

The Fatty Acids and Glycerides of Babassu Oil¹

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Babassu oil is obtained from the nut of the palm *Orbignya* (a subdivision of *Attalea*) *speciosa* which is abundant in some parts of Brazil. Until recently, this oil was finding increasing industrial use.

Several investigators have examined babassu oil previously. Heiduschka and Agsten (1), in 1930, determined the fatty acid content of babassu oil by vacuum distillation of the fatty acids. More recently, Nobori and Ono (2) studied babassu oil fatty acids using the methyl ester distillation technique. Preliminary investigations of babassu oil glycerides were undertaken by Bomer and Huttig (3) and Kaufmann (4).

The present investigation was undertaken to extend available information regarding the component acids of the oil and to obtain further information concerning the nature of the component glycerides in babassu oil.

Experimental

General Characteristics of Babassu Oil. The babassu oil was golden yellow in color and had an odor similar to that of coconut oil. Physical and chemical constants of the oil were as follows:

Melting point (F.A.C.).....	24°C.
Saponification equivalent.....	225.6
Iodine value (Wijs).....	16.1
Free fatty acids (Caled. as lauric acid).....	2.85%

Fatty Acid Analysis of Babassu Oil. The methyl ester fractionation procedure (5, 6, 7, 8, 9) was used for the analysis of "solid" and "liquid" fractions gained from a lead salt separation (10, 11) of the total fatty acids. Saponification equivalents and iodine values (Wijs) were determined on each distilled ester fraction and the composition was determined on the basis of these values (12, 13).

Mixed fatty acids (235.7 gm.) were prepared from 250 gm. of babassu oil. The iodine value of the mixed fatty acids was 17.0 (Wijs) and the saponification equivalent, 214.8. A portion of the mixed acids (218.4 gm.) was dissolved in 95% ethyl alcohol (1100 ml.), heated to boiling, and mixed with a boiling solution of lead acetate (131 gm.) in ethyl alcohol (1100 ml.) containing 3% glacial acetic acid. After standing overnight at room temperature, the white lead salts of fatty acids which precipitated were filtered, redissolved in 2200 ml. of ethanol containing 1.5% acetic acid and again allowed to crystallize. The "solid" lead salts were decomposed in a warm aqueous solution containing excess hydrochloric acid. The free fatty acids were recovered after repeated washings in the distilled water. The "liquid" lead salts were recovered after distillation of the alcohol from the combined filtrates. They were decomposed and the fatty acids recovered as described for the "solid" lead salts. The "solid" acid fraction weighed 131.7 gm. (60.3% of the total mixed acids) and had a saponification equivalent of 217.3 and an

iodine value of 3.9. The "liquid" acids (saponification equivalent, 211.0 and iodine value, 35.9) weighed 86.7 gm. and constituted 39.7% of the total mixed acids.

Both the "solid" and "liquid" acid fractions were converted to methyl esters with yields of 97.4% of theory for the "solid" acids (125.1 gm. of "solid" acids yielded 129.6 gm. of methyl esters) and 96.5% of theory for the "liquid" acids (80.5 gm. of "liquid" acids yielded 82.8 gm. of methyl esters). The resulting methyl esters were washed repeatedly to remove mineral acid (used to catalyze the esterification) and unreacted fatty acids.

The neutral methyl esters of both the "solid" and "liquid" acids were fractionally distilled at reduced pressure using a packed column with approximately 15 theoretical plates (8). The column was fitted with a distillation head especially designed for collection of small samples with minimum mixing of distillates. The data for the fractional distillation of the "solid" esters and the chemical analysis of the individual fractions are assembled in Table I. Similar data for the "liquid" esters are given in Table II. The fatty acid compositions of the "solid" and "liquid" acids are given in Table III.

On the basis of higher unsaturation in certain fractions than could be accounted for by oleic acid alone, the linoleic acid content was calculated as 1.1% of the total fatty acids. Heiduschka and Agsten (1) did not report the presence of linoleic acid, although its presence was reported by Nobori and Ono (2). Confirmatory evidence of the presence of linoleic acid was obtained by the isolation of tetrabromostearic acid (m.p. 115-116°) from the babassu oil fatty acids.

Preliminary Experimental Study of Babassu Oil Glycerides. A simple direct approach to the analysis of glyceride structures was provided by Hilditch and Lea (14) who demonstrated a practical means for

TABLE I
Distillation and Analysis of "Solid" Methyl Esters

Fraction number	Weight	Saponification equivalent	Iodine number (Wijs)
	<i>gm.</i>		
1	1.937	196.9	0.0
2	6.228	206.4	0.0
3	4.758	208.8	0.0
4	4.912	213.4	0.0
5	5.604	213.6	0.0
6	12.749	213.7	0.0
7	4.334	214.5	0.0
8	11.499	214.8	0.0
9	11.885	216.9	0.0
10	5.085	219.6	0.0
11	3.384	234.9	0.7
12	1.091	241.8	1.0
13	3.139	242.2	0.2
14	5.619	242.3	0.1
15	5.532	244.4	0.3
16	4.471	252.5	0.5
17	4.363	258.7	1.0
18	2.717	263.7	1.8
19	8.599	275.2	12.0
20	2.077	284.1	26.2
21	3.673	292.5	36.2
22	3.798	298.3	30.2
23 (residue)	0.733	432.0	24.5
		(330.0)*	
	118.192		

* Residual esters freed from unsaponifiable matter.

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TABLE II
Distillation and Analysis of "Liquid" Methyl Esters
(Fractions 1 to 5, inclusive, were distilled at 110 mm.;
fractions 6 to 18 were distilled at 2-3 mm.)

Fraction number	Weight	Saponification equivalent	Iodine number (Wijs)
	gm.		
1	0.987	152.6	3.6
2	6.300	158.1	0.6
3	3.695	168.1	0.0
4	1.973	179.5	0.5
5	3.838	185.8	0.6
6	4.592	196.8	0.2
7	3.799	210.0	0.3
8	10.668	213.8	0.0
9	8.323	215.1	0.0
10	1.675	223.0	0.0
11	3.918	238.6	0.5
12	1.100	256.7	17.0
13	4.635	288.1	76.1
14	3.937	294.1	95.2
15	5.844	295.8	95.6
16	6.825	295.8	94.5
17	4.754	295.8	93.6
18	2.940	295.9	92.1
19	1.595	360.6	86.4
	81.398	(296.0)*	

* Residual esters freed of unsaponifiable matter.

TABLE III
Fatty Acid Composition of Babassu Oil

Constituent	Weight percentage			Composition excluding unsaponifiable matter	
	"Solid" acids (60.3%)	"Liquid" acids (39.7%)	Total	Weight percentage basis	Molar percentage basis
Caproic.....	0.15	0.15	0.2	9.3
Caprylic.....	4.78	4.78	4.8	7.1
Capric.....	1.86	4.75	6.61	6.6	8.3
Lauric.....	32.10	11.94	44.04	44.1	47.3
Myristic.....	12.90	2.48	15.38	15.4	14.5
Palmitic.....	7.90	0.59	8.49	8.5	7.1
Stearic.....	2.65	2.65	2.7	2.0
Arachidic.....	0.16	0.16	0.2	0.1
Oleic.....	2.64	13.43	16.07	16.1	12.2
Linoleic.....	1.43	1.43	1.4	1.1
Unsaponifiable.....	0.09	0.15	0.24

measuring the content of trisaturated glycerides after removal of glycerides containing any unsaturated acids by permanganate oxidation in acetone solution (15). When an acid-free sample of babassu oil (133.7 gm.) was subjected to this treatment, the isolated trisaturated glycerides (iodine value, 0.3) weighed 84.00 gm. or 62.80% of the total glycerides. An acid analysis of the purified trisaturated glyceride fraction was performed as indicated above for the whole fat. Methyl esters of the acids were fractionally distilled and analyses were made for saponification equivalents and iodine values of each respective fraction (Table IV). The fatty acid composition of the trisaturated glycerides is summarized in Table VI.

Discussion

The Component Acids. Heiduschka and Agsten (1), who studied babassu oil in 1930, reported values for caproic, caprylic, lauric, and palmitic acids which agree essentially with the results of this investigation. However, differences were noted between their values for the percentage of capric, myristic, and oleic acids and those in this report. Stearic, arachidic, and linoleic acids were apparently not detected by the above investigators. The values of Nobori and Ono(2) for the component fatty acids of babassu oil agree well with the values found in this investigation.

The iodine values of the "liquid" methyl ester fractions indicated that there was unsaturated mate-

rial present in the lower boiling fractions. For the purpose of the calculations summarized in Table III, it was of little consequence whether this unsaturation be reckoned as oleic or some other acid. Calculating it as oleic acid, fractions one to seven, inclusive, contributed only 0.485 gm. to the total oleic acid. This weight represented less than 0.2% of the total weight of acids analyzed. Previous investigators did not report the presence of any unsaturation in their low molecular weight fractions.

The isolation of the characteristic derivative of linoleic acid, tetrabromostearic acid, establishes definitely the presence of the ordinary seed fat linoleic acid in the original oil.

Hilditch (13) has summarized the data for the component fatty acids of seed fats of various members of the Palmae family. The results reported in this paper for the quantity and identity of the component fatty acids of babassu oil closely resemble those given for other members of the Palmae family (Table V).

The Component Glycerides. The molar proportion of trisaturated glycerides in the babassu oil was found to be 67.3% of the total glyceride. It is interesting to note that this determined value is close to the theoretical value for the trisaturated glycerides, based on a completely random distribution of the saturated acids in the formation of the glycerides. The theo-

TABLE IV
Distillation and Analysis of F. S. G. Methyl Esters
(Acids from Trisaturated Glycerides)
Fractions 1 to 6, inclusive, were distilled at 46 mm.;
fractions 7 to 17 were distilled at 2 to 3 mm.)

Fraction number	Weight	Saponification equivalent	Iodine number (Wijs)
	gm.		
1	1.133	157.1	1.1
2	1.580	158.4	0.0
3	1.463	165.0	0.0
4	1.945	181.6	0.0
5	1.773	190.8	0.0
6	2.440	206.0	0.0
7	2.150	208.8	0.0
8	3.415	212.0	0.0
9	6.082	214.1	0.0
10	3.127	214.1	0.0
11	4.253	217.8	0.0
12	4.111	224.5	0.0
13	3.982	226.5	0.0
14	4.011	231.4	0.0
15	3.467	240.5	0.0
16	2.584	245.6	0.3
17	2.972	258.1	0.4
18	3.761	293.9	7.0
	54.249	(277.0)*	(4.3)*

* Residual esters freed from unsaponifiable matter.

TABLE V
A Comparison of the Composition of Babassu, Coconut, and Palm Oils
(Seed Fats of the Palmae)

Acids	Babassu oil			Coconut oil (19)	Palm oil (6)
	Present analysis	Heiduschka and Agsten (1)	Nobori and Ono (2)		
	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent
Caproic.....	0.2	0.1	0.8
Caprylic.....	4.8	6.5	4.1	5.4	3.0
Capric.....	6.6	2.7	7.6	8.4	3.0
Lauric.....	44.1	45.8	45.1	45.4	52.0
Myristic.....	15.4	19.9	16.5	18.0	15.0
Palmitic.....	8.5	6.9	5.8	10.5	7.5
Stearic.....	2.7	5.5	2.3	2.5
Arachidic.....	0.2	0.7	0.4
Hexadecenoic.....	1.3
Oleic.....	16.1	18.1	11.9	7.5	16.0
Linoleic.....	1.4	2.8	Trace	1.0

TABLE VI
Fatty Acid Distribution in the Glycerides of Babassu Oil

Acid	Molar percentage of acids in				Molar proportion of whole fat due to glyceride increments	
	Whole fat (dtd.)	Trisaturated glycerides		Mixed saturated-unsaturated glycerides (calcd.)**	Trisaturated glycerides (67.3%)	Mixed saturated-unsaturated glycerides (32.7%)
		(dtd.)	(calcd.)*			
Caproic.....	0.3	0.9	0.3	-0.9	0.6	-0.3
Caprylic.....	7.1	10.0	8.2	1.2	6.7	0.4
Capric.....	8.3	10.2	9.6	4.2	6.9	1.4
Lauric.....	47.3	48.4	54.4	42.9	32.6	14.7
Myristic.....	14.5	22.2	16.8	-1.2	14.9	-0.4
Palmitic.....	7.1	7.0	8.2	7.3	4.7	2.4
Stearic.....	2.0	1.0	2.3	4.0	0.7	1.3
Arachidic.....	0.1	0.1	0.3	0.1
Oleic.....	12.2	0.3	36.7	0.2	12.0
Linoleic.....	1.1	3.4	1.1

* Assuming a complete random distribution of the acids in the whole fat.

** From the (a) determined composition of the whole fat and trisaturated glycerides and (b) molar proportion of trisaturated glycerides in the whole fat.

retical value for the molar percentage of trisaturated glyceride, assuming random distribution of 86.7%

saturated acids, is $\frac{(86.7)^3}{(100)^3} \times 100 = 65.2\%$.

Hilditch (13) found that in eight samples of seed fats, in which the saturated acids formed between 85 and 94% of the total acids, the proportion of trisaturated glycerides was large, but at the same time, the glycerides were so constructed that the ratio of saturated acids to unsaturated acids (on a molar basis) in the mixed saturated-unsaturated glyceride portion of the fat was approximately constant (1.3 to 1.5:1). From the determined molar proportions of fatty acids in the whole fat and in the trisaturated glycerides, it was possible to calculate the acid composition of the mixed saturated-unsaturated glycerides. The corresponding "association ratio" (moles of saturated acids associated with one mole of unsaturated acids in the mixed saturated-unsaturated glycerides) found for babassu oil in this investigation was 1.5:1.

The detailed results given in Table VI show an apparent divergence from a random distribution of the acids throughout the glycerides. Caprylic, capric, and myristic acids were found almost entirely in the trisaturated glycerides. Furthermore, the acid present in highest proportion in babassu oil, lauric acid, was found to contribute almost as high a proportion of the total acids in the mixed saturated-unsaturated glycerides as in the trisaturated fraction. That this divergence is more apparent than real is shown clearly by the data given in Table VI which show the determined molar percentage of fatty acids in the trisaturated glycerides and the corresponding values calculated on the assumption that there was a complete random distribution of the acids in the whole fat. There is an agreement between these two columns of figures which indicates clearly a first approximation to the random distribution of all the acids available in the formation of the glycerides of babassu oil.

Longenecker has shown elsewhere (16, 17, 18) that animal body fats tend to be constituted according to a pattern described in terms of a complete random distribution of available acids during glyceride formation. Plant fats, for the most part, were not thought to fit this pattern. However, if the above indications are correct, then it may be anticipated that future research will reveal a pattern of organiza-

tion for babassu oil glycerides similar to that for animal fats. Work was in progress on the separation of specific glycerides from babassu oil to check this point until it became necessary to interrupt the progress temporarily.

Summary

The fatty acids of babassu oil were determined quantitatively by the ester fractionation procedure. The values found in molar percentages were: caproic 0.3, caprylic 7.1, capric 8.3, lauric 47.3, myristic 14.5, palmitic 7.1, stearic 2.0, arachidic 0.1, oleic 12.2, and linoleic acid 1.1. Confirmatory evidence for the presence of linoleic acid was obtained by the isolation of one of its characteristic derivatives, tetrabromostearic acid, m.p. 115°C. A similarity in fatty acid composition was shown between babassu oil and seed fats of other members of the Palmae family.

The molar proportion of trisaturated glycerides found in babassu oil (67.3%) was close to the proportion calculated (65.2%) on the assumption that all of the acids in babassu oil were distributed at random. Likewise, the determined fatty acid analysis of the trisaturated glycerides was a first approximation of the analysis calculated on the basis of complete random distribution of the component acids of the whole fat.

LITERATURE CITED

- (1) Heiduschka, A., and Agsten, R. Z. F. Prakt. Chem. 126, 53 (1930).
- (2) Nobori, H., and Ono, I. J. Soc. Chem. Ind., Japan 43, 435 (1940).
- (3) Bomer, A., and Huttig, H. Z. Untersuch, Lebensm. 75, 1 (1938).
- (4) Kaufmann, H. P. Z. Angew. Chem., 41, 1046 (1928).
- (5) Armstrong, E. F., Allan, J., and Moore, C. W. J. Soc. Chem. Ind. 44, 63T (1925).
- (6) Armstrong, E. F., Allan, J., and Moore, C. W. J. Soc. Chem. Ind. 44, 143T (1925).
- (7) Hilditch, T. P. Biochem J. 28, 779 (1934).
- (8) Longenecker, H. E. J. Soc. Chem. Ind. 56, 199T (1937).
- (9) Weitkamp, A. W., and Brunstram, L. C. Oil and Soap 18, 47 (1941).
- (10) Hilditch, T. P. Chem. Products 3, 78, 81 (1940).
- (11) Hilditch, T. P., and Priestman, J. Analyst 56, 354 (1931).
- (12) Longenecker, H. E. Oil and Soap 17, 53 (1940).
- (13) Hilditch, T. P. John Wiley and Sons, Inc., New York (1940). "The Chemical Constitution of Natural Fats."
- (14) Hilditch, T. P., and Lea, C. H. J. Chem. Soc. 3106, (1927).
- (15) Armstrong, E. F., and Hilditch, T. P. J. Soc. Chem. Ind., 44, 43T (1925).
- (16) Longenecker, H. E. Chem. Reviews 29, 201 (1941).
- (17) Longenecker, H. E., and Mattil, K. F. Federation Proc. 1, 122 (1942).
- (18) Longenecker, H. E. Paper presented before the American Oil Chemists' Society, Fall Meeting, October, 1942, Chicago, Illinois.
- (19) Longenecker, H. E. J. Biol. Chem. 130 167 (1939).