EFFECT OF ADDING OF UNSAPONIFIABLE MATTER OF WHOLE BARLEY GRAINS, WHEAT GERM AND RICE BRAN OILS, ON THE OXIDATIVE STABILITY OF SUNFLOWER OIL

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(Manuscript received 27 August 2007)

Abstract

The present study was conducted to study the effect of adding unsaponifiable matters of whole barely grains (WBG), wheat germ (WG) and rice bran (RB) oils on the stability of sunflower oil (SFO) at levels of 0.05, 0.1 and 0.15% compared to Butylated hydroxy tolune (BHT) at the level 0.02%.

Results showed that: WBG, WG and RB oils contains 55.9, 57.96 and 34.37%. Lenoleic acids respectively, 5.85, 4.7, and 4.09% unsaponifiable matter respectively, and it contain (2.92 , 7.05), (1240, 1562.22) and (21.5 , 58.62) ppm α- tocopherol and total tocopherols respectively. Also, unsaponifiable matter at 0.15% ratio of WBG, WG and RB oils increased the oxidative stability of SFO for 8.61, 6.73 and 7.78 hr. respectively and decreased the peroxide values and UV absorbance at 232 and 270 nm. From the previous resulted it could conduced that best results for oxidative stability of SFO is due to using unsaponifiable matters of WBGO followed by RBO and then WGO.

Keywords: whole barley grains oil, wheat germ oil, rice bran oil, unsaponifiable matters, α- tocopherol and stability.

INTRODUCTION

Barley is the preferred grain for cultivation in many areas in the world due to its resistance to drought and ability to mature in climates with a short growth season. Its use for poultry has however been limited by the considerable amounts of fiber contained in the grain (Villamide et al., 1997).

Svihus and Gullord (2002) determined the characteristies and chemical content in barley, they found that the starch content, protein content, ash content and crude fiber were 614, 107, 28, 23 and 49 g DM/kg respectively.

Wheat germ contains 8% oil with excellent source of polyunsaturated fatty acids, vitamin E. and high amount of unsaponifiable matters and naturally occurring antioxidants e.g. α- tocopherols. Therefore, it could be used with other oils to increase their stabilities (Mohamed et al., 2001, Wang and Johnson, 2001 and Amal, 2004).

Commercial rice bran contains from 11.5 to 17.2% protein, 12.8 to 22.67% fat , 6.2 to 14.4% total fiber and 8.0 to 17.7 % ash (depending on processing) with high

concentrations of unsapoifiable fraction (4.2 of total lipid content) and the tocopherol (V.E) which found at 1.0% V/V of the unsaponifiable fraction of RBG (Rogers et al., 1993 , Hui, 1996, Lloyd et al., 2000 and Sir, 2005).

The blend of rice bran oil (RBO) with maize oil (MO) and antioxidant vitamin E (0.03% wt/wt oil) reduced the acid and peroxide values thus the nutritional value of RBO may be enhanced by blending it with MO with vitamin E (Fan et al., 1995).

Vitamin E is thought to function primarily as a chain-breaking antioxidant that prevents the propagation of lipid peroxidation (López et al., 2005), α-tocopherol is the major contributor to the total vitamin E activity in some oils, but others contain a much greater proportion of α-tocopherol wheat germ oil contains appreciable amount of β-tocopherol while wheat germ sunflower, cotton seed and safflower oils contain about 1700,500, 400 and 350 mg α tocotrienol (α-TE kg^{-1}). Cereals are moderate sources of vitamin E, providing between 6mg α-TEKg^{-1} (barley) and 23 mg α-TE kg^{-1} (rye) (Bramley et al., 2000).

Tocotrienol as natural antioxidant in unsaponifiable matter are found in the bran and germ portions of cereals such as barley and rice. (Celina and Koh, 1999).

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Oils Refind sunflower oil was obtained from Misr Gulf oil processing Co(MiGOP) Atakah suez.

2.1.2. Whole barley grains (WBG): was obtained from Sakha-Kafr El sheikh, Egypt.

2.1.3. Rice bran (RB): was obtained from El-Sharkia Milling Company, Zagazig, Egypt.

2.1.4. Wheat germ (WG): Freshly granular milled wheat germ was collected from Middle Egypt flour Mills com.

2.1.5. Solvents: all solvents in this study were of analytical grade (Merck).

2.1.6. Commercial antioxidant (BHA): was supplied from East Man Chemical co.

Methods

1. Extraction of oil from WBG, WG and RB

Whole barley grains (WBG), wheat germ (WG) and rice bran (RB) were crushed separately twice using grinder model (MF10 microfine grinder drive), Soaked in pure n-hexane for 24 hours. The micella were collected and filtered. This process was repeated three times using fresh solvent each time. The solvent was evaporated

under vacuum at 40-45°C in rotary-evaporator, the oil was dried over anhydrous sodium sulfate, filtered, stored in dark brown bottles without any further purification and then kept at 5°C until analysis.

2. Gross chemical composition of WBG, WG and RB

Moisture, total lipid, crude proteins, fiber and ash contents were determined according to the method of the A.O.A.C. (2000). Total carbohydrates were estimated by diference.

3. Physical and chemical characteristics of WBG, WG and RB oils

- Refractive index: of the oils was determined at 25°C according to A.O.A.C. (2000) by using refractometer (NYRL-3 poland).

- Acid, peroxide, iodine values and unsaponifiable matter percentage were determined according to the methods described in A.O.A.C (2000).

- Absorpancy in ultraviolet

The U.V. absorption of 1% solution of the of oil in cyclohexane in 1cm cuvat was measured according to FAO/WHO (1970) at 232 and 270 nm. using Shemadzu sepectrophotometer CU.V.Vis (20-02).

- Separation of unsaponifiable matter

The unsaponifiable matter was separated from the whole barley grains oil (WBGO), wheat germ oil (WGO) and, rice bran oil (RBO) at room temperature according to the method of A.O.A.C. (2000).

Addition of unsaponifiable matter of WBGO, WGO, and RBO to sunflower oil (SFO): The unsaponifiable matter separated from these oils were added to sunflower oil at different percentages 0.05, 0.1 and 0.15% also BHA was added at percentage 0.02%.

- Fatty acid composition of the oils

The fatty acid of the analysed oil samples was determined by Gc-capillary column according to the method reported by Iooc (2001).

- The stability of oils

The oxidative stability of oils was estimated using a 679. Rancimat (Metrohn Herisou, Co., switzerland at 100°C with an air flow rate of 20 1/hr according to the method described by Mendez et al. (1997).

Determination of total tocopherols in oils

The total tocopherols content in oils were determined according to the method of Wong *et al.* (1988).

- Determination of α-tocopherols in oils

The α tocopherols of the analysed oil samples were determined by HPLC according to the method reported by (Dolde, et al., 1999).

RESULTS AND DISCUSSION

Gross chemical composition of whole barley grains (WBG), wheat germ (WG) and rice bran (RB)

Results of the chemical proximate analysis of WBG, WG and RB are given in table (1): it could be observed that WBG contain a higher percentage from total carbohydrates (75.53%) also it contain a considerable percentages of oil and protein 2.53 and 7.87 respectively, On the other hand rice bran is the richest source of total lipid 21.9, in addition its high contents of total carbohydrates (38.47%) and crude protein (15.63%). These results are in agreement with those given by Amal (2004) , Sir (2005) and Svihus and Gullord (2002).

Table 1. Gross chemical composition of whole barley grains wheat germ and rice bran.

Chemical composition %	Whole barley grains (WBG)	Wheat germ (WG)	Rice bran (RB)
Moisture content	8.19	8.8	9.0
Crude oil	2.53	9.65	21.9
Crude protein	7.87	25.62	15.63
Crude fibers	2.28	2.36	6.63
Ash content	3.6	4.96	8.8
Total carbohydrates by differance	75.53	48.61	38.4

Physical and chemical properties of oils

Physical and chemical properties of WBGO, WGO, and RBO were carried out and the results are given in data presented in table (2). From these results is clear that there is a little-change in refractive index absorbance 232 and 270nm, acid value and peroxide value of WBGO and WGO and RBO. Iodine value of WBGO and WGO recorded a higher increased value compared with RBO. This maybe due to the high amount of polyunsaturated fatty acid in WBGO and WGO.

On the other hand whole barley grains oil contain more unsaponifiable matter (5.85%) than wheat germ oil and rice bran oil (4.70 and 4.09%) respectively, although WGO and RBO are characterized by high content of unsaponifiable matter.

Table 2. Physical and chemical characteristics of whole barley grains oil (WBGO), wheat germ oil (WGO) and rice bran oil (RBO).

Physical and chemical properties	WBGO	WGO	RBO
Refractive index at 25°	1.4728	1.4705	1.4741
Conjugated diene UV. (absorbance at 232nm).	2.334	1.93	1.05
Conjugated triene UV. (absorbance at 270nm)	0.875	0.52	0.32
Free fatty acid (%)	4.5	13.31	9.58
Peroxide value (meq/kg oil)	3.73	27.77	27.52
Iodine value (I_2/100g oil)	120.54	125.69	105.05
Unsap (%)	5.85	4.70	4.090
Stability (hr.) at 100°C	4.78	5.94	4.08

Also the data presented in the same table revealed that the WBGO, WGO and RBO were almost the same in the oxidative stability at 100°C. The decrease in stability of these oils may be due to the lipase and lipoxygenase activities coupled with unsaturated fat pose problems regarding adequate shelf life of germ (Mohamed, et al., 2001). These results were in close agreement with these reported by Wang and Johnson (2001). The findings agree also with those reported by Mohamed et al. (2001) and Lloyd et al. (2000).

Fatty acid composition of oils

The data found in table (3) show the fatty acids composition of whole barley grains oil (WBGO), wheat germ oil WGO, rice bran oil (RBO), and sunflower oil (SFO). From these results it could be observed that WBGO was rich in lenoleic acid (Omega 6) 55.9% which were the same nearly from percentage of lenoleic acid of WGO and SFO 57.95 and 60.59% respectively. On the other hand the major fatty acid in RBO

was oleic acid which represented 47.99% followed by lenoleic acid 34.37% The data presented in the same table revealed that the content of total saturated fatty acid (TSFA) and total unsaturated fatty acid (TUSFA) in WBGO, WGO, RBO and SFO were the samene.

This results in greement with those obtained by Amal (2004) and Wang and Johnson (2001).

The ratio of C18:2/C16:0 as an indicator of deterioration of oil, from the results in table (3) it could be noticed that the C18:2/C16:0 ratio of SFO, more than other oils under study.

It is clear results this table that the oils under investigation contained a high amount of essential fatty acid (linoleic (ω6)) which improve the nutritional properties of investigated oils.

Table 3. Fatty acid composition of sunflower oil (SFO) whole barley grains oil (WBGO), rice bran oil (RBO), and wheat germ (WGO).

Fatty acid (%)	WBGO	WGO	RBO	SFO
$C_{14:0}$	-	-	-	-
$C_{16:0}$	19.31	18.89	17.64	8.13
$C_{18:0}$	-	-	-	4.45
$C_{18:1}$	19.26	14.56	47.99	26.61
$C_{18:2}$	55.91	57.96	34.37	60.59
$C_{18:3}$	5.52	8.59	-	-
$C_{18:2}/C_{16:0}$	2.895	3.068	1.948	7.452
Total sat. F.A.	19.31	18.89	17.64	12.80
Total unsat. F.A.	80.69	81.11	82.36	87.20

Effect of addition of unsaponifiable matter of oils and BHA on the physical and chemical characteristics of sunflower oil

The data obtained in table (4) indicated that the addition of unsaponifiable matters of WBGO, WGO and RBO at ratios of 0.05, 0.1 and 0.15% respectively (as natural antioxidant) caused decrease in the acid values, peroxide values and conjugated diene and triene at 232 and 270 nm of sunflower oil compared with SFO as control and SFO treated with BHA (as synthetic antioxidant) at ratio of 0.02%. This means that the sunflower oil had high quality by addition of unsaponifiable matters of these oils under study. This decrease may be due to that the unsaponifiable matter contain approximately 1.0 v/v from vitamin E α-tocopherol [Lloyd et al. 2000.] which is considered to function primarily as a chain breaking antioxidant that prevents the propagation of lipid peroxidation, [Lopez et al. (2005).] Also the unsaponifiable

fraction contain a unique complex of naturally occurring antioxidant compound Mohamed *et al.* (2001) and Lloyd *et al.* (2000) which, may be due to Vitamin E.

Table 4. Effect of addition of the unsaponifiable matter of whole barley grain, wheat germ and rice bran oils on the physical and chemical properties of sunflower oil.

Oils		Refractive index at 25°C	U.V. absorbance at		Free fatty	Peroxide value (meq/kg oil)
			232 nm	270nm		
Control sunflower oil (SFO)		1.4741	0.740	0.249	0.094	5.80
Sunflower oil + BHA (0.02)		1.4750	0.723	0.225	0.090	5.55
WBGO	0.05	1.4751	0.703	0.237	0.061	4.67
	0.1	1.4748	0.685	0.281	0.052	4.24
	0.15	1.4746	0.632	0.223	0.047	2.14
WGO	0.05	1.4752	0.713	0.235	0.092	5.50
	0.1	1.4745	0.700	0.230	0.073	4.75
	0.15	1.4740	0.652	0.200	0.070	2.47
RBO	0.05	1.4732	0.692	0.240	0.092	3.92
	0.1	1.4728	0.664	0.222	0.065	3.38
	0.15	1.4726	0.652	0.205	0.060	2.33

Effect of addition unsaponifiable matters of WBGO, WGO and RBO on oxidative stability of SFO

From the results summarized in table (5), it could be noticed that the oxidative stability of sunflower oil as control was 5.07hr. The addition of unsaponifiable of WBGO, RBO and WGO to SFO at ratio of 0.05, 0.1 and 0.15% caused gradually increasing in the stability of SFO also addition of BHA at ratio 0.02% caused a higher increase in stability of sunflower (6.2hr.). The results revealed that the best results for the oxidative stability was obtained at using unsaponifiable matters of WBGO followed by RBO then WGO at ratio 0.15% for SFO which were 8.61, 7.78 and 6.73 hr. respectively.

This increase in the stability by addition of unsaponifiable matter may be due to that fraction in RBO contains a unique complex of naturall occurring antioxidant compound i.e. tocopher, to controls and oryzanol (Lloyd et al., 2000), also tocotrienols antioxidant remaining in the bran and germ of barley and rice, which has more antioxidante than tocopherol (Celina and Koh, (1999).

Table 5. Effect of addition unsaponifiable matter % of WBGO, WGO and RBO on the oxidative stability of sunflower oil.

Oils	Oxidative stability at 100°C (hr.) of sunflower oil		
Control	5.07		
Control SFO BHA (0.02)	6.2		
Addition of unsaponifiable matters of oils:-	At percentages (%)		
	0.05	0.1	0.15
WBG	5.84	6.89	8.61
WG	6.20	6.40	6.73
RB	5.62	6.72	7.78

Total tocopherols and α-tocopherols

Tocopherols are important natural antioxidants that inhibit lipid oxidation in oils. Tocopherols and α tocopherols content of WBGO, WGO, RBO and SFO studied are presented in table (6).

These results indicate that wheat germ oil has the highest content of tocopherols and α tocopherols (156.22 and 1240 ppm respectively followed by sunflower oil (475.20 and 410.05ppm) while the whole barley grains (WBGO) oil was lower than these oils (WGO, RBO and SFO) (7.05 and 2.92 ppm). These results are in agreement with those reported by Bramley et al. (2000).

Table 6. Total tocopherols and α-tocopherols content of oils

Oils	α-tocopherols (ppm)	Total tocopherols (ppm)
Sunflower oil (SFO)	410.05	475.20
Whole barley grains oil (WBGO)	2.92	7.05
Wheat germ oil (WGO)	1240	1562.22
Rice bran oil (RBO)	21.50	58.62

CONCLUSION

Whole barley grains (WBG), wheat germ (WG) and rice bran (RB) oils are naturally contain a high amount of unsaponifible matters which used in this study to increase the stability of sunflower oil (SFO) compared to BHA especially WBGO at 0.15%.

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تأثير إضافة المواد الغير قابلة للتصبن لزيت حبوب الشعير الكاملة وجنين القمح وجنين الأرز على الثبات الأوكسيدى لزيت عباد الشمس

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– تهدف هذه الدراسة إلى دراسة تأثير إضافة المواد الغير قابلة للتصبن لزيوت حبوب الشعير الكاملة و جنين القمح وجنين الأرز على درجة ثبات زيت عباد الشمس بنسب ٠,٠٥ ، ٠,١، ٠,١٥ % مقارنة بمضاد الأكسدة الصناعي BHA بنسبة ٠,٠٢ % وتوضح النتائج الآتي :

– احتواء زيت الشعير وجنين القمح وجنين الأرز على نسبة حامض اللينوليك ٥٥,٩، ٥٧,٩٦ ، ٣٤,٣٧% على التوالي وأيضا تحتوي هذه الزيوت على نسبة من المواد الغير قابلة للتصبن ٥,٨٥ ، ٤,٧ ، ٤,٠٩% وأيضا تحتوي على (٢,٩٢ ، ٧,٠٥). (١٢٤٠، ١٥٦٢,٢٢) و (٢١,٥ ، ٥٨,٦٢) جزء في المليون من الفاتوكوفيرول والتوكوفيرولات الكلية على التوالي. كما أشارت النتائج إلى زيادة الثبات الأوكسيدي لزيت عباد الشمس باستخدام المواد الغير قابلة للتصبن لزيت حبوب الشعير وجنين القمح وجنين الأرز بنسبة ٠,١٥% إلى ٨,٦١، ٦,٧٣ ، ٧,٧٨ ساعة النوالي وحدث نقص في رقم البيروكسيد والامتصاص فى منطقة الـ UV على طول موجى ٢٣٢ و ٢٧٠ نانوميتر.

– وايضا يتضح من النتائج السابقة ان أفضل ثبات اوكسيدى لزيت عباد الشمس باستخدام المواد الغير قابلة للتصبن لزيت حبوب الشعير يليها زيت جنين الأرز ثم زيت جنين القمح.