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Interregional Seminar on the
Industrial Processing of Rice
Madras, 11 - 16 Oct. 1971

RICE BRAN OIL AND WAX [1/]

by

R. V. Harris
Tropical Products Institute
London, United Kingdom

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SUMMARY

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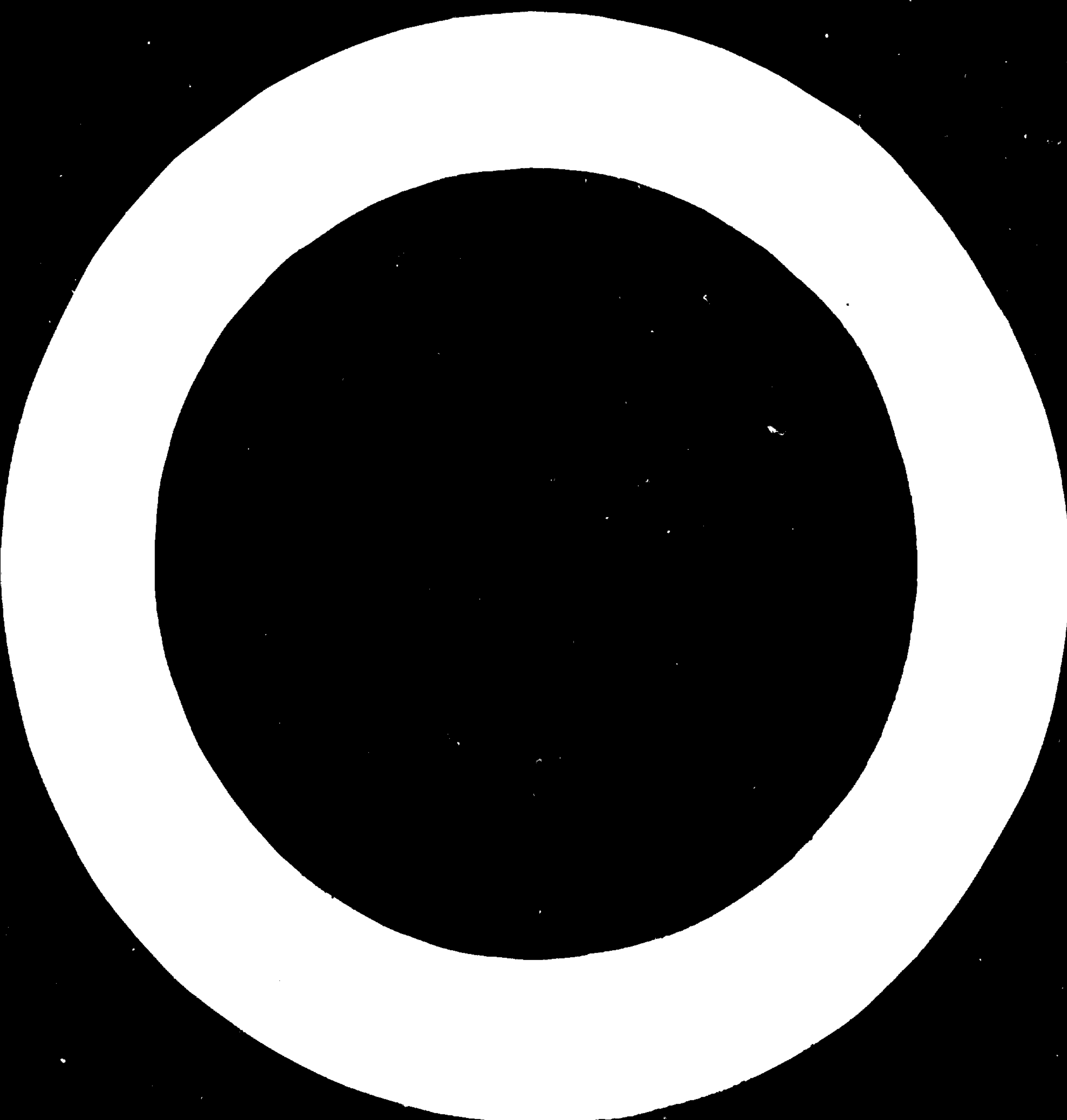


INTRODUCTION

1. Although the rice grain contains only about 2 - 3% fat, milling concentrates this in the bran from which it can be extracted to yield an oil with many potential edible and industrial uses. Development of this important new source of oil has up to now been hampered by a number of technical problems. Potential production of rice bran oil can be estimated from the current production of rice. This indicates that with the exception of a few countries only a minor proportion of this potential is realised. Full exploitation of available rice bran oil sources would make a substantial contribution to the world's edible oil supply in an area which is currently deficient in this commodity. Moreover, extraction of the oil increases the stability of the bran which could then be used in greater quantities as a high protein, high vitamin feedstuff for livestock. This increase in both edible oil and feedstuff production could be achieved without the employment of additional land, or the education of the farmer in the growing and harvesting of a new unfamiliar crop.

Production and Extraction of Rice Bran

2. The rapid deterioration of rice bran is caused by an active lipolytic enzyme which produces free fatty acids from the oil. This both renders the bran unsuitable for feedstuff and the oil extracted unsuitable for edible use. The breakdown of oil can be prevented by stabilising the bran by heat treatment before storage and transport or by the new XM process which mills the grain in the presence of hexane solvent. Alternatively the bran must be extracted immediately on milling whilst it is still fresh. Prior heat treatment also facilitates solvent extraction, the most efficient method of recovering the oil from low content material, by altering the physical nature of the bran particles and overcoming the problem of fines and channelling. Hexane is the preferred solvent for oil extraction although the use of alcohol yields a vitamin-rich syrup as well as the oil.

Nature of Crude Rice Bran Oil

3. Rice bran oil is an oleic/linoleic oil similar in composition and properties to

corn and cottonseed oils. It is low in saturated acids, the major saturated component being palmitic acid and is very low in linolenic acid. The physical characteristics of rice bran oil do not differ markedly from many other soft oils which are currently familiar commodities in World trade. The free fatty acid content is generally higher than most, due to the difficulties of stabilising the bran prior to extraction, as is the unsaponifiable content. Pigments present include carotenes with occasionally small amounts of chlorophyll. The oil has a high tocopherol content which increases oxidative stability. Along with the conventional sterols and squalene, the unsaponifiable content also includes oryzanol for which is claimed medicinal properties. The wax content is 3 - 9%, this can be recovered and purified to yield a valued hard wax with properties similar to those of carnauba wax.

Processing of Rice Bran Oil for Non-Edible Purposes

4. Oils of above 10% free fatty acid are uneconomic to refine for edible use and are generally used for soap manufacture or for the production of industrial fatty acids. A brief outline of the principles of soap manufacture is given. The soap produced from rice bran oil has good detergent properties and is soluble at low temperatures. It can be used to advantage in soft or liquid soaps and for washing of delicate surfaces, fibres and textiles which require low temperatures. A harder less soluble product can be obtained by blending with more saturated or lower chain length fats, or by hydrogenation.

5. A brief outline is given of the industrial production of industrial fatty acids from crude oils or acidulated soapstocks. With the use of hydrogenation and various methods of fractionation a wide range of fatty acid mixtures could be obtained from rice bran oil. The most evident uses for medium and high iodine value fatty acid mixtures would be in the surface coating field as components of alkyds and epoxy resins which find considerable use in paints, enamels, varnishes and lacquers. The low level of linolenic acid in rice bran oil fatty acids would minimise the after-yellowing properties which are a grave disadvantage in white and pastel shades. Esters of rice bran oil fatty acids could also find a use in plasticisers for synthetic rubbers, cellulosics and polymer resins giving flexibility and lubricity over a wide range of temperatures. Epoxidised rice bran oil and rice bran oil fatty acids would be suitable for use as stabilising prasticisers for polyvinyl chloride and other chlorine containing polymers.

6. Other uses for fatty acids include the manufacture of detergents and surfactants

for industrial use, emulsifiers for food use, lubricants and as constituents in cosmetics.

Processing of Rice Bran Oil for Edible Purposes

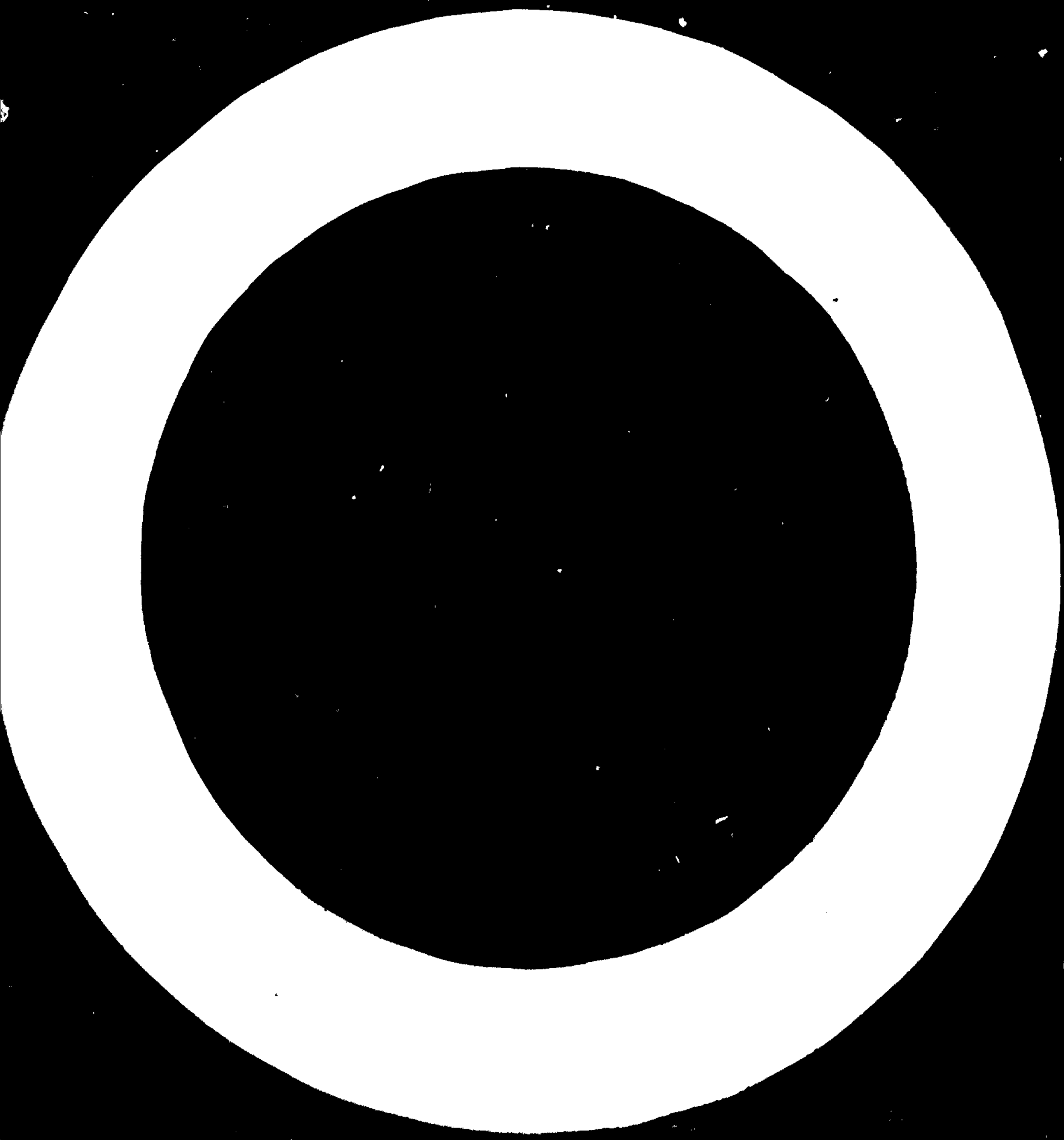
7. The difficulties experienced in the processing of rice bran oil for edible purposes arise largely at the neutralisation stage where separation of the soapstock presents problems and leads to refining losses far higher than theoretically calculated from the free fatty acid content. This can be partially overcome by the addition of certain chemicals during caustic refining but more recent work has suggested that a constituent of the wax fraction is principally responsible for the refining losses. There appears to be no outstanding problem with refining low free fatty acid dewaxed rice bran oil. Bleaching and deodorisation can be carried out by conventional means; the greenish hue often reported can be removed by using acidic clays.

8. Rice bran oil is particularly suitable for use as a salad oil, cooking oil and as the liquid portion of a margarine blend. Its low linolenic acid content and high tocopherol content gives it oxidative stability and minimises the formation of rancidity and off-flavours which can limit the use of other soft oils in blended fat products. For use as a salad oil where stability and absence of clouding at low temperatures is essential, winterisation is carried out to remove the high melting point saturated glycerides. Rice bran oil gives exceptionally high yields of fully winterised oils with consequent advantages in the economics of the operation. Well refined, low free fatty acid rice bran oils have high smoke and fire points and good frying characteristics. Low rates of peroxide, foam and polymer formation and good flavour characteristics have been reported. Hydrogenation of rice bran oil presents no unusual features and the hardened fat showed exceptional stability suggesting a use in shortenings.

9. The current intensified marketing of high linoleic oils, such as corn and safflower, is a result of the finding that polyunsaturated acids have a lowering influence on the plasma cholesterol levels. Intake of vegetable oils as opposed to saturated animal fats is being encouraged in the hope that they will reduce the incidence of vascular disorders such as atherosclerosis caused by deposition of cholesterol on the walls of blood vessels. The fatty acid composition of rice bran would enable it to take advantage of the movement evident in the U.S.A. and W. Europe towards cooking oils and softer, more unsaturated margarines and away from solid animal fats.

Rice Bran Wax

10. Hard, high melting point waxes can be produced from crude rice bran oil by taking advantage of this insolubility at low temperatures. Active chilling of the oil can be carried out or the normal tank settlings which are produced on storage and transport can provide a source of crude wax. Various ways of purifying the wax are described mostly by treatment with solvents and a final crystallisation from isopropanol. The major component of the hard wax fraction is myricyl cerotate with lesser amounts of similar wax esters. The purified wax is brown, hard, non-tacky and similar in many respects to carnauba wax. It can be readily bleached with hydrogen peroxide, sulphuric acid and chromium trioxide and can be expected to find application in wax polish formulations and in the wax coating of confectionaries and fruit.



CONTENTS

I. INTRODUCTION

1. In common with other cereals, the fat content of the rice grain is not high (2 - 3%) but the vast majority of it is in the embryo or germ. Consequently, milling which separates the germ, together with the pericarp, from the white rice also serves to concentrate the fat in the bran. The oil content of the isolated bran thus rises to between 14 - 18%.

2. As this article will attempt to demonstrate, this oil has comparable properties and a similar composition to corn and cottonseed oils. If it could be economically produced at an equivalent quality it would provide an important new source of valuable technical and edible grade vegetable oil in many countries of the world that at the moment suffer a shortage of these commodities. Moreover, another constituent of the bran, the wax, previously considered to be a hinderance to the successful processing of the oil, could, if economically recovered, become a valuable secondary product by virtue of its similarity in properties to carnauba wax, an established constituent of many commercial wax products. Extracting the oil has the additional advantage of vastly improving the keeping qualities of rice bran, thus enabling this to realise its full potential as a foodstuff with high protein and vitamin content.

3. Although in some countries (notably Japan and Burma) rice bran oil already makes a significant contribution to the edible oil supply, social and technological difficulties have so far prevented full exploitation elsewhere. Table 1 illustrates that only about 10% of the potential production is currently realised. Table 2 puts the situation in perspective showing that rice bran oil could become a major vegetable oil alongside other soft oils; current London prices for these other commodities will enable its possible commercial value to be estimated. More important, perhaps, than its actual value, is the ability of a new oil to satisfy the requirements of the ECAFE region for soft edible oil, thereby reducing the need for imports.

4. Considerable difficulties generally attend the promotion of a new oilseed

TABLE 1

Estimated Potential and Actual Rice Bran Oil Production in major ECAFE Countries

(All figures in 1000 ton units)

Country	Paddy (a)	Rice (b)	Rice Bran (c)	Rice Bran Oil Production Potential (d)	Actual
India	59,649	39,368	3,149	472	18
Pakistan	21,243	14,020	1,122	168	-
Indonesia	17,931	11,822	946	142	-
Japan	17,500	11,550	924	139	84
Thailand	13,200	8,712	697	105	6
Burma	8,216	5,422	434	65	22
S.Korea	5,493	3,625	290	44	7
Philippines	5,049	3,332	266	40	-
S.Vietnam	5,012	3,307	265	40	-
Taiwan	3,400	2,244	180	27	4
Cambodia	3,247	2,143	171	26	-
Nepal	2,450	1,617	129	19	-
Ceylon	1,538	1,015	81	12	-
Malaysia	1,476	974	78	12	-
			TOTAL	1,311	141

(a) From 'Rice Bulletin' Commonwealth Secretariat, November 1970.

(b) Estimated as ⅔ of Paddy.

(c) Calculated as 8% of Rice.

(d) Calculated as 15% yield of Oil.

TABLE 2

World Production of Edible Oils and Current U.K. Prices

Soft Oils	Production (a) (1000 tons)	Price (b)
Soybean Oil	5,509	£162/ton
Groundnut Oil	3,038	£187/ton
Sunflowerseed Oil	3,024	£199/ton
Cottonseed Oil	2,378	£165/ton
Olive Oil	1,485	£390/ton
(Potential Rice Bran Oil	1,311)	
Sesame Oil	574	-
Corn Oil	295	£189/ton
Others		
Coconut Oil	1,984	£170/ton
Palm Oil	900	£130/ton
Palm Kernel Oil	309	£170/ton

(a) From Commonwealth Secretariat, Vegetable Oils and Oilseeds Review 1970.

(b) Public Ledger, London, January 1971.

industry. Not the least are the efforts required for the location of suitable climate and soil conditions, the selection of optimum-yielding, disease and pest resistant strains, the evaluation of fertiliser, irrigation or drainage requirements, the preparation of land, and the education of the farmer in the planting, tending and harvesting of a new crop. In this respect, a rice bran oil industry is at an advantage; the source of the oil, the rice plant, is a well established and familiar crop in many parts of the world, and it is only in post harvest matters that education, new methods and technological improvements are required. This is an important factor which should stimulate the development of a rice bran oil industry in many countries.

5. It has become evident that difficulties still exist in the stabilisation of the bran for storage and transportation, in the extraction and processing of the oil and in the recovery and processing of the wax. Research and development experience are still needed in all these areas. This paper, however, will be mainly concerned with the potential uses and value of extracted rice bran oil and its by-products and will also give a brief description of the technology required.

II. PRODUCTION OF RAW RICE BRAN FOR OIL PRODUCTION

6. As is well known, raw rice bran contains an extremely active enzyme - lipase - which hydrolyses the triglycerides and releases free fatty acids (1). The major impediment to the development of rice bran oil industries in the past has been the invariably high free fatty acid content of the extracted oil due to the action of this lipolytic enzyme. High free fatty acid oils are not accepted by the edible oil refiner since removal of the acidity leads to considerable losses of neutral oil, and it is generally recognised that oils of more than 10% free fatty acid cannot be economically alkali refined. There is no objection to acid oils in the industrial fatty acid trade and, indeed, they represent the main feedstock for this area of utilisation.

7. In conventionally milled rice bran free fatty acid levels can rise to 10% in a matter of hours. It is thus quite clear that under practical conditions the rice bran unless fresh must be stabilised by destroying or inactivating the enzyme and preventing this rapid production of free fatty acids in order to extract an oil useful for edible purposes. Five basic approaches have been tried:-

(1) Heat treatment; (2) Chemical treatment; (3) Low temperature storage; (4) Control of relative humidity during storage; (5) Simultaneous milling and extraction.

(1) Heat Treatment - Extensive studies (2) have been carried out on the effect of heating samples of bran to various temperatures between 70°C and 110°C for periods of 1 to 3 hours. Changes in free fatty acid content were followed during subsequent storage at 25°C. Table 3 summarises the results from which it is evident that bran can be successfully stored without deterioration for considerable periods after subjecting it to heat treatment.

TABLE 3

Storage Characteristics of Rice Bran after Various Heat Treatments

(from data of Loeb et al (2))

Treatment		Free Fatty Acid Content after 25 days	Free Fatty Acid Content after 50 days
Time hrs.	Temperature °C	Storage at 25°C	Storage at 25°C
None		54%	85%
1	70	18%	29%
3	70	6%	8%
1	85	25%	36%
3	85	4%	5%
1	100	5%	8%
3	100	4%	4%
1	110	4%	7%
3	110	4%	4%

8. A very similar problem arises in the Palm Oil industry where the mesocarp oil is also accompanied by an active lipolytic enzyme. High free fatty acid palm oils were at one time commonplace and the introduction of a heat 'sterilisation' step resulted in a vast improvement in quality. In 1950, for instance, only 0.2% of the total Nigerian palm oil production was suitable for refining and edible use, by 1960, after the widespread introduction of 'sterilisation' the figure was 80%. In this case the ripe fruits are kept either

at 100°C for one hour, or under 20-40 lbs./sq.in. steam pressure in an autoclave for 15-20 minutes (3). Such a process could also be tried for rice bran.

9. A commercial grain expander has been evaluated for cocking and sterilising rice bran (4). In this case heating under pressure to about 300°F was carried out. 'Expanded' bran was found to be perfectly stable and showed no change in free fatty acid content over a period of 84 days. The process had the added attraction of increasing the cohesiveness of the particles of bran. This served to overcome the problems of 'fines' and 'channelling' which had given considerable trouble during solvent extraction of raw rice bran.

(2) Chemical Treatments and inert atmospheres, although the subject of a Japanese patent (5), have, on further examination proved to be ineffective (2).

(3) Low Temperature storage does tend to reduce the rate of free fatty acid rise (6) but unacceptably high levels are still reached in a comparatively short period.

(4) Control of Relative Humidity, at a low level, also retards free fatty acid formation, (2) but again not sufficiently to be of commercial importance unless preceded by heat treatment.

(5) Simultaneous Milling and Extraction, a recently developed process, overcomes the problem associated with the storage of raw bran by carrying out the milling actually in the presence of solvent, thereby yielding a de-oiled bran and a rice bran oil/hexane miscella in one operation (7). The process (X-M) shows considerable promise and is dealt with in more detail elsewhere.

10. It would seem from the foregoing that some form of heat sterilisation, and solvent extraction milling offer the only realistic alternatives for yielding a rice bran oil for the economic production of edible grade oil. Japanese workers (25) advocate the use of only very fresh bran for oil extraction, which also overcomes the free fatty acid problem. This is, perhaps, not a realistic suggestion for other countries owing to the transport difficulties resulting from the small and scattered nature of rice mills in the majority of producing areas.

III. EXTRACTION OF CRUDE RICE BRAN OIL

11. For oil contents as low as 10 - 20%, the only efficient method of recovering the oil is by solvent extraction and, indeed, attempts to extract it

by hydraulic pressing or screw expelling have resulted in rather poor recoveries (8). Modern solvent extraction plants can reduce the proportion of residual fat in a meal to 1 - 2% giving more economical yields and, in this case, a more stable defatted bran.

12. Although hexane is universally employed in commercial solvent extraction, other solvents have been examined on an experimental basis in an attempt to isolate other useful constituents from rice bran. Ethyl (9) and Isopropyl (10) alcohol have been shown to extract, as well as the oil, sugars, phospholipids and several B vitamins including biotin, pantothenic acid, pyridoxin, thiamin and niacin, which are recoverable as a syrup on cooling the miscella. However, the possible value of these materials as by-products is likely to be outweighed by the presence of a green pigment in the oil, which can then only be bleached with difficulty, the increased cost of solvent recovery and the reduction in nutritive value of the extracted bran.

IV. NATURE OF THE CRUDE OIL

(a) Physical Characteristics - The range of characteristics reported in the literature for solvent extracted fresh rice bran oils is given in Table 4 where comparison is made with the British Standard Specifications for a number of competitive crude oils. Requirements such as moisture and other volatile matter (such as residual solvent), sediment and other impurities are subjects of contractural agreement and are not generally included in specifications, although they are important commercially and if the levels are high will adversely affect marketability.

13. Except for generally high levels of free fatty acid and unsaponifiable material, rice bran oil does not, if carefully produced, differ markedly from other soft oils currently engaged in world trade.

(b) Fatty Acid and Glyceride Composition - The fatty acid composition is shown in Table 5 where rice bran oil is compared with competitive oils. Rice bran oil is a semi-drying oleic/linoleic oil. Its low linolenic acid content gives it a distinct advantage over cottonseed and soyabean oils for both edible and industrial use as will be discussed later.

14. A complete glyceride analysis has not been reported but from the low proportion of solid glyceride sedimented during winterisation it has been

TABLE 4

Characteristics of Crude Rice Bran Oil Compared with B.S.I. Specifications for Other Soft Oils

	Crude Rice Bran Oil	Crude Corn Oil	Crude Sunflower Oil	Crude Sesame Oil	Semi-Refined Cottonseed Oil	Crude Groundnut Oil	Crude Soyabean Oil
Colour (Lovibond 1 inch cell)	35Y 5R	<70Y 7R	<50Y 4R	<30Y 2.5R	<35Y 3.5R	<35Y 4R	60Y 6R
Specific Gravity (15.5°/15.5°)	0.918 - 0.921	0.921 - 0.928	0.922 - 0.927	0.921 - 0.924	0.921 - 0.924	0.917 - 0.919	0.924 - 0.928
Refractive Index (20°C)	1.472 - 1.470	1.472 - 1.474	1.471 - 1.476	1.472 - 1.476	1.472 - 1.475	1.468 - 1.472	1.473 - 1.477
Iodine Value	95 - 113	103 - 128	112 - 135	104 - 120	99 - 115	80 - 105	120 - 143
Saponification Value	181 - 189	187 - 195	>188	195 - 187	189 - 198	188 - 196	189 - 195
Free Fatty Acid	4 - 10%	< 4%	1 - 5%	< 2.5%	-	1 - 5%	1.5%
Unsaponifiable Matter	3 - 6%	2.8%	1.5%	2%	1.5%	1%	1.5%

TABLE 5

Fatty Acid Compositions of Some Common Soft Oils Compared with Rice Bran Oil

Fatty Acid	Rice Bran Oil	Corn Oil	Sunflower-seed Oil	Sesame Oil	Cotton-seed Oil	Ground-nut Oil	Soyabean Oil
Myristic (14:0)	0.4-1.0 (1)	0-1.7 (0)	0 (0)	0 (0)	0.5-1.5 (1)	0-1 (0)	0-1 (0)
Palmitic (16:0)	12-18 (15)	8-12 (8)	3-6 (4)	7-9 (8)	20-23 (21)	6-9 (7)	7-11 (8)
Stearic (18:0)	1-3 (2)	2-5 (4)	1-3 (3)	4-5 (4)	1-3 (2)	3-6 (4)	2-6 (4)
Oleic (18:1)	40-50 (45)	14-49 (46)	14-43 (34)	37-49 (45)	23-35 (29)	53-71 (62)	15-33 (28)
Linoleic (18:2)	29-42 (35)	34-62 (42)	44-75 (57)	35-47 (41)	42-54 (45)	13-27 (23)	43-56 (54)
Linolenic (18:3)	0.5-1.0 (1)	0 (0)	0 (0)	0 (0)	0-11 (3)	0 (0)	2-10 (5)
Arachidonic (20:0)	0 (0)	0 (0)	0-4 (1)	0-1 (1)	0.2-1.5 (1)	2-4 (3)	0-2 (0)

Range (typical analysis)

suggested that rice bran oil follows a more even distribution than these competitive oils (11).

(c) Other Constituents - Rice bran oil has been variously reported as dark greenish - brown to light yellow depending on the method of extraction and the extent of deterioration of the bran during storage. Pigments present include carotenes and, in the darker oils, chlorophyll. Carotenes contents have not been reported per se, but chlorophyll, of more concern to an edible oil processor, can rise as high as 20 p.p.m. (12, 13). Colour, usually measured by comparison with Lovibond Standard glasses, and how easily it can be removed are important criteria for the refining of edible oils. Most pigments can be readily absorbed by bleaching earths or destroyed by heat treatment but oxidation, particularly when traces of iron and copper are present, can lead to the colour being 'fixed' and resistant to bleaching. Conjugated fatty acids have also been found at a low level in rice bran oil (14) and also probably result from oxidation. Low free fatty acid rice bran oils are particularly resistant to oxidative rancidity; this is largely due to the high content of tocopherols, up to 0.47% having been reported (15). These are partially removed during deodorisation but the residue is still sufficient to give deodorised rice bran oils above-average stability. Moreover, they can be recovered from the deodorisation distillate and represent a valuable by-product as they can be used as anti-oxidants for other food items and in the manufacture of vitamins and pharmaceuticals. Squalene also occurs in rice bran oil at levels varying from 0.2 to 0.5% (9, 16, 17). Sterols probably represent the major class of compounds in the unsaponifiable material (18) and a proportion of these appear to occur as esters of ferulic acid (the monomethyl ether of 3:4 di-hydroxy cinnamic acid) (19). Oryzanol is the ferulate of cycloartenol (20) and is claimed to promote the growth of animals and alleviate disorder of menopause. In Japan, oryzanol is prepared commercially and included in medicinal products; it occurs in rice bran oil to the extent of 0.1% . Cycloartenol is the biosynthetic precursor of plant sterols (21). Hydrocarbons, long chain alcohols and their esters occur in the wax fraction which settles from the hot oil/hexane miscella on cooling. Rice bran wax, which could be a valuable secondary product of the rice bran oil industry varies greatly in content depending on the method of extraction employed but is typically 3 - 9%. It is dealt with in detail in a later section.

V. INDUSTRIAL USES OF CRUDE RICE BRAN OIL

15. It is intended to concentrate in this section on those uses of rice bran oil which do not involve the refining, bleaching and deodorising operations associated with the production of an edible grade oil. Rice bran oil industries are in their infancy in most potential producing countries and the bulk of research and development effort will of necessity be devoted to increasing the quantities of edible grade oil produced. Nevertheless, even in the most technologically advanced countries low quality inedible grade fats are often produced and these, together with the soap stocks recovered from alkali refining, enter the soap industry or, after 'splitting', the industrial fatty acid field. The wide range of materials that can be produced from fatty acids include emulsifiers and detergents, protective coatings, plasticisers and lubricants. It is anticipated that, recognising the difficulties involved in producing low free fatty acid oil from rice bran, considerable quantities of low grade material will continue to appear and attention should be drawn to the fact that these can be of great value to the chemical industry. Indeed, at the time of writing, the high price of soft edible grade oils such as corn, groundnut, cottonseed, and soybean has led to a parallel increase in the price of soap stocks and acid oils. Fatty acid based chemical manufacturers are searching for alternative sources of supply and it is felt that rice bran oil could have a role to play here.

16. Before considering the production and uses of the fatty acid mixtures which would be derived from rice bran oil, soap manufacture should be dealt with.

(a) Soap Manufacture

17. Many reports exist recommending that rice bran oil, with its high free fatty acid content would be highly suitable for soap production, thereby allowing other oils and fats to be diverted to the more important edible uses or exported (2, 22).

18. The name 'soap' strictly refers to any metal salt of any carboxylic acid, but the soluble washing agents to which this word is applied in common usage are confined to the sodium and potassium salts of fatty acids.

19. Chemically, the manufacture of soap consists of hydrolysing (saponifying) the glycerides with caustic soda or potash producing salts of the fatty acids and releasing glycerine. Technically the processes rest on the fact that soap is soluble in dilute electrolyte solutions but insoluble when the concentration rises above a certain level. Thus by simple addition of salt, soap can be separated from

glycerol, water, residual alkali and other impurities. In the classic process oil and alkali, in correct proportions, are boiled vigorously in a large vessel known as a 'kettle' until hydrolysis is complete. Solid salt or concentrated saline solution is added, bringing the soap out of solution. Due to its lower density the soap rises to the top with the lower layer containing the bulk of the salt, glycerine etc.. This can be withdrawn and processed to recover the salt and to produce glycerine, a valuable by-product.

20. The rest of the process consists essentially of repeatedly washing the soap by redissolving in boiling water and repeating the salting out procedure thereby reducing further the content of glycerine and impurities. The final salting out is done in a more careful manner and results in the separation of the soap into two layers, the upper layer being of greater purity and thus used for better quality products, the lower layer of lesser purity may be put through the process again or used for lower grade products. Potash soaps cannot be salted out, consequently the final product retains all the glycerine produced by the saponification reaction.

21. Neat soap direct from the kettle contains about 30% moisture, which is reduced by hot air drying, flash drying or vacuum drying. This is accomplished before pressing into bars, cutting into slabs, powdering, flaking or whatever final form is desired.

22. The basic procedure outlined above has been considerably modified and improved in recent years by the advent of centifuges to separate the soap, countercurrent washing towers, production of soap directly from fatty acids, and the introduction of compact and efficient continuous soap-making machinery.

23. Many other materials will be found in soap products to impart specific characteristics. Pigments, perfumes and emollients are most readily apparent in toilet soaps, and antibacterials are incorporated into deodorant soaps and surgical scrubs. Calcium and magnesium sequestering compounds such as polyphosphates and silicates serve as water softeners and suspending agents in laundry products which also will often contain bleaches; siliceous materials or other abrasives will be present in scouring powders and soaps.

24. The potential of a fat for soap manufacture is a matter entirely of its fatty acid composition. The fatty acids generally most useful are from twelve to eighteen

carbons long, those of ten or less have little surface activity whilst those of twenty and above are insoluble at ordinary temperatures. Sodium oleate and linoleate have very good detergent properties and have the advantage over saturated acids of being more soluble at lower temperatures and softer in constitution. The oxidative instability of the unsaturated acids is no great problem since a wide variety of antioxidants can be used in soaps. Thus rice bran oil is eminently suitable for soap manufacture. It can be used to particular advantage in soft or liquid soaps in dispensers, in hair shampoos, for floor and automobile cleaning and for the washing of delicate surfaces and certain textiles, fabrics and fibres which require lower temperatures. Oleic and linoleic soaps are less irritating to the skin than shorter chain or saturated acids and thus are ideally suited for infant and medicinal soaps. A further extension of its use can, of course, be provided by blending with tallow or a lauric oil (such as coconut and palm kernel) or hydrogenating. This yields a harder, less soluble product with a wide range of household and industrial applications.

(b) Industrial Fatty Acids from Crude Rice Bran Oil

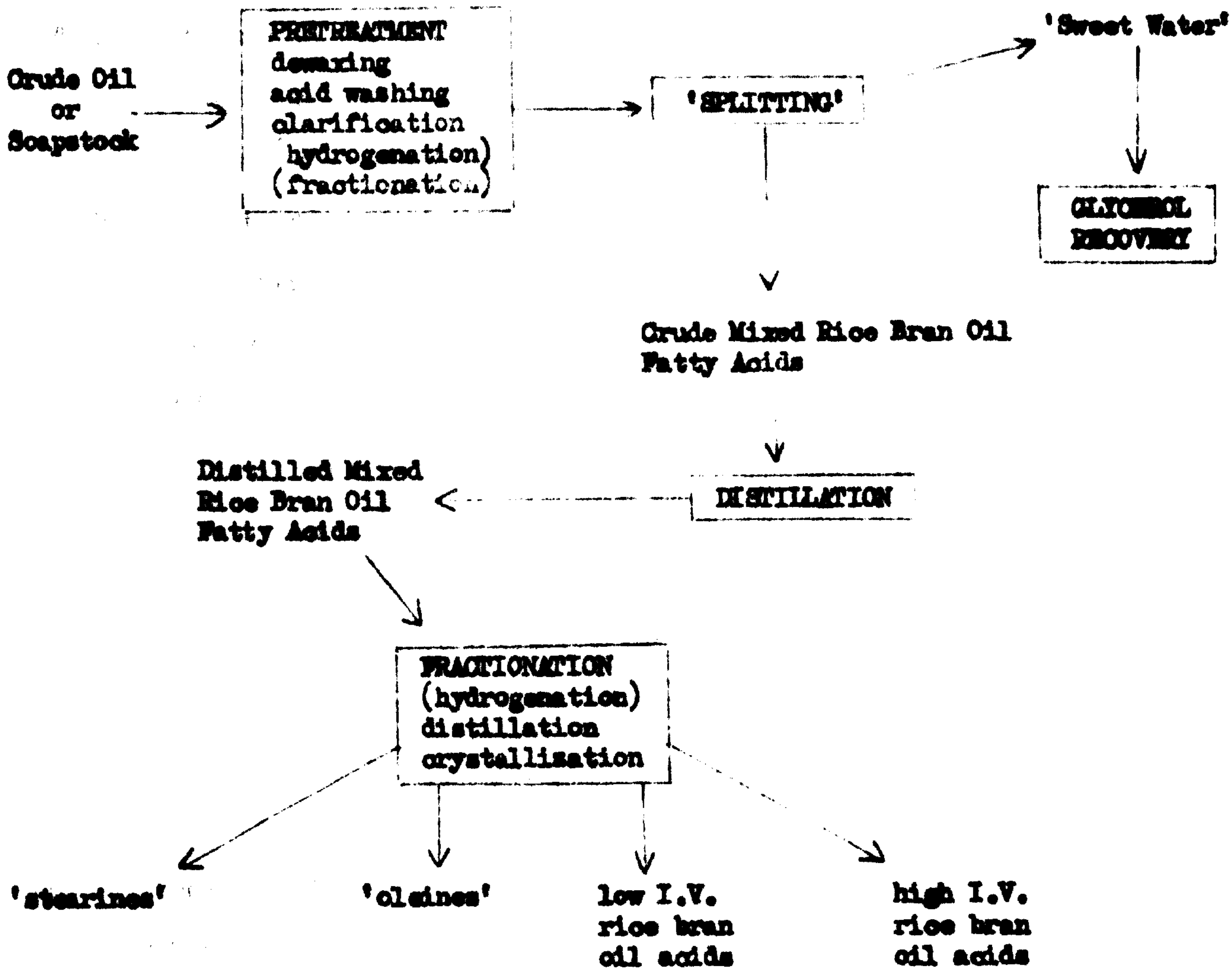
(i) Manufacture

25. Basically the process consists of the hydrolysis ('splitting') of the glycerides, separation of the glycerol, and purification of the mixed fatty acids by distillation. Refinements can include hydrogenation and fractionation, which may be by more sophisticated distillation or by solvent crystallisation at low temperature. Combination of these processes could lead to a wide variety of different fatty acid mixtures being produced from rice bran oil. A flow sheet for fatty acid manufacture from rice bran oil is shown in Figure 1.

26. '<u>Splitting</u>' can be accomplished by one of three methods which vary in sophistication, speed and efficiency. The simple Twitchell Method involves heating the oil to 100°C at atmospheric pressure in the presence of 1% Twitchell catalyst (sulphuric and sulphonic acid derivatives) and 50% water for two days in large wooden or stainless steel tubs. The water phase (termed 'sweet water' owing to its glycerol content) is withdrawn after 24 hrs. and replaced by fresh. The degree of split is not high by this method. More efficient is the use of an autoclave where higher temperatures (180 - 230°C) and pressures (150 - 450 psi) are employed. The most modern continuous splitting process employs countercurrent flows of water and oil at 250°C and 750 psi in a 60 ft. 'splitting' tower. Hydrolysis is rapid

FIGURE 1

Flow Sheet for Fatty Acid Manufacture from Rice Bran Oil



and efficient, sweet water emerging from the bottom of the tower whilst fatty acids are withdrawn from the top.

27. In all these processes oils containing high levels of free fatty acid hydrolyse more readily than neutral oils since they are able to dissolve more water.

28. Distillation can be carried out at low pressure as a batch process or continuously with or without a fractionating condenser column. It serves to purify the fatty acids from such impurities as residual triglycerides, non saponifiable material, oxidised and polymerised fatty acids and colouring matter which remain behind as 'still pitch'. This material finds use as a waterproofing agent.

29. Glycerine Recovery commences with the withdrawal of sweet water from the splitting process. After neutralisation of any entrained fatty acid, the 15 - 25% content of glycerol is concentrated by boiling, vacuum drying and distillation at reduced pressure. The product is frequently too highly coloured for immediate use

and requires bleaching usually with activated charcoal. Glycerol is used in the food, cosmetic and pharmaceutical industries.

(ii) Uses of Rice Bran Oil Fatty Acids

The traditional feedstocks for the industrial fatty acid industry are inedible tallows and greases, and the classic products are 'stearic acid' and 'oleic acid' obtained from the mixed distilled fatty acids by low temperature fractional crystallization aided by solvents or surface active agents. Commercial 'stearic' and 'oleic' acids are far from pure, and the names 'stearine' and 'oleine' are now in common use to distinguish them from the now available pure compounds. Fatty acid mixtures, either straight distilled, or fractionated, from the more common fats and oils are however now available to meet specific requirements. They are generally mixtures of C_{16} and C_{18} saturated fatty acids and specified by name, in the case of pure distilled grades, or by Iodine Value, indicating the degree of unsaturation, and Titre, representing the solidification temperature of the mixture. Exceptions to this generalisation include fish oils, with C_{20} - C_{24} acids, the lauric oils with C_{12} acid, and castor oil with its content, after hydrogenation, of hydroxy stearic acid. Rice Bran Oil is a semi drying oil and it would clearly be more economic to make use of it in products where a high Iodine Value is advantageous. Controlled hydrogenation is, however, capable of reducing the unsaturation to any desired degree. The use of this technique; plus various fractionation methods and blending with other more saturated fatty acid mixtures would enable rice bran oil to contribute to stearine and oleine manufacture. Thus the utilisation of stearines and oleines will also be briefly considered in addition to those more evident uses resulting from the oil's unsaturated nature.

Protective Coatings - After edible and detergent (including soap) uses, manufacture of surface coatings represent the third major area of utilisation for vegetable oils. It owes its rapid development to the shortage and high price of traditional drying oils such as tung and linseed during the second world war, at a time when non-drying and semi-drying fatty acids were becoming available. The most common types of compound used are the alkyds (fatty acid esters of polyhydric alcohols such as glycerol, pentaerythritol, sorbitol and xylitol, condensed with phthallic anhydride) and epoxy resins, (fatty acid derivatives of epichlorohydrin and bisphenol). The most common sources of fatty acids for this application currently are soyabean oil, cottonseed oil, and tall oil (a by-product of paper manufacture). The specifications of typical fatty acid mixtures derived from these oils are shown in Table 6, in terms of the most important features Iodine Value and Titre.

TABLE 6

Characteristics of Typical Fatty Acid Mixtures Used in Alkyd and Resin Manufacture for Protective Coatings

Iodine Value	110	122	130	134	138	142	145
Titre °C	31	27	26	21	10	5	4

32. The characteristics of straight distilled rice bran oil fatty acids has been reported as Iodine Value 104 - 106 with a Titre of 25 - 26°C (14). Since the bulk of the saturated acids in rice bran oil is palmitic acid (see Table 5) it could be readily removed by fractional distillation and crystallisation yielding a fatty acid mixture of higher I.V. and lower titre. This is currently done successfully with cottonseed and soyabean oils. For instance, fractional crystallisation will increase the Iodine Value of a cottonseed oil from 102 to 143 and a soyabean oil from 129 to 157. Fractional distillation will increase similar oils to 138 and 147 respectively. In addition, the linolenic acid content of rice bran oil is low, which minimises the after-yellowing characteristic of linseed oil, and to a lesser extent soyabean oil (58) which is a severe disadvantage in whites and pastel shades. Such a fatty acid mixture would find ready use in alkyd and resin based paints, enamels, varnishes and lacquers. Higher I.V. fatty acid mixtures are used in air drying varieties, but for baking enamels or softer films, lower Iodine Values can be tolerated. Dryers are added to hasten solidification and these will often themselves be metal (zinc, lead, cobalt or manganese) soaps of fatty acids; they act by catalysing oxidation and polymerisation. Metal soaps are also used to improve the flat finish of some paints.

33. Plasticisers - Fatty acid and fatty oil derived plasticisers have grown tremendously in importance in recent years due to the rapid expansion of the plastics and synthetic rubber industries. Butyl and higher chain length esters of unsaturated fatty acid mixtures have good compatibility with various synthetic rubbers, cellulosics and polymer resins providing flexibility and lubricity over a wide

range of temperatures. They have the additional advantage of being non-toxic and thus suitable for systems which come into contact with food.

34. Epoxidised semi-drying oils and esters of epoxidised fatty acid mixtures enjoy a major use as plasticisers for polyvinyl chloride and other chlorine containing polymers. They owe their importance to their additional stabilisation properties, the epoxy groups absorbing the hydrocholoric acid which is released on the ageing of these polymers. Plastic coated fabrics are the main outlet for these materials.

35. The C_9 dibasic azaleic acid can be derived from the ozonolysis of high oleic oils including rice bran oil (23, 54) and esters of this also find use as plasticisers, particularly with cellulosics.

36. Detergents and Emulsifiers - As mentioned earlier, fatty acids, as well as the triglyceride oils, can be employed as feedstock for the soap industry enabling more specialised products to be manufactured. Repeated washing and glycerol recovery is eliminated from soap making in this way. In addition to soap, an enormous range of synthetic surfactants are manufactured from fatty acids and it is clearly beyond the scope of this article to give more than a brief account of them. They range from the industrial and household detergents used for laundrying, textile manufacture, etc., to the emulsifiers, defoamers and softeners used in the food and cosmetic industries. A few examples of the more common types are given in Table 7. They are mainly derived from commercial stearines and oleines. In the light of the world-wide emphasis on biodegradable surfactants, fatty acid derived materials should assume increasing importance in the future.

TABLE 7

Material	Action	Use
Partial glycerides	Emulsifiers	food, cosmetics
Sulphated monoglycerides	Detergents	household, industrial
Fatty alcohol sulphates	Detergents	household, industrial
Fatty acid sulphonates	Detergents	household, industrial
Nitrogen derivaties of fatty acids (e.g. alkylolamides)	Detergents	laundry, textile manufacture
Ethylene oxide derivatives	Emulsifiers defoaming agents	food, cosmetics, industrial

37. Metal Soaps - The use of heavy metal soaps in surface coatings as dryers and flatting agents has already been mentioned. Aluminium, barium and calcium soaps find a considerable market as components of lubricants, being used as thickeners for mineral oils and greases and as dry lubricants in plastics manufacture. They are

also employed in waterproofing preparations for leather, rope and cement.

38. Metal soaps or the fatty acids themselves find extensive use in rubber manufacture. As well as their softening and lubricating properties which are utilised during the mixing, extrusion and moulding operations of natural rubber, zinc soaps play an important role as cross-linking accelerators during the vulcanisation process.

39. Cosmetics - Hand creams, hair creams, shaving creams and moisturising creams all employ stearines to impart lustre and sheen to their appearance. Glycerol, oleyl alcohol, liquid vegetable oils and fatty acid derived emulsifiers may also be important constituents of these products.

(c) Miscellaneous Uses for Crude Rice Bran Oil

40. Other than its obvious use for illumination several other uses for the crude oil have been reported but very little detailed information is available. They include carriers for insecticides and fungicides, anti-rust oils and mould release agents. They appear to be uses which any liquid oil could fulfil, cost being the prime factor influencing selection.

VI. PROCESSING OF RICE BRAN OIL FOR EDIBLE PURPOSES

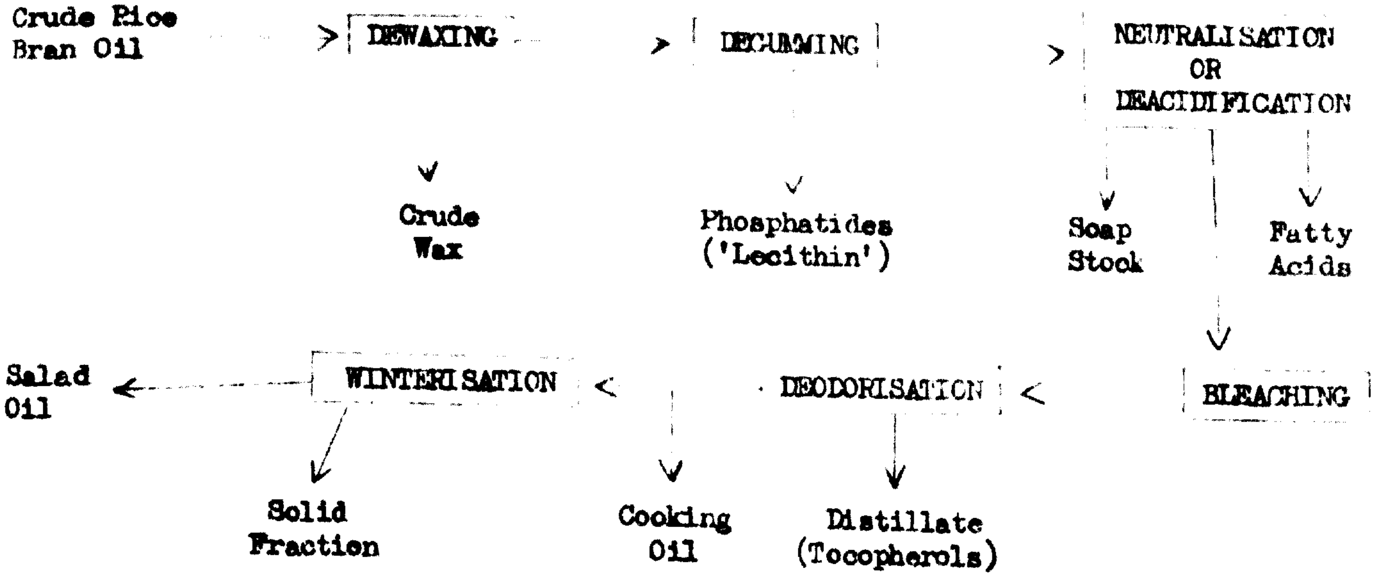
41. It has often been claimed that rice bran oil is difficult to refine and process, but the existence of a large flourishing rice bran oil industry in Japan and to a lesser extent in other countries indicates that the difficulties are not insurmountable. The major problems appear to arise not from the nature of the oil *per se* but from the high free fatty acid content that inevitably results from the extraction of bran that is not fresh, or has been stored even for a short period without some form of heat sterilisation. Japanese workers emphasise the importance of using only dried, fresh bran for obtaining a refinable oil (25).

42. The purpose of the various stages of processing rice bran oil for edible purposes is to remove the following impurities:- wax (dewaxing), phosphatides (degumming), free fatty acids (neutralisation or deacidification), pigments (bleaching), oxidative breakdown products (deodorisation), and, if the oil is required to be stored at refrigerator temperatures, high melting saturated glycerides (winterisation). Figure 2 summarises the process and the by-products obtained at the various stages.

43. (a) Dewaxing - Dewaxing of rice bran oils before processing is recommended not only by virtue of the possible value of the isolated wax but also because

FIGURE 2

Flow Sheet for Processing Rice Bran Oil for Edible Purposes



recent work strongly suggests that some component in the wax increases refining losses. Its removal from crude rice bran oil will be dealt with in a later section.

44. (b) Degumming - Gums and mucilages in vegetable oils are complex mixtures and only rarely has a detailed analysis been carried out. Almost certainly its constitution will vary from batch to batch. The most common impurities in solution in the oil comprise phospholipids and glycolipids but also included here are sugars and protein complexes which are often present in colloidal form (and therefore not filterable) but can be removed by the same methods as are used for phosphatides.

45. Removal of these gums from a crude oil is an important step for a variety of reasons. Most importantly, polar lipids have surface active properties and their presence causes losses during neutralisation due to the formation of emulsions. This leads to poor separation of the soapstock, entrainment of oil in the soapstock and residual soap in the neutral oil. The value of the soapstock for soap, or after acidulation for fatty acid manufacture, is also reduced by the presence of these impurities. Application of high temperatures to gummy vegetable oils (which can occur on several occasions during processing) can cause darkening and create difficulties during bleaching. Gums will also flocculate under such treatment and can cause blockages in pumps, filters or piping. Moreover, recovered phosphatides can have a value as by-products. Soyabean 'lecithin', for instance, is used extensively in the food, pharmaceutical and other industries.

46. The gum content of rice bran oil is variable and in most samples prepared by extraction of fresh or well stabilised bran does not appear to be high. Gums

do not seem to present the problems that are found with, for instance, soyabean, groundnut or rapeseed oils. Degumming was examined for its efficacy at reducing the refining loss of rice bran oils of up to 6.3% free fatty acids (24) and although reductions of 1 - 2% were found, this was not considered to be economic unless the phosphatides were of sufficient value to warrant recovery. In contrast, current Japanese practice favours an acid degumming treatment prior to alkali refining (25). If steam refining of rice bran oil is the method of choice for deacidification, however, degumming must be carried out since appreciable discolouration occurs which can render the oil virtually unbleachable.

47. The normal method of degumming involves the use of small quantities (1 - 1.5%) of concentrated phosphoric or sulphuric acids at moderate temperatures followed by filtration or settling. Another popular method, particularly if the phosphatides are to be isolated for selling, consists of warming the oil to about 80°C followed by addition of 2.5% hot water. Alternatively direct steam injection may be carried out until the temperature reaches 80 - 100° by which time sufficient steam will have condensed to achieve hydration and flocculation of the colloidal gum materials. These are then removed by centrifugation.

48. (c) De-acidification - The most widespread means of deacidification is by neutralisation of the free fatty acids by the addition of calculated amounts of caustic soda. Free fatty acids are converted to sodium salts to form the soapstock which is separated by allowing to settle or by centrifugation. It is this stage of rice bran oil processing that most problems in the past have been met. High refining losses have been found due to difficulties in separating the soapstock from the residual oil. The soapstock has been described as fluid, or fluffy and is found to entrain considerable amounts of neutral oil, or would remain suspended in the oil making withdrawal of clear neutral oil difficult. Refining factors in excess of 10 have been reported for relatively low free fatty acid rice bran oils which is clearly unacceptable for economic processing. Examples of typical refining losses are given in Table 8. Some of the difficulty can be overcome by separation of the soapstock by centrifugation (9, 52).

49. The cause of high refining loss is not entirely clear. The presence of gums and mucilages, as described above, is known to cause emulsions. However, a comparison of refining losses incurred by degummed and undegummed rice bran oil (24) did not reveal a drastic reduction, suggesting that presence of surface active agents of

type are not the primary cause.

TABLE 8

Examples of Refining Losses Obtained with Crude Rice Bran Oils

Reference	(20)	(29)	(30)	(24)	(31)	(24)	(12)	(26)	(29)	(29)
Free Fatty Acid of Crude Oil (%)	1.6	1.9	2.9	3.1	4	4.7	4.9	5.5	6.8	11.3
Refining Loss Reported (%)	12	24	20	14	17	19.6	28	44	51	56

50. Studies endeavouring to ascertain the optimum caustic concentration, stirring times, temperature (12, 26) have revealed that these variables can, as expected, alter the characteristics of the soapstock and can influence refining loss. Too high or too low a concentration of caustic can increase refining factor. It is well known that low iodine value fats yield a much firmer soapstock than liquid higher iodine value oils. But correctly adjusted conditions enable oils such as cottonseed, sunflower or soyabean to be alkali refined successfully without uneconomic losses. The Japanese, in particular, have carried out considerable work in establishing ideal conditions for the conventional alkali refining of rice bran oils (27) even those of high free fatty acids. Other groups have concentrated on exploring further the finding that certain chemicals are able to reduce refining losses (28). Sodium Silicate, ethanolamines, sugars (molasses and jaggery), certain alcohols and glycols have been examined in this respect with favourable results (26, 29, 12). These materials appear to act either by taking up some of the free fatty acid or by altering the physical properties of the soapstock allowing it to coalesce more satisfactorily. Examples of these studies are shown in Table 9.

51. The most recent reports point to the possibility that the high refining losses are principally caused by some constituent of the wax fraction. Low free fatty acid (4%) rice bran oils produced by the XM process were still found to give high losses on alkali refining, up to 1[illegible]%; but introduction of a special dewaxing step reduced this to an acceptable 6 - 8% level (31). Japanese workers emphasise the importance of removing wax prior to refining rice bran oils (25).

TABLE 9

Influence of Certain Chemicals on the Refining Characteristics of Rice Bran Oils

Reference	Free Fatty Acid of Crude Oil %	Additive	Refining Loss %
(29)	6.8	None	51
	6.8	1% Sodium Silicate	31
	6.8	2% Monoethanolamine	46
	6.8	3% Jaggery	27
(29)	9.8	None	62
	9.8	1% Sodium Silicate	32
	9.8	2% Triethanolamine	29
	9.8	2% Molasses	32
(26)	5.5	None	44.1
	5.5	1.8% Monoethanolamine	17.4
	5.5	1.9% Ethylene Glycol	20.3
	5.5	3% Ethanol	24
	5.5	2.5% Molasses	23.3

52. Other methods of deacidification do not seem to give the high refining losses which have characterised conventional alkali neutralisation of rice bran oil. Miscella refining, for instance, where neutralisation of the oil is carried out in hexane solution, has been successfully applied to rice bran oil without high loss (12). Steam distillation, to remove the bulk of the free fatty acid, followed by a mild alkali refine for the residue, has also been shown to give economically low refining losses, particularly with high free fatty acid oils (24, 32, 53). Deacidification by esterification, urea complexing (56) or ion-exchange resins (55) have not been reported commercially with rice bran oils, although these methods have been employed successfully on a laboratory scale.

53. (d) Bleaching - Removal of pigments from rice bran oil does not seem to have presented great problems despite the greenish hue frequently reported. A number of studies have been carried out (11, 12, 24), all of which indicate that conventional earth bleaching will readily give oils with Lovibond Colours of 2 - 3 red units (5¼ inch cell), an acceptable level for high grade cooking and salad oils. Removal of green colouration (resulting, it has been suggested, from the milling of immature

rice (31)) can be achieved without difficulty with the use of activated acidic clays. Japanese practice currently involves adding 3 - 5% activated earth to rice bran oil at 60 - 80°C, heating to 120°C with agitation, followed by filtration (25); this does not differ markedly from normal bleaching methods with other oils. Heat bleaching seems unlikely to be effective with rice bran oil owing to the occasional presence of chlorophyll.

54. (e) Deodorisation - The final stage in processing for a cooking oil involves removal of oxidative breakdown products such as ketones and aldehydes which cause undesirable odours and tastes. Thes breakdown products, in a carefully processed oil, should be present only at very low concentration but due to their extremely low taste thresholds, sometimes of the order of 1 part in 100 million, they are very readily detectable and must be removed to give the oil a bland or mild flavour. Deodorisation of rice bran oil can be carried out in the normal manner by heating the oil to temperatures of 200 - 250°C under high vacuum stripping out the undesirable volatiles in a current of dry steam. Any free fatty acids, and peroxides formed, for instance, during bleaching, are also removed as are a certain proportion of the natural tocopherol antioxidants. These latter can be recovered from the distillate, isolated and sold as a by-product as mentioned earlier.

55. Most vegetable oils in common use are particularly susceptible to oxidation after deodorisation due to removal of these natural antioxidants, but rice bran oil, with its high initial tocopherol content, retains sufficient to have above-average stability.

If the rice bran oil is to be used as a cooking oil, or as part of the formulation for a margarine blend, processing is now complete. However, if the oil is to be used as a salad oil, winterisation is required.

56. (f) Winterisation - This is carried out for the removal of saturated glycerides which have relatively high melting points and only a limited solubility in the unsaturated glycerides. It is a prerequisite of a high grade salad oil that it remains clear and liquid at refrigerator temperatures and does not become converted to a milky-looking product due to crystallisation of these saturated glycerides. Rice bran oil is eminently suitable for this application since its glyceride structure follows a more even distribution than most soft oils. This means that the saturated fatty acid chains are uniformly distributed among the glycerides and only a small proportion of totally saturated molecules are present. Winterisation consists of chilling the rice bran oil very slowly in large tanks, and holding it at 5°C or lower for a number

of days. The saturated glycerides crystallize out and are separated by filtration. With rice bran oil a high proportion remain liquid upon this treatment (94.5%), in contrast to cottonseed oil which yields only 57.7% of fully winterised oil (11). The separated saturated glycerides are not discarded but can find use as the solid fat fraction of a margarine or shortening formulation. For the manufacture of a salad oil, deodorisation would be carried out after winterisation.

57. Considerable development work has been carried out to determine optimum cooling rates, holding times and filtration techniques to give rapid winterisation and high yields of a fully winterised liquid fraction from rice bran oil for use as a salad oil.

VII. EDIBLE USES OF RICE BRAN OIL

58. Modern technology has provided many means of altering the chemical and physical properties of a refined liquid edible oil. Hydrogenation can reduce its content of unsaturated bonds and thus raise its melting point; fractional crystallization can be used to separate out triglyceride classes with different melting ranges; and interesterification can rearrange its molecular structure, sometimes with profound changes to physical characteristics such as crystal structure. A combination of these techniques makes it theoretically possible for a single oil, in skilled hands, to yield a variety of fat stocks suitable for many applications. Without resorting to these sophisticated, and, in some cases, costly techniques, however, the most evident uses of dewaxed, refined, bleached, deodorised rice bran oil remain in the salad oil and cooking oil fields, and as the liquid fraction of a margarine blend.

59. Two advantages that rice bran oil has over competitive products are its very low content of linolenic acid, and its high content of tocopherol, both important from the oxidative stability view point. The comparative rates of autoxidation of the three common unsaturated C18 acids oleic : linoleic : linolenic are 1 : 12 : 30, indicating how a content of linolenic acid can sharply reduce the keeping time of an oil. Linolenic is, in addition, suspected of being a key factor in the flavour reversion found with certain oils, notably soyabean (57), which limit its use in certain commodities. Flavour reversion has not been noted in connection with rice bran oils; its performance in accelerated storage tests has been shown to be excellent (11, 24) from both the peroxide formation standpoint and the organoleptic detection of off-flavours.

60. (a) Salad Oil - The most important features of a good grade salad oil are

cold stability, flavour stability, good colour, and the ability to form stable emulsions when used in a mayonnaise or emulsified salad dressing product. Emulsifiers and crystallization inhibitors can improve some of these characteristics. From reported figures (11), refined bleached deodorised rice bran oil can claim good cold stability as measured by the normal methods. Its performance is further improved by winterisation. Results are shown in Table 10 where rice bran oil is compared with competitive products (11, 24, 7, 31). The Cold Test, a requirement of salad oils in the U.S.A., is measure of the length of time before a bottle of oil, immersed in water at 0°C, will develop cloudiness. The high yield of liquid fraction on winterising rice bran oil is also of considerable benefit in the economics of salad oil production. Liquid oils of this type are also used extensively for fish canning.

61. (b) Cooking Oil - For nutritional reasons outlined later there has been a movement in the U.S.A. and W. Europe in recent years towards the use of cooking oils rather than solid fats for frying. Requirements for a cooking oil are rather more stringent than those for a salad oil since its use involves high temperatures. As well as oxidative stability, complete absence of free fatty acids must be assured since these tend to lower the temperature at which the oil will smoke or catch fire. Some oils foam excessively, the cause of which is not completely understood, but additives can prevent this from becoming a serious problem. Available evidence suggests that rice bran oil performs well in frying tests giving low peroxide, foam, free fatty acid and polymer formation (31) as well as an adequately high smoke point (415°F) and fire point (665°F) comparable with or superior to competitive oils in common use (11). There have also been reports of reduced losses (25), decreased sticking and a cleaner odour and flavour (31) than with other oils. It has been evaluated in a wide range of commercial and household applications with promising results (13, 31).

62. (c) Margarine and Shortenings - Margarine is a water-in-oil emulsion, the fat trapping the water phase within an interlocking network of crystals. The amount, nature and size of the crystals are important and determine the plastic properties of the material. The melting range must be wide so that over a range of temperatures the mixture is form retaining although plastic.

63. The fat phase is usually a carefully controlled blend of a liquid oil, a high melting solid fat together with a small proportion of intermediate stock. During

TABLE 10

CHARACTERISTICS OF SALAD OIL PREPARATIONS

	Unwinterised Rice Bran Oil	Ground-nut Oil	Cotton-seed Oil	Winterised Rice Bran Oil	Winterised Cottonseed Oil	Unwinterised X - M Rice Bran Oil	Winterised X - M Rice Bran Oil	Commercial Soyabean Oil Product
Cloud Point °C	+1	+5	+4	-6	+4	-6	-8	-
Pour Point °C	-	-	-	-7	-6	-	-	-
Solid Point °C	-7	+1	-2	-	-	-	-	-
Cold Test (hours)	-	-	-	9	5	0.5	36	22
Colour (Lovibond)	1.9R	-	-	-	-	2.0R	1.5R	1.7R
Iodine Value	102	95	109	-	-	103	103	112
A.O.M.Stability (hours)	24	-	-	-	-	20	20	21

manufacture the blend is well mixed in liquid form and then rapidly chilled so that solidification is homogeneous. This ensures that no graininess or large crystal structures are formed by early slow deposition of the solid fat content. Mechanical working also assists the production of uniform crystal size and even consistency. Virtually any oil or fat can be used as part of a margarine formulation and price and availability generally dictate which fats are used at any particular time. Currently in the U.S.A. and W. Europe, soyabean, cottonseed, sunflower and groundnut oils provide the bulk of the liquid stock with palm oil, animal fats or hydrogenated marine oils as the solid portion. It is evident that rice bran oil could contribute to margarine manufacture initially as an alternative to these liquid vegetable oils of similar properties; its low linolenic acid content once again being an advantage in not limiting the quantity that could be incorporated into such a blend.

64. Shortenings and other compound cooking fats, extensively used in the home and in the food industry, consist of a similar blend of various fats hydrogenated to the desired melting point together with a small amount of emulsifier. The behaviour of rice bran oil on hydrogenation appears to present no unusual difficulties. The Iodine Value, refractive index and colour have been found to decrease readily and evenly and in all respects paralleled those of other comparative oils hardened under the same conditions (11, 60). In the hydrogenated state rice bran oil is exceptionally stable and resistant to oxidation and when hardened to a consistency suitable for a shortening was found to have a keeping time somewhat in excess of hydrogenated cottonseed and groundnut oils (11).

65. (d) Nutritional Aspects of Rice Bran Oil Use - Aside from the value of fats in the diet as a major supply of calorific value and as a carrier for the fat soluble vitamins A, D and E, many years of investigation have established that certain fats have a specific inherent nutrient factor which cannot be supplied by other means. These studies have involved the effects of fat-free diets on experimental animals. Diets containing sufficient protein, adequate calories in the form of carbohydrates, and a full complement of water soluble and fat soluble vitamins still led to poor growth and other symptoms, and resulted in the recognition of a new deficiency disease. Further work demonstrated that the preventative and curative properties of certain fats could be traced to their content of certain polyunsaturated fatty acids and the expression 'essential fatty acids' was introduced. Early scepticism led to a thorough re-evaluation and there is

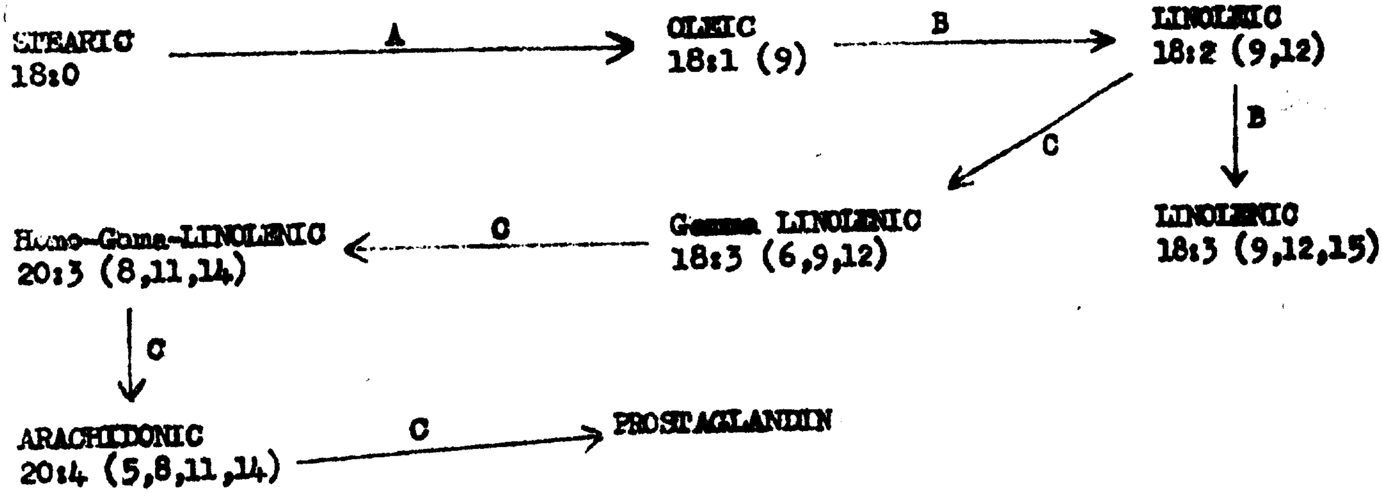
now no doubt that certain fatty acids, notably linoleic acid, are essential dietary components. It is beyond the scope of this article to describe the symptoms of essential fatty acid deficiency disease and the investigations which resulted in its eventual recognition which have been reviewed many times (33, 34).

66. The underlying reason is the inability of animals (ranging from insects to man) to synthesise linoleic acid, and thus must receive adequate supplies of this fatty acid in the diet. Animals tissues contain enzymes capable of introducing double bonds into (desaturating) fatty acid chains but not at a position 12 carbons from the carboxyl group. Plants do contain such enzymes and consequently linoleic acid is of wide occurrence in plant tissues including most seed fats.

67. Once received in the diet, linoleic acid undergoes several metabolic transformations which are of interest in that they may point to the fundamental cause of essential fatty acid deficiency and its symptoms. By a series of elongations and further desaturations linoleic acid is converted to the twenty carbon fatty acid arachidonic acid, once thought to be the end point of metabolism. Recent work has revealed, however, that arachidonic can be converted to an oxygenated cyclic compound known as prostaglandin which has important hormone-like properaties in connection with muscle contraction, reproduction and blood pressure regulation. Several recent reviews on the subject have appeared (35, 36). The metabolism of essential fatty acids is summarised in Figure 3.

FIGURE 3

Metabolism of Essential Fatty Acids



Enzyme reactions which occur:-

A - in both plant and animal tissues

B - only in plant tissues

C - only in animal tissues

68. Despite the essential nature of linoleic acid, the natural occurrence of essential fatty acid deficiency is most unusual, except as a side effect of other disorders or as part of general subnutrition, since linoleic acid is so widespread in nature. Of more immediate importance in the context of nutrition are the recent findings that suggest that there is a connection between the type of dietary fat intake and the incidence of atherosclerosis, currently a major cause of illness and death in many countries. Atherosclerosis is the term used to describe the accumulation of lipid on the inside walls of blood vessels. This leads to constriction of the vascular system and often ultimately complete blockage, with fatal results, the 'heart attack'.

69. Analysis of the accumulated lipid revealed phospholipids and cholesterol esters rather similar in composition to those of the plasma lipids. Since an elevated blood cholesterol level itself seems to increase the risk of atherosclerosis, a means of reducing these levels was sought in the hope that this would also lower the incidence of heart attacks. It has now been established that a diet high in polyunsaturated fatty acids, particularly linoleic acid, leads to a reduction in the plasma cholesterol level and long term trials are still underway to test the second hypothesis.

70. In 1965, the American Medical Association, after reviewing the field, issued a statement recommending that the public should eat less saturated animal fat, replacing it wherever possible with unsaturated vegetable oil. It should be stressed, however, that a direct casual relationship between dietary fat, serum lipid concentration and coronary heart disease is not proven, although there is much statistical evidence. Other factors such as cigarette smoking, lack of exercise, general overweight and emotional stress can be linked in much the same way with vascular disorders. Much controversy has followed the A.M.A. recommendation, but it is generally accepted that increasing the intake of unsaturated fat will, at the very least, do no harm, and may well ultimately prove to be beneficial.

71. In response to these findings there has been a massive swing in the U.S.A. and W. Europe towards the use of vegetable cooking oils rather than solid animal fats for frying, and a movement towards softer margarines with a higher content of polyunsaturated acids, particularly linoleic acid. The marketing of high linoleic oils such as corn and safflower, and margarines which contain them, has been

intensified and emphasise the possible health advantages of the high polyunsaturated fatty acid content. Other vegetable oils, such as soyabean, cottonseed, sunflower and groundnut, have also benefitted from this change in dietary habits, becoming increasingly used in margarines and other compound fat and oil products. Rice bran oil has a fatty acid composition not unlike these and is thus in a good position to take advantage from the situation. It can thus be expected that good quality, low free fatty acid rice bran oil, if produced at a price competitive with these other oils, could occupy a larger share of the world edible oil supply.

VIII. RICE BRAN WAX

72. (a) Introduction - Wax constitutes an appreciable fraction of the solvent extractable material of rice bran. Although its actual content appears to vary greatly according to method of preparation and the origin of the bran, typical analyses range from 3 - 9% of the oil. Recent studies on the processing of rice bran oil for edible use point to the wax fraction as the major cause of the difficulties and losses experienced on refining. It has, indeed, been stated that satisfactory refining of even relatively low acidity oil can only be carried out economically after dewaxing. The current emphasis on improving production of rice bran oil is thus likely to yield increasing quantities of crude rice bran wax. Not only should wax recovery improve the processing properties of the oil but it also has the potential of becoming a valued by-product capable of entering the hard wax market and playing a part in the overall economics of a rice bran oil industry.

73. Rice bran wax is not currently an major article of world trade and consequently it is unlikely that many wax processors (except in Japan) have had the opportunity of fully evaluating its performance in commercial wax products. Reports indicate, however, that rice bran wax is capable of replacing, at least partially, Carnauba wax in a variety of applications but more research and development experience is needed in this area.

74. (b) Production of Crude Rice Bran Wax - Wax is soluble in the triglyceride/hexane miscella at normal extraction temperatures (140 - 1[illegible]°F) but is virtually insoluble at ambient temperatures and below. Two alternatives thus suggest themselves for crude wax production:- firstly, extraction of bran with cold solvent to remove only the triglycerides, followed by hot solvent to yield a wax-rich product, and, secondly, conventional hot solvent extraction followed by cooling of the miscella or the desolventised oil and separation of the wax fraction by centrifugation, filtration or settling.

75. The dual extraction method has been studied in some detail (12, 30) and appears to have the additional advantage that the absence of substantial amounts of wax in the oil ensures more satisfactory refining. In these studies various flow rates, and solvent bran ratios were examined with an initial extraction of 40°F followed by extraction at 140°F. Cooling the second hexane miscella to 40°F resulted in a wax precipitate which was isolated by centrifugation. A preliminary cost study for this process has also been published (37) which suggest that it could be economic, the cost of minor modifications to a conventional extraction plant being rapidly recovered by the added value of the wax. It was estimated from these investigations that 500 lbs. of crude rice bran wax could be obtained from an oil production of 28,000 lbs.

76. Cooling of the extracted oil, of course, occurs naturally in practice on storage and transport and the wax comes out of solution during this period. The settlings, or crude rice bran oil 'sludge' provides a good source of crude wax although varying greatly in composition. Impurities present will include free fatty acids, triglycerides, gums (particularly if steam stripping has been used to desolventise the oil) and particles of tissue and dirt. This material has been examined as a starting material for wax production (38, 39, 40) with promising results. Active cooling of the crude oil, or a solution of it in acetone or hexane, to below ambient temperatures also leads to deposition of wax (25) but in this case would be accompanied by larger quantities of the saturated triglycerides. Current Japanese practice involves cooling the oil and isolating the crude wax by centrifugation (41) or filtration through unglazed porcelain cylinders covered with filter cloth (42).

77. A special process for dewaxing XM rice oils has recently been reported (43) and is the subject of an American patent (44). The wax content (2.5 - 3.5%) was found to have a specific gravity so close to that of the oil that filtration or centrifugation were ineffective. The problem was overcome by the addition of 4.5% sodium silicate solution to the chilled oil at 25°F firstly in hexane miscella and then in desolventised oil. Under these conditions the wax was found to bind water and become readily separable by centrifugation. This process also exerts a winterising action on the oil itself.

78. (c) Purification and Properties of Rice Bran Wax - The wax isolated by the above methods contains large amounts of triglycerides, free fatty acids and minor quantities of phospholipids and a variety of methods have been used to achieve initial

purification of the wax away from these impurities. Moreover, only a portion of the true wax consists of the hard, high melting fraction which is likely to have commercial value. Mild hydrolysis, washing and extraction with hot and cold solvents such as hexane, acetone, isopropanol, butanol, methanol or benzene have all been employed to obtain hard material desired (38, 39, 45 - 45, 50). Japanese practice involves hydrogenation of the crude rice bran wax to increase yield of hard, high melting, low iodine value fraction. It is difficult to compare the methods since the starting materials used varied widely in their content of wax and other impurities. Moreover, the final purified products varied in yield and properties. Isopropanol appears to be the solvent of choice for the final fractional crystallisation step for isolation of the hard wax fraction. It is a poor solvent at ambient temperatures but a good one at temperatures just below its boiling point. The melting point of the wax is just below the boiling point of isopropanol which is sufficiently low to allow ready removal from the isolated wax.

79. The products of the various purification methods are hard, non-tacky waxes, black or brown in colour, and approach carnauba wax in many of its properties. A summary of the properties of various preparations reported in the literature is given in Table 11; figures for carnauba wax, a likely commercial competitor, are given for comparison.

80. Bleaching of rice bran wax can be accomplished using hydrogen peroxide (38, 48) which yields a light brown product, or, if a completely white material is required, sulphuric acid and chromium troxide can be used (38, 39, 49). Bleaching earths or decolourising carbon have little effect. Bleaching also tends to slightly lower the melting point and iodine value whilst increasing the hardness of the wax (38). The hardness and melting point of rice bran wax can also be increased by compounding it with 25% stearyl α- or β-naphthylamide (49).

81. (d) Chemical Composition of Rice Bran Wax - Pure waxes are esters of long chain (20 - 32) alcohols with long chain (20 - 34) acids. The articles of commerce also contain varying proportions of triglycerides, free fatty acids, sterols, squalene and phospholipids depending on source and degree of purification. In rice bran wax the principal chain lengths of the wax acids are 22 (behenic), 24 (lignoceric), 26 (cerotic) and iso - 26 (isocerotic - 24 methylpentacosanoic) and of the wax alcohols, 26 (ceryl), iso-26 (isoceryl - 24 methylpentacosanyl), 28 (montanyl) and 30 (myricyl). Smaller amounts of shorter chain lengths occur in the softer constituents. The major esters

TABLE 11

Properties of Various Rice Bran Wax Preparations

References	(38)			(39)		(47)			
	Crude	Purified Method 1	Purified Method 2	Purified Method 1	Purified Method 2	Crude	Purified Method 1	Purified Method 2	Carnauba Wax
% Free Fatty Acids	21.6	2.7	2.7	21.1	15.4	34.1	14.8	-	2.9
Iodine Value	77	13.0	11.1	31.4	29	51.6	59.7	12.6	9.4
% non-saponifiable	14.0	57	56	47.7	49	-	31.7	48.7	56.9
Saponification No.	166	104	78	91.4	93.5	174.8	79.5	72.8	77.0
Melting Point	-	75.8	79.9	74	78	-	74.5	75.5	83.4
Yield %	-	13.7	9.1	17.2	17.6	-	18	1	-

appear to be myricyl cerotate (43 - 45%), ceryl cerotate (21 - 22%) and isoceryl - isocerotate (9 - 10%) with lesser amounts of the other possible esters, free wax acids and free wax alcohols (51, 47). The variable fatty acid content consists mainly of palmitic and oleic acids. Some of these may be esterified to the sterols. Sitosterol, stigmasterol and dihydrositosterol have been reported as major constituents of the unsaponifiable material (49, 51). Very little triglyceride, squalene, or phospholipid is found in purified rice bran wax.

82. (e) Uses of Rice Bran Wax - The hardness, high melting point and non-tacky nature suggest that the principal use for rice bran wax would be in polishes as a partial replacement for carnauba wax. Most preparations examined have had equivalent hardness and lustre-giving properties and were compatible with carnauba wax but were slightly lower in melting and softening points. The formulation of a wax polish is to some degree an art and different batches of any wax have to be evaluated separately and blended according to the exact properties required for the final product. Desirable features of a good polish wax include hardness and firmness without brittleness, the ability to produce a durable film, heat resistance, good solvent retention (to resist drying out) and good compatibility with dyes and other waxes. Stability in emulsions is also an advantage for incorporation into the many liquid and aerosol polishes currently being marketed.

83. Wax coatings for confections, such as chocolates, and fruits, is another application for which rice bran wax is suitable. Chocolate products are given a lustre and prevented from forming a 'bloom' of sugar or fat crystals on the surface. These wax 'chocolate enrobers' prevent spoilage and drying out and preserve appearance and flavour.

84. The coating of fruit and vegetables with wax after cleaning assists in retarding water loss, shrinkage and withering and basically consists of replacing the natural waxes which have been lost during the washing and cleaning process. A hard wax is necessary to impart gloss and improve appearance. It is of interest in this connection that in 1963 rice bran wax was approved by the U.S.A. authorities as a constituent of food articles in these wax coating applications (52). It was also approved for use as a plasticiser for chewing gum.

85. The availability of rice bran wax at a competitive price would stimulate the search for applications and enable it to be evaluated as a component in formulations such as carbon paper base, wax crayons, candles, cosmetics, and other commodities which currently utilize large quantities of carnauba and other waxes.

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