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RICE BRAN OIL AS ANTIFOAMER AND ANTIOXIDANT

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Abstract

Crude rice bran oil, from dehulled rice bran, was dewaxed and used to break and control the foam formation in crude soybean oil during frying. The dewaxed oil was evaluated as an antifoaming agent. It reduced the foam height from 6 cm to 0.7 cm after one hour by adding 10% dewaxed rice bran oil to crude soybean oil, and the foam disappered with increasing the amount of dewaxed rice bran oil. The oxidative stability of sunflower oil was evaluated after adding 10%, 20% and 30% rice bran oil. The induction period was increased by increasing the added rice bran oil and, also the stability was improved because rice bran oil contains high amounts of the natural antioxidants. Also, the effect of the methanolic extracts of rice bran hulls on the stability of sunflower oil was studied. Sunflower oil stability increased from 6 days to 8, 9 and 11 days when 1, 2 and 3% methanolic extracts of rice bran hulls was added, respectively due to its content of phenolic compounds. Characteristics of the oil, the unsaponifiable components (Hydrocarbon and sterols), the fatty acid composition were studied.

INTRODUCTION

Rice bran is produced in Egypt as a by-product of rice milling in large quantities.

Rice bran oil has attracted much attention as a health food because it was found to lower serum cholesterol. It contains oryzanol, tocopherol and sterol which are thought to have biochemical activities (Haumann, 1989 and Yoshitsugu *et al.*, 1994). Fully processed rice bran oil contains a high amount of unsaponifiable components compared to most other vegetable oils. Two groups of components found in the unsaponifiable fraction of rice bran oil have been investigated for possible health benefits. These are the tocotrienol and α-oryzanol. The tocotrienols are members of the vitamin E family, which possess antioxidants activity (Yamaoka *et al.*, 1991) and (Rogers *et al.*, 1993). This oil is usually rich in free fatty acids, which are developed by lipase hydrolysis in the bran directly after milling, and during storage prior to extraction (EL-Zanati and Zaher 1990). The addition of antioxidant to foods is one of the most effective means to retard the oxidation of fats. The addition of antioxidants has become popular as a method of increasing, the shelf life of food products and improving the stability of lipids and the foods containing lipids, thus preventing the loss of sensory and nutritional quality (Duh *et al.*, 1992). Crude rice bran oil usually contains 6-8% waxes in addition to free fatty acids and glycerides. Removal of waxy materials from its blends along with fatty acids was found to improve the efficiency of rice bran oil as a defoamer. So, dewaxing of crude rice bran oil is a recommended step perior to its use as antifoamer (El-Zanati and Zaher 1990), extracts from natural sources that have demonstrated strong antioxidant activity have been reported to be more effective in many instances than some major synthetic antioxidants. Sheabar and Neeman (1988), investigated the purified extracts from olives to obtain an effective antioxidants.

The antioxidant activity of methanolic extracts of peanut hulls (MEPH) has been demonstrated (Duh *et al.*, 1992) and it showed activity equal to BHA (Butylated hydroxy anisole) and stronger than α-tocopherol. However, if an antioxidant such as MEPH is to be used in foods, its effectiveness will depend on various factors such as the pH of the foods, storage temperature and the extent of thermal processing applied to the food. These factors have to be investigated to determine the feasibility of using MEPH as an antioxidant in foods. Therefore, the present work aims at the utilization of rice bran oil as antifoamer during frying, antioxidant and the antioxidative activity of MEPH to evaluate its effects on sunflower oil, and to study the fatty acid composition and unsaponifiable matter components of the oil.

MATERIALS AND METHODS

Materials :

1. Fresh rice bran with hulls was obtained from small mill.
2. Fresh dehulled rice bran was obtained from El-Sharkia Mill company, Zagazig Egypt.
3- Crude Soybean oil was obtained from Food Technology Research Institute-Giza.
4. Refined sunflower oil was obtained from Oil and Soap Company, El-Minia factory.

Methods :

1. Fresh rice bran with hulls and fresh dehulled rice bran were extracted with pure

η -hexane at room temperature, the solvent was evaporated under vaccum using rotary evaporator.

2. Crude rice bran oil (From the dehulled rice bran) was dewaxed by cooling to 17°C followed by centrifugation. The dewaxed oil was added at 10%, 20% and 30% levels to crude soybean oil to evaluate the dewaxed oil as an antifoaming agent during frying.
3. Crude rice bran oil, from the rice bran with hulls, was blended separetly with 10%, 20% and 30% of sunflower oil.

Methanol Extraction of rice bran hulls :

Rice bran hull powder (5g) was extracted with 50 ml methanol overnight at room temperature. The extracts was filtred, and the residue was re-extracted under the same conditions. The combined filtrate was evaporated under vacume below 40°C in a rotary evaporator to a final volume of 5 mL. Then it was added at 1, 2 and 3% levels to sunflower oil.

Analytical methods :

Free fatty acids (as oleic acid percent) peroxide value (as milliequivalent/Kg oil) and the unsaponifiable matter percent were determined according to methods described in the A.O.A.C. (1980).

Preparation and Identification of the fatty acid methyl esters :

The methyl esters of crude rice bran oil were prepared using a mixture of benzene: methanol : concentrated sulfuric acid (10 : 86 : 4) and methylation was carried out for one hour at 80-90°C according to Stahl, (1967). The composition of fatty acids were achieved by Gas liquid chromatography analysis using PYE Unicam model PV 4550 Capillary Gas chromatography fitted with flame ionization detector, the column (1.5 m x 4 mm) packed with diatomite C (100-120 mesh) and coated with 10% polyethylene glycol adipate (PEGA). The column oven temperature was programmed at 8'C/min from 70°C to 190°C then isothermally at this temperature for 20 min and nitrogen flow rate was 30 mL/min. Detector, injection temperatures, hydrogen and air flow rates and chart speed were 300°C, 250°C, 33 mL/min, 330 mL/min and 2 cm/min, respectively. The separated fatty acids were identified and calculated according to an authentic sample of fatty acids chromatographed under the same conditions.

Separation and identification of unsaponifiable matter by G.L.C. :

The unsaponifiable matter were extracted after saponification of the oil at room temperature according to the method outlined by Mordert (1968). The unsaponifiable constituents of the seed lipids were analysed directly using the unicam capillary gas chromatography PV 4550 fitted with flame ionization detector on a coiled glass column (2.8 m x 4 mm) packed with diatomite C (100-120 mesh) and coated with 1%. OV-17 as stationary phase. The oven temperature was programmed at 10°C/min from 70°C to 270°C then isothermally at this temperature for 15 min and the nitrogen flow rate was 30 mL/min. Detector injection temperatures, hydrogen and air flow rates and chart speed were 300oC, 250oC, 33 mL/min, 330 mL/min and 2 cm/min, respectively. The various fractions separated were identified and calculated according to an authentic sample of hydrocarbons and sterols chromatographed under the same conditions.

Measurement of stability :

Oven test:-

The oven test method suggested by Thompson (1966) was adopted for checking the stability of oils. Oil samples (50 gm) were placed in 250 ml beakers covered with watch glasses and incubated at 63°C until rancidity took place.

Rancidity was periodically assessed every 48 hours through determining the peroxide value.

RESULTS AND DISCUSSION

Antifoaming power of dewaxed rice bran oil :

The results presented in table (1) show the power of the dewaxed rice bran oil to break and control the foam formation in crude soybean oil during frying. The foam height could be reduced from 6 cm to 2 cm after half an hour from frying by adding 10% dewaxed rice bran oil to crude soybean oil. Then the foam height levelled off at 0.7 cm after one hour.

Meanwhile the foam height of crude soybeam oil during frying showed a noticeable gradual reduction, with increasing the added amounts of dewaxed rice bran oil to crude soybean oil, as the increase of dewaxed rice bran oil to 20% and to 30% breaks and controls the foam formation resulting from frying crude soybean oil. These results agree with the findings of perry and Chilton (1973), El-Zanati and Zaher (1990).

Table 1. Antifoaming power of dewaxed rice bran oil:

The oil	The foam hight	
	After half an hour	After one hour
1- S.O.	6 cm	6 cm
2- S.O. + 10% r.b.o.	2 cm	0.7 cm
3- S.O. + 20% r.b.o	2 cm	-
4- S.O. + 30% r.b.o.	-	-

Crude soybean oil (S.O.)
Dewaxed rice bran oil (r.b.o)

Stability of blended sunflower oil with rice bran oil by oven test:

Stability of Sunflower oil, as is, or blended with 10%, 20% and 30% rice bran oil were determined at 63°C + 1 and the changes in peroxide value are shown in table (2) and Fig. (1). It is obvious from these results that addition of rice bran oil to sunflower oil improved its stability. The stablity of sunflower oil showed noticeable and gradual increase with increasing the amount of rice bran oil. The induction period increased gradually from 6 to 7, 9 and 10 days for the added 10%, 20%, and 30% of rice bran oil to sunflower oil, respectively. The results show that crude rice bran oil increase the oxidative stability of sunflower oil because rice bran oil contains a high amount of natural antioxidants such as tocopherols as reported by Suk and Kim (1994) who said that crude rice bran oil was the most stable to oxidation and was the most advantageous for storage to avoid oxidation.

Table 2. Induction period at 63°C in days.

Sunflower oil alone	Sunflower oil + 10% rice bran oil	Sunflower oil + 20% rice bran oil	Sunflower oil + 30% rice bran oil
6	7	9	10

Effect of methanolic extracts of rice bran hulls on the stability of sunflower oil :

The antioxidant activity of methanolic extracts of rice bran hulls (MERH) with 1, 2 and 3% added to sunflower oil, the changes in peroxide value (Stability) of sun-

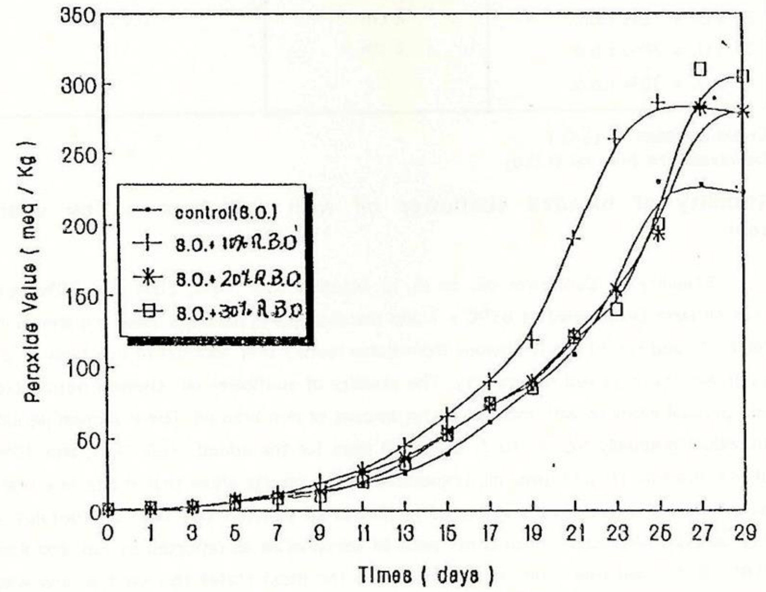

Fig 1. Stability of blended sunflower (S.O.) with rice bran oil (R.B.O.) .

flower oil and sunflower oil with (MERH as an antioxidant were determined and the obtained results are presented in table (3) and graphically illustrated in Fig. (2). It is clear that the addition of methanolic extracts of rice bran hulls at all concentration to sunflower oil increased its stability, from 6 days to 8, 9 and 11 days at 1, 2 and 3% respectively. This may be due to the strong antioxidant activity during oxidation and to the total phenolic compounds. Moreover, the hulls were selected as the best antioxidant material, since they may contain the high amounts of the phenolic compounds. Similar results were mentioned by Gutfinger, (1981) who discovered that a high polyphenal content was associated with high resistance to oxidation. Yen and Duh (1995), reported that total phenolic compounds are closely related to antioxidant activity, and this finding correlates with that reported by Duh, *et al.*, (1992) who said that the antioxidant activity of methanolic extracts of peanut hulls (MERH) has been demonstrated and it showed activity equal to BHA and stronger than α tocopherol.

Table 3. Effect of Methanolic extracts of rice bran hulls on the stability of sunflower oil.

Sunflower oil alone	Sunflower oil + 1% ME	Sunflower oil + 2% ME	Sunflower oil + 3% ME
6	8	9	11

ME : Methanolic extracts of rice bran hulls.

Chemical characteristics of rice bran oil :

The results in table (4) show that the acidity of the oil from rice bran oil with hulls or dehulled were 19 and 16.85 respectively. The bran must be stabilized by heating immediatly after milling to eliminate the formation of the free fatty acid in the bran because rice bran itself contains lipase which can increase the free fatty acids content of the extracted oil. This result is in accordance with the findings of Sevil and Selma (1993).

The peroxide values were 5.46 and 5.42 for the oils from rice bran with hulls and the dehulled respectively, similar results were mentioned by Suk and Kim (1994). Concerning the unsaponifiable matter, the results in the same table show that the rice bran oil contains a high amount of unsaponifiable matter, it were 7.31% and 6.42% for both oils of rice bran, respectively.

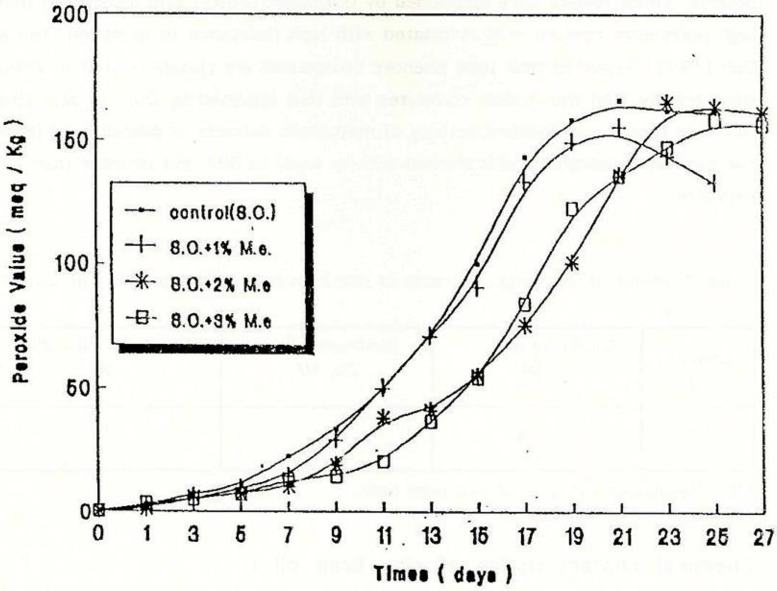

Fig 2. Effect of Methanolic Extracts (M.E.) of Rice bran hulls on the stablity of sun-

Table 4. Chemical characteristics of rice bran oil.

Properties	With hulls	Dehulled
Acidity	19	16.8
Peroxide value	5.46	5.42
Unsaponifiable matter %	7.31	6.42

Unsaponifiable matter components of crude rice bran oil from rice bran with hulls and the dehulled :

The unsaponifiable matter extracted from crude rice bran oil with hulls or dehulled were fractionated by Gas-liquid chromatography against authentic compounds. The obtained results are shown in table (5). From these results it can be noticed that the unsaponifiable matter consisted mainely of two groups, hydrocarbons and sterols. The first group hydrocarbons, represented about 27.84 and 27.38% of the total unsaponifiable matter of both oils respectively. Mean while, the second group of components (i.e. Sterols) represented 72.16 and 72.62% of the total unsaponifiable of both oils respectively. However B-Sitosterol represented the major component of the total sterols. The oil from rice bran with hulls contains C_{30} and C_{32} more than the oils from dehulled rice bran, Similar results were mentioned by Rogers *et al.*, (1993).

Fatty acid composition of rice bran oil from rice bran with hulls and dehulled.

The results in table (6) indicate the fatty acid composition of the oils from rice bran with hulls and dehulled. From these results it can be noticed that the unsaturated fatty acids represented 80.59% and 77.9% of the oils respectively.

Rice bran oil posses a well balanced fatty acid composition which is rich in linoleic acid (an essential fatty acid and is less in Linolenic acid, Smilar values were shown for sunflower oil, Corn oil and Sesame oil (Yesuhko 1986). The same results were reported by Bhattacharyya *et al.*, (1985).

Conclusion :

It may be recommended that dewaxed rice bran oil can be applied to break and control the foam formation, and rice bran oil with hulls as blended with oils to in-

Table 5. Unsaponifiable matter components of crude rice bran oil from rice bran with hulls and dehulled.

Name	Concentration	
	1	2
C_{12}	0.77	0.65
C_{14}	0.55	0.57
C_{16}	1.03	0.99
C_{17}	1.133	1.07
C_{18}	0.52	0.39
C_{19}	0.39	0.56
C_{20}	1.07	1.15
C_{21}	0.96	0.77
C_{22}	1.44	1.633
C_{23}	1.15	1.46
C_{24}	3.8	4.41
C_{26}	2.11	1.74
C_{28}	3.15	3.25
Squalene	1.03	1.12
C_{30}	3.66	3.12
C_{32}	5.08	4.50
CHo	17.04	19.00
Camp	18.15	18.12
Sitgma	10.69	9.50
B.Sito	25.92	26.00
Total hydrocarbons =	27.84	27.38
Total Sterols =	72.16	72.62

1) From rice bran with hulls
2) From dehulled rice bran.

crease their stability. On the other hand the methanolic extracts of rice bran hulls have strong antioxidant activity due to the high content of total phenolic compounds.

Table 6. Fatty acids components of crude rice bran oil from rice bran with hulls and dehulled.

Fatty acid	1	2
$C_{14:0}$	0.11	-
$C_{16:0}$	18.20	19.9
$C_{16:1}$	0.08	0.77
$C_{18:0}$	1.16	2.20
$C_{18:1}$	43.81	42.43
$C_{18:2}$	36.10	34.4
$C_{18:3}$	0.60	0.3
Saturated fatty acid	19.41	22.1
Unsaturated fatty acid	80.59	77.9

1) F.A. Composition of Rice bran oil from rice bran with hulls.
2) F.A. Composition of Rice bran oil from dehulled rice bran.

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زيت رجيع الكون كمثبط للرغوة وكمضاد للأكسدة

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يستخدم زيت رجيع الكون Rice bran المستخلص من الأرز بعد نزع القشرة الخارجية منه – وازالة الشمع منه (dewaxed) – لتثبيط الرغوة المتكونة عند استخدام زيت فول الصويا فى عملية التحمير. حيث يمكن استخدامه كمثبط للرغوة antifoaming agent حيث يعمل على تقليل الرغوة من ٦ سم إلى ٧ ر سم بعد ساعة من عملية التحمير باضافة ١٠.٪ من زيت رجيع الكون المنزوع منه الشمع (dewaxed rice bran oil) الى زيت فول الصويا – كما تختفى الرغوة تماماً عند إضافة زيت رجيع الكون بنسبة ٢٠ ٪ أو ٣٠٪ .

كما تم تقييم درجة ثبات زيت عباد الشمس بعد خلطه بنسبة ١٠٪، ٢٠٪، ٣٠٪، زيت رجيع الكون (مستخلص من الرجيع ومعه القشرة) – حيث زادت درجة ثبات الزيت مع زيادة نسبة رجيع الكون – حيث تزيد فترة التحضين لزيت عباد الشمس بزيادة نسبة الخلط لأن زيت رجيع الكون والقشرة يحتويا على كميات كبيرة من مضادات الأكسدة الطبيعية.

كما أظهرت النتائج انه بإضافة المستخلص الميثانولى لقشرة الأرز بنسبة ١ ، ٢ ، ٣٪ الى زيت عباد الشمس ودراسة الثبات – انه إرتفعت درجة ثبات زيت عباد الشمس مع زيادة نسبة المستخلص الميثانولى وذلك نتيجة لوجود المركبات الفينولية فى القشرة التى تعمل على تحسين الثبات حيث زادت فترة التحضين من ٦ أيام الى ١١ يوم باضافته بنسبة ٣٪.

كما تم دراسة الصفات الكيماوية للزيت والمواد الغير قابلة للتصين (الهيدروكربونات والاستيرولات).

وتمثل الاستيرولات المكون الأساسى للمواد الغير قابلة للتصبن ويمثل البيتاسيتوستيرول المكون الرئيسى للإستيرولات.

كما تم دراسة تركيب الأحماض الدهنية الموجودة – وهى تتمثل فى البالميتيك والأوليك واللينوليك.