CLXXXIV. THE KERNEL-FATS OF SOME MEMBERS OF THE PALMAE: *ACROCOMIA SCLEROCARPA* MART. (GRU-GRU PALM), *MANICARIA SACCIFERA* GAERTN., *ASTROCARYUM TUCUMA* MART., *MAXIMILIANA CARIBAEA* GRISEB., *ATTALEA EXCELSA* MART. (PALLIA PALM), AND *COCOS NUCIFERA* LINN. (COCONUT).

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UP to the present only five examples of the kernel-fats of this important family have been examined by the methods now available for the quantitative estimation of the component fatty acids [Armstrong *et al.*, 1925; Taylor and Clarke, 1927; Hilditch and Vidyarthi, 1928; Collin and Hilditch, 1928; Saraiva, 1929; Heiduschka and Agsten, 1930], and, of these, two only have been submitted to oxidation with potassium permanganate, whereby a general idea of the glyceride composition may be obtained. In the present paper the relevant data for six more seed-fats of this family are communicated. Of these, five are new, in the sense that they have not hitherto undergone detailed analysis, and one, a commercial specimen of coconut oil, is of interest as a useful addition to the example already reported upon in an earlier paper [Collin and Hilditch, 1928].

Of the five new fats, those from *Acrocomia sclerocarpa* Mart., *Manicaria saccifera* Gaertn., and *Astrocaryum Tucuma* Mart., were available in sufficient quantity for a fatty acid analysis of the normal standard of accuracy and for a determination of their content of fully-saturated glycerides. The amounts of fat available from the kernels of *Maximiliana caribaea* Griseb. and *Attalea excelsa* Mart. were so small that it was only possible to make a very rough estimate of their component fatty acids. In the case of *Maximiliana caribaea* the fatty acid mixture was subjected to a single fractionation, and its general composition was then deduced from the analytical constants of the primary fractions, in the absence of the systematic refractionation which is strictly necessary when dealing with the complex mixture of acids characteristic of the Palmae seed-fats. In the other case, the kernel-fat of *Attalea excelsa*, the primary fractionation was controlled so as to correspond as closely as possible, in size of fraction and range of boiling-point, with an average primary fractionation of a Palmae kernel-fat, and by comparison of the two sets of analytical data a general idea of the composition of its component acids was obtained.

To guard against any possibility of loss of low-boiling esters during the vacuum distillation, a single-surfaced water-condenser was inserted between the Willstätter bulb and the Perkin triangle during the primary fractionation

and the first two refractionations. Apart from this alteration, both the ester fractionations and the acetone-permanganate oxidations follow the procedures adopted in the examination of coconut and palm kernel-fats [Collin and Hilditch, 1928].

COMPOSITION OF THE FATTY ACID MIXTURES.

The tendency of the various species within the palm family to synthesise fats of similar composition is shown very strikingly by a comparison of the fatty acid mixtures of the five new fats examined in this paper, (i) with each other, and (ii) with the recent analyses already mentioned of the component acids from coconut, palm kernel, cohune nut, murumuru and *Attalea funifera* kernel-fats.

Table I.

	% acids.							
	Cap- rylic	Capric	Lauric	My- ristic	Pal- mitic	Stearic	Oleic	Lin- oleic
<i>Acrocomia sclerocarpa</i>	7.8	5.6	44.9	13.4	7.6	2.6	16.5	1.6
<i>Manicaria saccifera</i>	5.3	6.6	47.5	18.9	8.2	2.4	9.7	1.4
<i>Astrocaryum Tucuma</i>	1.3	4.4	48.9	21.6	6.4	1.7	13.2	2.5
<i>Astrocaryum Murumuru</i> [Saraiva, 1929]	1.1	1.6	42.5	36.9	4.6	2.1	10.8	0.4
<i>Maximiliana caribaea</i>	(?)	5.0	47.0	21.0	9.0	(?)	(18)	
<i>Attalea excelsa</i>	(Similar composition to that of <i>Acrocomia sclerocarpa</i>)							
Cohune (<i>Attalea cohune</i>) [Hilditch and Vidyarthi, 1928]	7.5	6.6	46.4	16.1	9.3	3.3	9.9	0.9
<i>Attalea funifera</i> [Heiduschka and Agsten, 1930]	6.5	2.7	45.9	19.9	6.9	—	18.1	—
Coconut I [Collin and Hilditch, 1928]	7.9	7.2	48.0	17.5	9.0	2.1	5.7	2.6
Coconut II	7.8	7.6	44.9	18.1	9.5	2.4	8.2	1.5
Palm kernel [Collin and Hilditch, 1928]	2.7	7.0	46.9	14.1	8.8	1.3	18.5	0.7

In each case the same range of fatty acids is present, but each genus, as it were, asserts its individuality by slight variations in particular components while conforming to the same general type. The comparative constancy of the major constituent of the mixtures, lauric acid, is particularly noticeable and, similarly, capric, myristic and palmitic acids all occur within fairly narrow ranges. The apparent absence of caprylic and stearic acids from the fat of *Maximiliana caribaea* may well be attributed to incomplete separation of the mixture due to lack of material.

GLYCERIDE STRUCTURE OF THE KERNEL-FATS OF *ACROCOMIA SCLEROCARPA* MART., *MANICARIA SACCIFERA* GAERTN. AND *ASTROCARYUM TUCUMA* MART.

The determination of the content of fully-saturated glycerides in these three fats and the consequent disclosure of the extent to which the unsaturated acids are distributed throughout the glyceride molecules has demonstrated that the usual tendency towards even distribution, characteristic of kernel-fats, holds throughout this group. The numerical expression of the extent of dispersion of the unsaturated acids, the "association ratio" [Collin and Hilditch, 1929], is in fair agreement in all three cases with the corresponding values for coconut and palm kernel-fats and indicates that all these fats possess similar glyceride structures. The case for the absence of triolein from coconut and palm kernel-fats has been put in a previous paper [Collin and Hilditch, 1928] and applies

with equal force to the present fats. Assuming triolein to be absent, the glyceride composition of the fats may be expressed in terms of saturated glycerides, mono-unsaturated disaturated glycerides, and di-unsaturated monosaturated glycerides (the figures refer to mols. per 100 mols. of fat) (Table II).

Table II.

	Fully-saturated glycerides	Mono-unsaturated disaturated	Di-unsaturated monosaturated
<i>Acrocomia sclerocarpa</i>	69	21	10
<i>Manicaria saccifera</i>	82	11	7
<i>Astrocaryum Tucuma</i>	73	18	9

Acrocomia sclerocarpa (*Gru-gru*) kernel-fat.

This tree, known locally as the gru-gru palm, is indigenous to Central America and Brazil, although the specimen from which this sample of nuts was taken grew in Trinidad. The nuts were kindly supplied by the Department of Agriculture, Port of Spain, Trinidad, to whom we are also indebted for the specimens of *Manicaria saccifera* and *Maximiliana caribaea* nuts.

The nuts contained 26 % of kernel, which, by extraction with low-boiling light petroleum, yielded 44.4 % of a white soft fat having saponification equivalent 222.3, acid value 0.6, iodine value 17.1, unsaponifiable matter 0.45 % and M.P. (open tube) 24°. The corresponding mixed fatty acids, containing the unsaponifiable matter, had saponification equivalent 210.4, iodine value 18.0, and setting-point 22°. A quantitative analysis of the component fatty acids has not been published but various workers have determined the constants of the fat, and obtained values for the saponification equivalent varying between 220–230, iodine value 16–21, M.P. 21–32.5° and Reichert-Meissl value 5.7–7.2.

The component fatty acids, determined by the ester fractionation process as described [Collin and Hilditch, 1928], are given in Table III.

Table III.

	% acids	
	Weight	Mols.
Caprylic	7.8	11.5
Capric	5.6	6.9
Lauric	44.9	47.6
Myristic	13.4	12.2
Palmitic	7.6	6.3
Stearic	2.6	1.8
Oleic	16.5	12.5
Linoleic	1.6	1.2

Fully-saturated glycerides. The fat (99.6 g.) was dissolved in acetone and treated with potassium permanganate in the usual manner. On working up the oxidation product there were obtained 69.4 g. crude fully-saturated glycerides (iodine value 0.3). After further purification with boiling aqueous potassium carbonate, the crude product was separated into (a) 42.9 g. of saturated glycerides (saponification equivalent 208.3, acid value 1.4), (b) 20.6 g. of saturated glycerides (acid value 2.2), and (c) 3.84 g. of acid product. This corresponds with a content of fully-saturated glyceride in the original fat of 64.5 % by weight or of 69.1 mols. per 100 mols. of fat. It also indicates an "association ratio" in the mixed saturated-unsaturated glycerides of 1.29 mols. of saturated acid with 1 mol. of unsaturated acid.

Manicaria saccifera kernel-fat.

As in the case of *Acrocomia sclerocarpa*, the palms from which the nuts were obtained, although indigenous to Central America and Brazil, were grown in Trinidad.

The kernels formed 15 % of the nut and gave 57.7 % of a soft white fat on extraction with low-boiling light petroleum. The fat possessed the following analytical characteristics: saponification equivalent 221.8, acid value 0.6, iodine value 10.7, unsaponifiable matter 0.05 %, and M.P. (open tube) 27.1°. The mixed fatty acids, containing the unsaponifiable matter, had saponification equivalent 208.0, iodine value 11.4 and setting-point 24.3°. Again there is no quantitative analysis of the fatty acids on record, but there is a reference in the literature [Olien en Vetten, 1919] to a specimen of this fat with a saponification equivalent of 232.2, iodine value 19 and M.P. 30°.

The results of the detailed analysis of the mixed fatty acids from the present specimen are given in Table IV.

Table IV.

	% acids	
	Weight	Mols.
Caproic	Trace	—
Caprylic	5.3	7.8
Capric	6.6	8.0
Lauric	47.5	49.9
Myristic	18.9	17.4
Palmitic	8.2	6.7
Stearic	2.4	1.8
Oleic	9.7	7.3
Linoleic	1.4	1.1

Fully-saturated glycerides. Permanganate-acetone oxidation of the fat (25.9 g.) yielded 20.6 g. of crude fully-saturated material; this was resolved, by further purification, into (a) 19.50 g. saturated glycerides (saponification equivalent 214.5, acid value 0.5), (b) 0.71 g. saturated glycerides (acid value 2.9) and (c) 0.39 g. acid product. The content of fully-saturated glyceride is therefore 79.5 % (weight) or 82.3 % (mols.), corresponding to an association ratio of 1.16 to 1.

Astrocaryum Tucuma kernel-fat.

The natural habitats of this palm are Brazil, Central America and the West Indies, but the palms from which the fat now examined was obtained were grown in Malaya. The nuts were collected through the kindness of Messrs E. Boustead and Co. (who also supplied the nuts of *Attalea excelsa*) from the Malakoff Rubber Estates.

The decorticated kernels yielded 39.8 % of a white fat, rather harder than in the previous instances, of saponification equivalent 230.3, acid value 1.8, iodine value 15.8, unsaponifiable matter 0.4 % and M.P. (open tube) 30.3°. The mixed fatty acids had saponification equivalent 218.9, iodine value 16.6 and setting-point 26.8°. The values recorded in the literature vary between the following limits: saponification equivalent 225–226, iodine value 9.4–11.6, M.P. 30.5–35.5°.

The results of the fractionation of the esters of the mixed fatty acids in the usual manner are given in Table V.

Fully-saturated glycerides. Oxidation of the fat (98.6 g.) with potassium permanganate in acetone yielded 72.1 g. of crude saturated glycerides which

Table V.

	% acids	
	Weight	Mols.
Caprylic	1.3	1.9
Capric	4.4	5.6
Lauric	48.9	53.1
Myristic	21.6	20.6
Palmitic	6.4	5.5
Stearic	1.7	1.3
Oleic	13.2	10.1
Linoleic	2.5	1.9

were further separated into (a) 61.7 g. saturated glycerides (saponification equivalent 220.5, acid value 0.6), (b) 4.40 g. saturated glycerides (acid value 2.6) and (c) 2.24 g. acid product. The original fat thus contained 69.7 % (weight) or 72.8 % (mols.) of fully-saturated glycerides and its "association ratio" was 1.25 : 1.

Maximiliana caribaea kernel-fat.

This species is also indigenous to Central America and Brazil, but the nuts studied were grown in Trinidad. The nuts, which were obviously immature, contained 59 % of kernel of which only 4.8 % was fat. The fat had the following characteristics: saponification equivalent 236.8, acid value 20.2, iodine value 22.7, unsaponifiable matter 0.23 %. There are no previous references to it in the literature. As already explained, the amount of fat at disposal only permitted a rudimentary fractionation of the esters of the mixed fatty acids to be undertaken. The results suggested the following approximate proportions of component fatty acids (Table VI).

Table VI.

	% acids	
	Weight	Mols.
Capric	5	6
Lauric	47	50
Myristic	21	21
Palmitic	9	8
Stearic	?	?
Oleic } Linoleic }	18	15

Attalea excelsa (Pallia palm) kernel-fat.

This batch of nuts came from palms grown in Malaya, but the tree is a native of Brazil. The kernel formed only 3 % of the nut and yielded 62.6 % of fat with saponification equivalent 231.7, iodine value 18.2, M.P. (open tube) 25.5°. The mixed acids had saponification equivalent 218.6, iodine value 19.3. Previous workers [Wittka, 1925; Allan and Moore, 1925] give the following values: saponification equivalent 218-241, iodine value 8-16, M.P. 18-19°.

The primary fractionation of the mixed esters may be compared with the primary fractionation of the mixed esters of *Acrocomia sclerocarpa* (Table VII).

The similarity in range of boiling-point, weights and analytical constants between the two sets of fractions is sufficient indication that the two mixtures are broadly the same in composition. The fat from *Attalea excelsa*, however, is not so rich in the group of acids below C₁₂ as *Acrocomia sclerocarpa* fat, and this is balanced by its increased content of myristic, palmitic and stearic acids.

Table VII.

<i>Attalea excelsa</i> Mixed esters					<i>Acrocomia sclerocarpa</i> Mixed esters				
	B.P.	Weight %	S.E.	I.V.		B.P.	Weight %	S.E.	I.V.
1	55-88°	24	196.6	0.5		50-95°	29	188.6	0.3
2	88-90	25	217.6	0.7		95-105	30	217.7	0.5
3	90-130	31	252.8	17.2		105-130	18	245.6	15.8
4	Residue	20	295.9	60.3		Residue	23	291.7	64.2

Coconut oil.

The coconut oil used was taken from a refined commercial specimen supplied by Messrs Lever Brothers, Ltd., and had saponification equivalent 217.2, iodine value 9.7 and acid value 0.3. The experimental determination of the fatty acid mixture and the fully-saturated glycerides was carried out by Dr R. Child; the final composition of the component acids is given in Table VIII.

Table VIII.

	% acids	
	Weight	Mols.
Caproic	Trace	—
Caprylic	7.8	11.2
Capric	7.6	9.2
Lauric	44.9	46.5
Myristic	18.1	16.5
Palmitic	9.5	7.7
Stearic	2.4	1.8
Oleic	8.2	6.0
Linoleic	1.5	1.1

Fully-saturated glycerides. Permanganate-acetone oxidation of the fat (400 g.), yielded (a) 244 g. saturated glycerides (saponification equivalent 211, acid value nil), (b) 82 g. saturated glycerides (acid value 6.6), and (c) 57.6 g. acid product. The original fat therefore contained 80.7 % (weight) or 84 % (mols.) of fully-saturated glycerides. The corresponding "association ratio" of saturated to unsaturated acids in the mixed non-fully-saturated glycerides is 1.4 : 1.

This result is of interest when compared with those for the only other coconut-fat glycerides previously examined [Collin and Hilditch, 1928]. The specimen of fat then studied contained slightly more combined oleic and linoleic acids than the present one and, correspondingly, slightly less fully-saturated glycerides. The ratio of saturated to unsaturated acids in the non-fully-saturated glycerides was, however, the same in both cases. In seed-fats wherein unsaturated acids do not form more than about 40 % of the total fatty acids, the amount of fully-saturated glycerides is determined by the excess of saturated acids over and above the quantity necessary to link with unsaturated acids in mixed glycerides with an "association ratio" of about 1.3 to 1.4 : 1.

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