J. Product. & Dev., 15(3): 309- 325 (2010)

EFFECT OF PHENOLIC COMPOUNDS EXTRACT FROM SOME HERBS AND SPICES ON THE STABILITY OF PALM OIL DURING DEEP FRYING

Rania E. El-Gammal * and AFAF-Haniem M. Ramadan **

** Food Industries Department, Faculty of Agriculture, Mansoura University, Mansoura, Egypt.*

***Home Economics Department, Faculty of Specific Education, Mansoura University, Mansoura, Egypt.*

ABSTRACT

Natural phenolic extracts from herbs and spices, namely Thyme (Thymus. Vulgairs), Marjoram (Origanum majorana) and Fennel (Foeniculum vulgare) were used as source of natural antioxidants to determine the stability refined, bleached and deodorized palm oil during deep of potato chip frying at 180° C for 12 hours .

Results of Total Phenolic Compounds (TPC) indicated that thyme extract have the highest total phenolic compounds represented 265.96 mg/g as Gallic acid in compare with marjoram and fennel extracts which were 194.08 and 52.25 mg/g as Gallic acid respectively.

HPLC results indicated that some major phenolic compounds were fractionated and identified namely Catechien, Caffien and some phenolic acids such as Ferrulic, P-Coumiric, Caffeic , Vanillic , Chlorogenic, Salsylic and Synergic acids.

Free Fatty Acid FFA% , peroxide value (PV) , P.Ansidine (p-A.V., Thiobarbituric acid (TBA), Iodine(IV) Values and Totox Number (TN) were determined. The statistical analysis of indicated a significant differences between untreated and treated palm oil during frying process up to 12 hours.

Results of chemical changes revealed that palm oil treated with thyme and marjoram were more stable than the other oil samples treated with fennel during deep fat frying at 180° C for 12 hours.

Also, significant changes in different chemical parameters were observed between control palm oil and treated oil with different phenolic extracts at the concentrates of 200 and 300 ppm during frying process.

So, Addition of Thyme and Marjoram phenolic extracts to palm oil improved the thermal stability and could extended the frying time in compare with Fennel phenolic extract.

Key words: Phenolic extracts and compounds, natural antioxidants from herbs & spices, frying process.

INTRODUCTION

Antioxidant is a substance that delays oxidation by inhibiting initial free radical formation or by preventing them from producing more free radicals which can perpetuate the reaction (Fasseas *et al.,* 2008). Antioxidants can bind metals, scavenge species that initiate or perpetuate oxidation, quench high-energy oxygen species-preventing formation of peroxides, or decompose lipid peroxides. They can improve both color and flavor stability in oils and fats . Since the addition of synthetic antioxidants to foods is very limited for legislative reasons. Natural antioxidants derived from plants, especially phenols, have become of considerable interest from the viewpoint of dietary antioxidant supplementation and food preservation. Many plants and herbs are considered to be excellent and rich sources of phenolic and terpenic compounds (Ramatho and Neuza, 2008).

Polyphenolic compounds are commonly found in edible oil and in edible plants and they have reported to have multiple biological effects, including antioxidants activity (Moure *et al.,* 2001).

Recently interest has considerably increased in finding naturally occurring antioxidants to use in foods which are being restricted due to the carcinogenicity effect

The plant kingdom offers a wide range of natural antioxidants. However, little known about the practical of most of them. Many herbal and plant in fusions frequently used in domestic medicine have antioxidative and pharmacological properties connected with the presence of phenolic compounds, especially flavonoids. Flavonoids very easily take part in oxidation-reduction processes, both inside and outside cells (Vinson *et al.,* 1995).

Herbs and spice and their extracts have been investigated for their antioxidants properties for at least 50 years. Crude extracts are rich in phenolics and have great interest in food industry because they retard oxidative deterioration of lipids .
(Ramadan and El-Gammal, 2010).

The presence of antioxidants is one of the fastest ways to reduce fat oxidation, although in their majority antioxidants present little stability when exposed to high temperature (Karpinska *et al*., 2001).

Deep fat frying may be defined as the process of cooking foods by immersing them in an edible oil for 150-180°C. During frying process oils and fats exposed to heat , air and moisture. These factors contribute to diminishing oil quality and changing the triglycerides structure. (Yamsaengsung and Moeria, 2002).

Within the spice thyme, fennel and marjoram are presented to be highest antioxidant ability , because of their natural compounds namely phenolics, these compounds delaying the deterioration of oil during frying as well as terpenes and have strong antioxidants characteristics during thermal treatments (Ramatho and Neuza, 2008).

This work aimed to evaluate and compare the phenolic compounds extracts from natural herbs and spices in retarding oxidation in palm oil during frying process at 180°C for 12 hours and to confirm that phenolic constitutes are responsible for antioxidants activity in edible oils.

MATERIALS AND METHODS

Materials:

Palm oil was directly purchased from Misr Oil and Soap Company, EL- Mansoura, Egypt.

Potato variety ***spunta,*** which used for frying experiment were obtained from Agricultural Research Center – Giza- Egypt.

Herbs and spices (Thyme, Fennel and Marjoram) were purchased from local market-Cairo- Egypt

Solvents, other reagents and dark glass bottles were purchased from El-Gomhoria for chemicals Company, Mansoura, Egypt.

Methods:

Extraction method: All herbs and spices firstly were dried at 45-50°C for an hour using air drying oven (Officine Specializzate, GARBUIO, Essiccatioi, TREVISO, ITALY). Then, it was extracted using a method of maceration with methanol (500 g dried leaves or seeds / 500 ml solvent) for 12 hours. After maceration, the extracts were collected, filtered and evaporated with vacuum rotary evaporator (BÜCH, RE 111, SWIZERLAND). The evaporated extracts were collected in dark glass bottles and stored at 3-5°C until using (Wojdylo *et al* ., 2007).

The preparation of potato chips: Fresh potato to be fried were manually peeled and sliced around 1.5 mm thickness , then slices soaked in 1.5% NaCl solution for 10 min. , filtered and dried using paper napkins before frying (Rossi *et al.,* 2007). All natural antioxidants extracts were added separately to palm oil before frying, at the beginning of the experiment the

concentrations of 200 and 300 ppm of different phenolic extracts were added.

Frying process :

2.500 kilogram peeled potato chips and Four liters of palm oil heated up to 180°C in domestic deep fryer (Moulinex) calibrated from 120°C to 200°C . Frying was started in 10 min. After the temperature reached 180°C , 100 gm of fresh potato chips were fried for 7 min. then stopped after that the temperature was allowed to return again to 180°C during 15 min . The process repeated twice per hour again , about 100 ml of treated Oil samples were taken for analysis each 0,3,6,9 and 12 hours. The treated and untreated oil samples stored at room temperature over night prior to analysis .(**Rossi *et al.*, 2007).**

Determination and identification of phenolic compounds :

Extraction of phenolic compounds of all herbs and spices extracts were carried out according to the method described by (Wojdylo *et al.*, 2007).

Total phenolic compounds of all extracts were determined according to the method described by Waskmundzka *et al*.(2007). At Food Technology Research Institute , Giza, Egypt . Phenolic compounds were calculated as mg gallic acid /100g of dry weight material.

Phenolic compounds of herbs and spices as methanolic extract were identified using high performance liquid chromatography (HPLC), "HP1050" At Food Technology Research Institute , Giza, Egypt .

Acid (AV), Peroxide (PV) and Iodine(IV) values were determined as described in A.O.A.C. (2000).

Oxidation rate was followed by the determination of *P*-Anisidine Value (*p*-A. V.) according to the method in AOAC (1999). The *p*-Anisidine value (*p*-A.V.) was calculated using the formula:

$$p\text{-A.V.} = 25x\ (1.2As\text{-}Ab)\ /mg$$

The absorbance was then measured at 350 nm.

Using Spectro UV-Vis Auto, (labomed, Inc. U.S.A).

Where, As = Absorbance of the fat solution after reaction with the *p*- Ansidine reagent, Ab = Absorbance of the oil solution, mg = Weight of the oil sample.

Thiobarbituric acid value (TBA) was determined according to Pearson (1986), which was expressed as mg malonaldehyde/ kg oil with the following equation:

$$TBA=7.8 \times O.D.$$

TOTOX number calculated by 2PV+ *p*-AV, according to the method described by (Shahidi and Wasundara, 2002).

Statistical analysis: The statistical analysis program was used to analyze data of variance (ANOVA), standard deviation was done using SPSS 17 program for windows (SPSS, 2007).

RESULTS AND DISCUSSIONS

Total phenolic content (TPC) in fennel, thyme and marjoram extracts:

Data in Table (1) showed the phenolic compounds content(TPC) in. methanolic extraction which more frequently used for isolation of antioxidants (phenolic compounds) and extraction yield was effective in the fractionation of active compounds as regarded in the mentioned figure. Methanolic extracts in Table (1) were always greater in total Polyphenolic compounds as gallic acid. Data indicated that, the total phenolic compounds of thyme extract represented 265.96 mg/g. Gallic acid followed by marjoram extract exhibited 194.08 mg/g as gallic acid and fennel extract exhibited the lowest amount of phenolic content, which was 59.5 mg/g gallic acid. Theses data were in accordance with (Moure *et al*., 2001) who found that phenolic compound have high total and active constitutes, these compounds resulted in the superiority, quenching and retarded oxidation of fatty products which herbs and spices where added.

Also, it could be noted that the variations in total phenolic content could be attributed to the specific nature of the plant type. Kim *et al.* (1994) who reported that the antioxidant activity of extracts produced from herbs and spices was dependent on the type of herbs than the solvent used These results were not doubtful because phenolic compounds in plant foods are largely influenced by genetic factors and environmental conditions. The difference in phenolic content could affect the antioxidant capacity of plants, because many phenolic compounds in plants are good sources of natural antioxidants (Juliani and Simon, 2002).

Table 1. Total phenolic Content (TPC) in herbs and spices extracts as mg/g gallic acid **.**

Total Phenolic Extract	Mg/g as Gallic acid
Thyme extract (TE)	265.96
Marjoram extract (ME)	194.08
Fennel extract (FE)	59.25

Fractionation and identification of phenolic compounds:

The methanolic extracts of herbs and spices namely thyme, fennel and marjoram as a source of natural antioxidants were subjected to HPLC for analysis.

Table 2 showed different phenolic compounds of each extract. The obtained results revealed that phenolic acids were the most abundant compounds in all examined extracts.

Thyme *(Thymus. vulgairs*) was rich in phenols these compounds which have high antioxidants capacity. Catechien has been identified as a major components which represents an important contribution especially in the taste of thyme , the action mechanisms of Catechien as anti carcinogenic agent could be attributed to its antioxidants property as a scavenger of the reactive oxygen species (Zeyada *et al.,* 2007).

Ferrullic acid have been identified with the amount of 49.19 mg/g from thyme extract and reported to be potent antioxidants inhibiting the photo peroxidation of linolenic acid (Zheng and Wang, 2001).

Other phenolic compounds were also detected namely P-coumric and Caffeic acid these separated compounds are nearly similar to those obtained with (Muira and Nakatani 1989), who found same flavonoids and biphenols dimmers in thyme .

Fennel (*Foeniculum vulgare*) is not widely used as natural antioxidants source of food flavouring but also had antioxidants properties The HPLC analysis of fennel extract showed a large number of flavonoids and phenolic acids (Table 2).

Salsylic Acid 9.29 mg/g and Ferrullic acid 2.75 mg/g where the most abundant phenolic constitutes in fennel extract. Catechien was presented with 3.36 mg/g. These data were in accordance with those given by (Yansihtevia *et al.,* 2006; Weinberg *et al.,* 1999 and Marinova and Yansihtevia, 1996).

Regarding to the same Figure, it could be noticed that Caffeic , Chlorogenic, salicylic and Vanillic have the lowest level of phenolic compounds followed by Cinnamic which recorded the least concentrate in compare with the major extracted phenolic matters.

Marjoram **(***Origanum majorana)* is natural antioxidants use for spicing and marenading in some areas. Data in Table (2) showed that Catechien was the predominant phenolic compounds with 27.14 mg/g which have polyphenols constituent and major peroxyl-radical-scavenging compound namely pigallocatechin-3-gallate (Lien *et al.,* 2008), followed by Salsylic acid 20.94 mg/g. Also, the amount of chlorgenic and benzoic acid

Table 2. Identification of some phenolic compounds in herbs and spices extracts as mg/gm**.**

Phenolic / Extract / Phenolic Compounds	Thyme Extract (TE)	Marjoram Extract (ME)	Fennel Extract (FE)
Catechien	94.75	27.14	3.36
Chlorogenic acid	22.16	4.97	0.66
Caffien	---------	----	0.45
P-OH Benzoic	20.80	4.65	1.34
Ferrulic	49.19	----	2.75
Caffeic Acid	14.12	2.21	0.98
Vanillic Acid	9.22	1.77	0.36
Synergic Acid	11.18	----	0.88
Salysilic Acid	----	20.94	9.29
P- coumaric Acid	47.51	----	----
Cinnamic Acid	8.13	-----	0.22

seemed to be equal. Only trace amounts of the phenolic acids were detected.

Some phenolic compounds were disappeared namely synergic, P-coumaric and cinnamic, however there were lower amount of phenolic acids chlorogenic, caffeic and vanillic acids, which were 4.97, 2.21 and 1.77 mg/g, respectively.

Changes in free fatty acids (FFA, %) of treated palm oil during frying process:

The amount of free fatty acids in fats and oils used to indicate the hydrolysis of fatty acids to glycerides. During frying process, the oil is continuously used to elevated temperature from 160 to 180°C. Data in Table (3) and Figure (1a) showed that the initial fatty acids % in untreated palm oil were 0.036, 0.19, 0.45, 1.71 and 3.38 %, respectively up to 12 hours of frying.

Also, the FFA (%) in all treated palm oil with different antioxidants extracts were increased gradually from zero time to 12 hours of frying, the statistical analysis of FFA content indicated a significant differences between treated palm oil during frying process. However there were no significant differences were observed in palm oil treated with thyme extract (TE) at the concentrate of 300 ppm and 200 ppm, followed by the treated palm oil with marjoram extract (ME). While, the treated palm oil with Fennel extract (FE) exhibited the highest amount of FFA% during frying process at 180°C, Data were in accordance with (Benmira *et al.,* 2007) who found that sunflower oil treated with lavender and thyme extract exhibited relatively reduced FFA and PV. Moreover, statistical analysis of obtained

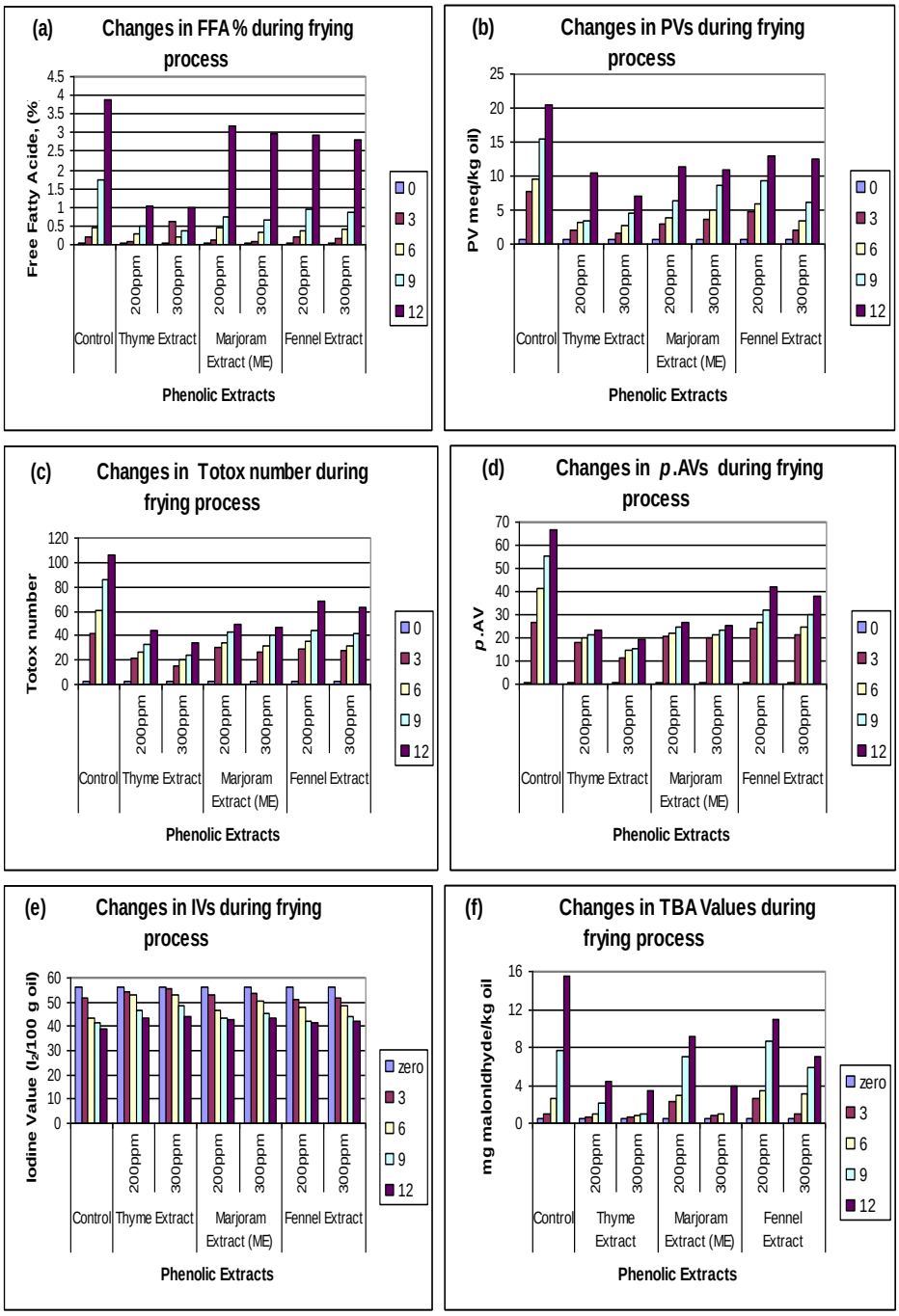

Figure 1(a, b….f). Chemical changes in palm oil during frying process at 180°C for 12 hours.

results proved that there are there a significant difference between untreated and treated oil samples during frying process at 180 °C.

However, FFA (%) of all untreated palm oil samples were more than those treated palm oil with different extracts at the concentrates of 300 and 200_ppm, the increase of FFA(%) content could be caused by increase the rate of hydrolysis of fatty acids to triglycerides or cleavage and oxidation of fatty acid double bonds.

On the other hand, FFA (%) thyme extract (TE) treated samples were in ascending order via frying time in compare with the other extracts, where it reached the maximum value at the end of frying for most samples.

So, it could be concluded that, there was no clear effect on FFA% content of all treated palm oil samples this could be attributed to natural antioxidants.

Changes in peroxide and *P*- Ansidine values during frying process :

Peroxide formation is a major concern from the point of view of rancidity and toxicology. The free radicals involved in their formation and propagation of malonaldhydes.

Data in Table (3) and Figure (1b) showed that during frying, the peroxide value of the treated palm oil tended to increase up to 9 hours and then slightly decreased.

Significant differences were observed between PV of treated palm oil samples with antioxidants and PV of untreated oil samples during frying process at 180°C. However, PV of treated palm oil with thyme extract (TE), marjoram extract (ME) at different concentrates were almost nearly from each other PVs for both of TE and ME reached to 6.97, 10.54, 12.54 and 11.33 meq o_2/kg oil after 12 hours of frying at 180° C.

The increasing of PVs in untreated palm oil reached, the maximum permitted limit and consequently losing the classification of palm oil while all treated palm oil showed a peroxide values below the maximum permitted for their classification in each category (20 meq O_2 / kg oil) (Malhenio *et al.,* 2009).

This could be due to when the oil was heated, an oxidative reaction occurred producing hydroperoxides, which is a volatile decomposition product (VDP), and the decomposition of hydroperoxides formed aldhydes, ketones, lipoperoxides and free radicals afterward. Since the peroxide value was used to determine the peroxide linkage of the reaction, in which decomposition resulted in a lower peroxide value. Similar results were reported by Che Man and Tan (1999).

During the frying process, the formation of secondary oxidation products especially after 6 hours of frying, that could be measured by the P-Ansidine value which increased after the first 3 hours of frying, the P- Av

sharply increased in untreated palm oil samples from 0.960 to 66.940 respectively from zero time to 12 hours (Table 3 and Figure d) this increase could be due to the temperature is a major factor influencing antioxidants activity during storage. This factor affected on different phenolic compounds for different extract concentrations. while the palm oil treated with TE and ME exhibited slight increase in compare with those treated with FE . these results almost in agree with Che Man and Jaswir (2000) who found that the addition of herbs extracts in palm oil decreasing the peroxides and P. Av during frying for 6 days. The Ansidine value is a good indicator of the freshness of an oil . for the fresh refined oils, the *P*-Ansidine value should be less than 10 .Yansihtevia *et al* ., (2006).

Also, Fassea *et al*.(2008) stated that frying process increase autooxidation then proceeds via traditional pathways. The reaction propagates from one fatty acid to another ultimately forming lipid hydroperoxides. Lipid hydroperoxides are tasteless and odorless; however, they decompose to products that are responsible for oxidation.

A purified component isolated from marjoram, which is likely a phenolic substance, is a better superoxide anion radical scavenger than BHT, BHA, alpha-tocopherol, and a variety of polyphenolic flavonoids (epigallocatechin gallate, quercetin, epicatechin; (Jun *et al.*, 2001). The inhibitory mechanism appears to depend on the action of an endogenous enzyme (superoxide dismutase) which destroys the superoxide anion by converting it to H_2O_2 ,this proposes that it is a phenolic substance

The ability of these compounds to protect fat from oxidation appeared to depend not only on their chelating and free-radical scavenging activities, but also on the stability of their free radical forms.

Statistical analysis of peroxide value data, showed a significant differences between all palm oil treatments during frying process.

Changes in total oxidation number (Totox number) during frying process

Results in Table (3) and Figure (1c) showed a significant changes in untreated palm oil samples The values of Totox number were found to be low in palm oil treated natural antioxidants extracts and could be arranged ascending as follows TE>ME>FE at the concentrates of 300 and 200 ppm during frying process at 180°C .Treated oil with thyme extract (TE) is more effective than the other extracts in retarding oxidation.

The highest Totox number was observed in treated palm oil with Fennel Extract at the concentrates of 200 and 300 ppm, this may be due to this extract have the lowest amount of total phenolic compounds in compare with the other two extracts.

These obtained results are confirmed with the results of PV, P.Av and TBA values. That showed the oil treated with Fennel extract was more susceptible to protect oil from oxidation at high temperature.

Changes in iodine value (IV) during frying process:

Iodine value indicates the degree of unsaturation of oils, a decrease of IV could be attributed to the destruction of double bonds by oxidation and polymerization .Changes in IV, are shown in Table (3) and Figure (1e) which decreased significantly at ($P < 0.01$) in untreated palm oil from 56.1 to 39.01 I_2/100 g from zero time to 12 hours in frying process . The results of IV showed slight deterioration between treated palm oil with different natural antioxidants. Mean while during frying process the palm oil treated with thyme extract decreased also, the IV were 56.1 to 44.1 ;56.1 to 43.5 I_2/100 g at the concentrations of 300 and 200 ppm also, the same trend was observed with marjoram extract. While, for the sample with fennel treatment, the decrease in IV was higher than those of oil treated with thyme and marjoram extracts the decrease of IV still faster up to 12 hour of frying.

The decline of Iodine value are indicative of increased rate of oxidation during frying and could be attributed to oxidation and polymerization reactions involving the double bonds, whether through chain reactions adjacent to the double bond to form volatile degradation products, or through direct interaction across the bond to form 1,2-diol (Alireza *et al.*, 2010).

Changes in thibarbituric acid (TBA) values during frying process :

Data in Table (3) and Figure (1f) illustrated the effect of adding phenolic leave extracts with different concentrates on thiobarbituric acid (TBA) values in palm oil during frying process.

TBA values of untreated palm oil ranged from 0.520 to 15.47 mg malonaldehyde/ kg oil**.** Although, TBA values of all treated oil samples were below 15 .47 malonaldehyde/ kg oil .

So, addition of antioxidants extracts leaded to decrease in TBA values in compare with control oil during frying process.

From the same results, TBA values of palm oil treated with thyme and marjoram extracts showed lower values than that of oil treated with fennel extracts after 6 hours of frying at 180°C. However, the highest antioxidant effect was clearly observed in 200 and 300 ppm for both treatments with TE and ME during frying time where TBA value reached 3.350 and 4.44 ; 3.95 and 9.08 mg malonaldehyde / kg oil, respectively.

Table 3. Chemical changes in palm oil during frying process at 180°C for 12 hours

Charact...	T.(hrs)		Thyme Extract(TE)		Marjoram Extract (ME)		Fennel Extract(FE)	
		Control	200ppm	300ppm	200ppm	300ppm	200ppm	300ppm
Free Fatty Acid Content (%	Zero	0.036± 0.008	0.036± 0.008	0.036± 0.008	0.036 ± 0.008	0.036± 0.008	0.036± 0.008	0.036± 0.008
	3	0.190± 0.005	0.073** ± 0.003	0.600** ± 0.005	0.136** ± 0.008	.093** ± 0.003	0.203** ± 0.006	0.176** ± 0.008
	6	0.453± 0.020	0.276** ± 0.008	0.220** ± 0.005	0.440** ± 0.005	0.340** ± 0.011	0.380** ± 0.005	0.400** ± 0.005
	9	1.716± 0.042	0.493** ± 0.008	0.366** ± 0.028	0.746** ± 0.176	0.640** ± 0.015	0.940** ± 0.015	0.870** ± 0.020
	12	3.883± 0.049	1.016** ± 0.008	1.010** ± 0.005	3.176** ± 0.014	2.966** ± 0.028	2.95** ± 0.027	2.823** ± 0.027
PV meq/kg oil	Zero	0.723± 0.01	0.723± 0.01	0.723± 0.01	0.723± 0.01	0.723± 0.01	0.723± 0.01	0.723± 0.01
	3	7.75± 0.12	2.12** ± 0.009	1.66** ± 0.028	2.96** ± 0.015	3.74** ± 0.020	4.86** ± 0.032	2.15** ± 0.011
	6	9.51± 0.03	3.13** ± 0.015	2.64** ± 0.018	3.95** ± 0.014	4.91** ± 0.014	5.93** ± 0.009	3.32** ± 0.045
	9	15.47± 0.02	3.35** ± 0.02	4.44** ± 0.03	6.37** ± 0.343.	8.59** ± 0.040	9.28** ± 0.011	6.08** ± 0.011
	12	20.51± 0.08	10.54** ± 0.023	6.97** ± 0.011	11.33** ± 0.012	10.99** ± 0.009	12.997** ± 0.57	12.54** ± 0.021
Totox number	Zero	2.406± 0.39	2.406± 0.39	2.406± 0.39	2.406± 0.39	2.406± 0.39	2.406± 0.39	2.406± 0.39
	3	41.866± 1.089	21.95** ± -0.37	14.553** ± 0.351	30.136** ± 0.239	26.980** ± 1.66	29.590** ± .015	27.220** ± 0.208
	6	60.300± 0.419	26.33** ± 0.310	20.476** ±. 043	33.833** ± 0.57	31.120** ± 0.08	34.913** ± 0.14	31.213** ± 0.0116
	9	86.516± 0.075	32.340** ± 0.058	24.280** ± 0.393	43.150** ± 0.480	40.810** ± 0.32	44.743** ± 1.62	42.066±** 0.033
	12	105.966± 0.124	44.10** ± 0.112	33.506** ± 0.143	49.263** ± 0.23	47.316** ± 0.34	68.140** ± 0.14	62.980** ± 1.173
p.AV	Zero	0.960± 0.152	0.960± 0.152	0.960± 0.152	0.960± 0.152	0.960± 0.152	0.960± 0.152	0.960± 0.152
	3	26.373± 0.087	17.726** ± 0.639	11.240** ± 0.387	20.503** ±. 204	19.740** ± 0.02	23.670** ± 0.036	21.033** ± 0.033
	6	41.266± 0.363	20.046** ± 0.341	14.583** ± .008	21.980** ± 0.04	21.660** ± 0.373	27.00** ± 0.015	24.573** ± 0.043
	9	55.583± 0.800	21.646** ± 0.021	15.580** ± 0.215	24.59** ± 0.460	23.596** ± 0.348	32.010** ± 1.58	29.906** ± 0.040
	12	66.940± 0.525	23.266** ± 0.323	19.566** ±. 120	26.603** ±. 233	25.330** ± 0.330	42.146** ± 0.026	37.900** ± 1.137

T.(hrs) : Time / hours

Each value is the mean of three replicates ± SD

** Means with a column are significantly different with control (P.< 0.01)

Table(3) .(Continued) **Chemical changes in palm oil during frying process at 180°C for 12 hours**.

Characteristics	T. / hrs	Control	Thyme Extract (TE)		Marjoram Extract (ME)		Fennel Extract (FE)	
			200ppm	300ppm	200ppm	300ppm	200ppm	300ppm
Iodine Value (gI_2/100 g oil)	Zero	56.1± 0.28	56.1± 0.28	56.1± 0.28	56.1± 0.28	56.1± 0.28	56.1± 0.28	56.1± 0.28
	3	51.5± 0.55	54.2** ± 0.48	55.30** ± 0.33	52.8** ± 0.69	53.7** ± 0.41	50.81** ± 0.48	51.70** ± 0.44
	6	43.34± 0.50	52.8** ± 0.069	52.81** ± 0.54	46.71** ± 0.77	50.21** ± 0.40	47.60** ± 0.55	48.7** ± 0.56
	9	41.80± 0.62	46.71** ± 0.77	48.8** ± 0.73	43.42** ± 0. 62	45.21** ± 0.48	42.41** ± 0.51	44.01** ± 0.66
	12	39.01± 0.52	43.42** ± 0.62	44.3** ± 0. 63	42.71** ± 0.65	43.41** ± 0.62	41.2** ± 0.56	41.90** ± 0.55
Thiobarbituric Acid Value Mg malomldhyde/kg oil	Zero	0.520± 0.020	0.520± 0.020	0.520± 0.020	0.520± 0.020	0.520± 0.020	0.520± 0.020	0.520 ± 0.020
	3	0.91± 0.06	0.723** ± 0.01	0.723** ± 0.01	2.33** ± 0.009	0.870** ± 0.020	2.69** ± 0.015	1.01** ± 0.005
	6	2.65± 0.02	0.940** ± 0.015	0.746** ± 0.176	2.96** ± 0.015	1.016** ± 0.008	3.47** ± 0.014	3.13** ± 0.015
	9	7.74± 0.27	2.15** ± 0.011	1.010** ±0.005	4.97** ± 0.011	2..99** ± 0.02	8.59** ± 0.040	5.93** ± 0.009
	12	15.47± 0.42	4.44** ± 0.03	3.35** ± 0.02	5.08** ± 0.011	3.95** ± 0.014	10.99** ± 0.009	6.97** ± 0.11

T. / hrs : Iime / hours

Each value is the mean of three replicates ± SD

** Means with a column are significantly different with control ($P < 0.01$)

Phenolic compounds are also related to inhibiting the activity of conjugated rings and hydroxyl groups and (Decker, 1995). Generally, addition of 200 and 300 ppm antioxidants extracts from thyme (TE) and marjoram (ME) extracts improved the stability of palm oil and had a special effect in preventing oxidation steps during frying process at 180° C also reducing the TBA values below to 6mg malonldhydes / kg oil that means treated oil in a good state for consumption (Che-Man and Jaswir, 2000).

Data of statistical analysis for TBA value, indicated that there were significant differences between all treated palm oil treated with natural antioxidants and untreated palm oil up to 12 hours of frying.

Changes in TBA values in treated palm oil with thyme and Marjoram extract nearly almost, these extracts inhibit oxidation to a certain extent and reducing the formation of carbonyl compounds namely aldhydes and ketones. Marangoni (2000) found that, antioxidants can quench the initiation and propagation steps of auto- oxidation chain reactions and the

radical scavenging activity of natural extracts, especially the phenolic acids and flavonoids have a protective effect against oil peroxidation.

Conclusively, this study recommended, that the addition of thyme and marjoram phenolic extracts at the concentrate of 200 and 300 ppm could retard effectively the palm oil deterioration during deep fat frying process of potato chips for 12 hours at 180° C.

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تأثير مستخلصات المركبات الفينولية لبعض التوابل والأعشاب علي ثبات زيت النخيل أثناء القلي الغزير

رانيا إبراهيم الجمال* - عفاف هانم محمود رمضان **
* قسم الصناعات الغذائية –كلية الزراعة- جامعة المنصورة- مصر
**قسم الاقتصاد المنزلي- كلية التربية النوعية –جامعة المنصورة- مصر

تم دراسة تاثير استخدام المستخلصات الطبيعية الفينولية لبعض التوابل والأعشاب كالزعتر والبردقوش والشمر كمصادر لمضادات الأكسدة الطبيعية بتركيزات ٢٠٠ و٣٠٠ جزء في المليون علي ثبات زيت النخيل المكرر المبيض المزال الرائحة أثناء عمليات التحمير العميق لشرائح البطاطس علي درجات حرارة ١٨٠° م لمدة ١٢ ساعة .

أثبتت النتائج أن المستخلصات الفينولية الكلية سجلت أعلاها للزعتر (٢٦٥.٩٦ مجم /جم مقدرةكـ Gallic acid) تليها البردقوش و الشمر (١٩٤.٠٩ و ٥٢.٢٥ مجم /جم مقدرةكـ Gallic acid)علي التوالي .

اظهرت نتائج التحليل الكمي والكيفي بـHPLC للمستخلصات الفينولية وجود مركبات **Catechien, caffeine** , بعض الأحماض الفينولية مثل **Ferrulic, P-Coumiric, Caffeic, Vanillic Chlorogenic, Salsylic and Synergic acids**

تم تقدير العديد من الثوابت الكيماوية للزيت شملت النسبة المئوية للأحماض الدهنية الحرة وقدرت كحمض أوليك – رقم البيروكسيد والـ *p*AV وحمض الثيوباربيتيوريك والرقم اليودي ورقم TOTOX .

أظهرت نتائج التحليل الكيماوي أن زيت النخيل المعامل بمستخلصات الزعتر والبردقوش بتركيز ٣٠٠و٢٠٠ جزء في المليون كانت أكثر ثباتا من الزيت المعامل بمستخلص الشمر بنفس التركيزين خلال عملية التحمير علي ١٨٠° م لمدة ١٢ ساعة

أظهرت نتائج التحليل الإحصائي انه توجد فروق معنوية واضحة بين عينات الكونترول والعينات المعاملة بالمستخلصات الفينولية للزعتر والبردقوش والشمر بتركيزات ٢٠٠و ٣٠٠ جزء في المليون لزيت النخيل خلال عملية التحمير تحت ظروف التجربة .

ولذا فان إضافة المستخلصات الفينولية لكلا من الزعتر والبردقوش بالمقارنة بالمستخلص الفينولي للشمر أدت إلي زيادة الثبات الحراري وإطالة زمن التحمير لزيت النخيل .