Edible Quality Rice Bran Oil from High FFA Rice Bran Oil by Miscella Refining

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Rice bran oils high in free fatty acids (FFA) can be converted to cooking oil having low unsaponifiable matter and light color by a combination of miscella dewaxing and miscella refining.

Among the methods of deacidification of high FFA vegetable oils, miscella refining involving hexane and alkali solution has proven its efficiency as a process. A great deal is known about the various parameters of this process, e.g. oil content in the miscella, alkali strength and excess, use of a nonionic surfactant, etc., on the extent of deacidification, refining loss and color. The suitability of the miscella refining process for high FFA rice bran oil of dark color has been studied little. There is, however, a report that the miscella refining process is quite suitable for rice bran oil of high acid values (1). In the interest of the production of edible quality rice bran oil from high FFA oils, the miscella refining process in hexane needs to be examined critically.

The refining of vegetable oils in miscella stage was first studied in 1951 in the U.S. (2). The effect of the concentration of miscella on oil color was reported by Thurman (3). There are other interesting papers and patents (4-7) pertaining to refining characteristics in the miscella phase. The effects of temperature, concentration and alkali and the rate of mixing on the refining of cottonseed oil in the miscella phase also have been investigated (6-8). The oils that have been deacidified by the miscella process appear to be mainly cottonseed, soybean, peanut (9) and sunflower (10).

Very little has been published about the miscella refining process, particularly as applied to rice bran oil.

The present study is concerned with the deacidification of high FFA rice-bran oil samples by the miscella refining process in hexane in the presence of caustic soda solution with a view to obtaining basic information on the factors that influence oil quality and oil loss.

EXPERIMENTAL

Crude rice bran oil of varying free fatty acid (FFA) content was obtained from local industries.

FFA and unsaponifiable matter in crude and refined oil were determined by AOCS methods (11). Color of the crude and refined rice bran oil was determined by Lovibond Tintometer (12).

The oils having 15.3, 20.5 and 30.2 FFA were degummed in the oil phase by phosphoric acid. The dewaxing was done in the hexane phase with calcium chloride and with a lipofrac agent at 15 ± 1 C. The wax crystallized was separated from the solution in hexane in a laboratory centrifuge. Appropriate concentration, e.g. 30, 45 and 60% of oil in miscella (w/v), was first made by adding hexane to the degummed and dewaxed oil. The required amount of the caustic solution based on oil was added drop by drop from a separating funnel to the miscella taken in a three-necked flask fitted with a stirrer, a condenser and the separating funnel to add alkali solution. After alkali addition, agitation was

TABLE 1

Effect of Oil Content in n-Hexane on Degumming[a] and Dewaxing[b] of Crude Rice Bran Oil

% Free fatty acid (FFA) in crude rice bran oil	Oil content in miscella (% w/v)	Characteristics of refined and bleached oil					
		% FFA in the oil	Lovibond color (1 cm. cell)			Unsaponifiable matter %	Refining factor
			Y	R	S		
15.3	—	—	26.0*	2.7*	0.4	3.9	—
	30	0.21	4.3	0.8	—	1.8	1.8
	45	0.20	4.2	0.7	—	1.7	1.8
	60	0.20	4.0	0.7	—	1.7	1.8
20.5	—	—	30.2*	4.0*	0.2	3.8	—
	60	0.18	3.1	0.7	—	1.8	1.8
30.2	—	—	34.0*	4.3*	0.5	4.2	—
	60	0.22	6.1	0.9	—	1.9	1.9

[a]Degummed by 85% phosphoric acid (1 kg/ton).
[b]Dewaxed by calcium chloride (2 kg/ton oil) as 10% aqueous solution in n-hexane at 15 ± 1 C.
*Crude rice bran oil.

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TABLE 2

Dewaxing[a] of Rice Bran Oil[b] in the Miscella Phase Without Additives

% Free fatty acid (FFA) in crude rice bran oil	Oil content in miscella (% w/v)	Characteristics of refined and bleached oil			Refining loss factor	Unsaponifiable matter %
		FFA in the oil	Lovibond color (1cm. cell)			
			Y	R		
15.3	60	0.20	4.0	0.7	1.4	1.6
20.5	60	0.18	3.0	0.6	1.4	1.6
30.2	60	0.22	5.7	0.7	1.6	1.7

[a]Miscella dewaxing at 15 ± 1 C for 6 hr.
[b]Degummed by 85% phosphoric acid (1 kg/ton).

TABLE 3

Dewaxing of Rice Bran Oil[a,b] in Hexane With Lipofrac Agent Combined with Miscella Neutralization

% Free fatty acid (FFA) in crude rice bran oil	Oil content in miscella (% w/v)	Characteristic of refined and bleached oil		Refining factor	Unsaponifiable matter %
		Lovibond color (1 cm. cell)			
		Y	R		
15.3	60	4.0	0.8	1.6	1.5
20.5	60	3.0	0.7	1.7	1.5
30.2	60	6.0	0.8	1.7	1.6

[a]Degumming by 85% phosphoric acid (1 kg/ton).
[b]Dewaxing in hexane in presence of alkylated phenol ethylene oxide condensate at 15 ± 1 C.

TABLE 4

Purification of Degummed[a] and Dewaxed[b] Rice Bran Oil by Miscella Refining and Bleaching of Desolventized Oil

% Free fatty acid (FFA) in crude rice bran oil	Oil content in miscella (% w/v)	Characteristics of refined and bleached oil		Total process loss %	Unsaponifiable matter %
		Lovibond color (1 cm. cell)			
		Y	R		
15.3	60	4.0	0.7	24.0	1.3
20.5	60	3.0	0.6	32.6	1.4
30.2	60	5.4	0.7	50.6	1.6

[a]Degummed by lipofrac process (alkylated phenol ethylene oxide condensate).
[b]Dewaxing in hexane in presence of alkylated phenol ethylene oxide condensate at 15 ± 1 C.

continued for 15 min to ensure intimate mixing between the FFA and alkali and absorption of color bodies by the soap. The whole neutralization operation was carried out at room temperature, 26 ± 1 C. The stirrer was then removed after washing with a known amount of hexane to recover as much oil as possible. The oil was then recovered by removing the supernatant by settling for two hr. The refined sample was decanted, washed with distilled water to remove traces of soap and the solvent was then distilled.

After the refined oil sample was dried, bleaching was carried out at 110 ± 1 C using 2% activated bleaching earth.

RESULTS AND DISCUSSION

The refining of rice bran oil in the miscella phase was investigated with respect to the effect of different methods of dewaxing and the effect of oil content in the miscella.

The effect of oil content in n-hexane is studied in rice bran oil of 15.3% FFA (Table 1). Both the color and the

refining factor improve when the miscella contains 60% oil. Degumming and dewaxing by calcium chloride at 15 ± 1 C in hexane also gives oil color with a refining factor of 1.9. Rice bran oil of 30.2% FFA refined well in the miscella phase with refining factor 1.9; however, the color is slightly darker than the samples with lower FFA. Rice bran oil dewaxed in the miscella phase without additives and then refined in the miscella phase can be converted into good quality rice bran oil with a refining loss factor of 1.4-1.6, as shown in Table 2. Bleaching in the oil phase effectively improves the color. The refining factor improves remarkably, and the unsaponifiable matter in refined oil is 1.6 to 1.7%. Dewaxing in hexane with lipofrac agent can be combined with miscella neutralization. The results obtained are included in Table 3. Lipofrac dewaxing before alkali neutralization in hexane enhances the refining factor in comparison with the hexane dewaxing by cooling only. Degumming and dewaxing by lipofrac process in hexane followed by miscella refining indicates (Table 4) that the unsaponifiable matter in two samples of rice bran oil decreases significantly without a significant change in the refining factor. The color of the samples also improves after bleaching.

The results shown in Tables 1-4 demonstrate the suitability of the miscella refining process preceded by miscella dewaxing for converting high FFA rice bran oils into edible quality oils that can be used in cooking.

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Cyclopropenoid Fatty Acids in *Gnetum scandens* and *Sterculia pallens* Seed Oils

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Seed oils of *Gnetum scandens* (Gnetaceae) and *Sterculia pallens* (Sterculiaceae) were found to contain sterculic (28.57, 6.97) and malvalic (11.27, 3.87) acids, respectively. Gas chromatographic analysis of silver nitrate/methanol-treated methyl esters was used to establish the co-occurrence of these two acids. *Sterculia foetida* methyl esters were used as a reference standard.

Cyclopropenoid fatty acids (CPFA) have been a subject of many investigations due to their carcinogenic (1,2), cocarcinogenic (3-5) and other biological effects on animals (6,7). As a part of our screening program aimed at the search for biologically active cyclopropanoid acids in minor seed oils, the present paper reports the results of the analysis of CPFA-containing seed oil of *Gnetum scandens* (Gnetaceae) and *Sterculia pallens* (Sterculiaceae). The seeds of *S. pallens* are eaten and the plant of *G. scandens* is used as a fish poison. Gnetaceae seed fats are rarely known for CPFA content.

EXPERIMENTAL PROCEDURES

The experimental procedures have been discussed elsewhere (8).

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RESULTS AND DISCUSSION

The analytical values of the seeds and oils are summarized in Table 1 (9). GLC chromatograms clearly established the presence of malvalic (11.27, 3.87) and sterculic (28.57, 6.97) acids in *G. scandens* and *S. pallens* seed oils. The GLC data (Table 2) were found close to those obtained by HBr-titration (10).

TABLE 1

Analytical Data of *Gnetum scandens* and *Sterculia pallens* Seed Oils

	G. scandens	*S. pallens*
Seeds		
Oil content (%)	15.7	30.2
Protein content N × 6.25 (%)	14.3	20.1
Moisture (%)	6.2	4.3
Seed oils		
Iodine value (Wijs)	85.93	85.30
Saponification value	191.51	195.39
Refractive index n_D	1.4769	1.4772
Halphen test	positive	positive
HBr equivalent	39.84	10.84