heating, which have been already referred to, apply fully to the potentiometric method. One factor which must be considered is that the potentiometric method is more time-consuming than the colorimetric technique. The shape of a typical titration curve is given in Fig. 2 along with a comparison of the inflection point with the colorimetric endpoints. A rather good correspondence is obtained with the phenolphthalein endpoint and the inflection point of the titration curve, but the thymolphthalein endpoint is considerably higher. A comparison of the colorimetric and the potentiometric methods both employing isopropanol-benzene as a titration solvent is given in Table III for a variety of fatty oils. These oils include a number of special interest to these laboratories, but their unusual nature and wide variety serve to emphasize the wide applicability of the methods. As may be seen, the correspondence between the colorimetric and potentiometric procedures is uniformly satisfactory.

With the exception of omitting the use of the cG nomenclature and expressing results in either "apparent pH readings" or "pH meter readings," the A.S.T.M. Official Method D 664-46T has been followed and may be referred to for more extensive detail. This method has been found to be satisfactory for the determination of acidic constituents in marine and vegetable oils, including chemical modifications of these oils and products and residues of refining processes. It is particularly suitable for dark or colored oils for which the colorimetric determination is difficult or impossible.

To avoid the confusion of titration data obtained in non-aqueous media with those in water, the term cG was introduced by Lykken *et al.* (3), to replace the term pH when using non-aqueous media. The use of cG units in millivolts involves calibration of two non-aqueous buffer standards. The value of these additional operations is questionable since there is a direct relationship between the pH meter reading and the cG scale. The A.S.T.M. potentiometric method (2) gives a factor of 0.000198 multiplied by the absolute temperature to convert pH meter readings to cG units. If this direct conversion is valid, then nothing is to be gained by the use of the term cG, and reference to "pH meter readings" or "apparent pH reading" should be satisfactory and avoid needless computation.

Summary

A discussion is presented of present official methods of determining the acid number of oils. A colorimetric method is presented for the determination of acid numbers of marine and vegetable oils and related products. It involves the use of alcoholic KOH, phenolphthalein, and a titration solvent consisting of 49.5% anhydrous isopropanol. 50% benzene, and 0.5% water. Most oils are completely soluble in the titration solvent, thus avoiding the disadvantages of two phase systems and of heating the oil. It compares satisfactorily with present official methods.

A potentiometric method which is at present an A.S.T.M. Standard Method for petroleum products is discussed. It has proved to be satisfactory for use with marine and vegetable oils.

A close correspondence has been shown with a number of different oils between acid numbers obtained colorimetrically and potentiometrically. This makes it possible to compare directly results obtained by the two methods.

Acknowledgment

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Rice Bran Oil. I. Oil Obtained by Solvent Extraction[1]

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RICE BRAN is a by-product of the rice milling industry and a potential source of edible oil. At present rice bran oil is produced by several mills in this country and by a considerably larger number in the Orient. In recent years Japan has produced as much as 17,000 tons of rice bran oil per year, for the most part by inefficient methods; and in pre-war years between 5 and 10 million pounds were imported into the United States, principally from Japan. Rice bran oil enters the United States at an import duty of 20% *ad valorem* in accordance with schedule 1, paragraph 53, of the Tariff Act of 1930 for expressed or extracted oils, not especially provided for. There are no established price quotations for this oil.

While rice bran oil will always be of minor importance in the vegetable oil industry of the United States, so far as total production of this commodity is concerned, it possesses considerable potential importance in certain limited areas.

The bran, which consists essentially of the outer portions and germ of the dehulled rice grain, amounts on an average to 8.5% of the rough rice. The approximately 1,600,500 tons of rough rice produced in the United States in the crop year 1945-1946 is equivalent to approximately 136,042 tons of bran. Assuming an extractable oil content of 10 to 14%, this amount of bran is equivalent to 27 to 38 million pounds of oil.

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The principal obstacle to the production and utilization of the oil is its reputed low quality. Ordinarily the crude oil has a high content of free fatty acid and it is difficult to refine and bleach.

When the bran is removed from the rice, the content of free fatty acid of the oil is usually below about 3%. After milling, however, an extremely active lipolytic enzyme system begins to function immediately, and it has been shown by Browne (3) and in this laboratory that during the first few hours after milling the content of free fatty acid of the oil increases about 1% per hour if the bran is stored at approximately 25°C. Within a month the content of free fatty acid of the oil may increase to 60-70%, and the bran becomes extremely rancid. When the content of free fatty acid of the oil is plotted against the time of storage of the bran, it is found that the rate of formation of the free fatty acid is highest at the beginning of lipolysis and decreases with time.

The action of the lipolytic enzyme can be inhibited to varying degrees by heating the bran at 90° to 105°C. for a short time, according to Browne (3) and West and Cruz (18). Chemical treatment has also been proposed (14) as a means of checking lipolysis. The first method is costly and tends to darken the oil; the second method has not yet been proved to be entirely successful. It is therefore more practical to extract the oil while the bran is still fresh. This procedure has some attraction owing to the fact that almost the entire crop of rice is milled in relatively few plants concentrated in a few processing centers in the rice-producing areas of this country. Another advantage to be gained by extracting the oil from the bran is that it obviates the formation of free fatty acid in the oil and spoilage of the bran. Hence the extracted bran may be stored for a longer time.

A high content of free fatty acid is not the only undesirable characteristic of the crude rice bran oil as ordinarily produced. With a relatively low content of free fatty acid, rice bran oil still may have refining losses up to 40-50% by the cup method. In addition the oil may be difficult to bleach. The high refining loss is generally attributed to surface active agents although the nature or source of these substances has not been established.

Solvent extraction is the most promising method for removing oil from rice bran since the bran is bulky and usually contains less than 18% of oil. Using a hydraulic press and employing the pressure commonly used for expressing coconut oil, Cruz *et al.* (5) could obtain practically no oil from rice bran. An unpublished report from Japan states that while 80% of the rice bran oil produced in Japan is pressed oil, the pressing, as customarily practiced, removes only 50% of the oil from the bran.

It will be shown here, among other things, that a good crude oil having a fairly low content of free fatty acid can be obtained by extracting fresh rice bran with commercial hexane; that this oil can be satisfactorily refined by the usual methods; and that the refined oil can be bleached in the usual manner to produce a high-grade edible product.

Extraction of the Oil

The crude oils used in most of these experiments were produced at the Southern Regional Research Laboratory from brans supplied on two separate days by a local rice mill. Both lots of bran were light in color and substantially free of broken rice. The history of the two brans was the same. This rice, Blue Bonnet variety grown in Texas, had been shocked and allowed to dry and cure in the field. The milled bran amounted to 12 to 15% of the rough rice. The first lot of bran was obtained from rice having a moisture content of 12.64%; the second lot was obtained from rice having a moisture content of 13.75%. Very little calcium carbonate was used in the milling operations.

The two lots of bran were solvent extracted under similar conditions. Extraction of the first lot was carried out as follows: The bran was collected as it came from the hullers and was immediately taken to the laboratory, divided into 3 lots of 120 pounds each and charged to three vertical batch extractors, after which it was immediately covered with commercial hexane (about 23 gallons of solvent per extractor). The following day (18 hours later) the extraction was started. Solvent was first pumped through the extractors in parallel and later through the three extractors in series.

Analyses of the bran before and after extraction and other pertinent extraction data are given below:

Total extraction time	8 hr. 35 min.
Rate of flow of solvent through meal	25 gal./hr.
Total solvent through bran	213 gal.
Ambient temperature	2°-5°C.
Temperature of solvent entering extractors	2°-13°C.
Lipids in bran before extraction	16.74%
Lipids in bran after extraction	1.98%
Moisture in bran before extraction	11.57%
Moisture in bran after extraction	8.40%

The miscella from the extractors was concentrated during the run to a content of about 60% of oil by evaporating the solvent at atmospheric pressure (60°-65°C.). The hot concentrated miscella was filtered to remove suspended meal particles after which it was entirely freed of solvent by stripping under reduced pressure with the aid of hydrogen at a temperature of about 90°C.

The recovered oil from this extraction was red-brown in color and perfectly clear while hot. On cooling a very small amount of solid material separated. The content of free fatty acid, calculated as oleic acid, was 5.7%. Over a storage period of two months at room temperature the content of free fatty acid did not change which indicates that filtered crude rice bran oil is probably as stable as other types of crude oil of the same relative degree of unsaturation.

The oil obtained from the second lot of bran had a content of free fatty acid of 4.2%, owing probably to the shorter time interval between milling and extraction of the oil. Preliminary tests indicated that the two samples of oil were otherwise relatively similar.

Hereinafter the oils obtained from the first and the second lots of bran are designated oil A and oil B, respectively, and the residual meals as meal A and meal B, respectively. Another lot of crude rice bran oil herein referred to was secured prior to these investigations and is designated as oil C.

Extraction and Solubility of the Wax

Extraction. Several investigators (10, 13, 15) have reported descriptions and data for various wax fractions which had been obtained from rice bran or rice

bran oil. A large fraction of this wax is reported to consist of melissyl cerotate. One report (13) states that rice bran wax is similar to beeswax and has a melting point of 75°C. It is stated in this same report that the melting point of the wax can be raised to 95°C. by hydrogenation; also that 100 pounds of rice bran oil will yield about 5.7 pounds of hardened rice bran wax. Another unpublished report states that the Japanese customarily remove wax from crude rice bran oil by cooling it to 5°C. and filtering it through heavy duck twill cloth. It is generally assumed that wax constitutes an appreciable and important fraction of the lipids extractable from rice bran.

However, several workers (5, 7, 12) who have investigated rice bran oil make no mention of any associated wax. This may have resulted from the fact that some solvents, especially when used under certain conditions, produce an oil comparatively free of wax, or that most of the wax separated from the oil more or less spontaneously and was inadvertently removed, for example, during filtration of the crude oil or micella. The experiences of the present authors indicate that either could have occurred.

Oil A contained practically no solids immediately after cooling to room temperature. On standing at room temperature over a period of several weeks, more solid material separated out of solution, but the total amount was appreciably less than one-tenth of 1% of the weight of the oil. Oil B behaved similarly, but under similar conditions about three times as much solid material separated. However, the total amount of solids which separated was still very little. The second extraction was carried out at temperatures 5°-8°C. higher than the first extraction, and about 13% more solvent was passed through the bran. Whereas oils A and B contained only small amounts of solids, the lipid material isolated on analyzing the brans before and after extraction in the pilot plant contained appreciable quantities of solids at room temperature. The only significant differences between the pilot-plant extractions and those made for analysis of total lipids were in the temperatures, the type of solvent, and the ratios of the solvent to bran which were used.

It was calculated that in the extraction of the first lot of bran, 90.5% of the total lipids in the bran were removed by cool hexane and produced an oil practically free of solid material. In the second extraction 96.2% of the total lipids were removed to produce a nearly wax-free oil. When a portion of meal A was re-extracted with commercial hexane at a temperature of 60°-65°C. additional lipids were readily obtained. These additional lipids, which solidified to a shortening-like consistency at room temperature, amounted to 1.9% on the meal A or exhausted meal basis and represented practically the entire amount of extractable material as shown by analysis of the meal. Apparently, when rice bran is extracted with commercial hexane it is possible by controlling the temperature to extract either nearly all of the oil and leave the wax or extract a mixture of oil and wax. When the oil is extracted first, the wax can be obtained in a concentrated form by subsequent extraction.

Other portions of meal A were extracted with other appropriate and commercially available solvents to determine whether more lipids than were indicated by the usual lipid analysis could be isolated from the meal. As stated above, meal A still contained 1.98% of lipids when re-extracted by the usual Soxhlet extraction method using a commercial hexane-pentane fraction of boiling range 95° to 138°F. Other extraction solvents which were used included benzene, ethanol (95%), and a mixture of benzene-ethanol. In each case extractions were carried out in a Soxhlet extractor having a capacity of about 1.75 liters or 800 g. of bran. The extraction cylinder was wrapped with an electrical heating element in order to carry out the extractions at elevated temperatures.

Extraction of meal A with benzene for 6 hours at 60°C. yielded a material somewhat darker in color than that obtained with commercial hexane. The recovered product, amounting to 2.6% on a meal A basis, was semi-solid at room temperature.

When benzene-alcohol (2:1) solvent, which is commonly used in extracting wood for lipid materials, was used there was obtained 4.3% of material after extraction of meal A for 6 hours at 65°C. Casual examination revealed the presence of considerable non-lipid material in the solvent-free extract. On diluting the extract with benzene and water and re-extracting with warm benzene, 2.9% of benzene-soluble material was obtained.

Hot, 95% ethanol was found to extract more material, both lipid and non-lipid, than any of the other solvents. The behavior of this solvent is in accord with the observations of Bloor (2), Maclean (11), and Conrad (4) with respect to the extraction of other types of lipid material from biological tissues. Extraction of meal A with 95% ethanol for 8 hours at 75°C. gave a mixture which after dilution with an equal weight of water yielded (on the meal A basis) 4.7% of material soluble in commercial hexane and 6.7% hexane-insoluble material. It was presumed the commercial hexane-soluble fraction contained all the lipid material and that the fraction remaining in the dilute alcohol solution consisted mainly of sugars and other alcohol-soluble, non-wax substances.

The wax-like extracts obtained by the four methods no doubt differed somewhat in composition. The products ranged in color from tan (commercial hexane extracted) to greenish-black (ethanol extracted). The various waxy products also varied in plasticity at room temperature, the wax obtained with ethanol being least plastic. Of the solvents tested, the rate of extraction was least with ethanol.

Solubility. Preliminary examination of the glyceride-free wax from crude rice bran oil showed that at room temperature it was insoluble in acetone and ethanol and only slightly more soluble in commercial hexane. Solubilities in the first two solvents are less than 0.1%. If rice bran oil is filtered free of solid wax and diluted with four parts of acetone, a small amount of additional wax will separate from the solution.

Since peanut oil is somewhat similar to rice bran oil in composition and chemical and physical characteristics, crude peanut oil was used to estimate the solubility of rice bran wax in oil. The wax used was separated from a sample of hexane extracted crude rice bran oil (oil C) which was relatively rich in this material. The wax was first concentrated by cooling the oil to 5°C. and filtering off most of the liquid oil. The filter cake was removed, mixed with 4 parts by weight of acetone, boiled for a short time, cooled, immersed in an ice-water slush for 2 hours, and fil-

tered. The wax, which remained on the filter was washed three times with cold acetone. After being freed of acetone, it was employed in the oil-solubility tests as follows:

Varying percentages of the wax were mixed with a clear, crude peanut oil. Each mixture was heated and shaken to dissolve the wax. On cooling to room temperature, the wax separated from all the oils containing 0.25% or more of added wax. After 48 hours at room temperature a small amount of solid wax was visible in the oil containing 0.1% of added wax. After 48 hours at 15°C., wax separated from oils containing 0.02% of added wax and after storage 15°C. for a slightly longer time, wax separated from oils containing 0.01% of added wax. The control oils remained perfectly clear in all cases. Detection of the added wax in all the oils was simplified because of the flocky and voluminous condition of the precipitated wax.

By applying the above-described method of separation with cold acetone, oil A was found to contain 0.44% of wax. By the same procedure it was found that the material extracted from meal A by hot commercial hexane contained 32.3% of wax. In other words, the total hexane extractable lipids from the first lot of rice bran contained about 3.5% of wax.

As stated above, when meal A was re-extracted with hot 95% ethanol there was obtained 4.7% of lipid material. Separation of this material with cold acetone indicated that it contained 42.9% of wax. This means that if the first lot of rice bran had been extracted with commercial hexane, followed by hot 95% ethanol, the total lipods extracted would have had a wax content of 8.8%.

Refining

Ordinary crude rice bran oil is reputed to be difficult to refine. Ueno, *et al.* (16, 17) reported a series of investigations describing the removal of free fatty acids by steam distillation, esterification of the free fatty acids with glycerol, and extraction of the oils with methanol and ethanol, as well as by refining with concentrated caustic soda at 100° to 150°C.

While a high free fatty acid content is often the principal difficulty encountered in refining rice bran oil, it is frequently not the only one. Many rice bran oils having a low free fatty acid content will not "break" when refined with caustic soda in the usual manner, and others may still be very dark in color after refining. The high refining losses encountered with oils having a relatively low free fatty acid content have been described by Dressler (6) and Kester and Van Atta (9). Dressler lowered the refining loss of a rice bran oil from 40% to 16% by adding with the lye and aqueous solution of 1% of sodium silicate followed by the addition of water just prior to settling the foots.

The crude oils described above were refined by several different methods as follows: The two oils (A and B) were mixed in equal proportions and after standing several days, were filtered through diatomaceous earth to remove any solids which may have separated. This filtered oil, which was used in the refining tests had a content of free fatty acid of 4.9%, calculated as oleic acid, and a Lovibond color (1) of 35 yellow and 5.3 red (1" column). The Wesson or theoretically minimum loss of the filtered oil mixture, determined by the method of Jamieson (8), was found to be 7.5%.

Refining tests, except as otherwise specified, were made exactly in accordance with the directions prescribed by the official American Oil Chemists' Society refining procedures for cottonseed and peanut oils. The results are collected in Table 1. Reference to the

TABLE 1

Refining Data on Rice Bran Oil [a]

No.	Lye, °Bé.	Excess lye used,[b] per cent	Time stirred in cold, min.	Time of stirring and temp. of hot bath, min. °C.	Refining loss,[c] per cent	Lovibond red color of refined oil, 70 yellow
R-5	12	0.5	45	20 — 65	21.0	6.6
R-6	16	0.5	45	20 — 65	19.6	8.1
R-13	20	0.5	45	20 — 65	47.7	10.1
R-11	16	0.5	20	20 — 65	19.3	8.2
R-8	16	0.5	90	20 — 65	20.3	8.4
R-9	16	0.2	45	20 — 65	47.9	9.9
R-12	16	0.5	45	20 — 80	16.4	10.3
R-10[d]	16	0.5	25	12 — 65	16.4	6.7

[a] 50:50 mixture of oils A and B. Free fatty acid content 4.9%, color 35 y, 5.3 r (1" column).
[b] Excess of solid sodium hydroxide based on the weight of the oil used.
[c] The foots remelted twice.
[d] 1.5% of 50% sodium silicate was mixed with the oil for 5 minutes before the lye was added.

data in this table shows that too concentrated a lye or a small excess of lye produces a high refining loss. In general, however, the refining losses for the rice bran oil are no higher than those which would be obtained with cottonseed oil of comparable content of free fatty acid.

Test R-6 of Table 1 was carried out with numerous variations, principally by the addition of sodium silicate or solutions of sodium silicate at various stages of the refining operation. Few refining losses below 19% were obtained and the lowest loss was obtained with the use of sodium silicate as indicated in R-10 of the table.

Rice bran oil was successfully refined in commercial hexane and the foots settled rapidly as a solid mass. The refining loss was quite low being only a few per cent higher than the Wesson loss. In a typical test 400 g. of oil was mixed with 400 g. of solvent; and sufficient 16° Bé. lye was added to neutralize the fatty acids and provide 0.5% excess of sodium hydroxide. After stirring the mixture at 24°C. for 30 minutes the flask was immersed in water at 60°C. and stirring continued for an additional 15 minutes. The foots were allowed to settle for one hour at 60°C. after which they were cooled to room temperature. The refining loss under these conditions was 11.7%, and the color of the refined oil was 70 yellow and 7.3 red on the Lovibond scale.

The lowest refining losses were obtained when the oil was refined with sodium carbonate. In a representative test 400 g. of the oil was heated to 50°C., and 61.3 g., or 2.5 times the theoretical amount of 15% sodium carbonate solution, was added with rapid mechanical stirring. After 30 minutes 20 ml. of 5% sodium carbonate solution was added and stirring was continued for an additional 15 minutes. The temperature was then raised to 60°C. and held at this level for one hour after which the foots were allowed to cool overnight. The refining loss was 10.5%; no foaming occurred and the foots settled readily. However, the refined oil still contained 0.37% of free fatty acids. The Lovibond color reading was 70 yellow and 4.4 red (1" column). On re-refining this oil by the official American Oil Chemists' Society method for "slow break" cottonseed oil

using 6% of 5° Bé. lye, a loss of 4.5% was obtained, and the Lovibond color was 70 yellow and 5.0 red.

Bleaching of the Refined Oils

The refined oils described in Table 1 were bleached with 6% of official American Oil Chemists' Society Fuller's earth. With the exception of the size of the sample and the size and shape of stirrer used, the procedure was the same as that of the official American Oil Chemists' Society method for refined cottonseed oil. The bleached colors of the oils are shown in Table 2, from which it is evident that all of the refined oils were readily bleachable. However, the colors of the refined oils usually were difficult to match exactly with the Lovibond color glasses because of their brownish green hue.

TABLE 2

Color of Refined and Bleached Rice Bran Oil [a]

Sample	Lovibond color of refined oil		Lovibond color of bleached oil	
	Yellow	Red	Yellow	Red
R-5	70	6.6	35	2.7
R-8	70	8.4	35	2.9
R-9	70	9.9	35	4.1
R-10	70	6.7	35	2.7
R-11	70	8.2	35	3.1
R-12	70	10.3	35	3.7
R-13	70	10.1	35	3.6
Refined in commercial hexane	70	7.3	35	3.8
Refined with sodium carbonate	70	4.4 [b]	70	4.5
Re-refined after refining with sodium carbonate	70	5.0	70	4.0

[a] Lovibond color of crude oil 35 y and 5.3 r (1" column). Oils bleached with 6% official American Oil Chemists' Society Fuller's earth.
[b] 1-inch column.

Because of the presence of a green color in the oils refined with caustic soda, several of them were combined and bleached by treatment with activated acidic clays, or small amounts of activated carbon. Bleaching and color readings were carried out as before except that various types and amounts of adsorbents and combinations thereof were substituted for the official American Oil Chemists' Society Fullers' earth. The adsorbents were a neutral activated clay (pH *ca.* 6.8), an acidic activated clay (pH *ca.* 4.0), and activated carbon. The results are recorded in Table 3.

TABLE 3

Effect of Bleaching Refined Rice Bran Oil With Various Adsorbents

No.	Quantity and type of adsorbents used for bleaching	Lovibond color of bleached oils	
		Yellow	Red
B-0	None	70	7.5
B-1	6% Official Fuller's earth	35	2.9
B-2	2% Neutral activated clay	35	3.1
B-3	4% Neutral activated clay	35	2.8
B-4	6% Neutral activated clay	35	2.7
B-5	4% Neutral activated clay and 0.4% activated carbon	35	2.6
B-6	4% Neutral activated clay and 0.2% activated carbon	35	2.7
B-7	2% Acidic activated clay	35	3.9
B-8	4% Acidic activated clay	35	3.5
B-9	4% Acidic activated clay and 0.4% activated carbon	35	3.3
B-10	2% Neutral activated clay and 2% acidic activated clay	35	3.3

Reference to Table 3 shows that the use of acidic clay gives a higher red color than does an equal amount of neutral clay; also that a mixture of acidic and neutral clays results in a higher red color than is obtained with an equal weight of neutral clay. These results are more apparent than real since the removal of the masking green coloring matter by the activated acidic clay makes possible a more accurate reading of the red color value, which becomes very evident from an examination of the absorption spectra of these oils.

Rice bran oils B-0, B-3, B-8, and B-10 of Table 3 and the crude oil (filtered 50-50 mixture of oils A and B) were dissolved in iso-octane and their spectra examined with a Beckman quartz spectrophotometer. The spectral curves corresponding to each of the oils are reproduced in Figure 1. Reference to this

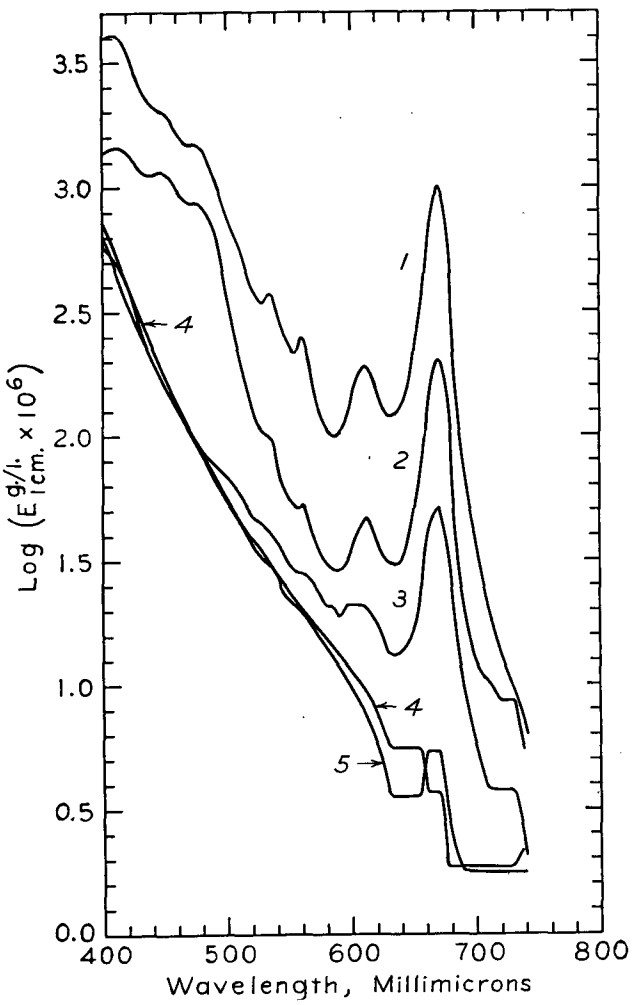

FIG. 1. Spectral absorption curves of rice bran oils. (1) Crude oil, (2) refined oil B-0, (3) oil B-3 obtained by bleaching B-0 with 4% neutral activated clay, (4) oil B-8 obtained by bleaching B-0 with 4% of acidic activated clay, (5) oil B-10 obtained by bleaching B-0 with a mixture of 2% neutral activated clay and 2% acidic activated clay.

figure indicates that at any given wavelength the oil bleached with 4% acidic clay and that bleached with a mixture of 2% acidic clay and 2% neutral clay generally exhibit a lower absorption than does the oil bleached with 4% neutral clay, whereas the last mentioned oil has a lower Loviband red color reading. Spectroscopically the most marked difference in the three bleached oils is in the greater content of chlorophyll of the oil bleached with the 4% neutral clay.

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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