Oxidative Stability of Healthful Frying Oil Medium and Uptake of Inherent Nutraceuticals During Deep Frying

Nasirullah* and Baby Latha Rangaswamy

Department of Lipid Science and Traditional Foods, Central Food Technological Research Institute, Mysore-570 020, India

ABSTRACT: Four healthful frying oil mediums have been formulated using sunflower (FOB-I), groundnut (FOB-II), mustard (FOB-III), and palm olein (FOB-IV) oils as base oils, and fortified with rice bran and crude sesame oils separately in the ratio of 60:20:20 (by vol). Oxidative stabilities have been ascertained by deep-frying potato bajji (potato slices sandwiched with Bengal gram flour) continuously for 60 min for three cycles with a gap of 7 d each. The product had moisture between 12.8 and 16.0% and absorbed fat between 32.5 and 38.1%, making the oil media vulnerable to oxidation. The *p*-anisidine values for leftover FOB-I and FOB-IV ranged from 10.8 to 24.4 and from 1.5 to 10.7, respectively, indicating that the former was a less and the latter a more stable combination. Hydroperoxide and conjugated dienes were assessed by UV spectrometry at λ_{max} 230 nm. The O.D. was maximal (1.4) for FOB-I samples for both leftover and absorbed oils for third-cycle experiments. That there was no absorbance for the FOB-III and -IV samples indicated their absence. Estimation of oryzanol and sesamol in oil left over after deep frying and in the oil absorbed by the products indicated that distribution was equal and there was no loss of these active factors during deep frying. The study indicated that sunflower oil blend was the least stable and the palm olein blend was most stable.

Paper no. J11106 in *JAOCS 82*, 753–757 (October 2005).

KEY WORDS: Antioxidants, frying, healthful oil, nutraceuticals, stability.

Deep fat frying imparts a good taste, flavor, pleasing golden brown color, and crisp texture to food products along with excellent mouth feel. Less attention has been paid to the vegetable oils used for frying, although all the desirable properties of deep-fried foods are attributed to the quality and variety of edible oil used for frying (1). During frying, oil is exposed to atmospheric oxygen and moisture at a high temperature (180–190°C). As a result, various chemical changes in the frying oil produce a number of harmful compounds and reduce the quality of the frying oil (2,3). Hence, a formulated vegetable oil to be used for frying that can offset the undesirable effects of heat and moisture is desirable. In our research (4), we have explored ways to improve the heat resistance during frying of vegetable oils such as sunflower, groundnut, mustard, and palm olein. Rice bran oil and crude sesame oil have been used as sources of nutraceuticals and antioxidants, i.e., oryzanol and sesamolin, respectively. The beneficial effects of rice bran oil and sesame oil are well documented (5–8). In the present investigation frying oil blends were prepared by incorporating rice bran and crude sesame oils, in a fixed ratio, into the base oils. Their stability against heat and moisture and the distribution of nutraceuticals in the fried products and leftover oil after fryings also were studied.

*To whom correspondence should be addressed.
E-mail: lipid@cscftri.ren.nic.in

EXPERIMENTAL PROCEDURES

Composition of healthful frying oil blends. Healthful frying oil blends were prepared using sunflower oil, double-filtered groundnut oil, crude mustard oil, and palm olein separately as base oils. Each base oil was fortified with rice bran and crude sesame oils in the ratio of 60:20:20 (by vol). The blends were made up in quantities of 5 kg each. After thorough mixing with an agitator, the blends were stored for 1 wk before use. Phase separation was noticed in the palm olein oil blend; hence, it was shaken and mixed occasionally. Before samples were drawn for experiments, the blends were further mixed for sake of homogeneity.

Preparation of product in healthful frying oil blends. Bengal gram flour (250 g), rice flour (25 g), chilli powder (3.5 g), and salt (4.5 g) were mixed together. After mixing, the water (300 mL) was added slowly to the mix to make a smooth batter for bajji (a potato slice coated with a seasoned Bengal gram flour/rice flour mix and subsequently deep fried, used as snack). The batter was held for 10 min for a better equilibration and homogenization. The peeled and sliced potatoes were dipped into the batter and fried at 180–190°C using the four different healthful frying oil blends. The potato bajji were continuously prepared for about 1 h, batch after batch. The bajji and leftover oil were stored separately for further experiments. The leftover oil was kept at room temperature (26–32°C) for 5 to 7 d in contact with air before a second cycle of product preparation was carried out.

Sunflower, double-filtered groundnut, mustard, palm olein, rice bran, and crude sesame oils were procured through the consumer cooperative society of the Central Food Technological Research Institute (Mysore, India) in unit packs from reputable vegetable oil firms in India. All the chemicals and solvents were of analytical reagent grade obtained from chemical companies on rate contract. Ethyl alcohol was refluxed with sodium hydroxide before distillation. *p*-Anisidine was recrystallized in hot water in the presence of sodium sulfite and active carbon before preparing the reagent for estimation.

Fat percentage, moisture percentage, and *p*-anisidine value were determined by AOCS procedures (9).

UV-vis spectroscopy. UV-vis spectra were recorded on a Shimadzu spectrophotometer (Model UV01601) using 1-cm width quartz cuvettes. The stock solutions were prepared by taking 50 mg of the oil samples in a 20-mL graduated test tube and making up to 5 mL with spectroscopic-grade hexane. Stock solution (0.5 mL) was further diluted to 3 mL. This final solution was taken for recording spectra between 200 and 800 nm.

FTIR spectroscopy. FTIR spectra were recorded on a PerkinElmer spectrophotometer (Model-2000 GC-IR). Spectra were from a film on a potassium bromide cell. The recording was done between 800 and 4000 cm^{-1}.

Estimation of oryzanol. Oryzanol content of the oil was estimated by determining the O.D. of the oil dissolved in hexane at 314 nm and using the specific extinction coefficient $E_{314nm}^{1\%,1cm} = 358.9$ (5).The percent oryzanol content was calculated using Equation 1:

$$\% \text{ oryzanol content} = \text{O.D.} \times 100/358.9 \times W \quad [1]$$

where W = weight of the oil sample. Gram% oryzanol can be converted to ppm by calculating back to mg per kg of oil sample.

Estimation of sesamol. Estimation of sesamol was done with the Villavecchia/Boudouin reaction (10,11), which depends on the release of sesamol from sesamolin, present in sesame oil, by acid hydrolysis and its subsequent condensation with furfuraldehyde to generate a pink-colored complex. This basic reaction has been refined by using a very dilute solution of alcoholic furfural (2% furfural in 95% ethyl alcohol). The pink complex has a λ_{max} of 520 nm.

A spectrophotometric method was developed in which 5 mL of vegetable oil, 5 mL of concentrated hydrochloric acid, and 5 mL of furfural solution were mixed together and shaken to give a pink complex. The acid layer separated on standing. The absorbance of the pink-colored acid layer was recorded at 520 nm. A preconstructed calibration curve was used to calculate the amount of sesamol present in the oil.

Standardization of the spectrophotometric method for estimation of sesamol in sesame oil and its healthful frying oil blends. (i) Preparation of the stock solution. Sesamol (11.5 mg; Spectrochem Pvt. Ltd., Hyderabad, India) was dissolved in 11.5 mL of concentrated hydrochloric acid (35% from E. Merck, Darmstadt, Germany) to produce a stock solution (1 mL of stock solution containing 1 mg of sesamol).

(ii) Preparation of the working solution. The stock solution (1 mL) was made up to 10 mL in a 20-mL graduated test tube by the concentrated hydrochloric acid used for the preparation of the stock solution. One milliliter of working solution contained 0.1 mg of sesamol.

(iii) Development of the pink-colored complex for spectrophotometric estimations. Five different aliquots (0.5, 0.75, 1.0, 1.5, and 2.0 mL) of working solution were taken in 20-mL graduated test tubes and made up to 5 mL using concentrated hydrochloric acid. Then 0.4 mL of reagent solution (2 mL of furfuraldehyde in 100 mL of ethyl alcohol) was added to each reaction tube and the contents were subsequently shaken. A pink color developed immediately. The color was allowed to stabilize for 30 s before recording the spectra.

(iv) Recording of UV-vis spectra. UV-vis spectra of the pink complex between 200 and 800 nm were recorded on a Shimadzu UV-vis recording spectrophotometer (UV-240, Graphicord, model 1802212/240) coupled with a Shimadzu PR-1 graphic printer. The absorbance maximum of the solution was at 520 nm. The pink complex generated by the reaction of sesamol and furfural absorbs at λ_{max} 520 (12). O.D. values at 520 nm were plotted against the concentration of the solution to construct the calibration curve to be used as a ref-

TABLE 1
Physicochemical Properties, Oxidative Stability, and Nutraceutical Content of Frying Oil Blend-I[a] (FOB-I)

Sample/code	Fat (%)	Moisture (%)	*p*-Anisidine value	Sesamol content (ppm)	Oryzanol content (ppm)	Absorbance at λ_{max} (230 nm)	FTIR frequency (cm^{-1})
FOB-I control	NA	NA	1.0	750	600	Nil	1745, 2854, 2923, 3472
Cycle 1							
Product	36.7	15.9	NA	NA	NA	NA	NA
Leftover oil	NA	NA	10.8	707	600	1.1	1745, 2030, 2336, 2855, 2924, 3473
Absorbed oil	NA	NA	15.1	684	600	Nil	1745 (*d*), 2031, 2332, 2854, 2926, 3472
Cycle 2							
Product	37.0	14.0	NA	NA	NA	NA	NA
Leftover oil	NA	NA	11.7	681	500	1.3	1745, 2030, 2332, 2854, 2926, 3472
Absorbed oil	NA	NA	15.1	765	600	1.0	1120, 1163, 1744 (*d*), 2030, 2331, 2854, 2929, 3473
Cycle 3							
Product	34.8	13.9	NA	NA	NA	NA	NA
Leftover oil	NA	NA	24.4	714	500	1.4	1744, 2028, 2360, 2886, 2927, 3472, 3852
Absorbed oil	NA	NA	15.1	748	600	1.4	1505, 2030, 2162, 2359, 1746, 2854, 2925, 3473, 3852

[a]Control; leftover oil after frying; and corresponding oil absorbed by the potato bajji. FOB-I, refined sunflower oil/rice-bran oil/crude sesame oil, 60:20:20 by vol; NA, not applicable; *d*, doublet.

TABLE 2
Physicochemical Properties, Oxidative Stability, and Nutraceutical Content of FOB-II[a]

Sample/code	Fat (%)	Moisture (%)	*p*-Anisidine value	Sesamol content (ppm)	Oryzanol content (ppm)	Absorbance at λ_{max} (230 nm)	FTIR frequency (cm^{-1})
FOB-II control	NA	NA	1.3	823	800	Nil	1746, 2855, 2922, 3473
Cycle 1							
Product	35.7	15.7	NA	NA	NA	NA	NA
Leftover oil	NA	NA	8.8	815	800	Nil	1740, 2857, 2922, 3473
Absorbed oil	NA	NA	3.6	800	700	0.03	1744 (*d*), 2853, 2922, 3473
Cycle 2							
Product	34.9	14.3	NA	NA	NA	NA	NA
Leftover oil	NA	NA	5.0	836	600	1.0	1748, 2856, 2926, 3473
Absorbed oil	NA	NA	7.6	886	700	1.1	1745 (*d*), 2855, 2926, 3473
Cycle 3							
Product	32.5	12.8	NA	NA	NA	NA	NA
Leftover oil	NA	NA	10.0	858	600	1.3	1746, 2854, 2926, 3473
Absorbed oil	NA	NA	10.1	836	700	1.4	1747 (*d*), 2854, 2926, 3473

[a]FOB-II, double-filtered groundnut oil/rice bran oil/crude sesame oil, 60:20:20 by vol. For other abbreviations see Table 1.

erence for estimation of sesamol in actual samples. Each value was the average of six replications.

RESULTS AND DISCUSSION

Oilseeds provide a variety of phytochemicals, some of which may possess harmful effects when consumed in large amounts, others of which have beneficial health effects (6). Use of intact or crushed whole seeds, such as those of flax and sesame, together with other plant-based material, in food formulations and in baked products is recommended. Two lignans, sesamin and sesamolin, were found in crude sesame oil at 0.44 and 0.25%, respectively. However, during the refining process these lignans may be converted to their corresponding alcohols—sesamol, sesamolinol, sesaminol, and pinoresinol—which are potent antioxidants (13). Similarly, rice bran oil contains oryzanol, an ester of ferulic acid having hypocholesterolmic properties (5).

Preparation of a medium-moisture product. Potato bajji, a medium-moisture product (12.8–16.0%), was prepared in all the oil blends, namely, sunflower (FOB-I), groundnut (FOB-II), mustard (FOB-III), and palm olein (FOB-IV), as described in the Experimental Procedures section. The purpose was to assess the effect of moisture on the heat stability of the oil absorbed by the potato products, as moisture may act as a protectant to a certain extent. During deep frying, the core temperature of the product is about 30–40°C less (14) than the temperature at the surface.

The amount of oil absorbed by the product ranged between 32.5 and 38.1% in the four blends studied. Three 60-min cycles of product production were performed, with a gap of 7 d beween each cycle, to provide enough time for the oxidative

TABLE 3
Physicochemical Properties, Oxidative Stability, and Nutraceutical Content of FOB-III[a]

Sample/code	Fat (%)	Moisture (%)	*p*-Anisidine value	Sesamol content (ppm)	Oryzanol content (ppm)	Absorbance at λ_{max} (230 nm)	FTIR frequency (cm^{-1})
FOB-III control	NA	NA	0.3	907	800	Nil	1745, 2879, 2925, 3472
Cycle 1							
Product	38.0	16.0	NA	NA	NA	NA	NA
Leftover oil	NA	NA	0.3	883	800	Nil	1745, 2030, 2330, 2854, 2925, 3472
Absorbed oil	NA	NA	0.3	850	800	Nil	1746 (*d*), 2854, 2924, 3473
Cycle 2							
Product	37.5	14.3	NA	NA	NA	NA	NA
Leftover oil	NA	NA	2.2	869	800	Nil	1745, 2031, 2335, 2854, 2926, 3473
Absorbed oil	NA	NA	5.6	859	800	Nil	1745 (*d*), 2031, 2330, 2854, 2926, 3472
Cycle 3							
Product	37.6	15.0	NA	NA	NA	NA	NA
Leftover oil	NA	NA	2.5	859	700	Nil	1747, 2031, 2330, 2854, 2924, 3473
Absorbed oil	NA	NA	5.3	891	700	Nil	1747 (*d*), 2031, 2336, 2854, 2962, 3473

[a]FOB-III, mustard oil/rice bran oil/crude sesame oil, 60:20:20 by vol. For abbreviations see Table 1.

TABLE 4
Physicochemical Properties, Oxidative Stability, and Nutraceutical Content of FOB-IV[a]

Sample/code	Fat (%)	Moisture (%)	*p*-Anisidine value	Sesamol content (ppm)	Oryzanol content (ppm)	Absorbance at λ_{max} (230 nm)	FTIR frequency (cm^{-1})
FOB-IV control	NA	NA	1.5	795	600	Nil	1745, 2854, 2924, 3473
Cycle 1							
Product	37.5	15.9	NA	NA	NA	NA	NA
Leftover oil	NA	NA	1.5	788	600	Nil	1744, 2855, 2928, 3473
Absorbed oil	NA	NA	1.5	750	600	Nil	1745, 2854, 2927, 3472
Cycle 2							
Product	36.9	13.9	NA	NA	NA	NA	NA
Leftover oil	NA	NA	5.8	768	600	Nil	1745, 2854, 2926, 3473
Absorbed oil	NA	NA	6.1	795	600	Nil	1746, 2854, 2926, 3473
Cycle 3							
Product	38.1	14.9	NA	NA	NA	NA	NA
Leftover oil	NA	NA	10.7	646	600	Nil	1746, 2854, 2924, 3474
Absorbed oil	NA	NA	8.6	689	600	Nil	1747, 2854, 2923, 3474

[a]FOB-IV, palm olein/rice bran oil/crude sesame oil, 60:20:20 by vol. For abbreviations see Figure 1.

changes to take place in the oil due to the presence of atmospheric oxygen. The oils remained open to the atmosphere after deep frying. The products were sensorily acceptable during all three cycles of production.

Oxidative stability of healthful frying oil medium and of oil absorbed by the products during deep frying. FOB-I, FOB-II, FOB-III, and FOB-IV were used in three cycles of product preparation. The control, oil left over after frying, and oil absorbed by the products were used for physicochemical and spectral studies. The results are presented in Tables 1–4.

In examining Tables 1–4, one can see that the *p*-anisidine value, which is a measure of the carbonyls produced from peroxides and hydroxides by thermal/oxidative rancidity, is an effective tool to use in assessing oxidative stability. It ranged from 10.8 to 24.4 and from 1.5 to 10.7 for leftover oil of FOB-I and FOB-IV, respectively. Ranges for FOB-II and FOB-III fell in between, indicating that FOB-I was the least stable and FOB-IV was the most stable combination. That *p*-anisidine value ranges for absorbed oils in all four cases were lower than in the corresponding leftover oil may be a consequence of storing the leftover oil in contact with atmospheric oxygen, whereas the product oil was kept in an enclosed system.

These findings are supported by spectral data, where UV-vis spectra showed an absorbance maximum at 230 nm, representing hydroperoxides and conjugated dienes. The absorbance was maximal for FOB-I samples, both for leftover oil and oil absorbed by the products during the third cycle of product preparation. FOB-II was similar to FOB-I, but the deterioration of fat in the third cycle in FOB-II was less than for FOB-I. No conjugated dienes formed in mustard and palm olein blends, i.e., FOB-III and -IV, as evidenced by the lack of absorbance at 230 nm. This indicated that FOB-III and -IV were oxidatively more stable than sunflower oil (FOB-I) and groundnut oil (FOB-II) blends. FTIR spectra showed peaks at 3400 to 3480 cm^{-1} for water-associated hydroxyl groups, 2854 to 3008 cm^{-1} for hydrocarbon chains, and 1740 to 1750 cm^{-1} for ester carbonyls. These frequencies appear for all the TAG molecules. None of the four blends showed any unusual absorbance (Tables 1–4) except for the third-cycle sample of FOB-I, the sunflower oil frying medium, where peaks were observed at 3852 cm^{-1} for a polyhydroxy polymer that might have been generated *in situ*.

Distribution of nutraceuticals/antioxidants in healthful frying oil medium and oil absorbed by the products during deep frying. Although vegetable oils consist of simple TAG, the distribution of FA in TAG is not random. That is, unsaturated FA preferentially occupy the *sn*-2 position, and saturated FA are located at *sn*-1 and *sn*-3 positions (15). Hence, nonglyceride components such as nutraceuticals/antioxidants or other related phytochemicals also may have a selective distribution between oil and the products during deep frying, more so when the product has many other components such as starch, carbohydrates, and protein.

Oxidation is not restricted to the TAG and FA alone. It also occurs in the case of phytosterols, β-sitosterol, stigmasterol, and other hydrocarbons (16). Therefore, efforts have been

TABLE 5
Uptake of Sesamol by the Product (potato bajji) During Deep Frying Using an Enriched Sunflower/Rice Bran/Sesame Oil (60:20:20 by vol) Frying Oil Blend

	Sesamol content[a] (ppm)			Sesamol content[a] (ppm)	
Cycle no.	Leftover oil	Absorbed oil	Cycle no.	Leftover oil	Absorbed oil
I	4511	4628	III	4620	4581
II	4549	4562	IV	4636	4606

[a]Sesamol content of control frying oil blend 4333 ppm.

made to assess the quantity and distribution of oryzanol and sesamol in oil left over after frying and in oil absorbed by the products. Comparison of the results presented in Tables 1–4 show that the distribution of nutraceuticals/antioxidants in the oil medium and the product was almost equal, and there was no loss during deep frying, as the values compared well with the control samples.

Enrichment study of sesamol and its distribution in products during deep frying. In our previous experiments the sesamol content of the oil was below 1000 ppm in all samples for all four oils. In the present experiments, we also considered a sunflower/rice bran/sesame oil (60:20:20 by vol) combination (FOB-V) in which sesamol content was raised to 4333 ppm by incorporating synthetic sesamol to assess the distribution pattern of sesamol at a higher level. Four cycles of product (potato bajji) were prepared during 60-min intervals, with a gap of 3 d between cycles. The sesamol contents of oil left over after frying and of oil absorbed were 4511–4636 and 4606–4628 ppm, respectively (Table 5). Sesamol content in the leftover oil was nearly equal to that in the oil from the product, and there was no loss during deep fryings.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Vishveshwaraiah Prakash, Director, Central Food Technological Research Institute, Mysore, India, for his keen interest in the work and facilities provided to carry out the investigation. Thanks are also due to Dr. Belur R. Lokesh, Head, Department of Lipid Science and Traditional Foods, for his helpful suggestions.

REFERENCES

1. Thompson, J., *Chemistry and Technology of Deep Fat Frying*, Short Course at University of California at Davis, May 16–18, 1990.
2. Clark, W.L., and G.W. Serbia, Safety Aspects of Frying Fats and Oils, *Food Technol. 45*:84–89 (1991).
3. Perkins, E.G., The Analysis of Frying Fats and Oils, *J. Am. Oil Chem. Soc. 65*:520–522 (1988).
4. Nasirullah, Development of Deep Frying Edible Vegetable Oils, *J. Food Lipids 8*:295–304 (2001).
5. Seetharamaiah, G.S., and J.V. Prabhakar, Oryzanol Content of Indian Rice-Bran Oil and Its Extraction from Soap Stock, *J. Food Sci. Technol. 23*:270–273 (1986).
6. Beardsell, D., J. Francis, D. Ridley, and K. Robards, Health Promoting Constituents in Plant Derived Edible Oils, *J. Food Lipids 9*:1–34 (2002).
7. Hemalatha, S., and Ghafoorunnisa, Lignans and Tocopherols in Indian Sesame Cultivars, *J. Am. Oil Chem. Soc. 81*:467–470 (2004).
8. Suja, K.P., J.T. Abraham, S. Nhamizh, A. Jayalekshmy, and C. Arumughan Antioxidant Efficacy of Sesame Cake Extract in Vegetable Oil Protection, *Food Chem. 84*:393–400 (2004).
9. AOCS, *Official Methods and Recommended Practices of the AOCS*, 5th edn., edited by D. Firestone, AOCS, Champaign, 1997, Methods Ab 3-49, Ca 2d-25 (97), Cd 18-90.
10. Committee on Analysis of Commercial Fats and Oils, Analysis of Commercial Fats and Oils, *Ind. Eng. Chem., Anal. Ed. 12*:379 (1940).
11. Mordret, F., Detection of Sesame Oil, *J. Crops Grass 6*:389–397 (1968).
12. Ranganna, S., *Manual of Analysis of Fruits and Vegetable Products*, Tata McGraw-Hill, New Delhi, 1977, pp. 236–237.
13. Fukuda, Y., T. Osawa, M. Narmiki, and T. Ozaki, Studies on Antioxidative Substances in Sesame Seeds, *Agric. Biol. Chem. 49*:301–305 (1985).
14. Indira, T.N., Baby Latha R, and M. Prakash, Kinetics of Deep Fat Frying of a Composite Product, *J. Food Sci. Technol. 36*:310–315 (1999).
15. Che Man, Y.B., T. Haryati, H.M. Ghazali, and L. Buana, Randomness Test of Fatty Acids Distribution in Triacylglycerol Molecules of Palm Oil, *J. Food Lipids 5*:113–123 (1998).
16. Boskou, D., Frying Temperature and Minor Constituents of Oils and Fats, *Grasas Aceites 49*:326–330 (1998).

[Received April 11, 2005; accepted August 8, 2005]