Menoufia J. Food & Dairy Sci., Vol. 3 February (2018): 1 - 13

POTENTIAL ANTIOXIDATIVE ACTIVITY OF RICE MILLING BY-PRODUCTS

M. A. Salem[(1)] , A. M. Sorour[(2)] and M.A. El-Bana[(2)]

(1) Food Sci. and Tech. Dept., Fac. of Agric. Tanta Univ., Egypt.
(2) Food Tech. Res. Inst., Agric. Res. Center, Giza, Egypt

Received: Oct. 18 , 2017 **Accepted: Nov. 21 , 2017**

ABSTRACT : *This investigation was carried out to study the possibility of extraction of some natural antioxidative phenolic compounds from rice milling by-products (defatted black rice bran, defatted white rice bran, black rice hull and white rice hull). The extracted phenolic compounds were tested as natural antioxidants using cotton seed oil after deep frying (170-180)°C of potato for 25 hours.*

The results indicated that Ethanol gave the highest extract yield of all extracts. Ethanol exhibited the highest extraction ability for phenolic compound (5.31, 4.80, 2.90 and 2.10 mg/g), for Defatted black rice bran, Defatted white rice bran, white rice hull, and black rice hull extracts, respectively and also showed the strongest antioxidant activity of Defatted black rice bran extract activity owing to its high content of phenolic and flavonoids compounds.

Ferulic acid was the major phenolic compounds presented and identified in defatted black rice bran; defatted white rice bran and black rice hull while, Caffeic acid was the major phenolic compounds presented and identified in White rice hull. The highest inhibition ratio IC50 was (0.097) found in TBHQ extract following by Defatted black rice bran, Defatted white rice bran, Black rice hull and White rice hull.

Peroxide value, Thiobarbituric acid (TBA) value and polymer content of cotton seed oil increased by increase of frying time, furthermore, defatted black rice bran ethanolic extract (400 ppm) was more effective as antioxidant than those of the other studied by-products of the rice milling .

Key word: *Rice milling-phenolic-deep frying - Peroxide value*

INTRODUCTION

Lipid oxidation has been identified as the major deterioration process of vegetable oils affecting both the sensory and the nutritional quality of foods. Frying is one of the most common cooking techniques used in domestic and industrial food preparation. Flavour, shelf-life and nutrient composition of fried food and vegetable oils are altered by this process, and also some of the compounds formed may have undesirable consequences on consumers' health (Hosseini *et al*., 2016).

Antioxidant compounds are gaining importance due to their dual role in the food industry as lipid stabilizers and in preventive medicine as suppressors of excessive oxidation that causes cancer and ageing Devi *et al*. (2007)

Synthetic antioxidants such as butylated hydroxy toluene (BHT), butylated hydroxyl anisole (BHA) or tertabutyl hydroquinone (TBHQ) are often used to retard lipid oxidation in food systems. Due to their low thermal stability, the concern about their long term effects on human health and the increasing demand by consumers for natural products, plant extracts emerged as good alternatives to synthetic antioxidants (Sahin *et al.*, 2017).

Studies have shown that cereal grains, especially rice, contain special phenolic acids (such as ferulic acid, p-coumaric and diferulate) that are not present in significant

quantities in fruit and vegetables (Adom and Liu, 2002).

Rice, being one of the most produced and consumed cereals in the world, has an important role in the relation between the diet and health. Several compounds with antioxidant activity have been identified in rice, including phenolic compounds, tocopherols, tocotrienols and ϒ-oryzanol (Iqbal *et al*., 2005). The phenolic compounds are mainly associated with the pericarp in rice, hence, the milling process reduces the concentration of these compounds in the grain. Besides, grains with darker pericarp colour, such as red and black rice, contain higher amounts of polyphenols (Walter and Marchesan,2011). In addition, the concentration of total phenolics in the grain has been positively associated with the antioxidant activity, with potential beneficial effects on health, such as reduction of oxidative stress, aid in the prevention of cancer, in the control of blood lipids and related diseases, which may help in the prevention of cardiovascular problems, and in the prevention of the complications of diabetes (Zhang *et al*., 2006 and Yawadio *et al.*, 2007).

Jeon *et al*. (2006) reported that phenolic compounds, from methanolic extracts of rice hull, exhibit high antioxidant activity against scavengers of singlet oxygen and inhibit high hydrogen peroxide -induced damage to cellular deoxy nucleic acid (DNA) in human lynphocytes. Furthermore, in black rice hull , cyaniding glucoside has been reported to be one of the major antioxidant compounds (Osawa, 1999).

Colored rice are reported as potent sources of antioxidants and encourage ments as viable sources of antioxidants for functional foods (Yawadio, *et al.*, 2007).

The present study was under taken to evaluate the efficiency of the polyphenolic extracts from different rice milling by-products (defatted black and white rice brans, black rice hull and white rice hull) as a new sources of natural antioxidants for inhibiting the rancidity of fried cotton seed oil.

MATERIALS AND METHODS

1.Materials:

White rice hull and bran of Sakha 101 as well, black hull and bran were obtained from the Rice Research and Training Center (RRTC), Sakha, Kafer El-Sheikh, Egypt, Season 2016 and stored at -20°C until further use. Commercial antioxidant; Tetra butyled hydroxyl quinone (TBHQ), 1,1-diphenyl -2 –picrylhydrazyl (DPPH) , Folin-ciocalteau reagents , Thiobarbituric acid (TBA 98%) were purchased from Sigma-Aldrich Co. (St. Louis, Mo., U.S.A.) and cotton seed oil (antioxidant free)were: obtained from Tanta Company for Oils and Soap, Tanta, Egypt, (2016)

2.Methods:

2.1.Samples preparation:

The black rice bran and white rice bran (20g) were soaked in 100 ml n-hexane at room temperature (25±2) °C for 48 hr, then filtrated through Whatman No.1 filter paper. The residues were re-extracted three times using fresh solvent each time to extract most of the oils from the samples.

2.2.Extraction of natural antioxidants from rice by-product:

The prepared ground materials (10 g) of each sample were soaked in 100 ml of each solvent (Ethanol, Ethyl acetate, Acetone and Diethyl ether) overnight in a shaker at room temperature according to Mohdaly *et al* (2010). The extracts were filtrated through Whatman No.1 filter paper. The residues were re-extracted three time under the same conditions. The combined filtrates were evaporated under vacuum in a rotary evaporator below 40ºC. The extracts obtained after evaporation of organic solvents were weighted to determine the extract yield and stored at -20° C until further analysis.

2.3.Determination of total phenolic compounds:-

Total phenolic compounds of the extracts were determined spectrophoto metrically using Folin-ciocalteau reagent according to the method described by Bonoli *et al.* (2004) and used to estimate the phenolics-acid content using a standard curve prepared using tannic acid.

2.4.Determination of total flavonoids:

Total flavonoid was determined by the method of Ordonez *et al.* (2006). and used to estimate the flavonoids content using a standard curve prepared using catechol acid.

2.5.Identification of phenolic compounds by HPLC:

Phenolic compounds of rice by-products samples were extracted according to the method outlined by Evangelisti *et al.,* 1997.

2.6.Evaluation of Antioxidant activity of extracts(AA):

Determination of DPPH· radical scavenging capacity:

The1,1-diphenyl-2-picrylhydrazyl (DPPH) assay (Lee *et al*., 2003) .

IC_{50} values, which correspond to the concentration of rice by-products extracts that caused a 50% neutralization of DPPH•, were calculated from the plot of percent DPPH• scavenging versus concentration.

2.7.Measurement of stability:

The oxidative stability of oils were estimated according to the method described by the Tsaknis *et al*. (1999) by rancimate method using 679 Rancimate (Metrohm, Herisav, Switzerland) at 100^{o}C with air flow rate at 20 L/hr.

2.8.Antioxidative assay of phenolic extracts:

The antioxidative activities of poly phenolic extracts were assayed by addition of each extract at 400 ppm level of its polyphenols content and TBHQ 200 ppm to cotton seeds oil free of antioxidants.

2.8.Frying performance:

Cottonseed oil (3 kg) were heated in a domestic fryer (Model 7122 A, Tefal Super 500 deluxe, France) to 185 $\pm$ 5^{o}C. Potato tubers were first washed with tap water then manually peeled, cut into 5.0 x 0.7 x 0.7 cm pieces using mechanical cutter (type chef, La Minerva, Italy) and submerged in tap water until frying. After draining off excess water, 200 g of them were placed in a wire basket and deep fried in the tested cotton seed oils as follows:

1. Free from antioxidants, heated control.
2. Containing (200 ppm) Tetra butyled hydroxyl quinone (TBHQ).
3. Containing (400 ppm) from ethanolic extracted rice milling by- products .

The frying process was daily repeated for five hours. The heating frying cycle was continued for five days. At the end of each frying period, the oil was filtered through muslin to remove the remaining fried particles, allowed to cool overnight at room temperature. Two hundred ml of the filtered oils were taken and preserved in dark glass bottles with stoppers in a refrigerator until analyzed.

2.8.1.Peroxide value (PV): was determined by potassium iodide method according to Leonard *et al.* (1987).

2.8.2.Thiobarbituric acid (TBA): values were determined according to Sidwell *et al.* (1990). The concentration of malonaldehyde in oil samples were calculated from standard curve. Absorbance was read at 532 nm against distilled water.

2.8.3. Polymer content: were determined according to the method outlined by Wu and Nawer (1986)

2.9.Statistical analysis:

Most of the received data were analyzed statistically using the analysis of variance

and the means were further tested using the least significant difference test (LSD) as outlined by Steell and Torrie (1980).

RESULTS AND DISCUSSION

1.Effect of using different solvents on Total polyphenols content of extracted from rice milling by-products:

Phenolics are antioxidants, and there is a general belief that the phenolics present in plant food contribute to prevent the oxidative damage that is implicated in a range of diseases, including cancer, cardiovascular diseases and aging (Scalbert *et al*., 2005).

The data in Table (1) concluded that ethanol was the best solvent for extracting polyphenols from rice milling by-products. The amounts of ethanolic could be arranged in the following decreasing order extracted polyphenolic compounds by ethanol from defatted black rice bran (5.31 mg/100g), defatted white rice bran (4.80 mg/100g, black rice hull (2.90 mg/100g) and finally white rice hull (2.10 mg/100g). These results are agreement with the results obtained by Butsat and Siriamornpun (2010).; Araba *et al.* (2011) and Pitchaporn, and Sirithon (2016). On the other hand, the data in the same Table showed that, defatted black rice bran contained highest amounts of polyphenolic compounds with all using solvents comparing with other different by-products in the rice milling. These result agreement with Zhang *et al*. (2006) whom reported that black rice contains rich of polyphenolic compound much more white rice.

2.Effect of solvent on extracted total flavonoids from rice milling by-products:

Data in Table (2) showed that, defatted black rice bran extracts had the highest total flavonoids contents, with values ranging from 0.21 to 0.53 mg Catechol equivalent／g followed by defatted white rice bran extracts with values ranging from 0.19 to 0.36 mg Catechol equivalent／g then Black rice hull extracts with values ranging from 0.10 to 0.27 mg Catechol equivalent／g and finally White rice hull extracts with values ranging from 0.08 to 0.19 mg Catechol equivalent／g, depending on the solvent used for extraction. The highest flavonoids contents were observed in ethanolic extracts. These results are in agreement with Goufo *et al.* (2014).

Table (1): Effect of using different solvents on extracted Total polyphenols content from rice milling by-products. (mg Tannic acid/100g of Dry Weigh)

Extraction solvent	Tot Total polyphenols (mg Tannic acid/100g of Dry Weigh)			
	defatted Black rice bran	defatted white Rice bran	Black Rice hull	white rice hull
Ethanol	5.31 [a]	4.8[a]	2.9[a]	2.1[a]
Acetone	4.1[b]	2.4[b]	2.3[b]	1.7[b]
Ethyl acetate	2.7 [c]	2.3[c]	1.3[c]	1.0 [c]
Diethyl ether	2.4 [d]	1.9[d]	1.0[d]	0.8[d]

Each value is an average of three determinations

Values followed by the same letter in columns are not significantly different at P<0.05

Table (2): Effect of solvent on extracted total flavonoids from rice milling by-products.

Extraction solvent	Total flavonoid content(mg Catechol equivalent／g)			
	Defatted black rice bran	Defatted white rice bran	Black rice hull	White rice hull
Ethanol	0.53[a]	0.36[a]	0.27[a]	0.19[a]
Ethyl acetate	o.39[b]	0.26[b]	0.21[b]	0.16[b]
Acetone	0.25[c]	0.20[c]	0.13[c]	0.11[c]
Diethyl ether	0.21[c]	0.19[c]	0.10 c	0.08[c]

Each value is an average of three determinations

Values followed by the same letter in column are not significantly different at P<0.05.

3. Identification of polyphenols compound of rice milling ethanolic extracts.

The aforementioned set of experiments relevant to the antioxidant efficiency of the total polyphenols extracts (defatted black rice bran, defatted white rice bran, black rice hull and white rice hull) and demonstrated that the total polyphenols compounds possessed remarkable antioxidant activity. Therefore, it is quite necessary to characterize the phenolic compounds of total polyphenols extracts. High performance liquid chromatography (HPLC) was used for the qualitative and quantitative determination of total polyphenols. Table (3) indicated that, the most abundant phenolic acids in by- products of the rice milling were Ferulic, p-coumaric, vanillic and Caffeic acids furthermore Ferulic acid was the major phenolic compounds presented and identified in defatted black rice bran; defatted white rice bran and black rice hull while, Caffeic acid was the major phenolic compounds presented and identified in White rice hull .These result agree with Zaupa *et al*. (2015)

On the other hand, our finding that ferulic acid is the major component found in bran rice makes sense if it is linked to arabinoxylan in cell walls of the aleurone layers (McKeehen, *et al.*, 1999*) .*

4. Antioxidant activity (DPPH) of crude rice milling by-product ethanolic extracts.

The free redical scavenging of the ethanolic extracts of crude rice milling by-product were evaluated using the DPPH method and the results showed that antioxidant activity of by-products of the rice milling ethanolic extract in ranged from 100 ppm to 400 ppm (compared with synthetic antioxidant TBHQ). The results cleared that antioxidant activity of TBHQ was higher than all extracts at different level (table4). These findings are in close agreement with previous findings of (Butsat and Siriamornpun ,2010.; Yao *et al*., 2010.and Pitchaporn, and Sirithon (2016). In addition, The DPPH radical scavenging of defatted black rice bran, defatted White rice bran, black rice hull, white rice hull and TBHQ in concentration of 400 ppm were 82.75, 80.3 ,74.4 ,72.9 and 95.2 %. The varied radical scavenging activity of the extracts depended on the amount of total phenolic. Also, the highest inhibition ratio IC_{50} (0.097) was found in TBHQ extract following by defatted black rice bran (0.182) , defatted White rice bran (0.195), black rice hull (0.215) and white rice hull (0.223). This finding supports the data previously reported in a study where the antioxidant activity was dependent on the actual composition of milling fraction (Liyana-Pathirana and Shahidi 2007).

Table (3): Identification of polyphenolic compounds (mg/100g) of defatted black rice bran, defatted white rice bran, black rice hull and white rice hull:

Phenolic compounds contents	by- products of the rice milling			
	defatted black rice bran	defatted white rice bran	black rice hull	white rice hull
Benzoic acid	ND	ND	1.02	22.3
Catechol acid	0	1.38	ND	ND
Chtechin acid	4.01	4.06	ND	1.78
Protocatechuic acid	2.6	ND	ND	ND
Caffien acid	25.5	ND	1.98	44.8
EL lagalic acid	ND	ND	ND	21.3
p-coumaric Acid	37.7	29.5	22.3	4.53
Vanilic acid	11.84	85.5	8.16	13.2
Gallic acid	0	0.43	1.26	1.08
Ferulic acid	121.9	87.4	40.01	29.93
Pyrogallol acid	ND	8.83	ND	8.54
Syringic acid	0.71	ND	ND	ND
Caffeic acid	27.55	16.09	36.5	84.1
Chlorogenic acid	1.54	0.97	4.79	2.27
Salicylic acid	ND	ND	10.3	ND
Chrysin	0.77	ND	ND	ND

ND : not detected

Table (4): Antioxidant activity by (DPPH) assays of crude rice milling by-product ethanolic extracts.

Samples	DPPH Scavenging(%)				$IC_{50\%}$ mg/ml
	100(ppm)	200(ppm)	300(ppm)	400(ppm)	
TBHQ	80.2[a]	86.31[a]	92.8[a]	95.2[a]	0.097
Defatted black rice bran	46.6[b]	63.2 [b]	74.4[b]	82.75[b]	0.182
Defatted white rice bran	42.2[c]	60.01[c]	71.3 [c]	80.3[c]	0.195
Black rice hull	37.4[d]	56.1[d]	68.8[d]	74.4[d]	0.215
White rice hull	35.9[e]	54.5[e]	66.75[e]	72.9[e]	0.223

Each value is an average of three determinations
Values followed by the same letter in columns are not significantly different at P<0.05

5.Effect of polyphenolic extracts on the oxidative stability of cotton seed oil:

The polyphenolic compounds extracted from rice milling by-products were added to cotton seed oil with the concentration of 100, 200 and 400 ppm and 200 ppm of TBHQ. The stability of cotton seed oil was measured at 100C^{o} by rancimat method. It is clear that the addition of ethanolic extracted from rice milling by-products increase the stability of cotton seed oil at all levels. Induction period of cotton seed oil increased to 10.60, 9.40, 8.90, and 8.80 hrs. With 400 ppm of ethanol extracts of defatted black rice bran, defatted white rice bran, black rice hull and white rice hull respectively. While, it was increased to 8.3 hr. by addition of TBHQ at 200 ppm concentration. These compounds are considered to be beneficial to health since, they act as antioxidants in the body by inhibiting lipid peroxidation scavenging, free radical and displaying antimutagenic properties. Similar results were obtained by Delfanian, *et al*. (2016), who discovered that a high polyphenol content was associated with high resistance of oxidation.

The percentage of antioxidant activity (A.A.) was calculated and also presented in Table (5). Hence, it could be noticed that defatted black rice bran extract had the highest antioxidant activity among the investigated extracts followed by defatted white rice bran, black rice hull then white rice hull extract which had the lowest antioxidant activity. The antioxidant activity of the phenolic compounds had been also investigated by Nam *et al.* (2006), who reported that pigmented of rice extracts scavenged superoxide anions more effectively than hydroxyl radical. Furthermore, Pyo *et al.* (2004) found that a positive linear correlation (R = 0.943) was demonstrated between radical scavenging activity and total phenolic content of each extract.

In addition, all rice fractions (except for milled rice) showed the ability to scavenge the DPPH_ radical at a rate higher than TBHQ (0.2 mg/ml) (Liyana-Pathiranaand Shahidi, 2007).

Table (5): Effect of ethanolic extracts on the oxidative stability of cotton seed oil.

Polyphenolic sources	ethanolic concentration					
	100ppm	200 pm	400ppm	100ppm	200ppm	400 pm
	Induction period (hr)			Antioxidant activity(A.A%)*		
Cotton seed oil (control)	4.2			0		
TBHQ		8.3	-	-	98	-
defatted black rice bran	8.1.	9.40	10.60	93	124	152
defatted white rice bran	7.80	8.90	9.40	86	112	124
Black rice hull	7.20	8.40	8.90	71	100	112
black rice hull	7.0	8.20	8.80	67	95	110

$$\text{A.A. \%} = \frac{\text{Induction period of sample - induction period of control}}{\text{Induction period of control}} \times 100$$

6.Effect of using ethanolic extracts from rice milling by-product on chemical properties of cotton seed oil:

6.1.peroxide value (PV):

The data presented in Table (6) illustrate that, PV of cotton seed oil was increased by increasing the frying hours. On the other hand, PV for oils treated by defatted black rice bran, defatted white rice bran, black rice hull, white rice hull phenolic extracts at 400 ppm concentration, TBHQ at 200 ppm concentration and control were increased to 19.40, 19.60, 19.80, 19.90, 19.80 and 26.30 meq/kg oil for 25 hours, respectively. Defatted black rice bran phenolic extract had the highest activity in increasing the thermal oxidation. These results are consistent with findings of Upadhyay *et al*. (2017) Who reported that lipid peroxides were significantly reduced by the addition of antioxidants in Thermal processed oil.

6.2.Thiobarbituric acid (TBA)

There are two stages of oil oxidation, i.e., the first stage is the formation of hydro peroxides and the second one is the decomposition of hydroperoxides to produce secondary oxidation products which could be react with TBA reagent to produce coloured compounds which absorb usually at 530 nm (Orthoefer, *et al.,* 1996).

Thiobarbituric acid (TBA) of fresh and fried cotton seed oil was determined and the results are presented in Table (7). The rates of TBA values were rapidly increased with increasing the frying period of control. Comparing to heated control (8.0 mg malonaldhyde/kg oil) for 25 hours frying, all antioxidant extracts and TBHQ decreased the TBA value to 3.1, 3.4, 3.9, 4.2 and 4.05 mg malonaldhyde /kg oil, when defatted black rice bran, defatted white rice bran, hull black rice, hull white rice at 400 ppm concentration and TBHQ at 200 ppm concentration were used, respectively. Generally, Table (7) also cleared that, defatted black rice bran extract was more effective as antioxidant than those of the other studied by-products and TBHQ. Similar results were obtained by. Devi *et al*. (2007) showed that the defatted rice bran (DRB) extracts were stable at high temperatures and therefore capable of protecting soybean oil against oxidation even at elevated temperatures.

Table (6): Effect of ethanolic extracts from rice milling by-product on peroxide value (PV) during the deep frying of cotton seed oil.

Treatments / Frying time(h)	Control*	TBHQ 200 ppm	ethanolic extracts from rice milling by-product at 400 ppm conc.			
			Defatted black rice bran	Defatted white rice bran	black rice hull	White rice Hull
	Peroxide value (meq/kg oil)					
0	7.0^{Af}	7.0^{Af}	7.0^{Ae}	7.0^{Af}	7.0^{Af}	7.0^{Af}
5	12.5^{Ae}	10.5^{Be}	10.3^{Dd}	10.4^{Ce}	10.3^{De}	10.5^{Be}
10	15.6^{Ad}	11.9^{Cd}	12.6^{Bc}	11.9^{Cd}	12.1^{Bd}	11.9^{Cd}
15	18.4^{Ac}	14.2^{Bc}	13.8^{Cc}	14.0^{Cc}	14.4^{Bc}	14.3^{Bc}
20	19.3^{Ab}	16.9^{Bb}	16.9^{Bb}	16.8^{Cb}	17.1^{Bb}	16.9^{Bb}
25	26.3^{Aa}	19.8^{Ba}	$19.4^{C\ a}$	19.6^{Ba}	19.8^{Ba}	19.9^{Ba}

Each value is an average of three determinations ± standard devasion
in column; means with the same small supercript letters are not significantly different at 0.05%.
in a raw means with the same capital superscript letters are not significantly different at 0.05%
* Free from antioxidants.

Table (7): Effect of ethanolic extracts from rice milling by-product on Thiobarbituric acid (T.B.A) during the deep oil.

Treatments / Frying time (h)	Control*	TBHQ (200 ppm)	ethanolic extracts from rice milling by-product at 400 ppm conc.			
			Defatted black rice bran	Defatted white rice bran	black rice hull	white rice hull
	TBA (mg malonaldhyde/kg oil)					
0	0.71^{Ae}	$0.71A^{de}$	0.71^{Ad}	$0.71^{Ad\ e}$	0.71^{Ade}	0.71^{Ad}
5	1.89^{Ad}	0.61^{Ce}	0.66^{Bd}	0.62^{Ce}	0.60^{Ce}	0.61^{Cd}
10	2.85^{Ac}	0.80^{Cd}	0.75^{Bd}	0.80^{Cd}	0.83^{Cd}	0.75^{Bd}
15	3.9^{Ab}	1.80^{Bc}	1.60^{Cc}	1.75^{Cc}	1.85^{Bc}	1.9^{Bc}
20	7.9^{Aa}	2.92^{Cb}	2.01^{Db}	2.8^{Cb}	3.10^{Bb}	3.3^{Bb}
25	8.0^{Aa}	$4.05^{B\ a}$	3.1^{Ca}	3.4^{Ca}	3.9^{Ba}	$4.2^{B\ a}$

Each value is an average of three determinations ± standard devasion

in column; means with the same small supercript letters are not significantly different at 0.05%.

in a raw means with the same capital superscript letters are not significantly different at 0.05%

TBHQ: tetra butyled hydroxyl quinine

* Free from antioxidants.

6.3. Effect of ethanolic extracts from rice milling by-product on insoluble polymer (%) content during the deep frying of oil.

The result in Table (8) illustrated that, the insoluble polymer content values of oil increased during frying and were strongly correlated with prolonging the frying period. During frying, oils are hydrolysed to form FFA, monoglyceride , diglycerides and these compounds accumulate in the frying oil with repeated use. In addition, oils also oxidized to form hydroperoxide, conjugated dienoic acids, epoxides, hydroxides, aldehydes and ketones. These compounds may undergo fission into smaller fragments or may remain in the triglyceride molecule and cross-link with each other, leading to dimeric and higher polymeric triglycerides (Innawonga *et al* ., 2004).

On the other hand, insoluble polymer content for oil contained ethanolic extracted from by Defatted black rice bran, Defatted white rice bran, Black rice hull, White rice hull at 400 ppm concentration, TBHQ at 200 ppm concenteration and control were increased to 2.38, 2.42, 2.48, 2.52, 2.4 and 3.2 %oil for 25 hours respectively These result agreement with Ali. (2010) and Basuny *et al*. (2013) .

Table (8): Effect of using ethanolic extracts from rice milling by-product on insoluble Polymer content (%) of oil during the deep frying of oil.

Treatment / Frying time(h)	Control*	TBHQ (200ppm)	ethanolic extracts from rice milling by-product (400ppm)			
			Defatted black rice bran	Defatted white rice bran	Black rice hull	White rice hull
0	0.17^{Af}	0.17^{Af}	0.17^{Af}	0.17^{Af}	0.17^{Af}	0.17^{Af}
5	0.82^{Ae}	0.52^{Ce}	0.50^{Ce}	0.57^{Be}	0.59^{Be}	0.6^{Be}
10	1.64^{Ad}	0.98^{Cd}	0.98^{Cd}	1.04^{Bd}	1.14^{Bd}	1.2^{Bd}
15	2.4^{Ac}	1.48^{Dc}	1.45^{Dc}	1.58^{Cc}	1.59^{Cc}	1.68^{Bc}
20	2.85^{Ab}	1.7^{Db}	1.73^{Db}	1.82^{Cb}	1.89^{Cb}	1.96^{Bb}
25	3.2^{Aa}	2.4^{Ca}	2.38^{Ca}	2.42^{Ca}	2.52^{Ba}	2.54^{Ba}

TBHQ: tetra butyled hydroxyl quanine
Each value is an average of three determinations ± standard devasion
in column; means with the same small supercript letters are not significantly different at 0.05%.
in a raw means with the same capital superscript letters are not significantly different at 0.05%
* Free from antioxidants

CONCLUSION

From the previous results, it could be concluded that, the antioxidative activity of Defatted black rice bran ethanolic extracts was greater than those of Defatted white rice bran, Black rice hull and White rice hull. The use of ethanolic extracted from defatted black rice bran, defatted white rice bran, black rice hull and white rice hull could be added at levels of 400 ppm to increase the heat stability of oils

REFERENCES

Adom, K. K. and R. H. Liu (2002). Antioxidant activity of grains. J. Agric. Food Chem. 50:6182-6187.

Ali, R. M. (2010). Improvement the stability of fried sunflower oil by using different levels of Pomposia (Syzyyium cumini). Elec. J. Env., Agric. Food Chem., 9(2): 396–403.

Araba, F., I. Alemzadehb and V. Maghsoudib (2011). Determination of antioxidant component and activity of rice bran extract . Chemistry and Chemical Engineering , 4 : 120 -128 .

Basuny, A.M., M. A. Shaker and M. K. Sahar (2013). Polyphenolic compounds of eggplant peel juice as a natural antioxidant for the stability of sunflower oil during deep-fat frying. Curr. Res. Microbiol Biotechnol., 1(1): 1-8

Bonoli, M., V. Verardo, E. Marconi and M. F. Caboni (2004). Antioxidant phenols in barley (*Hordeum vulgare L.*) flour: comparative spectrophotometric study among extraction methods of free and bound phenolic compounds. Journal of Agricultural and Food Chemistry, 52: 5195-5200.

Butsat, S. and S. Siriamornpun (2010). Antioxidant capacities and phenolic compounds of the husk, bran and endosperm of Thai rice. Food Chem., 119, 606–613.

Delfanian, M., E.R. Kenari and A.M. Sahari (2016). Utilization of Jujube Fruit (*Ziziphusmauritiana Lam.*) Extracts as Natural Antioxidants in Stability of Frying Oil. International Journal of Food Properties, 19:789–801.

Devi, R. R., A. J. Jayalekshmy and C. Arumughan (2007). Antioxidant efficacy

of phytochemical extracts from defatted rice bran in the bulk oil system . Food Chem., 104: 658–664.

Evangelisli, F., P. Zunin, E. Tisconia, R. Petacchi, G. Drava and S. Lanteri (1997). Stability to oxidation of virgin olive oils as related to olive conditions: Study of polar compounds by chemometric methods. J. of Am. Oil. Chem. Soc., 74(8): 10 17-1022.

Goufo, P., J. Pereira, N. Figueiredo, M. B. P. P. Oliveira, C. Carranca and E. A. S. Rosa (2014). Effect of elevated carbon dioxide (CO2) on phenolic acids, flavonoids, tocopherols, tocotrienols, c-oryzanol and antioxidant capacities of rice (Oryza sativa L.). J. Cereal Sci. 59:15–24.

Hosseini, H., M. Ghorbani, N. Meshginfar and A.S. Mahoonak (2016). A Review on frying: procedure, fat, deterioration progress and health hazards. J. of Am .Oil .Chem .Soc., 93, 445–466.

Innawonga, B., P. Mallikarjunana and J. E. Marcyb (2004). The determination of frying oil quality using achemosenory system. Lebensm-Wiss.u-Technol. 37:35-41

Iqbal, S., M. I. Bhanger and F. Anwar (2005). Antioxidant properties and components of somecommercially available varieties of rice bran in Pakistan. *Food Chem.*, 93:265-272.

Jeon, K. I., E. J. Park, H. R. Park, Y. J. Jeon, S. H. Cha and S. C. Lee (2006). Antioxidant activity of far-infrared radiated rice hull extracts on reactive oxygen species scavenging and oxidative DNA damage in human lymphocytes. J. of Medicine and Food , 9: 42–48.

Lee, S.C., J.H. Kim, K.C. Nam and D.U. Ahn (2003). Antioxidant properties of far infrared-treated rice hull extract in irradiated raw and cooked turkey breast. J. Food Sci. 68: 1904-1909

Leonard, W.A., A.E. Woods and M.K. Wells (1987). Food Composition and Analysis.Publ. by Van Nastr and Rinhold Com. New York. pp. 255-258.

Liyana-Pathirana, C.M. and F. Shahidi (2007). Antioxidant and free radical scavenging activities of whole wheat and milling fractions. Food Chem. 101, 1151-1157.

McKeehen, J. D., R. H. Busch and R. G. Fulcher (1999). Evaluation of wheat (Triticum aestivum L.) phenolic acids during grain development and contribution of Fusarium resistance. J. of Agric. and Food Chem ., 47: 1476–1482.

Mohdaly, A., M. A. Sarhan, I. Smetanska and A. Mahmoud (2010). Antioxidant properties of various solvent extracts of potato peels, sugar beet pulp, and sesame cake. J. of the Sci. of Food and Agric., 90: 218-226.

Nam, S. H., S. P. Choi, M. Y. Kang, H. J. Koh, N. Kozukue and M. Griedman (2006). Antioxidative activities of bran extract from twenty one pigmented rice cultivars. Food Chem., 94 : 613–620.

Ordonez, J. D., M. A. Gomez and M. I. Vattuone (2006). Antioxidant activities of *Sechiumedule* (Jacq.) *Swartz extracts*. Food Chem., 97: 452–458.

Orthpoefer, F.T. (1996). Rice Bran Oil: Healthy lipid Source. Food Tech. December: 62-64.

Osawa, T. (1999). Protective role of rice polyphenols in oxidative stress. Anticancer Res., 19: 3645- 3650 (inJapanese).

Pitchaporn, W., K. Niwat and N. S. Sirithon (2016). Bioactive compounds and antioxidant properties of different solvent extracts derived from Thai rice by-products.Appl Biol Chem ., 59(3): 373–384

Pyo, Y., T. LE, L. Logendra and R.T. Rosen (2004). Antioxidant activity and phenolic compounds of Swiss chard (*Beta vulgaris* subspecies cycla) extracts. Food Chem., 85, 19-26.

Sahin, S., M. Bilgin, E. Sayım and B. Suvenilir (2017). Effects of natural antioxidants in the improvement of corn oil quality: olive leaf vs. lemon balm.

International Journal of Food Science and Technology,52, 374–380.

Scalbert, A., I.T. Johnson and M. Saltmarsh (2005). Polyphenols: antioxidants and beyond. Am. J. of Clin.Nutr., 81: 215–217.

Sidwell, C. G., H. Saiwin, M. Benca and J.H. Mitechell (1990). The use of thiobarbituric acid as a measure of fat oxidation. Am. of Oil Chem. Soci., 3(12): 603-606.

Steell, R.G. and J.H. Torrie (1980). Principles and procedures of statistics.2nd Ed. pp 120. McGraw-Hill, New York, USA.

Tsaknis, J., V. Spiliotis, S. Lalas, V. Gergis and V. Dourtoglou (1999). Quality Changes of Moring aoleifera, Variety Mbololo of Kenya Seed Oil During Frying. GrasasYAceites, 50: 37–48

Upadhyay, R., S. Sehwag and Niwas Mishra H. (2017). Chemometric approach to develop frying stable sunflower oil blends stabilized with oleoresin rosemary and ascorbyl palmitate. Food Chem, 218, 496–504.

Walter, M. and E. Marchesan (2011). Phenolic compounds and antioxidant activity of rice.Braz. arch. biol. technol.,.54 (.2) Curitiba Mar./Apr.

Wu, P.F. and W.W. Nawar (1986). A technique for monitoring the quality of used frying oils . J. of the Am. Oil Chem, Soci., 63: 1363-1367

Yao, Y., W. Sang, M. Zhou and R. Ren (2010). Antioxidant and α-glucosidase inhibitory activity of colored grains in China. J. Agric Food Chem., 58(2):770–4.

Yawadio, R., S. Tanimori and N. Morita (2007). Identification of phenolic compounds isolated from pigmented rices and their aldose reductase inhibitory activities. *Food Chem*, 101, 1616-1625.

Zaupa, M., L. Calani, D.D. Rio, F. Brighenti and N. Pellegrini (2015). Characterization of total antioxidant capacity and polyphenolic compounds of differently pigmented rice varieties and their changes during domestic cooking. Food Chem, 187, 338–347.

Zhang, M., B. Guo, R. Zhang, J. Chi, Z. We, Z. Xu, Y. Zhang and X. Tang (2006). Separation, purification and identification of antioxidant compositions in black rice. *AgricSci China*, **5**, 431- 440.

النشاط المضاد للاكسده المحتمل لمخلفات ضرب وتبيض الارز

موسى عبده سالم[1] ، أحمد محمد عبدالرازق سرور[2] ، محمد أحمد البنا[2]

[1] قسم علوم و تكنولوجيا الأغذية كليه الزراعه جامعه طنطا

[2] معهد بحوث و تكنولوجيا الاغذية مركز البحوث الزراعية

الملخص العربى

أجرى هذا البحث بهدف الحصول على بعض المركبات الفينولية المضادة للأكسدة الطبيعية المستخلصة من ضرب وتبييض الأرز مثل رجيع الكون الأسود منزوع الدهن ورجيع الكون الابيض منزوع الدهن وقشور الأرز الأبيض وقشور الأرز الأسود وإمكانية استخدامها كمضادات أكسدة طبيعية بالمقارنة برباعى بوتيل هيدروكس كينون"مضادات الأكسدة الصناعية" بإضافتها إلى زيت بذرة القطن أثناء تحمير البطاطس على فترات بمعدل 5 ساعات يوميا لمدة تصل إلى 25 ساعة.

وقد أظهرت النتائج أن الايثانول كان أفضل مذيب لاستخلاص المواد المضادة للأكسدة حيث كانت الكمية المستخلصة من رجيع الكون الأسود منزوع الدهن ، رجيع الكون الابيض منزوع الدهن ، قشورالأرز الأسود ، قشورالارزالابيض هى: (5.31 - 4.80 - 2.9 –2.1) ملليجرام كل جرام على التوالى وبناءا علية تم استخدام الايثانول لاستخلاص المواد المضادة للاكسدة ا للازمة لاستكمال باقى التجارب.

واظهر النتائج ان المستخلص الايثانولى لرجيع الكون الأسود منزوع الدهن يملك اعلي نسبه نشاط من بين المستخلصات المختلفه .

وبتفريد المركبات الفينولية لمستخلصات المخلفات السابقة الذكر أظهر أنها تحتوى على حامض (الفيريوليك والفاليك والكافييك والبيكوماريك) بالاضافه لذلك نجد ان حامض الفيريوليك هو اهم المركبات الفينولية لرجيع الارز الاسود والابيض منزوع الدهن و قشور الارز الاسود بينما كان حامض الكافييك هو اهم المركبات الفينولية لقشور الارز الابيض.

وكانت اعلى نسبه لتركيز المثبط ل % 50 من الشقوق الحرة هي.0.097 مجم /مل TBHQ يليه مستخلص رجيع الكون الاسود منزوع الدهن ورجيع الكون الابيض منزوع الدهن وقشرة الارز الاسود والابيض على التوالى.

حدث زياده في رقم البيروكسيد واختبار حامض الثيوبابيوتريك واختبار محتوى الزيت من البوليمرات الغير ذائبه فى الزيت المضاف له المستخلصات الفينوليه من رجيع الكون الأسود منزوع الدهن ، رجيع الكون الابيض منزوع الدهن ، قشور الأرز الأسود ، قشور الارز الابيض عند مستوي 400 جزء فى المليون و200 جزء فى المليون من رباعى بوتيل هيدروكس كينون"مضادات الأكسدة الصناعية" بزياده وقت التحمير بالاضافه لذلك نجد ان مستخلص الايثانولى لرجيع الارز الاسود اكثر المستخلصات الفينوليه فاعليه من المستخلصات الايثانوليه لمخلفات ضرب وتبيض الارز عند مستوي 400 جزء فى المليون 200 جزء فى المليون من رباعى بوتيل هيدروكس كينون"مضادات الأكسدة الصناعية".

أسماء السادة المحكمين

أ.د/ علاء الدين السيد البلتاجى كلية الزراعة - جامعة المنوفية

أ.د/ سحر رمضان عبدالهادى كلية الزراعة – جامعة كفر الشيخ