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ORIGINAL ARTICLE

Retention of natural antioxidants of blends of groundnut and sunflower oils with minor oils during storage and frying

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Abstract Unrefined groundnut oil (GNO) and refined sunflower oil (SFO) were blended with four minor oils including laboratory refined red palmolein (RRPO), physically refined rice bran oil (RBO), unrefined sesame oil (SESO), and unrefined coconut oil (CNO) containing natural antioxidants viz., β-carotene, tocopherols, oryzanol and lignans. The five blends prepared were GNO+RRPO (80:20), GNO+RBO (80:20), GNO+SESO (80:20), SFO+RRPO (50:50) and SFO+CNO (60:40). Prepared blends contained saturated fatty acids (SFA) (16.7–53.3 %); monounsaturated fatty acids (MUFA) (16.0–45.5 %) and polyunsaturated fatty acids (PUFA) (29.2–37.8 %). GNO blends viz., GNO+RRPO, GNO+RBO and GNO+SESO contained β-carotene (10.7 mg/100 g), oryzanol (0.12 g/100 g) and lignans (0.35 g/100 g) respectively as natural antioxidants. SFO was enriched with β-carotene (28.7 mg/100 g) and medium chain fatty acids (34.2 %) by blending with RRPO and CNO respectively. The oil blends (200 ml) were packed and stored at 38 °C/90 % relative humidity (RH) and 27 °C/65 % RH and samples were withdrawn at fixed intervals for analysis. Freshly prepared blends were also investigated for their frying performance. During storage, GNO+RBO blend showed highest oxidative stability probably due to the presence of oryzanol in the order GNO+RBO>GNO+SESO>GNO+RRPO. During frying, the peroxide value of GNO blends with RBO (rich in oryzanol) and SESO (rich in lignans) was less while the free fatty acid value was less in SFO blends with RRPO and CNO. Hence, blending of natural antioxidants rich minor oils (RRPO, RBO and SESO) with the major vegetable oils (GNO and SFO) may preserve them by lowering their rate of oxidation during storage and frying.

Keywords Coconut oil · Natural antioxidants · Oxidation · Groundnut oil · Radical scavenging activity · Red palmolein · Rice bran oil · Sesame oil · Sunflower oil

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Introduction

In the recent years, emphasis is made on the natural antioxidants present as minor components in any vegetable oil. The minor constituents uniquely present in certain vegetable oils are associated with medicinal qualities and hence helpful in preventing/delaying onset of diseases and promoting health. These natural antioxidants include tocopherols, β-carotene, oryzanol and lignans. Oryzanol is uniquely present in rice bran oil (RBO), which is shown to have hypocholesterolemic activity (Reena and Lokesh 2007). Palm oil is a rich source of β-carotene, which functions as provitamin-A and a scavenger of oxygen free radicals and has several health benefits (Basu et al. 2001). Tocopherols and tocotrienols present in unrefined and physically refined oils such as palm oil and RBO, have antioxidative and hypocholesterolemic properties and are beneficial in preventing cardiovascular diseases (Minhajuddin et al. 2005; Edem 2002). Sesame oil is a rich source of lignans, which are known to have antioxidant, hepato-protective, hypolipidemic, hypotensive and anticarcinogenic activities (Namiki 2007). With the growing health awareness among consumers, the health promoting minor components of vegetable oils are being isolated and used as nutritional supplements. Blending of major vegetable oils with natural antioxidants rich minor oils is an available option for improving the quality and health benefits of oils. The different vegetable oils of known fatty acid composition can be combined in

appropriate ratios to obtain products of improved composition and better functional properties besides enhancement of oxidative stability (Anwar et al. 2007).

The major vegetable oils commonly used in different regions of India are groundnut oil (GNO) with annual production and consumption of 1.43 million tonnes and sunflower seed oil (SFO) with annual consumption of 0.83 million tonnes during 2009–2010 (FAO 2013). These oils do not contain the health-improving minor components such as β–carotene, oryzanol and lignans while groundnut oil naturally contains small amounts of tocopherols, sunflower oil is depleted of its natural tocopherols content during refining. However both the oils have less of tocopherols. Coconut oil with annual consumption of 0.40 million tonnes, sesame oil with annual consumption of 0.1 million tonnes, rice bran oil with annual consumption of 0.56 million tones (FAO 2013) and palm oil (imported) are the minor oils available in India with limited consumption based on regional preferences.

Indian food laws do not permit external addition of minor components as concentrates/isolates to vegetable oils, but a vegetable oil (unrefined or refined grade) containing minor components can be incorporated at a level of 20 to 80 % in any other vegetable oil (FSSAI Food Safety and Standards Authority of India et al. 2011). The oils can be blended even to derive the protective advantage due to the presence of specific ingredients that offer protection against oxidation to improve frying recyclability (Toliwal et al. 2005). Previous reports on oil blends have focused on total tocopherols and fatty acid composition in relation to stability (Warner and Mounts 1993; Chu and Kung 1998; Bhatnagar et al. 2009) and storage stability of oil blends (Khatoon and Gopala Krishna 1999). Blending of corn oil with black cumin and coriander seed oils improved its stability and radical scavenging activity (Ramadan and Wahdan 2012). Blending of high linoleic sunflower oil with selected cold pressed oils improved its functionality, stability and antioxidative characteristics (Ramadan 2013). Another report regarding stability during storage under packed conditions of oil blends containing minor components such as β–carotene, tocopherols, oryzanol, and lignan antioxidants is available (Shiela et al. 2004). Despite several studies on the quality and stability improvement of the oils through blending, literature is scarce on the retention of natural antioxidants in oil blends during storage and frying. In the present study, we have attempted to improve the stability of major oils by blending them with minor oils containing natural antioxidants and the blended oils were assessed for their stability and retention of natural antioxidants under accelerated storage conditions of high temperature, high humidity and also frying conditions, the results of which are reported in this paper.

Materials and methods

Unrefined groundnut oil (GNO), physically refined rice bran oil (RBO), unrefined sesame oil (SESO), refined sunflower oil (SFO), unrefined coconut oil (CNO) were procured from the local super market of Mysore city, Karnataka, India. Crude red palm oil was obtained from M/s Palmtech Pvt. Ltd. Mysore and was fractionated and the olein fraction refined in the laboratory and used as such without bleaching and labeled as refined red palmolein (RRPO); 2,2–diphenyl–1–picryl hydrazyl free radicals (DPPH), α-tocopherol, β-carotene and sesamin were procured from Sigma Chemical Co., St. Louis, USA and Sesamol was procured from M/s Spectrochem Pvt. Ltd. Mumbai, India. Other chemicals and reagents used for analysis were of analytical reagent grade.

Fatty acid composition by Gas chromatography Fatty acid methyl esters (FAME) of the oil samples were prepared by transesterification, according to AOCS Method No: Ce 1–62, 1998 (AOCS 1998). FAMEs were analyzed on a Fisons 8000 series gas chromatograph (Fisons Co., Italy), equipped with a flame ionization detector (FID) and a fused silica capillary column (100 m X 0.25 mm i.d.), coated with 0.20 μm SP2560 (Supelco Inc., Bellefonte, PA) as the stationary phase. The oven temperature was programmed from 140 to 240 °C at 4 °C/min with an initial hold at 140 °C for 5 min. The injector and FID were at 260 °C. A reference standard FAME mix (Supelco Inc.) was analyzed under the same operating conditions to determine the peak identity. The FAMEs were expressed as relative area percentage.

Tocopherols content Total tocopherols content was determined by using IUPAC Method No. 2.301, (Paquot and Havtfenne 1987) and expressed as total tocopherols (as α-tocopherol) in mg/100 g.

Oryzanol Oryzanol content in RBO and its blends was determined by a spectrophotometric method by dissolving 0.01 g of the sample in 10 ml of hexane and reading the absorbance at 314 nm in a 1–cm cell (double beam UV–visible recording spectrophotometer model UV–1601, Shimadzu Corporation, Kyoto, Japan). The oryzanol content was calculated by using the formula: [(A/W)×(100/358.9)]. Where A is the absorbance of the sample, W is the weight of the sample in gram/100 ml, 358.9 is the specific extinction ($E^{1\%}_{1cm}$) value for oryzanol (Gopala Krishna et al. 2006).

β-carotene β-Carotene content of the samples were determined by dissolving the oil sample in acetone and absorbance was recorded at 450 nm using computerized Shimadzu Spectrophotometer (Kyoto, Japan) according to PORIM method (1998).

Lignans by HPLC Analysis of lignans in SESO and its blends was performed by HPLC (model LC–10A VP Shimadzu corporation, Kyoto, Japan) equipped with a UV–detector set at 290 nm on a C18 phenomenex column (250 mm length *x* 4.6 mm i.d.) using 70 % methanol as the mobile phase according to Kamal-Eldin and Appelqvist (1994). Standard sesamol and sesamin were used for the quantification of lignans in the sample.

Preparation, packaging and storage of oil blends The five blends prepared were GNO+RRPO (80:20), GNO+RBO (80:20), GNO+SESO (80:20), SFO+RRPO (50:50) and SFO+CNO (60:40). The blends were prepared by placing them in a beaker in the desired ratio and mixing at 120 rpm for 15 min at 65 °C and blends cooled to room temperature. These were immediately taken up for packing using the packaging material Nylon (poly amide) based co-extruded film material (PA). The oil blends (200 ml) were packed in 16×10 cm uniform pouches with minimum air space, by driving out air from the pouches manually. The pouches were stored at two temperatures and relative humidity (RH) conditions i.e. accelerated condition 38 °C/90 % RH, normal condition 27 °C/65 % RH. All blends were analyzed initially and after withdrawal at 15, 30, 45, 60, 75 and 90 days for their chemical parameters such as peroxide value, free fatty acids value, fatty acid composition (AOCS 1998), oryzanol, lignans, β–carotene and total tocopherols contents on triplicate samples.

Frying of papads in the oil blends A domestic stainless steel frying pan with internal diameter 20 cm x height 8 cm was used for frying experiments. The pan was filled with 500 ml of the oil and was heated to 180 °C and *papads* were fried for 20 min once in 24 h for a total of 120 h. No oil replenishment was done during frying. Oils were allowed to cool to room temperature after each frying operation and about 50 ml of oils were withdrawn and stored at 4 °C each day for subsequent analysis. *Papad* frying was performed in the morning hours and their sensory analysis was conducted in the afternoon hours.

Radical Scavenging activity (RSA) RSA towards DPPH radicals was determined according to Bhatnagar et al. 2009. RSA and the presence of hydrogen donors in the oils were examined by reduction of DPPH radicals in toluene. A toluenic solution of DPPH radicals was freshly prepared at a concentration of 10^{-4} M. The oil samples (50±1 mg) were placed in test tubes and a 4-ml aliquot of DPPH toluenic solution was added and vortexed for 20 s at ambient temperature. Against a blank of pure toluene without DPPH radicals, the decrease in the absorption at 515 nm was measured in a 1–cm quartz cell after 1, 30, and 60 min of mixing, using a UV–visible

Table 1 Fatty acid composition of primary oils and their blends with minor oils

Fatty acids	GNO	RRPO	RBO	SESO	SFO	CNO	GNO: RRPO (80:20)	GNO: RBO (80:20)	GNO: SESO (80:20)	SFO: RRPO (50:50)	SFO: CNO (60:40)
C8:0	Nd	Nd	Nd	Nd	Nd	7.4±0.5	Nd	Nd	Nd	Nd	2.0±0.02
C10:0	Nd	Nd	Nd	Nd	Nd	5.1±0.4	Nd	Nd	Nd	Nd	1.9±0.1
C12:0	Nd	Nd	Nd	Nd	Nd	51.2±1.0	Nd	Nd	Nd	Nd	30.3±0.2
C14:0	0.1±0.02	1.0±0.2	Nd	Nd	Nd	22.4±0.9	0.2±0.04	Nd	Nd	0.5±0.01	9.4±0.2
C16:0	15.9±0.4	54.8±0.9	30.3±0.7	12.7±0.6	7.4±0.2	9.2±0.4	23.3±0.4	19.0±0.5	16.0±0.9	26.6±0.9	9.6±0.1
C18:0	1.4±0.1	0.5±0.1	Nd	0.9±0.3	1.2±0.1	0.1±0.01	0.8±0.1	0.5±0.1	0.7±0.04	1.8±0.2	0.1±0.02
C18:1	46.2±0.6	36.7±0.5	37.8±0.6	40.3±1.0	31.5±0.6	4.0±0.1	45.5±1.2	45.5±0.8	45.4±1.1	36.1±0.8	16.0±0.5
C18:2	36.1±0.8	6.8±0.3	31.8±0.7	45.8±0.8	59.7±0.8	0.3±0.05	29.9±1.1	34.8±0.7	37.8±0.9	34.6±0.9	30.3±0.8
SFA	17.4	55.8	30.3	13.6	8.6	95.4	24.3	19.5	16.7	28.9	53.3
MUFA	46.2	36.7	37.8	40.3	31.5	4.0	45.5	45.5	45.4	36.1	16.0
PUFA	36.1	6.8	31.8	45.8	59.7	0.3	29.2	34.8	37.8	34.6	30.3
S:M:P Ratio	1:2.6:2.1	1:0.7:0.1	1:1.2:1.1	1:2.9:3.4	1:3.6:3.9	1:0.04:0.003	1:1.9:1.2	1:2.3:1.8	1:2.7:2.3	1:1.2:1.2	1:0.3:0.6

Nd not detected

GNO Groundnut oil, *RRPO* Red Palmolein, *RBO* Rice bran oil, *SESO* Sesame oil, *SFO* Sunflower oil, *CNO* Coconut oil

Values reported are mean±SD (n=6).

spectrophotometer (model UV–1601, Shimadzu corporation, Kyoto, Japan). RSA towards DPPH radicals was estimated from the differences in absorbance of toluenic DPPH solutions with or without sample (control) and the inhibition percent was calculated using the following equation: % Inhibition=[{absorbance of control− absorbance of test sample}/absorbance of control] × 100.

Sensory evaluation of papads Freshly fried papads were subjected to sensory analysis to determine the acceptability. Twelve panelists were selected from among the post graduate students in the Department of Food science and Nutrition, University of Mysore, Mysore on the basis of their willingness to participate and also a sweet threshold test. Six differently coded samples were served to the panelists. The data were pooled, analyzed statistically and product acceptability determined.

Statistical analysis The experiments were carried out in duplicate. All the quality parameters were analyzed in triplicate (n=6) and the data obtained for each parameter was expressed as mean±standard deviation. One-way anova was used to calculate significant difference among the blends (Steele and Torrie 1980). A two-tailed p value was determined to show the significant differences. A significant difference was considered only when the p value≤0.05.

Results and discussion

Fatty acid composition The fatty acid composition of the individual oils and blends is given in Table 1. Data reveals that the individual oils contained saturated fatty acids (SFA) (13.6–95.4 %); monounsaturated fatty acids (MUFA) (4.0–46.2 %) and polyunsaturated fatty acids (PUFA) (0.3–59.7 %) while the blends contained SFA (16.7–53.3 %); MUFA (16.0–45.5 %) and PUFA (29.2–37.8 %). Among the oil samples, RBO, SESO and SFO were good sources of MUFA and PUFA while CNO was significantly rich in SFA (95.5 %). The PUFA content of the individual oils was found to be in the order of SFO>SESO>GNO>RBO>RRPO>CNO. The MUFA content of individual oils was found to be in the order of GNO>SESO>RBO>RRPO>SFO>CNO. The SFA content of the individual oils was found to be in the order of CNO>RRPO>RBO>GNO>SESO>SFO. The blending of the oils resulted in an even distribution of PUFA, MUFA and SFA and thus balanced the fatty acid composition in the prepared blends. In case of SFO after blending with RRPO and CNO a significant decrease was observed in PUFA content. All the blends of GNO with other minor oils (RRPO, RBO and SESO) showed an increase in MUFA and PUFA contents. Literature suggests that by decreasing the PUFA content oxidative stability of oil blends can be increased (Bhatnagar et al. 2009). The PUFA rich SFO can be made stable by decreasing its PUFA content through blending it with SFA rich CNO and RRPO.

Natural antioxidants content The natural antioxidants content of individual oils and their blends is shown in Table 2. The total tocopherols content of individual oils ranged from (2.9–80.0 mg/100 g). The total tocopherols content of the individual oils agreed well with the literature reports (Kamal-Eldin and Andersson 1997; Bhatnagar et al. 2009) Among the oils, CNO contained the least amount of tocopherols (2.9 mg/100 g) while RBO contained the highest amount of tocopherols (80.0 mg/100 g). The tocopherols content of the individual oils was found to be in the order of RBO>RRPO>SESO>GNO>SFO>CNO. The β-carotene was found only in RRPO (45.5 mg/100 g). Similarly, oryzanol and lignans were found only in RBO (0.60 g/100 g) and SESO (1.4 g/100 g). The results for β-carotene in RRPO agreed well with the literature reports of Yap et al. 1991 and Jalani et al. 1997 while the results for oryzanol in RBO agreed well with

Table 2 Natural antioxidants content of different oils and their blends

Oil/blends	Total tocopherols (mg/100 g oil)	β-carotene (mg/100 g oil)	Oryzanol (g/100 g oil)	Lignans (g/100 g oil)
RRPO	73.8±2.5	45.5±5.0	Nd	Nd
RBO	80.0±2.2	Nd	0.6±0.05	Nd
SESO	57.5±1.6	Nd	Nd	1.4±0.05
CNO	2.9±0.2	Nd	Nd	Nd
SFO	49.7±1.1	Nd	Nd	Nd
GNO	50.7±0.9	Nd	Nd	Nd
GNO: RRPO	55.2±1.5	10.7±2.5	Nd	Nd
GNO: RBO	54.6±1.2	Nd	0.12±0.1	Nd
GNO: SESO	53.1±0.5	Nd	Nd	0.35±0.05
SFO: RRPO	62.6±1.0	28.7±3.0	Nd	Nd
SFO: CNO	30.3±0.8	Nd	Nd	Nd

Nd not detected

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Values reported are mean±SD (n=6)

the report of Gopala Krishna et al. 2006 and lignans in SESO agreed well with the literature report of Bhatnagar et al. 2009. The resultant blends of RRPO were enriched with 23 & 63 % of β-carotene after blending (10.7 & 28.7 mg/100 g), while the blends of RBO and SESO contained 20 % (120 mg/100 g) and 25 % (350 mg/100 g) of oryzanol and lignans respectively after blending.

Oxidative stability

Changes during storage at 38 °C/90 % RH The oxidative changes in the blended oils incubated at the different storage conditions for 90 days are given in Table 3. The initial values of PV were within 10 meqO_2/kg of oil, except SFO: RRPO whose initial PV was 11.99 meqO_2/kg of oil. A constant increase in the PV was observed in all the blends, although the rate of peroxides formation in the blends of groundnut oil was significantly less (PV 32–50 meqO_2/kg of oil) compared to the blends of sunflower oil (70 and 103 meqO_2/kg of oil). Among the GNO blends, no significant difference was observed in PV during the storage period while the SFO blends with RRPO (103 meqO_2/kg of oil) and CNO (70 meqO_2/kg of oil) showed a significant difference in PV during the storage period. Whereas in case of FFA, the SFO oil blends (0.02 and 0.03 %) found to be significantly stable compared to the GNO blends (0.24–0.33 % oleic acid). PUFA content is an important factor influencing oxidative stability of oils and their blends than the antioxidants. Oxidative stability index (OSI) is inversely proportional to PUFA content and the oxidative stability of high PUFA oil can be increased by blending with high MUFA or SFA oil (Bhatnagar et al. 2009). In other words, if the PUFA content of oil is reduced through blending with MUFA or SFA, the oxidative stability of the blend would increase. Similarly, in the present study blending of GNO with the minor oils (RRPO, RBO and SESO) an increase in MUFA and SFA was observed, which illustrates the stability of oil blends towards oxidation, whereas the MUFA content of the SFO blends was significantly less than the GNO blends. In case of FFA values, the SFO blends were found to be more stable and the hydrolytic reaction was slower than in GNO blends, which is indicated by a higher increase in FFA, and this may be due to high MUFA and PUFA of GNO blends. The slower increase in FFA may be due to the refined form of the SFO, as refining removes FFA and the initial values were low and remained almost same during the storage period (0.01-0.03 %). Under accelerated storage conditions i.e. 38 °C/90 % RH, the PV rise of the blends was found to be in the range 8.1–17.5 folds and the FFA rise of the blends was found to be in the range 1.4–2.0 folds indicating a higher rate of PV and FFA development (Table 4).

Table 3 Storage behavior of packed blends at different storage conditions

Parameters	Blends (ratio)	Days of storage											
		38 °C/90 % RH						27 °C/65 % RH					
		0	15	30	45	60	75	90	30	60	90		
PV (meq O_2/kg)	GNO: RRPO	6.0±0.014^{a}	18.0±0.017^{b}	23.95±0.05^{e}	32.08±0.04^{d}	36.16±0.000^{e}	42.61±0.29^{f}	50.19±0.04^{g}	14.01±0.025^{b}	19.0±0.94^{e}	30.09±0.012^{d}		
	GNO: RBO	3.98±0.018^{a}	97±0.067^{b}	14.04±0.015^{c}	15.00±0.97^{d}	22.07±0.005^{e}	24.98±0.89^{f}	32.12±0.052^{g}	7.02±1.010^{b}	12.05±0.02^{c}	21.03±0.884^{d}		
	GNO: SESO	3.94±0.030^{a}	7.9±0.000^{b}	16.03±0.034^{c}	19.98±0.00^{d}	20.07±0.022^{d}	26.0±0.04^{e}	39.07±0.942^{f}	7.975±0.025^{b}	12.07±0.005^{c}	25.81±0.287^{d}		
	SFO: RRPO	11.99±0.01^{a}	28.07±0.00^{b}	50.0±0.2^{c}	62.06±0.00^{d}	72.2±0.145^{e}	88.18±0.045^{f}	103.46±0.965^{g}	20.06±0.025^{b}	26.06±0.138^{c}	47.11±1.036^{d}		
	SFO: CNO	4.00±0.006^{a}	12.05±0.02^{b}	33.82±0.16^{c}	39.73±0.23^{d}	44.07±0.106^{e}	39.08±1.133^{f}	70.13±0.076^{g}	8.01±0.000^{b}	15.03±1.025^{c}	29.86±0.105^{d}		
FFA (%)	GNO: RRPO	0.17±0.003^{a}	0.18±0.000^{b}	0.21±0.000^{c}	0.22±0.001^{d}	0.23±0.007^{e}	0.23±0.0005^{e}	0.24±0.000^{f}	0.17±0.000^{a}	0.18±0.0005^{b}	0.18±0.0003^{b}		
	GNO: RBO	0.17±0.001^{a}	0.17±0.00^{a}	0.20±0.001^{b}	0.21±0.000^{c}	0.21±0.000^{c}	0.23±0.002^{d}	0.24±0.002^{e}	0.17±0.001^{b}	0.18±0.000^{c}	0.18±0.003^{c}		
	GNO: SESO	0.23±0.000^{a}	0.25±0.000^{b}	0.27±0.001^{c}	0.28±0.002^{d}	0.29±0.002^{e}	0.30±0.000^{f}	0.33±0.000^{g}	0.23±0.001^{a}	0.23±0.001^{a}	0.24±0.001^{b}		
	SFO: RRPO	0.02±0.000^{a}	0.02±0.000^{a}	0.02±0.000^{ab}	0.03±0.003^{c}	0.03±0.000^{d}	0.03±0.000^{d}	0.03±0.003^{d}	0.02±0.000^{a}	0.02±0.000^{a}	0.02±0.000^{a}		
	SFO: CNO	0.01±0.000^{a}	0.01±0.000^{a}	0.01±0.001^{a}	0.01±0.001^{a}	0.01±0.000^{a}	0.01±0.000^{a}	0.02±0.000^{b}	0.01±0.000^{a}	0.01±0.000^{a}	0.01±0.000^{a}		

GNO Groundnut oil, *RRPO* Red Palmolein, *RBO* Rice bran oil, *SESO* Sesame oil, *SFO* Sunflower oil, *CNO* Coconut oil

Values reported are mean±SD (n=6)

Values in rows followed by different superscripts are significantly different (p <0.05)

Table 4 Stability of natural antioxidants during different storage conditions

Parameters	Blends (ratio)	Days of storage											
		38 °C/90 % RH							27 °C/65 % RH				
		0	15	30	45	60	75	90	30	60	90		
β-carotene (mg/100 g)	GNO: RRPO	10.7±9.00^{a}	10.7±0.55^{a}	6.6±0.6^{b}	6.5±0.65^{b}	7.3±6.04^{b}	7.0±5.0^{b}	6.3±4.58^{b}	10.1±5.47^{b}	9.3±2.49^{b}	9.5±3.0^{b}		
	SFO: RRPO	28.7±15.00^{a}	22.6±2.05^{b}	14.3±12.75^{c}	12.2±1.mn	6.7±0.86^{e}	6.2±6.1^{e}	5.8±2.00^{e}	17.7±0.00^{b}	17.4.±11.02^{b}	17.2±10.0^{b}		
Oryzanol (g/100 g)	GNO: RBO	0.12±0.007^{a}	0.11±0.024^{a}	0.11±0.002^{a}	0.11±0.012^{a}	0.11±0.012^{a}	0.11±0.01^{a}	0.10±0.01^{a}	0.11±0.005	0.11±0.018	0.11±0.579		
Lignans (g/100 g)	GNO: SESO	0.35±0.015^{a}	0.35±0.005^{a}	0.23±0.00^{b}	0.27±0.005^{c}	0.25±0.003^{bc}	0.25±0.017^{bc}	0.26±0.005^{c}	0.28±0.028	0.28±0.002	0.27±0.015		

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Values reported are mean±SD (n=6)

Values in rows followed by different superscripts are significantly different (p<0.05)

Changes during the 27 °C/65 % RH Oxidative changes in the blended oils stored at the different storage conditions for 90 days are given in Table 3. The results indicate that, at the storage conditions followed in the study, the GNO blended with RRPO, RBO and SESO were more effective in preventing peroxides formation and in case of SFO blended with RRPO and CNO had low amounts of free fatty acids. Among the two storage conditions, the 27 °C and 65 % RH was found to be significantly more effective in preventing and retaining the antioxidants in the blends. The overall characteristics of the blends indicated that the MUFA, PUFA and natural antioxidants were incorporated in different levels into the GNO and SFO through blending, which played a major role in preventing the rancidity in the blends. Generally oil needs good oxygen barrier coupled with a good sealant layer even when the contamination of the sealing area occurred. Nylon is a good oxygen barrier. Hence five layer nylon based co-extruded material satisfying both the requirement and also of low cost was selected. The two storage

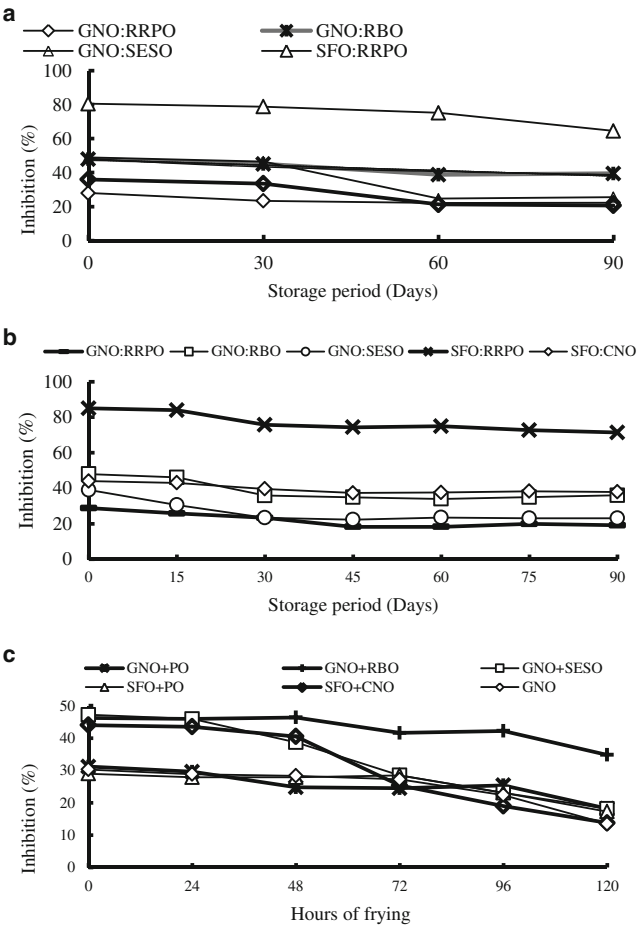

Fig. 1 Radical scavenging activity of vegetable oil blends stored at different temperatures i.e. (**a**) 38 °C & 90 % RH; (**b**) 27 °C & 65 % RH and (**c**) after frying. *GNO* Groundnut oil, *RRPO* Red Palmolein, *RBO* Rice bran oil, *SESO* Sesame oil, *SFO* Sunflower oil, *CNO* Coconut oil. Values reported are mean (n=6)

conditions of 90 % RH/38 °C and 65 % RH/27 °C were selected as per BIS which stimulate the conditions of average and coastal regions climatic conditions of other places. Under normal storage conditions i.e. 27 °C/65 % RH, the PV rise of the blends was found to be in the range 3.9–7.4 folds during the storage period and the FFA rise of the blends was found to be in the range 1.0–1.1 folds during the storage period. Based on the rise in PV and FFA, it can be concluded that normal storage conditions (27 °C/65 % RH) preserves the oil blends better than the accelerated storage conditions (38 °C/90 % RH) irrespective of the packaging material and composition of oil blends.

Stability of natural antioxidants Antioxidants play a vital role in the stability of oils and the most common antioxidant found in the oils are tocopherols while some unique antioxidants like oryzanol, lignans and β–carotene are found only in RBO, SESO and RRPO respectively. β-carotene (RRPO), oryzanol (RBO) and lignans (SESO) were determined in blends during the experimental period at both storage conditions. Under accelerated storage conditions i.e. 38 °C/90 % RH, the β–carotene retention in RRPO blends was 20-58 % while the oryzanol retention in the RBO blend was 83 % and the lignans retention in SESO blend was 74.2 % during the storage period. Under normal storage conditions i.e. 27 °C/65 % RH, the β-carotene retention in RRPO blends was 65.2–88.7 % while the oryzanol retention in the RBO blend was 91.6 % and the lignans retention in SESO blend was 77.1 % during the storage period. Based on the retention values of oryzanol, lignans and β–carotene, it can be concluded that normal storage conditions (27 °C/65 % RH) preserves the natural antioxidants of oil blends better than the accelerated storage conditions (38 °C/90 % RH) irrespective of the packaging material and composition of oil blends.

The radical scavenging activity of blends The RSA of the blends incubated at different temperature and humid conditions are represented in Fig. 1a and b. From the figures it is observed that at both the storage conditions, SFO+RRPO blend showed significantly higher RSA, which may be due to the presence of high amounts of carotenoids and tocopherols in RRPO. RRPO was also blended with GNO albeit in a smaller amount than SFO+RRPO blend and hence showed lower RSA. Among other blends, GNO with RBO and SESO were found to exhibit good RSA of 40–50 % which may be due to the presence of oryzanol and lignans present in RBO and SESO respectively. The radical scavenging activity of different blends after frying is given in Fig. 1c. A decrease in the radical scavenging activity (RSA) was observed in the all the blended oils and GNO (as control) during the frying period. On the first day of frying, no significant difference was observed in radical scavenging activity among the blends and GNO (as control). Among all the blends GNO+RBO was most stable and showed maximum RSA (45.9 %) during the frying period compared to the other blends and GNO (as control) which ranged between 13–43 % of RSA. The high RSA of the GNO+RBO blend during frying may be due to the presence of oryzanol which is a potent antioxidant and can withstand high temperature conditions (Gopala Krishna et al. 2006). Even though, RRPO and SESO are good

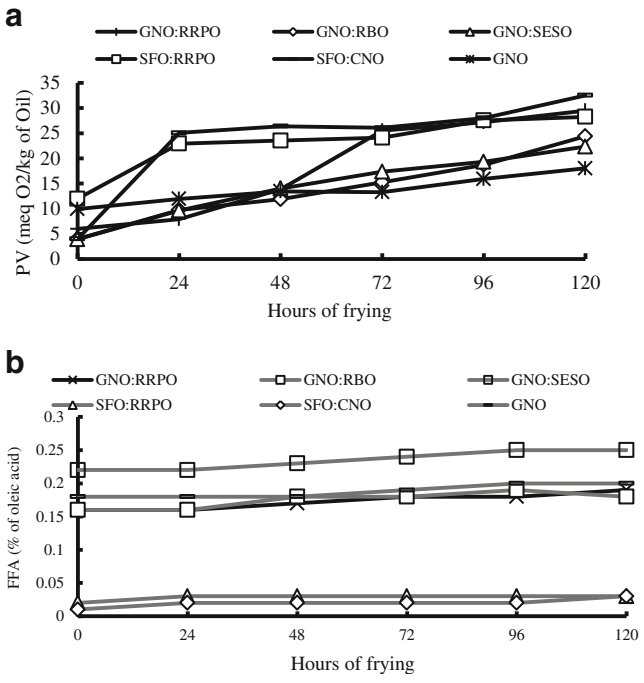

Fig. 2 (**a**) Peroxide value and (**b**) free fatty acids value of blended oils during frying. *GNO* Groundnut oil, *RRPO* Red Palmolein, *RBO* Rice bran oil, *SESO* Sesame oil, *SFO* Sunflower oil, *CNO* Coconut oil. Values reported are mean (n=6)

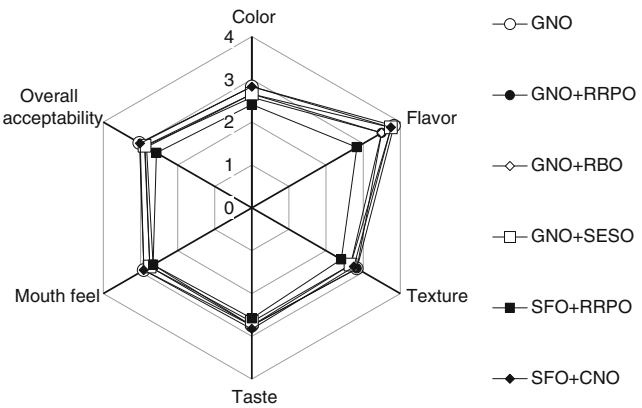

Fig. 3 Sensory evaluation of fried papads. *GNO* Groundnut oil, *RRPO* Red Palmolein, *RBO* Rice bran oil, *SESO* Sesame oil, *SFO* Sunflower oil, *CNO* Coconut oil. Values reported are mean (n=6)

source of β-carotene and lignans but could not exhibit high RSA which indicates their sensitivity to the high temperature.

Effect of frying papads on the oxidative stability of blends Frying of papads in the oil blends resulted in a constant rise in peroxide value (PV) and free fatty acids value (FFA) (Fig. 2a and b). The PV of the GNO blends with RRPO, RBO and SESO was significantly increased during the 120 h of frying period. Similarly in case of SFO blends with RRPO and CNO there were a significant increase in PV during the frying period. The PV of GNO blends after first day of frying was found to be less (7.95–9.65meqO_2/kg) than GNO (as control) i.e. 11.96 meqO_2/kg, whereas from the period between 72nd h of frying to 120th h of frying, there was a small increase in PV i.e. (15.26–25.52 meqO_2/kg of oil) to (22.34–29.50 meqO_2/kg oil). The PV of SFO blends after 24 h of frying was found to be more (22.93–25.08 meqO_2/kg of oil) than GNO (as control) i.e. 11.96 meqO_2/kg of oil (Fig. 2a). During the 120 h of frying period there was slight increase in FFA of the blends and GNO (as control) (Fig. 2b). Among the blends and GNO (as control), the FFA of SFO blends was significantly lower (0.017–0.03 %) than GNO (as control) and other GNO blends. The low FFA values may be due to the minimum hydrolytic reactions during frying as dry *papad* usually contains ~15 % of moisture and allows less moisture exposure to the oil (Choe and Min 2007).

Sensory evaluation Sensory scores of the fried *papads* in different blends are given in Fig. 3. The sensory scores indicated high acceptability to the *papads* fried in SFO+CNO blend and were comparable with *papad* fried in GNO (as control). No significant difference among any of the blends and GNO (as control) indicates the acceptability of the prepared blends by the panelists to be used as frying medium.

The present study was planned to ascertain the suitability of minor oils as a source of natural antioxidants in major oils. The overall characteristics of the blends indicated that the MUFA, PUFA and natural antioxidants were incorporated at different levels into GNO and SFO through blending, which played a major role in delaying the rancidity in their blends. Fair amounts of natural antioxidants were detected in the blends depending on the oil source i.e. β-carotene in the blends with RRPO, lignans in SESO blend and oryzanol in RBO blend. During the storage period, the antioxidants of all blends were stable. From the results it is evident that, at the storage conditions followed in the study, the GNO blended with RRPO, RBO and SESO were more effective in preventing peroxides formation and in case of SFO blended with RRPO and CNO had low amounts of free fatty acids. In case of radical scavenging activity, the blends with antioxidant rich oils i.e. GNO+RBO, SFO+RRPO were effective in scavenging the free radicals. During the 120 h of frying period, the GNO and SFO blends showed significant difference ($p \leq 0.05$) in peroxide value whereas, no significant difference was observed in free fatty acids value of the blends ($p > 0.05$). The radical scavenging activity was significantly high in GNO+RBO blend ($p \leq 0.05$) which correlates well with the improved oxidative stability. The sensory scores of the *papads* fried in the oil blends and GNO (as control) showed no significant difference ($p > 0.05$) which indicates the acceptability of the above prepared oil blends by the panelists to be used as frying medium.

Conclusions

In the present study on retention of natural antioxidants and balancing of saturated and unsaturated fatty acids, the major oils (GNO and SFO) blended with minor oils (RRPO, RBO, SESO and CNO) exhibited a balanced fatty acid profile. The SMP ratio were found to be 1:1.9:1.2, 1:2.3:1.8, 1:2.7:2.3, 1:1.2:1.2 and 1:0.3:0.6 for GNO+RRPO, GNO+RBO, GNO+SESO, SFO+RRPO and SFO+CNO blends. The minor oils rich in natural antioxidants also enriched the blends (GNO+RRPO, GNO+RBO, GNO+SESO, SFO+RRPO, SFO+CNO) with β-carotene, lignans, oryzanol and tocopherols which have contributed towards the oxidative stability of the blends, during the different storage conditions and withstood the frying temperature conditions.

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