Blends of rapeseed oil with black cumin and rice bran oils for increasing the oxidative stability

Magdalena Rudzińska¹ · Minar M. M. Hassanein² · Adel G. Abdel-Razek² · Katarzyna Ratusz³ · Aleksander Siger²

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Abstract For the increase of oxidative stability and phytonutrient contents of rapeseed oil 5, 10 and 20 % blends with rice bran oil and black cumin oil were prepared. Profiles of different bioactive lipid components of blends including tocopherols, tocotrienols, phytosterols and phytostanols as well as fatty acid composition were carried out using HPLC and GLC. Rancimat was used for detecting oxidative stability of the fatty material. The blends with black cumin seed oil characterized higher level of α - and γ -tocopherols as well as all isomers of tocotrienols. Presence of rice bran oil in blends leads to increased tocotrienols amounts, β -sitosterol and squalene. Blending resulted in lowering ratio of PUFA/SFA and improves stability of these oils. The ratio of omega-6/omega-3 raises from 2.1 in rapeseed oil to 3.7 and 3.0 in blends with black cumin and rice bran oils, respectively. Addition of 10 and 20 % of black cumin and rice bran oils to rapeseed oil were influenced on the oxidative stability of prepared blends. The results appear that blending of rapeseed oil with black cumin seed oil or rice bran oil enhanced nutritional and

functional properties via higher oxidative stability as well as improved phytonutrient contents.

Keywords Blends · Black cumin · Rice bran · Rapeseed · Phytonutrients · Oxidative stability

Introduction

In recent decades, oil crop production has been among the most vibrant activities in world agriculture. Over the 2000–2010 decade the sector grew by almost 5 % per year following the growth of food consumption in developing countries. The four most important oil crops—oil-palm, soybean, rapeseed and sunflower seed – account about 75 % of world production (FAO Statistical Yearbook, 2013). The total production of oil crops used for culinary and industrial oil processing in 2010 ranged in Egypt 1.5 mln t, and in Poland 2.5 mln t. Whereas, rapeseed dominated in Polish breeding and small amount of other oils is brought from other countries, nearly 85 % of oils and fats in Egypt are imported, mainly palm oil (FAO Statistical Yearbook). Although a wide range of vegetable oils are available in the market, some vegetable oils are not up to standards to meet consumer satisfaction in terms of their stability (Mostafa et al. 2013). Nutritionists recommend 30–35 % of energy (%E) level or lower of calories as fat with the intake of saturated fat not to exceed 10 %E (Simopoulos 1996). The ratio of saturated to monounsaturated and polyunsaturated fatty acids in good quality fat like 1:1:1 is prescriptive (FAO Fats and Fatty Acids in Human Nutrition 2010). World Health Organization suggested that for adult people estimated average requirement level for total PUFA is 11 %E and total n-3 fatty acids 2 %E, so the resulting acceptable range for n-6 fatty acids intake is 2.5 to 9 %E (Przybylski et al. 2005). Besides fatty acids composition, the content of tocopherols and sterols

Research highlights In the experimental part a new products were obtained—blends of plant oils
In the analytical part were investigated oxidative stability of blends
Blending of rapeseed oil with black cumin or rice bran oil increased their oxidative stability

✉ Magdalena Rudzińska
magdar@up.poznan.pl

¹ Faculty of Food Science and Nutrition, Poznan University of Life Sciences, Poznań, Poland

² Fats and Oils Department, National Research Centre, Cairo, Egypt

³ Faculty of Food Sciences, Warsaw University of Life Sciences - SGGW, Warsaw, Poland

play an important role in quality of vegetable oils. Tocopherols are recognized as very efficient natural antioxidants, about 250 times more effective than BHT (Choe 2008). Their high potency is based on their ability to be transformed back from the oxidized form into the active structure (Przybylski et al. 2005). Phytosterols, which reduced blood cholesterol level, especially its LDL fraction, are present in vegetable oils as free sterols, esterified with fatty acids/cinnamic acid, or as glycosides. They are added to food products, like margarines, as functional compounds (Gylling et al. 2009). Blending of different oils as objective for modifying their quality is to develop oils with enhanced nutritional and functional properties and which require no further processing for specific end-use markets (Reyes-Hernandez et al. 2007). World vegetable oil markets are highly competitive requiring a steady improvement in oil quality to increase market prospects.

Rapeseed oil is characterized by a low level of saturated fatty acids (SFA) and high levels of monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids, especially n-3 α -linolenic acid. Additionally, the ratio of n-6:n-3 is favorable and equal 2:1. Rapeseed oil content high level of phytosterols, and relatively high amounts of tocopherols (Przybylski et al. 2005). It is effective in reducing plasma total and LDL cholesterol levels, to affect the fatty acid composition of blood platelet phospholipids and to alter platelet activity and thrombogenesis (Choe 2008).

Rice bran oil (RBO) is an excellent cooking medium because it contains high level of phytosterols—anti-polymerize agents (Blekas and Boskou 1989), prove a longer shelf life, more stable at higher temperature, gives better taste and flavour to food items (Liang et al. 2014; Sharma 2002). RBO has cholesterol-lowering properties due to the presence of oryzanol (Soehnlein et al. 2009). Rice bran oil's other components like tocotrienols and squalene have powerful anti-cancer and anti-ageing properties (Kannappan et al. 2010). Taking advantage of the micronutrient present in rice bran oil, it was considered that value of other edible oils could be nutritional improved by blending it with RBO (Choudhary et al. 2013; 2015).

Black cumin seed oil contain typical fatty acids, like linoleic, oleic, palmitic, and stearic. The main component of sterols was β -sitosterol (48.35–51.92 %), followed by Δ^5 -avenasterol, campesterol, and stigmasterol (Matthaus and Özcan 2011). In our previous work we found high content of total tocochromanols, β - and γ -tocotrienol and γ -tocopherol in cold pressed black cumin seed oil (Hassanien et al. 2014). The presence of fat-soluble bioactive compounds such as tocopherols and phytosterols at elevated amounts makes it a good reason for blending with other oils.

It was objective to upgrade and strengthen the oxidative stability of rapeseed oil via blending with some selected oils of higher stability characteristics. It is known that rapeseed oil

is widely used in many countries especially European countries and Canada.

In presented study, rapeseed oil was blended with uniquely stable oils, like rice bran oil or cold pressed black cumin seed oils at ratios 5, 10 and 20 %. This study is mainly concerned on the stability evaluation of prepared blends, which was measured by Rancimat test. The content of tocopherols and tocotrienols by HPLC, phytosterols and fatty acid composition by GLC were also determined in parent oils and all blends. As far as we know, no such previous studies have yet been conducted on the blending of rapeseed oil with rice bran or cold pressed black cumin seed oils. This study helps in development of newer blends oils with improved stability characteristics.

Experimental

Materials

Refined rapeseed (RO) and rice bran oils (RBO) were purchased from the commercial market in Poland. Cold pressed oil from black cumin seeds (BCO) was purchased from National Research Centre, Cairo, Egypt.

All solvents of HPLC grade, 1 M methanolic KOH, sterol standards and anhydrous pyridine were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standards of tocopherols were obtained from Calbiochem-Novobiochem (San Diego, CA, USA), FAME standards and Sylon BTZ was purchased from Supelco (Bellefonte, PA, USA).

Vegetable oil blends preparation

Rapeseed oil was blended with rice bran oil or black cumin seed oil in the following weight proportions: 95:5, 90:10 and 80:20. Three blends from every kinds of mixture were prepared.

Phytosterols

Sterol content and composition were determined by GC following the procedure described by AOCS Official Method Ch 6-91(1997). Briefly, 50 mg of lipids were saponified with 1 M methanolic KOH for 18 h at room temperature, then water was added and the unsaponifiables extracted three times with hexane/methyl tert-butyl ether (1:1, v/v). Silylated by Sylon BTZ derivatives of the sterols were separated on a gas chromatograph HP 6890 series II Plus (Hewlett Packard, Palo Alto, USA) equipped with DB35MS capillary column (25 m x 0.20 mm, 0.33 μ m; J&W Scientific, Folsom, CA). Sample was injected in splitless mode. The column temperature was held at 100 °C for 5 min, and then programmed to 250 °C at 25 °C/min, held for 1 min, then further programmed

to 290 °C at 3 °C/min and held for 20 min. The detector temperature was set at 300 °C. Hydrogen was used as the carrier gas at a flow rate of 1.5 mL/min. An internal standard, 5 α -cholestane, was used for sterols quantification. Phytosterols were identified by comparison of retention data with standards. Samples from autonomous parental oils and blends were analyzed in triplicate.

Fatty acids

Methyl esters of fatty acids (FAME) were prepared according to AOCS Official Method Ce 1 k-07 (2007). Diluted FAME were separated on a gas chromatograph HP 5890 series II (Hewlett Packard, Palo Alto, USA) equipped with an Innowax capillary column (30 m x 0.20 mm x 0.20 μ m) and flame ionization detector (FID). Hydrogen was used as the carrier gas at flow rate of 1.5 mL/min. The column temperature was isotherm at 210 °C. Detector and injector temperatures were set at 240 °C. Fatty acids were identified by comparison of the retention times with authentic standards and the results were reported as weight percentages after integration and calculation using Chem. Station (Agilent Technologies). Samples from autonomous parental oils and blends were analyzed in triplicate.

Oxidizability Cox value

The Cox value of the oils was calculated by applying the formula proposed by Fatemi and Hammond (1980):

$$\text{Cox value} = \{[\text{C18 : 1}(\%)] + 10.3*[\text{C18 : 2}(\%)] + 21.6*[\text{C18 : 3}(\%)]\}/100$$

Tocochromanols

For the determination of tocochromanols (tocopherols and tocotrienols), a solution of 250 mg of oil in 25 mL of n-heptane was used for the HPLC. The HPLC analysis was conducted using a Merck-Hitachi low-pressure gradient system, fitted with aL-6000 pump, a Merck-Hitachi F-1000 fluorescence spectrophotometer (detector wave lengths for exCitation 295 nm, for emission 330 nm), and a D-2500 integration system. The samples in the amount of 20 μ L were injected with a Merck 655-A40 autosampler onto a Diol phase HPLC column 25 cm x 4.6 mm ID (Merck, Darmstadt, Germany) using a flow rate of 1.3 mL/min. The mobile phase used was n-heptane/tert-butyl methyl ether (99: 1, v/v) (Balz et al. 1992). Samples from autonomous parental oils and blends were analyzed in triplicate.

Oxidative stability index

For determination of oxidative stability of oils AOCS Official Method Cd 12b-92 (1997) was used. The test was performed on an automated Metrohm Rancimat model 743 (Herisau, Switzerland) at 110 $\pm$ 0.1 °C and an air flow of 20 L/hr to determine the induction period (IP) of the oils. Samples from autonomous parental oils and blends were analyzed in triplicate.

Statistical analysis

Results are presented as the mean $\pm$ standard deviation from three replicates of each experiment. A P-value < 0.05 was used to denote significant differences between mean values determined by the analysis of variance (ANOVA) with the assistance of Statistica 7.0 (StatSoft Inc., Tulsa, OK) software.

Results and discussion

Phytosterols

The contents of desmethylsterols (brassicasterol, campesterol, Δ 5- and Δ 7-stigmasterol, β -sitosterol, Δ 5- and Δ 7-avenasterol), 4-monomethylsterols (gramisterol, citrostadienol) and 4,4-dimethylsterols (cycloartenol, 24-methylenecycloartenol) in parent and blended oils were detected (Table 1). Brassicasterol was characteristic of rapeseed oil (RO) whereas squalene was characteristic of rice bran oil (RBO). The total phytosterol content in RBO was at the highest level (7.4 mg/g). Rapeseed oil was the second-richest source of total phytosterols content (3.3 mg/g), followed by BCO (1.7 mg/g). Obtained results agreed with literature data (Schwartz et al. 2008; Kritchevsky 1997). The content of phytosterols in prepared blends was adequate to their amount in parent oils. Blending of RO with BCO has not influenced on the phytosterols contents. Their amount ranged from 3.0 mg/g to 3.4 mg/g of oils. While the quality of the phytosterols remained unchanged when adding BCO into RO, the quantities of some phytosterols were modified without modifying the total phytosterol contents of oil blend. There was a decrease in brassicasterol and β -sitosterol while an increase in Δ 5-stigmasterol, cycloartenol and citrostadienol was observed. Adding of RBO to RO caused an increase of total phytosterols amounts from 3.4 mg/g to 4.0 mg/g (Table 1).

β -Sitosterol and campesterol were the main phytosterols in parental oils and their blends. The addition of RBO (5, 10 and 20 %) to RO had influenced on the level of squalene and β -sitosterol which the content gradually increased. As a result of

Table 1 The phytosterols and phytostanols content in parental and blended oils ($\mu\text{g/g}$)

Phytosterols	Samples of oils			Samples of oils blended with rapeseed oil					
				Black cumin			Rice bran		
	Rapeseed	Black cumin	Rice bran	5 %	10 %	20 %	5 %	10 %	20 %
Squalene	Nd	Nd	1017 $\pm$ 40	Nd	Nd	Nd	51 $\pm$ 2	102 $\pm$ 5	203 $\pm$ 9
Brassicasterol	442 $\pm$ 21	Nd	Nd	416 $\pm$ 18	388 $\pm$ 24	354 $\pm$ 15	420 $\pm$ 18	403 $\pm$ 18	304 $\pm$ 11
Campesterol	1241 $\pm$ 52	169 $\pm$ 8	1189 $\pm$ 41	1221 $\pm$ 61	1163 $\pm$ 51	1082 $\pm$ 47	1235 $\pm$ 58	1244 $\pm$ 57	1231 $\pm$ 59
Campestanol	116 $\pm$ 5	27 $\pm$ 1	95 $\pm$ 4	122 $\pm$ 5	107 $\pm$ 5	98 $\pm$ 4	125 $\pm$ 6	120 $\pm$ 6	52 $\pm$ 3
Δ 5-Stigmasterol	11 $\pm$ 1	243 $\pm$ 10	657 $\pm$ 27	25 $\pm$ 1	44 $\pm$ 2	59 $\pm$ 2	46 $\pm$ 2	86 $\pm$ 4	130 $\pm$ 6
β -Sitosterol	1443 $\pm$ 62	593 $\pm$ 27	2552 $\pm$ 88	1461 $\pm$ 62	1351 $\pm$ 60	1239 $\pm$ 51	1598 $\pm$ 74	1624 $\pm$ 72	1665 $\pm$ 80
Sitostanol	47 $\pm$ 2	71 $\pm$ 3	106 $\pm$ 5	43 $\pm$ 2	48 $\pm$ 2	52 $\pm$ 2	55 $\pm$ 3	59 $\pm$ 3	63 $\pm$ 3
Δ 5-Avenasterol	50 $\pm$ 2	Nd	158 $\pm$ 7	49 $\pm$ 2	44 $\pm$ 1	40 $\pm$ 2	59 $\pm$ 3	66 $\pm$ 3	83 $\pm$ 4
Gramisterol	Nd	Nd	333 $\pm$ 14	Nd	Nd	Nd	12 $\pm$ 1	25 $\pm$ 2	57 $\pm$ 3
Cycloartenol	Nd	436 $\pm$ 18	387 $\pm$ 15	20 $\pm$ 1	45 $\pm$ 1	89 $\pm$ 4	20 $\pm$ 1	40 $\pm$ 2	77 $\pm$ 4
Δ 7-Stigmasterol	Nd	Nd	48 $\pm$ 2	Nd	Nd	Nd	2 $\pm$ 1	5 $\pm$ 1	10 $\pm$ 1
24Methylene-cycloartenol	Nd	Nd	286 $\pm$ 12	Nd	Nd	Nd	16 $\pm$ 1	31 $\pm$ 1	60 $\pm$ 3
Δ 7-Avenasterol	Nd	Nd	128 $\pm$ 6	Nd	Nd	Nd	6 $\pm$ 1	13 $\pm$ 1	26 $\pm$ 1
Citrostadienol	Nd	123 $\pm$ 6	182 $\pm$ 8	8 $\pm$ 1	15 $\pm$ 1	29 $\pm$ 1	9 $\pm$ 1	18 $\pm$ 1	36 $\pm$ 2
Others	Nd	Nd	221 $\pm$ 9	Nd	Nd	Nd	22 $\pm$ 1	25 $\pm$ 2	44 $\pm$ 2
Total	3350 $\pm$ 146 ^b	1662 $\pm$ 66 ^a	7359 $\pm$ 194 ^d	3365 $\pm$ 148 ^b	3205 $\pm$ 141 ^b	3042 $\pm$ 127 ^b	3676 $\pm$ 148 ^c	3861 $\pm$ 154 ^c	4041 $\pm$ 158 ^c

Nd not detected

a...d Means within the row with different superscripts are significantly ($P < 0.05$) different

addition of RBO or BCO to RO cycloartenol and citrostadienol, which were not observed in individual RO, started to appear in reasonable amounts.

In recent years, increased interest in consumption of phytosterols. γ -Oryzanol is a mixture of ferulic acid esters of triterpene alcohols and phytosterols and is chiefly responsible for many health benefits rice products (Lerma-García et al. 2009). Enrichment of human diet in natural phytosterols is favorable for the decreasing of plasma cholesterol level and coronary mortality (Cusak et al. 2013). Blending of RO with RBO positively influenced on the phytosterols content and can be recommended as a safe and cheap way of increasing the content of these compounds in other edible fats and oils. To improve the phytosterols composition of rapeseed oil, it can be blended with BCO as a source of stigmasterol and cycloartenol.

Fatty acids composition

The main fatty acids in the RO were oleic (62 %), linoleic (20 %) and linolenic (9 %) acids. BCO was characterized by a high percentage of linoleic acid (C18:2, 61 %), followed by oleic acid (C18:1, 22 %) and palmitic acid (C16:0, 12 %) (Table 2). RBO constituted 41.4, 34.1 and 20.4 % of oleic, linoleic and palmitic acid, respectively (Table 2). These results were typical of oils from identical sources and agreed with

previously reported results (Przybylski et al. 2005; Choudhary et al. 2013; Hassanien et al. 2014).

Due to the blending of RO with RBO or BCO (5, 10 and 20 %) increased in the content of C16:0 and C18:2 were observed. Blending caused decrease in linolenic acid and PUFA/SFA ratios.

Cox value was greater in BCO (6.6) than in RO (4.7) and RBO (4.1). Prepared blends characterized similar Cox value which ranged from 4.6 to 5.1 (Table 2). The ratio of PUFA/SFA and Cox value are usually accepted as a measure of oxidative stability (Fatemi and Hammond 1980; Mendez et al. 1996). Karupaiah and Sundram (2013). reported that decreasing PUFA/SFA ratios in human diet were associated with a significantly greater postprandial level of HDL-C in plasma. Choudhary et al. (2013) found that RBO blended with olive oil (70:30) contained highest amount of MUFA. Blends prepared in this study characterized lower level of MUFA compared to parent oil.

In prepared blends the ratio of omega-6/omega-3 raises from 2.1 in RO to 2.5, 2.8 and 3.7 when blended with 5 %, 10 % and 20 % of BCO respectively, and to 2.3, 2.5 and 3.0 in blends with 5 %, 10 % and 20 % of RBO. Some studies reported that a ratio of omega-6/omega-3 fatty acids equal 2.5/1 influence on the reducing of rectal cell proliferation in patients with colorectal cancer (Simopoulos 2002). A ratio of

Table 2 The fatty acid composition in parental and blended oils (%)

Fatty acids	Samples of oils			Samples of oils blended with rapeseed oil					
				Black cumin			Rice bran		
	Rapeseed	Black cumin	Rice bran	5 %	10 %	20 %	5 %	10 %	20 %
C12:0	Nd	0.6±0.1	Nd	Nd	0.1±0.1	0.1±0.1	Nd	Nd	Nd
C14:0	Nd	0.2±0.1	Nd	Nd	Nd	Nd	Nd	Nd	Nd
C16:0	4.6±0.3	12.0±0.5	20.4±0.9	4.9±0.2	5.3±0.2	6.1±0.3	5.4±0.2	6.2±0.3	7.7±0.3
C16:1	0.4±0.1	0.4±0.1	Nd	0.4±0.1	0.4±0.1	0.4±0.1	0.4±0.1	0.3±0.1	0.3±0.1
C18:0	1.7±0.1	2.4±0.1	1.9±0.1	1.7±0.1	1.8±0.1	1.8±0.1	1.7±0.1	1.7±0.1	1.7±0.2
C18:1 n-9	62.2±3.1	21.6±1.1	41.4±1.9	60.2±2.5	58.1±2.8	54.1±2.5	61.2±3.2	60.1±2.8	58.0±2.5
C18:2 n-6	20.0±0.8	60.9±2.6	34.1±1.7	22.0±1.1	24.1±1.3	28.2±1.3	20.7±1.5	21.4±1.1	22.8±1.0
C18:3 n-3	9.4±0.4	0.4±0.1	1.0±0.4	8.9±0.4	8.5±0.4	7.6±0.4	9.0±0.4	8.6±0.4	7.7±0.4
C20:0	0.3±0.1	1.1±0.1	0.7±0.1	0.3±0.1	0.4±0.1	0.5±0.1	0.3±0.1	0.3±0.1	0.4±0.1
C20:1	0.9±0.1	0.1±0.1	0.5±0.1	0.9±0.1	0.8±0.1	0.7±0.1	0.9±0.1	0.9±0.1	0.8±0.1
SFA	6.6 ^a	16.3 ^c	23.0 ^f	7.1 ^a	7.5 ^b	8.5 ^c	7.4 ^b	8.2 ^c	9.9 ^d
MUFA	63.5 ^d	22.1 ^a	41.9 ^b	61.4 ^d	59.3 ^d	55.2 ^c	62.4 ^d	61.3 ^d	59.2 ^d
PUFA	29.4 ^a	61.3 ^d	35.1 ^c	31.0 ^a	32.6 ^b	35.8 ^c	29.7 ^a	30.0 ^a	30.5 ^a
PUFA/SFA	4.5 ^d	3.8 ^{bc}	1.5 ^a	4.4 ^d	4.3 ^{cd}	4.2 ^c	4.0 ^c	3.6 ^{bc}	3.1 ^b
n-6/n-3	2.1 ^a	174 ^c	33 ^b	2.5 ^a	2.8 ^a	3.7 ^a	2.3 ^a	2.5 ^a	3.0 ^a
Cox value	4.7 ^b	6.6 ^c	4.1 ^a	4.8 ^b	4.9 ^b	5.1 ^{bc}	4.7 ^b	4.7 ^b	4.6 ^b

Nd not detected

^a–^c Means within each row with different superscripts are significantly ($P < 0.05$) different

2–3/1 suppressed inflammation in patients with rheumatoid arthritis (Cleland et al. 2003). High intakes of omega-6 fatty acids were associated with an increased risk of postmenopausal breast cancer (Wirfält et al. 2002), promote adipogenesis and increase expression of lipogenic genes (Muhlhausler and Ailhaud 2013).

Tocopherols and tocotrienols

Results of tocopherols and tocotrienols composition in Table 3 are presented. BCO contained the highest amount of total tocochromanols (1731 µg/g) followed by RO and RBO (689 and 392 µg/g) respectively.

Table 3 The tocochromanols content in parental and blended oils (µg/g)

Tocochromanols	Samples of oils			Samples of oils blended with rapeseed oil					
				Black cumin			Rice bran		
	Rapeseed	Black cumin	Rice bran	5 %	10 %	20 %	5 %	10 %	20 %
α-Tocopherol	323.7±1.4	112.1±1.3	110.0±1.1	287.0±1.1	272.6±1.3	248.7±3.3	288.8±2.0	279.0±5.0	256.5±4.7
β-Tocopherol	9.9±0.5	3.8±0.3	3.5±0.6	Nd	1.1±0.1	1.6±0.1	1.0±0.1	1.4±0.1	1.8±0.1
γ-Tocopherol	350.2±2.5	938.5±2.6	80.3±1.6	409.7±1.7	455.1±1.9	491.5±1.8	328.1±3.5	312.8±5.1	284.2±2.5
δ-Tocopherol	4.9±0.6	4.5±1.0	3.5±0.8	4.7±0.4	5.4±0.5	5.6±0.5	4.6±0.2	5.1±0.4	6.1±0.5
α-Tocotrienol	Nd	3.0±0.4	16.5±1.0	Nd	Nd	Nd	0.5±0.1	1.2±0.1	2.3±0.1
β-Tocotrienol	Nd	284.3±5.1	Nd	10.5±0.8	25.4±1.2	56.2±1.5	Nd	Nd	Nd
γ-Tocotrienol	Nd	376.7±3.1	170.6±0.8	15.3±1.2	35.2±1.6	73.8±0.9	8.2±0.2	15.9±0.6	33.6±1.3
δ-Tocotrienol	Nd	8.6±0.5	7.9±0.6	Nd	0.9±0.1	1.6±0.1	Nd	1.1±0.1	1.5±0.1
Total	689.0±4.7 ^c	1731.5±14.3 ^f	392.3±6.5 ^a	727.2±5.2 ^{cd}	795.7±6.7 ^d	879.0±9.2 ^{de}	631.2±6.1 ^b	616.5±9.8 ^b	586.0±9.3 ^b

Nd not detected

^a–^f Means within the row with different superscripts are significantly ($P < 0.05$) different

The main isomers present in RO were α - and γ -tocopherols and their contribution was 47 and 50 %, respectively. No tocotrienols were detected in RO, while all tocopherol and tocotrienols isomers were observed in RBO and BCO. Tocochromanols in BCO consisted of 61 % of tocopherol and 38.8 % of tocotrienols, whereas in RBO were nearly at equal proportion. Tocochromanols profile, especially α - and γ -tocopherols and tocotrienols of RO was enriched upon blending with BCO or RBO.

It was noticed that the addition of 5, 10 and 20 % of RBO to RO slightly decreased the amount of α - and γ -tocopherols. On the other side, β - γ - and δ - tocotrienols were observed in reasonable amounts which are not found in RO. In case of blending RO with BCO at 5, 10 and 20 %, it was noticed gradual increase in the amount of α - and γ -tocopherols. Also, β - and γ tocotrienols were found in reasonable amounts, these compounds are not present in RO.

Isomers of tocopherols have different antioxidative activity *in vitro* and *in vivo*. In food system the antioxidative activity decreases in the following order: $\gamma > \delta > \beta > \alpha$ isomers (Przybylski et al. 2005). BCO content very high level of γ -tocopherol, what plays an important role in products rich in PUFA. Addition of this oil to RO caused significant increase of total tocochromanols, especially γ -tocopherol.

Tocotrienols in recent years have received much more attention than tocopherols, because they exhibit a different suite of biological activities (Miyazawa et al. 2009). Tocotrienols demonstrates also great potential as an antiosteoporotic agent (Chin et al. 2013). BCO is especially rich in tocotrienols, what could be a good reason to enrichment of RO in these compounds.

Oxidative stability

The results of oxidative stability, in terms of measurement of induction periods (IP) of the pure RO, RBO and BCO and their blends are shown in Fig. 1. It was observed that BCO had the highest IP, while blends RO with BCO or RBO shown better stability than parent oils. It could be explained by the increased level of tocopherols and tocotrienols observed in oil blends, as well as steryl ferulates and composition of individual phytosterols. The blending 20 % of RBO or BCO with RO resulted in a significant increase in the IP, which is a characteristic of the oxidative stability of the oil and fats. The results are in the agreement with data published by Hoffman et al. (2002) for the rapeseed/palm olein blend. They reported that the oxidative stability of 1:1 (v/v) rapeseed/palm olein blend was improved up to 60 % in comparison with rapeseed oil. Frankel and Huang (1994) reported that blend of rapeseed oil and high oleic sunflower oil had comparable or better stability than hydrogenated canola oil containing 1 % linolenate. Islam et al. (2009) observed that phytosterol ferulates from RBO are responsible for the antioxidant activity via the reactive oxygen species scavenging and inhibition of their production.

Conclusion

The new RO blends reach the target in raising and improving the nutritional and functional properties than that of original one. At different concentrations of BCO blended with RO, the amount of γ -tocopherol was increased and appeared of β and γ -tocotrienols (which are not found in individual RO). It was noticed that blends of RO with BCO or RBO increased the

Fig. 1 The induction time of parental and blended oils

total amounts of phytosterols and phytostanols. On the other side, decrease in linolenic acid in oil blends can confer excellent properties upon the oil blends. When blending of RO with BCO or RBO at a level of 10 and 20 % showed better oxidative stability than parent RO. The ratio of omega-6/omega-3 PUFA in RO blends, reaches to desirable ratios having positive effects in reducing the risk of some diseases. These new and unique oils blends are rich in bioactive lipids such as phytosterols, phytostanols and tocochromanols which may improve nutritional and functional properties to the foods.

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