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NATURAL ANTIOXIDANT ACTIVITY OF RICE HULL AND BLACK RICE HULL EXTRACTS ON SUNFLOWER OIL

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ABSTRACT

Hull from rice (RH) and black rice (BRH) were treated by methanol, ethanol and water to extract natural antioxidant. Anti-oxidative activities of RH, BRH extracts as natural antioxidant and butylated hydroxyl-tolunene (BHT) as synthetic antioxidant were determined using a linoleic acid system and measurement at 500nm. Natural and BHT antioxidants exhibited strong and close anti-oxidative activities from 94.29 to 84.29%. The RH, BRH extracts and BHT were add separately to sunflower oil at levels of 0.01 , 0.02 , 0.05 and 0.10 % to keep its quality during heating at 180 ± 5C° for 28hour (4hour/day). Thiobarbituric acid reactive substances (TBARS) and saponification number (SN) were determined in the sunflower oil at the end of heating period. The results showed that the addition of natural antioxidant extracts and BHT at 0.05 and 0.10% inhibited lipid peroxidation and improved its frying quality during heating with respect to the above mentioned properties.

INTRODUCTION

Rice is one of the major cereal crops in Egypt. Rice hull is a major waste co-product of the rice industry comprises 20% of the rice grain. The annual rice production of paddy rice in Egypt amounts to about 6.0million ton. It gives about 1.2million ton rice hull Badawi, (2000). Rice hull is found in over 75 countries where rice is grown and represents, according to variety, 14–35% of the tonnage of harvested rice Bhattacharya *et al.*, (1984). Since the world production of rice is over 350 million tons, resulting in more than 70 million tons of rice hull, it can be realized that this problem is very important. It is disposed of in many countries by burning, which has caused much environmental pollution. Rice hull, an agricultural residue obtained during milling process, has been widely used as a fuel in rice mill and electricity generating power plant Chatveera and Lertwattanaruk (2009). However, rice hulls are wasted or destined to undervalued uses. Currently, agricultural and industrial residues are attractive sources of natural antioxidants Moure *et al.*, (2001). The extraction of antioxidant compounds from residue materials such as hulls, seed coats, peels, grape seeds, olive rape, and cocoa byproduct has been reported Moure *et al.*, (2000). In general, seed coat plays an important role in protecting seeds from oxidative damage because the seed coat possesses large quantities of endogenous antioxidants such as phenolic compounds Moure *et al.*, (2001). Rice hull also contains an antioxidant defense system to protect rice seed from oxidative stress. Ramarathnam *et al.*,(1989) identified isovitexin as a natural component in white rice hull, which showed a strong antioxidant effect.

Another study Asamarai *et al.*, (1996) showed that rice hull contained several kinds of strong antioxidants such as anisole, vanillin, and syringaldehyde. Thus, rice hull is an attractive source of natural antioxidants.

Antioxidants prevent rancidity, improve sensory scores, and provide improved consumer acceptance of food products Salih *et al.,* (1989). Some synthetic antioxidants are suspected as being possible cancer etiologic agents Addis and Hassel (1992). It is expected that these antioxidants will be banned or that food companies may decide not to use synthetic antioxidants like BHA to keep the label more appealing to consumers. Most food companies would prefer natural antioxidants to BHA and are interested in novel, new, natural antioxidants. Therefore, it would be tremendously advantageous to identify potent natural antioxidants. On the other hand, tocopherols are widely used as safe antioxidants, but they are not as effective as the synthetic antioxidants and the manufacturing cost is high Addis and Hassel (1992).

The aim of this investigation was to evaluate the effectiveness of natural antioxidant extracted from rice hull and black rice hull than butylated hydroxyl-toluneene at different levels (0.01, 0.02, 0.05 and 0.10%). The natural and synthetic antioxidants were tested using sunflower oil.

MATERIALS AND METHODS

Materials:

Rice hull dehulled from raw rice (Giza 175) and black rice (October 2008) were obtained from Rice Breeding Section, Field Crops Research Institute, Agricultural Research Center, Egypt.

BHT was obtained from Naarden International Company, Holland. Sunflower oil was obtained from Arma Food Company, El – Asher of Ramadan, Egypt.

Methods:

Extraction of natural antioxidants from RH and BRH :

Air dried RH and BRH (50g of each) were finely powdered and extract with petroleum ether (40-60 C°) to remove fats and resinous materials. The residues were exhaustively extracted separately with 500 ml of methanol, ethanol and water. The extract was filtered through Whatman No. 1 filter paper, and the filtrate was evaporated to dryness under reduced pressure on rotary evaporator (RE 300/MS) at 40 C°.

Determination of antioxidant activity:

Natural antioxidant extracts from RH and BRH were evaluated as antioxidant activity and compared with BHT by thiocyanat method as described by Tsuda *et al.,* (1994).

Addition of natural antioxidants to sunflower oil:

Sunflower oil was used as a substrate for oxidations studies. Natural antioxidant extracted from RH and BRH and synthetic antioxidant effect (BHT) were added to oil at 0.01, 0.02, 0.05 and 0.10% on dry weight basis to test their antioxidant effectiveness according to Buford, (1988). Control sample without additive was prepared under the same conditions.

Sunflower oil with and without antioxidants (natural and synthetic) were heated in 500 ml glass beaker at 180± 5 C° for 28 hour (Total heating hours) intermittent heating period was 4h/day. The oil samples for heating were taken periodically and stored in glass bottles at – 10 C° tell analysis according to Zandi and Gordon (1999).

Physico – chemical characteristics of sunflower oil:

Thiobarbituic acid reactive substances was determined in oil samples after 28 hours (heating period) as described by Ohkawa *et al.,* (1979). The thiobarbituic acid reactive substances values were calibration curve construction using malonaldhyde/ kg sample. Saponification number (SN) was determined in oil samples after the end of heating period as the recommended methods of A.O.A.C. (2000).

Statistical analysis of data:

Mean values of data were obtained from three riplicates determination. Values expressed are mean ±SD. Significance of differences between control and treated samples were evaluated using Duncan's multiple range test at 5% level.

RESULTS AND DISCUSSION

Amounts of natural antioxidant from rice hull and black rice hull :

Table (1): Water, ethanolic and methanolic antioxidant extracts percentage of RH and BRH.

Samples	Water extract	Ethanolic extract	Methanolic extract
RH	0.6051 ± 0.033	0.0122 ± 0.001	0.6614 ± 0.038
BRH	2.5032 ± 0.131	0.6798 ± 0.038	1.4368 ± 0.079

Values are mean ± SD, n = 3

Water, ethanolic and methanolic antioxidant extracts percentage of RH and BRH results are shown in Table (1). The results showed that the, RH ethanolic extract contained lower amount (0.0122%) of antioxidant. BRH aqueous extract (2.5032%) gave a best result than ethanolic and methanolic extracts (0.6798% and 1.4368%). Meanwhile, RH methanolic extract (0.6614%) gave a high amount of antioxidants than water and ethanolic extract (0.6051% and 0.0122%). This means rice hull contained several kinds of strong antioxidants. Thus rice hull is an attractive source of natural antioxidants Asamarai *et al.,* (1996).

Antioxidant activity of rice hull and black rice hull extracts :

Antioxidant activity was determined for extracts prepared from RH and BRH in comparison with BHT as synthetic antioxidant. The results are recorded in Table (2). From the obtained results it could be noticed that activity in the linoleic acid system of control (no additives) represent 100% lipid peroxidation, with absorbance value at 500 nm. This means that antioxidant activity 0.00%. Whereas the synthetic antioxidant, BHT showed 94.29% activity followed by methanol and ethanol extracts from BRH and RH, which showed 92.86%, 91.43%, 90.0% and 88.57% respectively, while, the aqueous extracts in the same samples showed the lowest activity. These data agreed with those reported by Lee *et al.*, (2003) who found that the methanolic extracts of rice hull contained several phenolic compounds such as o-methoxcinnamic acid, 4.7 dihydroxy-benzoic acid and p-coumaic acid, which are known to have antioxidant effects. Thus, rice hull should receive greater attention as economical natural antioxidant source. Moreover, Kyung *et al.*, (2006) evaluated the antioxidative effects of methanol extracts of rice hull against reactive oxygen species and they found that this extracts possess significant antioxidant activity. It also showed metal chelating actives and protective effect against oxidative DNA damage.

Table (2) : Antioxidant activity of rice hull and black rice hull extracts as compared to BHT.

Antioxidants	Absorbance at 500 nm.	Lipid peroxidation	Activity %
No additive	0.7	100	0
RH			
Methanol	0.64	8.57	91.43
Water	0.59	15.71	84.29
Ethanol	0.62	11.43	88.57
BRH			
Ethanol	0.63	10.00	90.00
Water	0.60	14.29	85.71
Methanol	0.65	7.14	92.86
BHT	0.66	5.71	94.29

The effect of different extracts from rice hull and black rice hull on oxidative stability of sunflower oil:

a. Thiobarbituic acid reactive substances (TBARS):

Different concentrations and extracts from RH, BRH and BHT at level 0.01, 0.02, 0.05 and 0.10% were added to sunflower oil. The satiability of all samples were determined by the measuring the changes in TBARS after incubation of heating period. The obtained results are presented in Table (3).

The obtained results indicated that the addition of RH and BRH extracts methanolic at levels 0.05 and 0.10% to sunflower oil after heating period gave approximately the same effect of BHT at concentration of 0.05 and 0.10% for the same conditions. TBARS values for sunflower oil with addition levels of 0.05 and 0.10% for sunflower oil with addition methanol extracts were 0.0076, 0.0086, 0.0076 and 0.0083mg malonaldehyde/ kg and 0.0089, 0.0091, 0.0087 and 0.0090mg malonaldhyde / kg in ethanol extracts from BRH and RH than 0.0076mg malonaldehyde/ kg for sunflower oil with BHT at 0.05 and 0.10%.

The results inducted that the added at 0.05 from methanol and ethanol extracts gave nearly effect of added 0.10%. It could be observed that the antioxidant activity was parallel with the content of these compounds.

Table (3) : Effect of antioxidants and heating temperature on TBARS on sunflower oil

Levels of antioxid-ants	Control at Zero time	Control after 7 days	TBARS mg malonaldehde / kg oil						
			RH			BRH			S.A
			Ethanolic	Methanolic	Water	Ethanolic	Methanolic	Water	BHT
0.01%	0.0076 ±.0004	0.7900 ±.0416	0.2770 ±.0154	0.2010 ±.0112	0.1980 ±.0116	0.2280 ±.0120	0.1690 ±.0094	0.2370 ±.0132	0.2180 ±.0136
0.02%			0.0790 ±.0044	0.0710 ±.0009	0.0730 ±.0041	0.0700 ±.0040	0.0560 ±.0031	0.0960 ±.0060	0.0490 ±.0055
0.05%			0.0091 ±.0008	0.0086 ±.0005	0.0160 ±.0010	0.0089 ±.0005	0.0076 ±.0004	0.0180 ±.0009	0.0076 ±.0011
0.10%			0.0090 ±.0007	0.0083 ±.0005	0.0140 ±.0008	0.0087 ±.0005	0.0076 ±.0004	0.0140 ±.0008	0.0076 ±.0008

Values are mean ± SD, n = 3 **S.A: synthetic antioxidants**

b. Saponification number (SN) :

Saponification number was determined in RH and BRH extracts and compared with BHT at different levels and the results are reported in Table (4). The results showed that no changes in SN to different extracts at different levels relatively RH and BRH, which means that the increased of short acids were very small. These results may be due to RH and BRH are attractive sources of natural antioxidant.

From the obviously results it could be recommended that the RH and BRH contain of height amounts from natural antioxidant. The addition of antioxidant at 0.05 and 0.10% to sunflower oil retarded the peroxidation and improving its frying quality during continuous heating.

Table (4) : Effect of antioxidant extracts and heating temperature on saponification number on sunflower oil.

Levels of antioxid-ants	Control at Zero time	Control after 7 days	Saponification number						
			RH			BRH			S.A
			Ethanolic	Methanolic	Water	Ethanolic	Methanolic	Water	BHT
0.01%	199.89 ±1.1520	204.18 ±1.1343	201.00 ±1.1823	201.11 ±1.1767	200.91 ±1.1720	200.88 ±1.1715	201.13 ±1.1107	201.13 ±1.1107	201.18 ±1.1111
0.02%			200.27 ±1.1056	201.17 ±1.1726	201.15 ±1.1108	201.08 ±1.1109	200.71 ±1.1706	201.00 ±1.1108	201.12 ±1.1727
0.05%			200.99 ±1.1100	200.89 ±1.1099	201.10 ±1.1722	201.01 ±1.2410	201.00 ±1.1722	201.27 ±1.1726	201.16 ±1.1727
0.10%			200.99 ±1.2411	200.79 ±1.1094	200.99 ±1.2411	200.79 ±1.1094	201.18 ±1.2416	201.19 ±1.1727	201.14 ±1.2416

Values are mean ± SD, n = 3 **S.A: synthetic antioxidants**

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نشاط مستخلصات مضادات الأكسدة الطبيعية لقشور الأرز وقشور الأرز الأســود على زيت عباد الشمس

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قشور الأرز وقشور الأرز الأسود تم معاملتها بالميثـانول والأيثـانول والمـاء للحصول على مستخلصات مضادات أكسدة طبيعية. تم تقدير نشاط مستخلصات مـضادات الأكسدة ومقارنتها بمضادات الأكـسدة الـصناعية BHT بيوتيلاتيدهيدروكـسى تولـوين بواسطة حامض اللينوليك. النتائج أوضحت أن مستخلصات مضادات الأكـسدة الطبيعيـة والصناعية ذات نشاط عالي ويتراوح مابين ٨٤,٢٩ إلى ٩٤,٢٩%. أضـيفت مـضادات الأكسدة الطبيعية المستخلصة من قشور الأرز وقشور الأرز الأسود ومـضادات الأكـسدة الصناعية إلى زيت عباد الشمس بنسب ٠,١،٠,٠٥،٠,٠٢،٠,٠١% للحفاظ علـى جـودة الزيت أثناء التسخين على درجة ١٨٠± ٥°م لمدة ٢٨ ساعة (٤ ساعات / يوم) وتم تقـدير قيم TBARS ورقم التصبن في نهاية مدة التسخين. أوضحت النتائج أن إضافة مـضادات الأكسدة الطبيعية والصناعية على نسب٠,١،٠,٠٥% تحدث تثبيط لعملية الأكسدة بالنـسبة لليبيدات كما أنها تعمل على تحسين صفات الزيت عند درجة الحرارة المرتفعة (١٨٠°م).

قام بتحكيم البحث

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