THE CHEMICAL COMPOSITION OF RICE OIL

By GEORGE S. JAMIESON

Rice oil, which has been produced on a small commercial scale from the bran at various times in England, Italy, and in this country in Louisiana, has been the subject of several investigation.[1, 2, 3] C. A. Browne,[4] who suggested the present study, determined the chemical and physical characteristics of the oil and demonstrated that rapid hydrolysis which the oil undergoes was due to a lipase. He fed rice bran and polish to steers and found that the feces contained considerable quantities of undigested fat and fatty acids. The insoluble fatty acids obtained in the usual manner had a mean molecular weight of 320.2, which is higher than that of arachidic acid (312.3).

Although in 1903 Browne had shown that rice oil contained fatty acids with a molecular weight greater than that of palmitic acid, Tsujimoto[6] stated that the oil which he examined contained palmitic, oleic and linolic acids. It will be shown that rice oil also contains myristic, stearic, arachidic and lignoceric acids.

The oil used in this investigation was extracted from rice bran by ethyl ether and given to the writer by Charles E. F. Gersdorff of the Protein Investigation Laboratory of this Bureau.

Chemical and Physical Characteristics

The characteristics of rice oil which were determined given in Table I. The percentages of saturated and unsaturated acids were determined by the lead salt ether procedure. The saturated acids as determined had an iodine number of 4.8 and contained 0.78 per cent of unsaponifiable matter for both of which corrections have been made.[7] Also unsaturated acids have been corrected for the 5.63 per cent of unsaponifiable matter which they contained.

Table I—CHARACTERISTICS OF RICE OIL

Refractive index 25°C	1.4690
Acid value	73.67
Iodine number (Hanus)	99.9
Saponification value	185.3
Saponification value corrected for unsaponifiable	194.2
Unsaponifiable matter (per cent)	4.64
Saturated acids (corrected) (per cent)	14.70
Unsaturated acids (corrected) (per cent)	74.30
Reichert-Meissl value	0.3
Polenske value	0.3

The acid value was determined about 2 weeks after the extraction of the oil. Both the iodine number and saponification value are in close agreement with the values obtained by Garelli for extracted rice oil.[8]

Unsaponifiable Matter

The unsaponifiable matter (3.8 g.) was separated from about 200 g. of the oil by the modified Kerr-Sorber method.[9] It was dissolved in 50 cc. of absolute alcohol and allowed to stand over night in a cool place. A small crop of colorless flat prisms were obtained. After recrystallization from alcohol, they melted at 83° C. When mixed with an equal quantity of melissyl alcohol (M. P. 84-5) the mixture melted at 83 to 84° C., indicating that the substance was melissyl alcohol. The quantity separated was too small for further identification tests.

After concentrating the alcoholic filtrate to about 35 cc. and allowing it to stand over night in the ice box, 0.4 gram of small brilliant crystals was obtained. This substance after recrystallization from alcohol melted at 137 to 138° C. without decomposition. It gave the Liebermann-Burchard test, showing that it was a phytosterol. The purified acetyl derivative melted at 124° to 125° C. Further concentration of the original alcoholic solution and cooling for several days failed to yield any more crystals. The concentrated solution was heated with 25 cc. of 95 per cent alcohol and a slight excess of a one per cent alcoholic solution of digitonin was added. One gram of the digitonin-sterol compound was obtained, which was equivalent to 0.24 g. of sterol. The total quantity of sterol isolated amounted to 16.7 per cent of the unsaponifiable matter.

The alcoholic filtrate was evaporated and the residue taken up in 30 cc. of ether. The insoluble digitonin was removed by filtration. The ether was evaporated and the residue was dissolved in 25 cc. of 95 per cent alcohol. After standing in the ice box for over 2 weeks, some brown crystalline aggregates, which had separated, were removed and recrystallized first from ether, then from alcohol. The purified substance melted at 138 to 139° C. The acetyle derivative was prepared. It melted at 132 to 132.5° and gave an intense Liebermann-Burchard test, indicating that it was not a dihydrosterol. The alcoholic filtrate, after concentration, deposited a small quantity of a sterol which melted at 142 to 143° C. This also gave the Liebermann-Burchard test. The quantity of this sterol was too small for the preparation of the acetyl derivative.

It was found that when a dilute alcoholic solution of either of these sterols was treated with an alcoholic one per cent solution of digitonin and allowed to stand, no precipitation took place. However, upon rubbing the sides of the flask with a rod, a copious precipitate of the digitonin-sterol compound quickly separated. Presumably, if the original alcoholic solution of the unsaponifiable matter after the addition of the digitonin solution had been thoroughly rubbed with a rod, a complete precipitation of the sterols would have been obtained. This experiment indicates that similar treatment should be made in other cases when it is desired to completely precipitate the sterols with digitonin.

The total quantity of sterols isolated amounted to about 25 per cent of the total unsaponifiable matter.

The non-crystallizable portion of the unsaponifiable matter was not investigated.

Unsaturated Acids

The iodine number of the unsaturated acids was 133.2, indicating that they consisted of a mixture of oleic acid (iodine number 90.1) and linolic acid (iodine number 181.4). Using these data the following percentages were calculated:

	%	In original oil %	Glycerides in original oil %
Oleic acid	52.77	39.21	40.97
Linolic acid	47.23	35.09	36.67
	100.00	74.30	77.64

Saturated Acids

A quantity of the saturated acids (iodine number 2.8) prepared by the lead salt ether method was esterified with methyl alcohol.[10] This mixture of methyl esters was fractionally distilled under diminished pressure. The data for this distillation are given in Table II. A preliminary distillation of the esters was made from a liter Claisson flask. Seven fractions (A, B, C, D, E, F, G) and a residue were obtained. These fractions and residue were redistilled from a 250 cc. Ladinburg flask according to the manner indicated in the table. Seven fractions and a residue were obtained.

Table II—Fractional Distillation of Methyl Esters of Saturated Acids.
(134.85 g. subjected to distillation)

Distillation at 2.5 mm. pressure.

	Fraction	Temperature C.°	Weight G.
	A	148	23.00
	B	149	22.66
	C	150	21.10
	D	151-5	23.00
	E	156-162	22.70
	F	163-180	10.90
	G	181-205	7.30
	Residue		4.20
Fractions A and B redistilled	1	146-148	4.80
Fraction C added	2	148-149	46.42
Fractions D and E added	3	150	43.98
Fractions F and G added	4	152-157	14.10
Residue added	5	158-165	13.80
	6	175-185	6.75
	7	195-215	4.80
	Residue		0.20

The iodine numbers which are measures of the esters of the unsaturated acids present, and the saponification values of fractions 1 to 7 are given in columns 2 and 3 of Table III. Using these data, the mean molecular weights of the saturated acid esters in each fraction were calculated[11] (recorded in column 6).

The results in column 6 indicate what saturated acids may be present in the fractions. The mean molecular weight of the saturated acid esters in fractions 1 and 2 is somewhat less than that of methyl palmitate (270.3) and indicates that these fractions contain some methyl myristate. The results for fractions 3-5 lie between the molecular weights of methyl palmitate and methyl stearate (298.4), which indicates that the fractions contain these esters in various proportions. The molecular weight of the saturated acid esters of fraction 6 indicates a mixture of stearic and arachidic esters (326.4), while that of fraction 7 indicates a mixture of methyl arachidate and lignocerate (382.5).

The free mixed acids were recovered from these fractions by saponifying with alcoholic potash and acidifying the soap solution with hydrochloric acid. The constituent acids were isolated by fractional crystallization from alcohol of the mixture which had been completely freed from mineral acid and salt. The identity of the acids was established by the melting points and by the fact that these melting points were not lowered when the substances were mixed with equal quantities of the respective acids which they were suspected of being, the purity of which had been established previously by elementary analysis.

In all cases the melting points of the isolated acids confirmed the deductions drawn from the mean molecular weights of the fractions.

TABLE III RICE OIL

Fractional Distillation of Methyl Esters of Saturated Acids

Fractions	Iodine number	Saponification value	Mean molecular weight	Esters of unsaturated acide %	Mean molecular weight of esters of saturated acids	Myristic-acid		Palmitic acid		Stearic acid		Arachidic acid		Lignoceric acid	
						%	G	%	G	%	G	%	G	%	G
1	0.6	211.4	265.4	0.53	265.2	17.15	0.823	76.97	3.695						
2.	0.6	208.3	269.4	0.53	269.3	3.34	1.550	90.95	42,219						
3	1.54	206.2	272.0	1.36	271.8			88.55	38.945	5.02	2.208				
4	4.7	203.1	276.3	4.16	275.4			77.53	10.509	16.58	2.338				
5	8.6	194.3	288.7	7.62	288.1			32.33	4.461	56.10	7.742				
6	6.7	178.3	314.7	5.94	315.8					34.85	2.352	54.93	3.708		
7	5.9	153.3	366.0	5.32	371.5							17.42	0.736	73.56	3.531
							2.373		99.829		14.640		4.444		3.531

Lignoceric acid ($C_{24}H_{48}O_2$) which melted at 80 to 80.5° C. was isolated from fraction 7. Arachidic acid ($C_{20}H_{40}O_2$) which melted at 77° C. was separated from fractions 6 and 7. Stearic acid ($C_{18}H_{36}O_2$)

which melted at 69° C. was isolated from fraction 6. Palmitic acid ($C_{16}H_{32}O_2$), melting at 63° was obtained from fractions 1 and 2. Myristic acid ($C_{14}H_{25}O_2$), melting at 53 to 54°, was separated from fraction 1.

This establishes the identity of the saturated acids in the fractions of the esters. The quantities were calculated from the mean molecular weights given in Column 6, Table III, and the theoretical molecular weights of the two esters in each fraction. These results are given in column 7-16. The small residue given in Table II was found to contain only decomposition products.

In Table IV the percentage composition of the saturated acids is given in column 3, the percentages of saturated acids in the original oil in column 4, and the equivalent percentages of glycerides in column 5.

Table IV RICE OIL
Saturated Acids

Acids	Weight G	Saturated Acids %	Acids in Original Oil %	Glycerides in Original Oil %
Myristic	2.373	1.9	0.28	0.30
Palmitic	99.829	79.9	11.74	12.32
Stearic	14.640	11.8	1.73	1.81
Arachidic	4.444	3.6	0.52	0.54
Lignoceric	3.531	2.8	0.42	0.43

The mean molecular weight of the total insoluble fatty acids as calculated from the data presented is 277.8, which is 11.5 lower than the value actually found by Browne in the oil of the rice bran used in his feeding experiments upon steers. The latter oil unquestionably contained a much larger percentage of arachidic and lignoceric acids, as is confirmed by the high mean molecular weight, 320.2, of the undigested insoluble fatty acids found by Browne in the oil from the feces of the steers. The supposition advanced by Browne in 1903 as to the existence in rice oil of such higher homologues as arachidic and lignoceric acids has been confirmed by the present work, although the actual percentage of these constituents in rice oils of different origin is no doubt subject to a wide varaition.

Summary

A sample of extracted rice oil with an acid value of 73.7 contained 14.7 per cent of saturated and 74.3 per cent of unsaturated acids. The oil had an iodine number of 99.9 and a saponification value of 185.3. The composition of the oil has been determined with the following results:

	Acid	%
Glycerides of	Oleic	41.0
	Linolic	36.7
	Myristic	0.3
	Palmitic	12.3
	Stearic	1.8
	Arachidic	0.5
	Lignoceric	0.4
Unsaponifiable Matter		4.6

Sterols, which amounted to about 25 per cent of the unsaponifiable matter, were isolated. The several fraction of sterols ranged in their melting points from 137° to 143° C. Also a small quantity of what appears to be melissyl alcohol was obtained from the unsaponifiable matter.

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