated hydroxytoluene (BHT) was supplied by Eastman Chemical Co.

### 6- Standard phenols compounds for HPLC analysis

Gallic acid, catechin, epicatechin, tannic acid and procyanidin were obtained from Koch- light laboratories Ltd. Colubrook, Buckingham, Shira, England.

### 7- Preparation of potatoes

The potatoes were washed, peeled and sliced to chips 2 mm thick using a manual chips slicer.

### 8- Extraction of Polyphenolic compound

Crushed red grape seed ( *Vitis vinifera* (20 g ) was extracted overnight with 200 ml methanol at room temperature according to the method described by Duch and Yen (1997). The extracts was filtered, and the residue was re-extracted under the same conditions and the combined filtrates were evaporated to 5 ml in a rotary evaporator at 40° C. The extract were evaporated to dryness and kept at -4° C until analysis.

### 9- Determination of total phenolic compounds

The total phenolic compounds in red grape seed were determined spectrophotometrically using Folin-Ciocalteu reagent according to the method described by Duch and Yen (1995). The methanolic extracts (0.1ml) of sample in a volumetric flask were diluted with glass-distilled water (15 ml). Folin - Ciocalteu reagent (5 ml) was added and the content of the flask mixed thoroughly. After 3 min., sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution ( 10 ml , 10% W/V ) was added and finally quantified to 100 ml glass-distilled water and then the mixture was allowed to stand for 30 min. with intermittent shaking. The blue color was measured with a UV-Vis Spectrophotometer. The concentration of total phenolic compounds in samples, mg/ Kg of dry product, were determined as caffeic acid.

### 10- Qualitative and quantitative determination of phenolic compounds with high performance liquid chromatography ( HPLC )

A Hewlett-Packard series 1, 100 liquid chromatographic system (waldbronn, Germany) ( loop 20  $\mu\text{l}$  ) equipped with a diode array detector and a lichrosorb RP 18 column ( 4.0 mm id  $\times$  250 mm; partical size 5  $\mu\text{m}$  ) ( Merck, Darmstadt) was used. Elution was performed at a flow rate of 1.0 ml / min with Mobil phase of water/acetic acid ( 98:2, V/V, solvent A) and methanol/acetonitril (50:50, V/V, solvent B), starting with 5% B and increasing B to levels of 30% at 25 min ., 40% at 35 min., 52 % at 40 min., 70 % at 50 min ; 100 % at 55 min., and kept at this stage for 5 min . A re-equilibration time of 1 min. was then required. Quantitation was achieved at 280 nm by internal standard method Evangelisti, *et al* (1997).

### 11-Preparation of oils

System 1 : Sunflower and cotton seed oils ( control).

System 2 : Control + 200 ppm BHT.

System 3 : Control + 200 ppm grape seed phenolic compound (GSPC).

System 4 : Control + 400 ppm (GSPC).

System 5 : Control + 800 ppm (GSPC).

### 12-Frying process

Sunflower: cottonseed oil blends (1:1 V/V) with or without antioxidant (control) and other systems were used for frying potato chips as follows: Two kg. of oil was placed in an aluminum frying container with 35 cm. diameter and 20 cm. high, oil was heated at  $180^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 4 hr / day for 5 days. After frying of potatoe chips and at the end of each day, samples of oils were withdrawn and stored in brown bottles at  $20^{\circ}\text{C}$  until analysis.

### 13-Physico-chemical properties of frying oils

Color, refractive index (RI), viscosity (V), ultraviolet absorption ( $E^{1\%}$  at 232 and 268nm.), acidity, peroxide value(PV), Thiobarbituric acid (TBA) value, iodine value (IV) and oxidized fatty acid (OFA) content were determined according to the methods described by A.O.A.C. (2000), Polar and non polar components in oil were measured by column chromatography according to the method described by Waliking and Wessels (1981), polymer content was analyzed according to the method of peled *et al* (1975), and oxidative stability (OXS) by rancimat method at  $100^{\circ}\text{C} \pm 2^{\circ}\text{C}$  were determined according to the method of Evangelisti *et al* (1997).

### 14-Statistical analysis

Statistical analysis involved used of the statistical analysis systems (SAS , 1985) software Package. Analysis of variance was performed by ANOVA procedures. Significant differences between means were determined by Duncan's Multiple Range test.

## Results and Discussion

### Total phenolic compounds content

The concentrations of total phenols of grape seed as determined by the Folin-Ciocalteu method was 950 ppm of dry product as caffeic acid.

### HPLC analysis of polyphenols extracted from grape seed

Table (1) shows the chemical composition of polyphenols of grape seed determined with HPLC analysis. It could be noticed that procyanidin was the major phenolic compounds present in grape seed, followed by gallic acid, catechin, epicatechin and tannic acid.

**TABLE 1. Chemical composition of polyphenols of grape seed .**

Name	%
Gallic acid	10.30
Catechin	22.50
Epicatechin	9.70
Tannic acid	4.50
Procyanidin	53.00

These results are in good agreement with those reported by Jayaprakasha *et al.* (2001) and, Kaga *et al.* (1999).

#### *Characteristics of fresh oils used in frying experiments*

The initial physico-chemical characteristics of fresh sunflower: cotton seed oils used in this study are given in table (2). The fresh sunflower: cotton seed oils were of good quality, as evidenced by their initial low peroxide value of 0.6 meq/kg oil, acidity of 0.12 % and iodine value of 120 gI<sub>2</sub>/100g oil. This is mainly due to the type of oil as sunflower: cotton seed oils relate to semi-drying oils which have iodine value ranging between 90-130. Besides sunflower: cotton seed oils contain a high percent of unsaturated fatty acids (about 90%). The stability of oils was 10.5 hr by Rancimat. These results are in agreement with the Egyptian standard Organization, (1993).

#### *Antioxidant activity of grape seed phenolic compounds*

The antioxidant activity of phenolic compounds extracted from the red grape seed were assessed by the Rancimat method. This method assigned the induction period for the onset of oxidative rancidity in sunflower: cottonseed oils at 160 °C ± 0.2 °C. The longer the induction period the stronger the antioxidant activity which was tested in triplicates using different GSPC concentrations of 200, 400 and 800 ppm. Table (3).

In the present study, model systems comprising of sunflower: cottonseed oils boosted with phenolic compounds were designed to assess their stability. Another experiment was performed where sunflower: cottonseed oils were boosted with BHT (200 ppm) in order to compare the antioxidant efficiency of the phenolic compounds under study with the most commonly used synthetic antioxidant material. The induction period for the system containing phenolic compounds increased with the increase in the phenolic compound's concentration. However, there were no significant differences in the induction period for the systems 2 and 3, conversely systems 4 and 5 exhibited remarkable antioxidant effect compared with the other systems. It is worth nothing that GSPC at 800 ppm was superior to BHT in retarding sunflower: cottonseed oils oxidative rancidity. Therefore, it could be suggested to add GSPC to increase the shelf life of edible oils.

**TABLE 2. Characteristics of fresh sunflower : cotton seed (1:1 V/V) oil blend .**

Characteristics of the oil	Value
Refractive index at 25° C	1.4721
Viscosity (Centipoise)	44.00
Color Red	2.00
Yellow	35.00
E <sup>1%</sup> at 232 nm	0.75
E <sup>1%</sup> at 268 nm	0.09
Acid value (% as oleic acid)	0.12
Peroxide value (meq./kg oil)	0.60
Induction period (hr)	10.50
TBA value at 532 nm	0.001
Iodine value (Hanus)	120.00
Polar content (%)	0.50
Polymer content (%)	0.01
Fatty acid composition (%)	
C <sub>12:0</sub>	1.52
C <sub>14:0</sub>	4.80
C <sub>16:0</sub>	5.30
C <sub>18:0</sub>	2.30
C <sub>18:1</sub>	25.50
C <sub>18:2</sub>	65.30
C <sub>18:3</sub>	9.50

**TABLE 3. Effect of grape seed phenolic compounds on sunflower : cotton seed (1:1 V/V)oil blend oxidative rancidity .**

System	Induction period (hr) <sup>a</sup>
Sunflower : cottonseed oil blend (Control)	10.50 <sup>a</sup>
Control + BHT (200 ppm)	12.30 <sup>a</sup>
Control + GSPC (200 ppm)	12.50 <sup>a</sup>
Control + GSPC (400 ppm)	15.30 <sup>b</sup>
Control + GSPC (800 ppm)	21.50 <sup>b</sup>

Induction period refers to the time (h) at the break point of the two extrapolated straight parts of the curve obtained by Rancimat apparatus.

L.S.D = 2.20 at p > 0.05.

#### *Changes in characteristics of sunflower: cottonseed oil blend during frying*

The changes in quality parameters of sunflower: cotton seed oils used for intermittent frying of potato chips in the presence and absence of antioxidants are given in. Table (4).

#### *Changes in peroxide value*

The changes in PV during frying are presented in Table (4). The results of this study showed that in system I (control), the formation of peroxides seemed

to increase rapidly from the beginning until the 5<sup>th</sup> day of frying. Sunflower: cottonseed oils with the addition of antioxidants (systems 2,3,4,5) had significantly lower PV than those of the control, throughout the duration of the study. System 2 (200 ppm BHT) and system 3 (200 ppm GSPC) were not significantly different from each other. However, the PV of system 5 (800 ppm GSPC) was significantly lower than the PV of systems 2 and 3. In general, the oxidative stability was in the order GSPC (800 ppm) > GSPC (400 ppm) > GSPC (200 ppm) = BHT (200 ppm) > control (Perkins, 1967).

#### *Changes in TBA value*

The changes in TBA values during frying are presented in Table (4). TBA values of all systems increased progressively with the frying time. The TBA test has been widely used as an objective measure of secondary oxidation products of oils. It relates to the level of malonaldehyde formed during oxidation of lipids. It was assumed that accumulation of these products during consecutive days of frying affected the oil quality and were responsible for the development of rancid odors and off flavor of the oil (Gordon, 1990). The control (system 1) consistently had the highest TBA values among the five systems throughout the 5 days of frying. The increase in TBA values for systems 2,3,4 and 5, were in the following order: BHT (200 ppm) = GSPC (200 ppm) > GSPC (400 ppm) > GSPC (800 ppm).

The effectiveness of GSPC as lipid antioxidants has been attributed mainly to their ability to remain stable at high temperature (Jaswir *et al.*, 2000). GSPC contain gallic acid, catechin, epicatechin, tannic acid and, procyanidin as their primary phenolic antioxidants that react with lipid or hydroxyl radicals and convert them into stable products (Namiki, 1990 and Gordon, 1990).

#### *Changes in acidity*

The changes in acidity during frying are presented in Table (4). Acidity is a measure of the acidic components in the oil. Generally, the determination of the acidity by titration does not differentiate between acids formed by oxidation and those formed by hydrolysis (Sherwin, 1968). It was nevertheless measured, because free acids contribute to the development of off-flavors and off-odors in the product. The increase in the level of acidity in oil systems with antioxidants was in the order of: GSPC (800 ppm) < GSPC (400 ppm) < GSPC (200 ppm) = BHT (200 ppm), < control the higher acidity of the control oil system compared to systems with antioxidants is due to the presence of the phenolic antioxidants that act by inhibiting oxidation reactions but have no direct effect on hydrolytic reactions Cuvelier *et al.*, (1994).

TABLE 4. Physico-Chemical changes of Sunflower : Cottonseed (1:1 v/v) oilblend during deep-fat frying .

Systems	Peroxide Value	acid value	Iodine Number	TBA Value	Viscosity	Color		Polar components	Polymer content	E <sub>1%</sub> <sub>1cm</sub> at 232nm	E <sub>1%</sub> <sub>1cm</sub> at 268nm	Oxidized Fatty acid	
						R	Y						
System1 (control)	0	0.60	0.12	120.00	0.001	7.50	2.00	35.00	0.50	0.01	0.75	0.09	0.12
	4	4.30	0.30	116.00	0.30	13.00	4.50	35.00	9.50	2.30	0.06	0.40	0.50
	12	19.00	0.72	110.00	0.80	34.00	12.50	35.00	15.50	4.50	1.80	0.60	1.05
	20	30.20	0.90	100.00	0.99	60.00	18.00	35.00	20.70	7.20	1.95	0.90	1.60
System 2 (BHT200ppm)	0	0.61	0.11	120.00	0.001	7.30	2.00	35.00	0.50	0.01	0.73	0.08	0.13
	4	4.00	0.28	117.00	0.27	10.00	3.50	35.00	9.00	2.10	0.90	0.21	0.49
	12	17.50	0.65	111.00	0.75	28.00	11.30	35.00	14.30	4.00	1.30	0.39	1.00
	20	28.00	0.80	101.00	0.92	48.00	16.50	35.00	18.00	6.90	1.63	0.52	1.40
System 3 (grape seed Polyphenols 200ppm)	0	0.60	0.12	120.00	0.001	7.50	2.00	35.00	0.50	0.01	0.72	0.08	0.13
	4	3.95	0.27	116.00	0.25	10.20	3.50	35.00	8.90	2.00	0.89	0.20	0.48
	12	17.32	0.60	110.00	0.73	28.00	11.00	35.00	14.00	3.80	1.25	0.35	1.00
	20	28.01	0.73	100.00	0.89	47.00	16.00	35.00	17.82	6.90	1.60	0.50	1.40
System 4 (grape seed Polyphenols 400ppm)	0	0.60	0.11	120.00	0.001	7.50	2.00	35.00	0.50	0.01	0.72	0.08	0.13
	4	3.00	0.19	118.00	0.13	9.00	3.00	35.00	7.01	1.20	0.79	0.13	0.35
	12	15.20	0.49	115.00	0.30	23.00	9.00	35.00	12.30	2.10	1.00	0.21	0.80
	20	20.03	0.60	105.00	0.45	40.00	12.00	35.00	15.00	4.50	1.20	0.34	0.99
System 5 (grape seed Polyphenols 600ppm)	0	0.60	0.11	120.00	0.001	7.50	2.00	35.00	0.50	0.01	0.72	0.08	0.13
	4	2.01	0.13	118.00	0.08	8.00	2.90	35.00	3.00	0.90	0.75	0.10	0.20
	12	9.40	0.22	117.00	0.18	18.00	6.30	35.00	7.00	1.50	0.85	0.15	0.35
	20	12.30	0.30	113.00	0.25	29.00	10.00	35.00	10.00	2.30	0.92	0.20	0.47
L.S.D	$P > 0.05$	3.10	0.50	2.00	0.50	2.50	1.00	-	1.5	0.90	0.40	0.25	0.12



#### *Changes in iodine value*

Changes in IV during 5 days of frying in all systems are given in Table (4). IV is a measure of overall unsaturation and is widely used to characterize oils and fats. Thus, a decrease in IV is consistent with the decreasing number of double bonds in oil as it becomes oxidized Coppen, (1989). A significantly larger change in IV in the control (system2) compared to the other systems indicated that the rate of oxidation of unsaturated fatty acids was reduced in the presence of antioxidants. The changes in IV also confirm that GSPC (800 ppm) was more effective in protecting oxidation of unsaturated fatty acid than GSPC (400 and 200 ppm) and BHT(200 ppm).

#### *Changes in Polymer content*

The changes in polymer content of all systems is presented in Table (4). It is well known that as oxidation of oil exposed to frying temperatures proceeds, the polymer content increases. Increases in polymer content are due to formation of higher molecular weight substance by polymerization (Yoon *et al*.,1985). The results showed that the polymer content of all systems increased slowly after the 5 days of frying. It was noted that the rate of polymer formation was faster in the oil system without antioxidants than in oil systems with antioxidants. The polymer content in systems 2 and 3 were not significantly different from each other. Within oil systems with antioxidants, systems 4 and 5 showed significantly lower formation of polymers than systems 2 and 3. System 5 showed significantly less formation of polymers compared to the other systems. Therefore, the GSPC (800 ppm) had the strongest effect in retarding formation of polymers during frying, followed by GSPC(400 and 200 ppm), synthetic antioxidants (BHT, 200 ppm), and the control.

#### *Changes in viscosity*

The changes in viscosity of all systems are presented in Table (4). The observed increases in viscosity were due to polymerization, which resulted in formation of higher molecular weight compounds, *i.e.*, Carbon-to-carbon and carbon-to-oxygen-to-carbon bridges between fatty acids (Gray, 1978). The control had a consistently higher level of viscosity during frying, and other systems showed less increase in viscosity.

#### *Changes in color*

The changes in color of all systems are presented in Table (4). The color of oil systems increased significantly throughout the 5 days of frying. The color of frying oil darkens during frying as a result of oxidation and formation of brown pigments from the potato chips (Gray,1978). The results showed that system 5 (GSPC 800 ppm) was significantly darkened at a rate less rapid than the other systems.

### The changes in $E^{1\%}_{1\text{cm}}$ at 232 and 268 nm

The changes in  $E^{1\%}_{1\text{cm}}$  at 232 and 268 nm throughout the 5 days of frying are shown in Table (4). Oxidation of polyunsaturated fatty acids is accompanied by increased ultraviolet absorption. Unlike the peroxide value,  $E^{1\%}_{1\text{cm}}$  at 232 nm

which also measures the degree of primary oxidation, shows a trend of increasing diene content with progress in frying times for all systems. The oil systems with antioxidants showed significantly less formation of conjugated dienes compared to the system without antioxidants (control). The  $E^{1\%}_{1\text{cm}}$  at 232 nm

of the oils after 5 days of frying was lowest in system 5. System 4 showed significantly less formation of conjugated diene, followed by systems 2 and 3. The  $E^{1\%}_{1\text{cm}}$  at 268 nm, which is an indicator of the formation of conjugated triene,

increased significantly across the 5 days of frying in all systems. The changes in  $E^{1\%}_{1\text{cm}}$  at 268 nm paralleled the changes in  $E^{1\%}_{1\text{cm}}$  at 232 nm. According to peled *et al.*

(1975), besides dienes, trienes could form from polymers during frying. These results, like those for peroxide values and  $E^{1\%}_{1\text{cm}}$  at 232, indicate that the stabilizing effect

of antioxidants on sunflower and cotton seed oils was in the order of: GSPC (800 ppm) > GSPC(400ppm) > GSPC(200ppm) = BHT (200ppm).

### Changes in polar components

The changes in polar components during 5 days of frying in all systems are given in Table (4). The results showed that the polar components of all systems increased after the 3 days of frying. The rate of polar components was faster in the oil system without antioxidants than in oil systems with antioxidants. Systems 4 and 5 showed significantly lower formation of polar components than systems 2 and 3. System 5 showed significantly least formation of polar components compared to the other systems.

### Changes in oxidized fatty acids

The changes in OXF of all systems are presented in Table (4). The results showed that system 1 (control) had a consistently higher level of OXF during frying. The increase in OXF for the other systems were BHT (200ppm) = GSPC (200 ppm) > GSPC (400 ppm) > GSPC (800ppm).

It could be concluded from the results of this study that the addition of grape seed phenolic compounds to frying oils offers a good protection against oxidation especially at a level of (800 ppm). GSPC also proved to be superior to BHT especially at 800 ppm. level The higher advantage of using GSPC is that they have no health hazard effects.

## References

- Abdel-Rahman, M.k. (2001)** Effect of feeding rats on thermally oxidized sunflower oil and antioxidants on their oxidases activity, *Ph. D Thesis*, Fac. of Agric., Cairo Univ .
- Amorowicz, R., Naczkn, and Shahidi, F. (2000)** Antioxidant activity of crude tannins of canola and rapeseed hulls. *J.Am. Oil Chem. Soc.* **77** (9), 957.
- A.O.A.C. (2000)** Official methods of analysis 16<sup>th</sup> ed. Association of official analytical chemists international., Arlington, Virginia, U.S.A.
- Bastida, S. and Sanchez- Muniz, E.J. (2002)** Polar content vs. TAG oligomer content in the frying – life assessment of monounsaturated and polyunsaturated oils used in deep- frying. *J. Am. Oil chem. Soc.* **79** (5), 447 .
- Coppen, P.P (1989)** The use of antioxidants, in rancidity in foods. 2<sup>nd</sup> edn., edited by J. C. Allen and R.J. Hamilton, A. Elsevier, London, PP. 83 – 104 .
- Cuvelier, M.E., Berest, C. and Richard, H. (1994)** Antioxidant constituents in sage (*Salvi officinalis*). *J. Agric. Food Chem.* **42** , 655 .
- Duh, P.D. and Yen, G.C. (1995)** Changes in antioxidant activity and components of methanolic extracts of peanut hulls irradiated with ultraviolet light. *Food Chem.* **54** , 127 .
- Duh, P.D. and Yen, G.C. (1997)** Antioxidant efficacy of methanolic extracts of peanut hulls in soybean and peanut oils. *J. Am. Oil Chem. Soc.* **74** (6), 745 .
- Eder, K. and Stangl, G.I. (2000)** Plasma thyroxine and cholesterol concentrations of miniature pings are influenced by the thermally oxidized dietary lipids *J. Nutr.* **130**, 166 .
- Egyptian Standard Organization (1993)** Vegetable oils st. No. 49. Egyptian organization for standardization.
- Evangelisti, F., Zunin, P., Tisconia, E., Petacchi, R., Drava, G. and Lanteri, S. (1997)** Stability to oxidation of virgin olive oils as related to olive conditions: study of polar compounds by chemometric methods . *J. Am. Oil Chem., Soc.* **74** (8), 1017 .
- FAO Production Year Book (1997)** FAO statistics No. 51 . Rome: Food and agriculture organization of the united nations.
- Gamez-Meza, N., Noriega-Rodriguez, J.A., Medina-Juarez, L.A., Ortega-Garcia, J., Cazarez-Casanova, R. and Angulo- Guerrero, O. (1999)** Antioxidant activity in soybean oil extracts from thompson grape bagasse. *J. Am. Oil chem. Soc.* **76** (12), 1995.
- Gertz, C. and Kochhar, S.P. (2001 a)** New theoretical and practical aspects about frying process. 24<sup>th</sup> world congress and Exhibition of the International society for fat research (ISF), Berlin, Germany, 16-20 September.

- Gertz, C. and Kochhar, S.P. (2001 b)** New analytical criteria for fresh and used deep-frying fats and oils. 24<sup>th</sup> world congress and exhibition of the International Society for fat research (ISF), Berlin, Germany, 16-20 September.
- Gordon, M.H. (1990)** The mechanism of antioxidant action in vitro, in food antioxidants. Edited by B.J.F. Hudson, Elsevier, New York, pp 1- 18 .
- Gray, J.I. (1978)** Measurement of lipid oxidation – A Review. *J. Am. Oil Chem. Soc.* **55**, 539 .
- Halliwell, B., Murcia, M.A., Chirico, S. and Aruoma, O.I. (1995)** Free radicals and antioxidants in food and in vitro: what they do and how they work. *Crit. Rev. food Sci. Nutr.* **35** , 7 .
- Irwandi, J., Che-Man, Y.B. and Kitts, D.D. (2000)** Use of natural antioxidants in refined palm olein during repeated deep – fat frying. *Food Res. Int.* **33** , 501.
- Ito, N. Hirose, M., Fukishima, S., Tsuda, H., Shirai, T. and Tatematsu, M. (1986)** Studies on antioxidants: Their anticarcinogenic and modifying effects on chemical carcinogenesis. *Food Chem. Toxicol.* **24** , 1099 .
- Jaswir., Che-Man, Y.B. and Kitts, D.D. (2000)** Optimization of physico-chemical changes of palm olein with phytochemical antioxidants during deep-fat frying *J.Am. Oil Chem. Soc.* **77** (11), 1161.
- Jayaprakasha, G.K., Singh, R.P. and Sakariah, K.K. (2001)** Antioxidant activity of grape seed (*Vitis vinifera*) extracts on peroxidation models *in vitro*. *Food Chemistry*, **73**, 285.
- Kanner, J., Frankel, E., Granit, R., German, B. and Kinsella, J.E. (1994)** Natural antioxidants in grapes and wines. *J. Agric food Chem.* **42** , 64.
- Koga, T., Moro, K., Nakamor, K., Yamakashi, J., Hosoyama, H., Kataoka, S. and Ariga, T. (1999)** Increase of antioxidative potential of rat plasma by oral administration of proanthocyanidin rich extract from grape seeds *J. Agric. Food Chem.* **47**, 1892 .
- Kovac, V. and Pekic, B. (1991)** Proanthocyanidols from grape and wine Contemporary Agriculture, **39**, 5.
- Macheix, J. J., Fleurient, A. and Billot, J. (1990)** The main phenolics of fruits, In “ fruit phenolics”. CRC press, Boca. Raton, PP. 1-103 .
- Mayer, A., Ock – Sook, S., Person, D., Waterhouse, A.L. and Franke, E.N. (1997)** Inhibition of human low-density lipoprotein oxidation in relation to composition of phenolic antioxidants in grapes (*Vitis vinifera*). *J. Agric. Food Chem.* **45** , 1638.
- Namiki, N. (1990)** Antioxidants / antimutagens in food. *Crit-Rev. Food Sci. Nutr.* **29**, 273.

- Peled, N. , Gutfinger, T. and Letan, A. (1975)** Effect of water and BHT on stability of cottonseed oil during frying. *J. Sci. Food Agric.* **26** , 1655 .
- Perkins, E.G. (1967)** Formation of non-volatile decomposition products in heated fats and oils. *Food Technol.* **21** , 125.
- Saito, N., Hosoyama, H., Arigata, T., Kataoka, S. and Nobuyuki, Y. (1998)** Antiulcer activity of grape seed extract and procyanidins. *J. Agric. Food Chem.* **46** , 1460 .
- SAS , (1985)** SAS, user's guide: statistics, ver. 5. SAS institute Inc. Cary, N.C.
- Sherwin , E.R. (1968)** Methods for stability and antioxidants measurement *J.Am. Oil Chem. Soc.* **45**, 632.
- Waltking, A.E. and Wessels , H. (1981)** Chromatographic separation of polar and non-polar components of frying fats. *J. Assoc. of Chem.*, **64** (6), 1329 .

(Received 25/2/2003)

## تأثير المركبات الفينولية لبذور العنب على الثبات الحرارى لزيتو التحمير

أمانى محمد محمد بسيونى

قسم بحوث الزيوت والدهون - معهد بحوث تكنولوجيا الأغذية - مركز  
البحوث الزراعية - جيزة - مصر .

تأثير المركبات الفينولية على خصائص جودة المخلوط الناتج من زيت بذور عباد الشمس وزيت بذرة القطن أثناء تحمير البطاطس الشيبسى على درجة مئوية لمدة 4 ساعات على مدار 5 أيام . حيث تم عمل خمسة أنظمة للتحمير وهى عينة زيت بدون اضافات ، وعينة مضاف إليها 200 جزء فى المليون BHT ، و عينة مضاف إليها 200 جزء فى المليون من المركبات الفينولية المستخلصة من بذور العنب وأخرى مضاف إليها 400 جزء فى المليون وأخرى مضاف إليها 800 جزء فى المليون من المركبات الفينولية المستخلصة من بذور العنب .

- تم سحب عينة بعد كل 4 ساعات تحمير وأجراء كلا من الاختبارات الاتية عليها :  
" رقم البيروكسيد - ورقم حمض الثيوباربيوتريك - والحموضة - والرقم اليودى -  
والمرکبات القطبية - والمحتوى من البوليمير - واللزوجة - والامتصاص فى  
منطقة الأشعة فوق البنفسجية على طول موجى 222، 268 نانومتر - واللون -  
والمحتوى من الأحماض الدهنية المؤكسدة " ووجد ان اضافة 800 جزء فى  
المليون من المركبات الفينولية لبذور العنب أدى إلى انخفاض الزيادة فى كل  
خصائص الجودة للزيت وذلك مقارنة بباقى التركيزات .
- ومن هذا يتضح أن أفضل النتائج لإضافة مضادات الاكسدة والتي أدت إلى تحسين  
الثبات الحرارى للزيت أثناء التحمير هى 800 جزء فى المليون من المركبات  
الفينولية لبذور العنب . ووجد أن تركيز المركبات الفينولية الموجودة فى بذور  
العنب هى 950 جزء فى المليون مقدرة كحمض كافيك .
- ووجد أن المركبات الفينولية الموجودة فى بذور العنب بعد تغريدها بجهاز HPLC  
والتي تم التعرف عليها هى حمض الجالليك والكاتشين وأبيكاتشين والتانينك  
والبروسياندين .