The distinct maxima at 612 mμ and 670 mμ observed in some of the curves of Figure 1 are characteristic of chlorophyll A. The chlorophyll A content of each sample was calculated from the maxima at 670 mμ and these data together with the transmission and extinction coefficients at 670 mμ are given in Table 4.

TABLE 4

Effect of Refining and Bleaching on the Chlorophyll Content of Rice Bran Oil

Oil	Extinction coefficient, $E^{g./l.}_{1cm.} \times 10^5$ at 670 mμ[1]	Transmission at 670 mμ, per cent	Chlorophyll in oil,[2] per cent
Crude	100.0	24.7	98×10^{-5}
Refined (B-0)	20.0	76.2	20×10^{-5}
Bleached (B-3, 4% neutral clay)	5.1	94.0	5×10^{-5}
Bleached (B-8, 4% acidic clay)	0.4	99.5	0.04×10^{-5}
Bleached (B-10, 2% neutral and 2% acidic clay)	0.5	99.3	0.05×10^{-5}

[1] Measured in iso-octane. Chlorophyll A maximum occurs at 660 mμ when measured in ethyl ether (19).

[2] Estimated on the assumption that all absorption at 670 mμ was due to chlorophyll A, using Zschiele's average extinction coefficient of 102.1 for chlorophyll A.

It is evident from this table that the actual percentage of chlorophyll in the various oils is extremely small and that practically all of the green color can be removed from rice bran oil by bleaching with a few per cent of activated acidic clay.

Summary

1. Freshly milled rice bran has been extracted with commercial hexane and the recovered oil and extracted meal examined for their respective content of wax. The oils were refined and bleached by standard as well as several special methods. The crude, caustic soda refined, and several refined and bleached oils were examined spectrophotometrically.

2. When freshly milled rice bran of good quality is extracted with commercial hexane, an oil of relatively low free fatty acid content is obtained. This oil possesses good color and is as stable as other similar types of crude oils.

3. If the oil is extracted from the bran at a temperature below about 10°C. and the extraction is discontinued at the right time, the extracted oil represents 90-95% of the total lipids in the bran and contains very little wax. This wax, which is readily extracted with hot commercial hexane as well as other types of solvents, amounts to about 3-9% of the total extractable lipids.

4. When subjected to ordinary caustic soda refining methods, good rice bran oils behave much like cottonseed oils of comparable free fatty acid content. Both caustic soda refining in a hydrocarbon solvent and refining with sodium carbonate result in refining losses approximating the absolute or Wesson loss.

5. Some of the refined oils when bleached according to usual practice produce products acceptable for use in the edible trade. However, refined rice bran oil has a definitely greenish cast resulting from the presence of chlorophyll, but this color can be removed by bleaching with a small amount of activated acidic clay.

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Rice Bran Oil. II. Composition of Oil Obtained by Solvent Extraction

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Introduction

THE characteristics and composition of rice bran oil have been reported by a number of investigators. Most of the published data refer to oils obtained from rice of foreign origin and some of them to samples of unknown origin and agronomic history. Furthermore, the free fatty acid content of the oils on which data has been reported has often been abnormally high. Previous investigations may be briefly summarized as follows:

In 1903 C. A. Browne (1) reported data with reference to the chemical and physical constants of bran oil from Louisiana-grown rice. This oil had a free fatty acid content of 83.5%. In 1911 Tsujimoto (2) reported data on the characteristics and composition of a commercially-extracted Japanese rice bran oil which contained 17.4% free fatty acid. Jamieson (3) applied the ester fractionation method to the determination of the composition of oil extracted with ethyl ether from rice bran produced in the United States. The extracted oil had a free fatty acid content of 36.9%. Cruz *et al.* (4, 5) applied the ester fractionation method to determine the composition of

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ethyl ether-extracted rice bran oil obtained from rice of the Hambas and Ramai varieties grown in the Philippine Islands. These oils had a free fatty acid content of 20.5 and 21.1%, respectively. Trevithick and Lewis (6) reported data on the characteristics of an imported rice bran oil having a free fatty acid content of 51.0%, and calculated its composition from the iodine and thiocyanogen values.

The Report of the Oil Characteristics Committee of the American Oil Chemists' Society of 1937 (7) contains the results of an analysis by Mitchell and Lauro for expressed rice bran oil imported from Japan. The characteristics are reported on a refined oil obtained from a crude oil having a free fatty acid content of 3.8%. The composition was calculated from the iodine and thiocyanogen values. The composition of a Japanese rice bran oil has also been reported by Ueno and Ueda (8).

In view of the interest in the recovery of rice bran oil from bran produced in Southern and Southwestern rice mills and the lack of data on the characteristics and composition of these oils, an analysis has been made of two samples of crude and one refined oil extracted from bran obtained by commercial milling of two varieties of rice (Blue Bonnet and Zenith) grown in Texas and Arkansas, respectively. The method of extraction and refining of the first of these two oils (Blue Bonnet has been described previously (9). The second oil (Zenith) was extracted in a similar manner.

The first oil was extracted with commercial hexane from fresh bran obtained from commercially milled Blue Bonnet rice grown in Texas during 1946. The rice was cured in the shock and had an average moisture content of 13.2% at the time of milling. The second oil was extracted with commercial hexane from fresh bran obtained from commercially milled Zenith rice grown in Arkansas during 1946. This rice was also cured in the shock and had an average moisture content of 13.1% at the time of milling. Filter aid (Hyflo Super-Cel)[2] was added to each of these oils prior to filtration at room temperature to remove the wax and wax-like constituents.

The refined oil consisted of a composite of several samples which were produced from the crude rice bran oil (Blue Bonnet variety), obtained during a series of previously reported (9) refining tests.

Methods of Analysis

Iodine values, saponification values, and titer were determined by the methods of the American Oil Chemists' Society (10). Unsaponifiable matter (11), thiocyanogen values (12), and hydroxyl numbers (13) were determined by the methods described in the references cited. Saturated acids were determined by a modification of the method of Pelikan and von Mikusch (14) using sintered glass filter sticks for filtration. Spectrophotometric analyses were made by the method now under collaborative test by the Spectroscopy Committee of the American Oil Chemists' Society. This method is a modification of the Mitchell, Kraybill, and Zscheile (15) technique in which an atmosphere of nitrogen is used during preparation of the reagent and the isomerization reaction (16). The results were calculated by the method of Brice and Swain (17).

[2] *Hyflo* Super-Cel is named as part of the specification of the exact experimental conditions and does not imply that this product is particularly endorsed or recommended by the Department of Agriculture over other commercial filter aids having the same or similar properties.

Results and Conclusions

Data on the composition of the Blue Bonnet and Zenith rice brans are shown in Table I.

TABLE I

Composition of Moisture-Free Rice Bran [1]

Variety of rice	Blue Bonnet [2]	Zenith [3]
Origin	Texas	Arkansas
Nitrogen, %	2.06	1.91
Protein (N×6.25), %	12.88	11.94
Ash, %	15.93	23.19
Potassium, %	1.18	0.86
Phosphorus, %	2.08	1.17
Calcium, %	1.92	4.32
Acid-insoluble ash, %	3.17	7.33
Crude fiber, %	10.7	11.4
Total sugar, calc'd as invert sugar, %	2.16	3.0
Lipids, %	16.90	11.90

[1] Analysis by the Analytical, Physical Chemical, and Physical Division of this Laboratory
[2] Original moisture 10.34%.
[3] Original moisture 11.05%.

The bran from the Blue Bonnet variety of rice was practically free of hulls and broken kernels. The mill from which the bran was obtained stated that the rice was milled with the minimum addition of calcium carbonate commensurate with the moisture content of the rice, and that the yield of bran was approximately 13%.

The bran from the Zenith variety of rice contained an appreciable quantity of hulls and broken kernels, which accounts in part for its lower content of oil and higher content of ash and acid insoluble ash constituents.

The physical and chemical characteristics of the crude and refined rice bran oils are shown in Table II, from which it is evident that the refined oil had a somewhat lower specific gravity, refractive index, and percentage of unsaponifiable matter and a slightly higher saponification value than the crude oil from which it was produced.

TABLE II

Physical and Chemical Characteristics of Extracted Rice Bran Oils

Characteristic	Crude oil Blue Bonnet	Crude oil Zenith	Refined oil Blue Bonnet
Specific gravity, 25°/25°	0.9187	0.9212	0.9166
Refractive index, $n_D^{25°}$	1.4720	1.4700	1.4708
Lovibond color			
5¼" cell	70Y 12.7R	35Y 24.2R	35Y 6.5R
1" cell	35Y 4.1R	35Y 5.0R	....
Free fatty acids, as % oleic	4.6	6.1	0.11
Iodine value, Wijs	102.0	100.3	102.3
Thiocyanogen value	75.9	74.4	75.7
Saponification value	185.4	183.4	187.6
Unsaponifiable matter, %	3.86	4.98	2.70
Titer, °C	25.2	26.5	25.2
Hydroxyl number	8.7	14.0	5.0
Saturated acids, %	16.3	16.5	16.3
Iodine value of mixed acids	105.7	104.2	105.4

The composition of the oils calculated from spectrophotometric data and saturated acids determined by a modified Bertram oxidation method is shown in Table III along with the composition calculated from iodine and thiocyanogen values (10). Spectrophotometric analysis of the original oils indicated the presence of 0.9 to 1.2% of conjugated diene and traces of conjugated triene and tetraene constituents. Analysis of the alkali-isomerized samples shows that the oil contained 0.8 to 1.06% of linolenic and 30.6 to 33.2% of linoleic acids calculated as glycerides. Saturated acids were determined by Bertram oxidation.

TABLE III

Composition of Solvent-Extracted Rice Bran Oils

Constituent	Blue Bonnet crude [1]	Zenith crude [1]	Blue Bonnet refined [1]	Blue Bonnet crude [2]	Zenith crude [2]	Blue Bonnet refined [2]
Conjugation						
Diene, %	0.97	1.26	1.01	.....	.....	.....
Triene, %	0.0055	0.029	0.0041	.....	.....	.....
Tetraene, %	0.063	0.095	0.015	.....	.....	.....
Glycerides of						
Linolenic acid, %	0.80	1.06	0.84	.....[3]	.....[3]	.....[3]
Linoleic acid, %	33.2	30.6	33.1	32.0	31.8	32.6
Oleic acid, %	45.0[4]	46.0[4]	46.3[4]	54.2	52.7	53.2
Saturated acids, %	17.1[5]	17.3[5]	17.1[5]	9.9	10.5	11.5
Unsaponifiable matter, %	3.9	5.0	2.7	3.9	5.0	2.7

[1] Calculated from spectrophotometric data and results of Bertram oxidation method.
[2] Calculated from iodine-thiocyanogen data.
[3] Linolenic acid assumed to be absent.
[4] Calculated by difference; % oleic = 100 − (% linolenic + % linoleic + % saturated + % unsaponifiable matter).
[5] Determined by a modified Bertram oxidation method.

Because of the high percentage of unsaponifiable matter, the oleic acid was calculated by difference rather than from the iodine value of the oil. The percentage of linolenic acid in rice bran oil has not been previously reported although Mitchell and Lauro (7) obtained traces of ether insoluble bromides from the rice bran oil which they analyzed.

When the compositions of the oils were calculated from the iodine and thiocyanogen values, assuming linolenic acid to be absent, the values obtained for saturated acids were much lower than the corresponding analytically determined values. The calculated values for oleic acid are probably correspondingly high. This discrepancy may be attributed to the presence in the oils of a large percentage of unsaponifiable matter. Attempts to calculate the composition on the basis of the data for the iodine and thiocyanogen values and determined saturated acid content assuming linolenic acid to be present also gave erroneous results, the calculated linolenic acid content ranging from 7.4 to 9.3%.

Summary

The characteristics and composition of two crude and one refined rice bran oils have been determined. These oils were obtained by solvent extraction of commercial rice brans from Texas-grown Blue Bonnet and Arkansas-grown Zenith varieties of rice. The glyceride composition of the two crude and one refined oils was found to be: 0.80, 1.06, and 0.84% linolenic acid; 33.2, 30.6, and 33.1% linoleic acid; 45.0, 46.0, and 46.3% oleic acid; 17.1, 17.3, and 17.1% saturated acids; and 3.9, 5.0, and 2.7% unsaponifiable matter, respectively.

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