142. *The Configuration of Naturally Occurring Mixed Glycerides. Part IV. The Configuration of the Major Component Glycerides of Palm Oil.*

By M. L. Meara.

Palm oil has been separated by exhaustive fractional crystallisation into fractions consisting of fully saturated, mono-unsaturated di-saturated, and mono-saturated di-unsaturated glycerides respectively. Component fatty acid analyses considered in conjunction with thermal data obtained for individual glycerides isolated from crystallisation of the fully hydrogenated derivatives of each fraction indicate the presence of both α- and β-oleodipalmitin (in approximately equal amounts) in the mono-unsaturated di-saturated portion of the oil, whereas α-palmitodioleins and α-palmito-oleolinoleins greatly predominate over the accompanying β-isomers in the mono-saturated di-unsaturated fractions.

The determination of the component acids and glycerides of palm oil has been the subject of a number of investigations. Brash (*J. Soc. Chem. Ind.*, 1926, **45**, 438T) from a study of the crystallisation of palm oil and of the same oil after hydrogenation concluded that palm oil contained about 10% of tripalmitin and about the same amount of triolein. Hilditch and Jones (*ibid.*, 1930, **49**, 863T) isolated and examined the fully saturated glycerides from four different palm oils and found that the amount (7—10%) varied with the ratio of saturated to unsaturated acids in the fat as a whole, and that 70—80% of the fully saturated glycerides consisted of tripalmitin. A more detailed examination of the component glycerides of palm oils is due to Banks, Dean, and Hilditch (*ibid.*, 1935, **54**, 77T) who examined the fully saturated glycerides obtained by hydrogenating palm oils progressively to varying degrees of unsaturation. From comparative rates of hydrogenation it was suggested that the mono-palmito-oleins which form 60% of palm oil consisted of both α- and β-palmitodioleins with the β-isomer predominating, whereas the melting points of the palmitodistearin fractions obtained on repeated crystallisation of the hydrogenated oils indicated that a considerable amount of α-palmitodiolein was present. From similar evidence these authors indicated the presence of both α- and β-oleodipalmitins with the β-isomer predominating. They also produced evidence of increasing proportions of the unsymmetrical isomer as the amounts of palmitic and unsaturated C_{18} acids approached equality. Hilditch and Maddison (*ibid.*, 1940, **59**, 67) investigated two palm oils by resolving them into a series of simpler fractions by recrystallisation from acetone at 0° and above. They were able to state the proportions of the various glyceride groups present, within narrow limits, but no individual glyceride fraction was obtained in these crystallisations and the configuration of the component glycerides lay outside the scope of their investigation.

These somewhat indefinite conclusions, supported by little conclusive proof, called for further study of the configuration of the glycerides of palm oil, and a specimen of the oil has therefore been re-investigated according to the methods employed in the investigation of Piqui-a fruit-coat fat (Part III, *J.*, 1947, 773).

Experimental.

The neutralised and deodorised palm oil [*ca.* 500 g., sap. equiv. 282·3, iod. val. 52·3; component fatty acids % (mol.): myristic 2·8, palmitic 43·4, stearic 3·4, oleic 43·1, linoleic 7·3%] was exhaustively

crystallised from acetone and from ether. It was realised at a very early stage that the crystallisation would have to be much more exhaustive than that required for Piqui-a fruit-coat fat (*loc. cit.*), difficulties of separation experienced by Banks, Dean, and Hilditch occurring with the parent glycerides in much the same manner as with their fully hydrogenated derivatives.

Crystallisation of the oil (acetone, 3 c.c. per g.) at 0° gave 343·6 g. of crystalline material (iod. val. 34·2), leaving 158·4 g. (iod. val. 68·8) in solution. The latter recrystallised under the same conditions gave 64·1 g. (iod. val. 62·6) and 94·3 g. (iod. val. 70·2) respectively. The 64·1 g. fraction further recrystallised under the same conditions gave 22·3 g. (iod. val. 53·0) and 41·2 g. (iod. val. 69·5). The 343·6 g. fraction crystallised from acetone (5 c.c. per g.) at 0° gave 233·6 g. (iod. val. 33·8) and 110·0 g. (iod. val. 69·2). The former was recrystallised from acetone (5 c.c. per g.) at 15° and the latter from acetone (5 c.c. per g.) at 0°. The palm oil had thus now been separated into the following fractions :—

Wt. (g.)	51·6	149·4	22·3	8·3	24·5	110·0	41·2	94·3
Iod. val.	12·0	34·1	53·0	55·1	65·1	69·2	69·5	70·2

At this stage the 51·6 g. fraction was crystallised from ether (10 c.c. per g.) at 15°, the crystalline deposit being successively recrystallised from ether at 15° with dilutions increasing from 10 to 50 until the fully saturated glycerides had been isolated, together with small fractions containing the residual traces of fully saturated glycerides together with some mono-oleo-glycerides.

The 149·4 g. fraction was then crystallised from acetone (10 c.c. per g.) at 0°, and the crystalline material deposited recrystallised from acetone (20 c.c. per g.) at 0°, the material remaining in the mother liquors being united with the fraction of iodine value 53·0. The insoluble portion was then crystallised from ether (5 c.c. per g.) at 0° (which at this stage gave a much sharper separation of mono-oleo- from di-oleo-glycerides than acetone), the soluble portion being recrystallised from acetone (20 c.c. per g.) at 0°. Successive recrystallisations of the insoluble fractions from ether (5 c.c. per g.) at 0° and of soluble portions from acetone (20 c.c. per g.) gave rise to a considerable number of fractions. Fractions of very similar iodine value were ultimately combined to give the final fractions F—K (see below).

Fractions of iodine value 60 and over were combined and recrystallised from ether (10 c.c. per g.) at − 55° and − 45° successively, ultimately giving fractions K—N.

Thus the oil was finally resolved into the following fractions A—N :

Fraction	A	B	C	D	E	F	G	H	J	K	L	M	N
Wt. (g.)	20·5	4·9	4·0	0·7	1·4	22·2	52·5	33·3	30·2	7·7	115·0	89·5	96·8
% (wt.)	4·3	1·0	0·8	0·2	0·3	4·6	11·0	7·0	6·3	1·6	24·0	18·7	20·2
Iod. val.	0·0	1·2	6·6	15·0	24·1	29·5	30·2	33·0	43·2	50·0	57·9	70·0	86·9

Fractions A, F, G, H, J, L, M, and N consisting of concentrates of individual glyceride groups were further investigated, the small complex intermediate fractions B—E and K being neglected.

The component fatty acids of fractions L, M, and N were determined by ester fractionation after preliminary separation of the acids by lead salt–alcohol or low temperature crystallisation methods. The composition of fractions F, G, H, and J was arrived at by ester fractionation of a portion of the fully hydrogenated fraction after due allowance had been made for the unsaturated acids, determined iodometrically and spectrophotometrically on a small portion of the unhydrogenated fraction. The component glycerides are calculated from the data so obtained (see Table I).

Table I.

Component Acids and Glycerides of Fractions F—J and L—N (% mol.).

Fraction	F	G	H	J	L	M	N
Acid (% mol.) :							
Myristic	0·9	0·3	2·3	5·1	2·9	1·2	0·8
Palmitic	67·6	65·6	62·0	44·5	32·4	26·1	16·1
Stearic	—	1·2	1·1	13·7	9·6	5·6	3·0
Oleic	30·9	30·9	31·8	} 36·7 {	48·6	59·7	63·7
Linoleic	0·6	2·0	2·8	} 36·7 {	6·5	7·4	16·4
Component glycerides (% mol.) :							
Trisaturated	5·5	1·3	—	—	—	—	—
Disatd. mono-unsatd.	94·5	98·7	96·2	89·9	34·7	—	—
Mono-satd. di-unsatd.	—	—	3·8	10·1	65·3	98·7	59·7
Tri-unsaturated	—	—	—	—	—	1·3	40·3

Since the solid fractions F, G, H, and J could not be obtained (as in the case of the corresponding fractions from Piqui-a fruit, Part III) in sharply-defined crystalline forms, each fraction was hydrogenated at 100° in the presence of Raney nickel catalyst, as also were fractions L, M, and N, the fully saturated glycerides obtained therefrom then being exhaustively crystallised from ether. Much greater dilutions are required for the fractional crystallisation of fully hydrogenated material than for the fractional crystallisation of mono- and di-oleo-glycerides, and a more or less standard procedure was adopted. The fraction was first crystallised from ether (100 c.c. per g.) at 10°, the deposited crystals being filtered off. The mother liquor was then cooled to 5°, refiltered, and finally cooled to 0° to give a further crop of crystalline material, the final mother liquors then containing small amounts of fully hydrogenated material together with incompletely hydrogenated material. Each fraction was then recrystallised at 10° and 0° under the same conditions, and fractions of the same melting point combined and recrystallised from ether (200 c.c. per g.) at 10° and 0°. Thus fraction GH (18·5 g.) gave 10·28 g. of crystalline material (GHl, m. p. 67—68°) at 10°, which on further repeated recrystallisation did not change in melting point; 1·52 g. (m. p. 62—65°) were deposited at 5°, and 3·57 g. (m. p. 62—64°) at 0°.

The 1·52 g. fraction on recrystallisation at 10° gave 0·89 g. (GH2, m. p. 67—67·5°) and at 0°, 0·56 g. (m. p. 63—63·5°). Similarly, the 3·57 g. fraction on recrystallisation at 10° gave 1·63 g. (m. p. 62—65°), and at 0°, 1·70 g. (m. p. 62—64°). The three fractions of similar melting point were recombined and crystallised from ether (200 c.c. per g.) at 10° and 0° and the process repeated on the fractions obtained, leading ultimately to the fractions GH3, GH4, and GH5, which did not alter in melting point on further recrystallisation. When a fraction remained constant in melting point after repeated recrystallisations it was submitted to detailed thermal examination in the manner described in Part I (*J.*, 1945, 22).

Discussion.

In this investigation it was possible to separate the fully saturated glycerides almost completely from the remainder of the oil. It was not possible, however, to separate stearodipalmitin from tripalmitin, as is seen from the saponification equivalents of the four fractions into which fraction A was finally resolved (Table IIa). The melting point of each fraction varied but little and lay near to that of tripalmitin. Had β-stearodipalmitin occurred in quantity a more marked separation on crystallisation might have been expected, with the melting point of the most insoluble fraction approaching 68°. The lack of separation observed due to very close similarity in solubility, coupled with the only slight differences in melting points observed, point, although not conclusively, to the presence of unsymmetrical α-stearodipalmitin occurring together with tripalmitin in the fully saturated portion of palm oil.

From Table I it is seen that fractions F, G, and H consist almost entirely of oleodipalmitins, while Table IIb shows that the material obtained after hydrogenation of fractions F and G consists of approximately 80% of β-stearodipalmitin together with small but definite amounts of the unsymmetrical isomer. In H, a fraction of greater solubility, it is seen that the amount of unsymmetrical isomer increases as might have been predicted since unsymmetrical isomers have considerably greater solubility under the same conditions than their corresponding symmetrical isomers. It is clear from the data recorded that in palm oil a considerable amount of the oleodipalmitin occurs as the α-oleo-isomer, in contrast to Piqui-a fruit-coat fat where it was found that the mono-unsaturated glyceride consisted entirely of symmetrical β-oleodipalmitin.

From Table I it is seen that fraction J will contain both oleodipalmitins, oleomyristopalmitins, and oleopalmitostearins, together with increasing amounts of dioleo-glycerides. No crystallisation occurred on treating the hydrogenated fraction under conditions similar to those used for FH, GH, and HH, indicating the probable absence of symmetrical glycerides. Exhaustive crystallisation of this fraction confirms this since the fraction of highest melting point melted at 62—63°, indicating that the stearodipalmitins and palmitodistearins in this fraction, derived from oleodipalmitins and oleopalmitostearins, consist for the most part of the α-palmito-isomer. Further, the component fatty acid analysis shows that together with fraction L this fraction contains the bulk of the myristic acid present in the fat, this being present as myristo-oleopalmitins, thus being in harmony with the now fully established principle of " even distribution ", according to which any minor component acid will tend to be associated, in any one glyceride molecule, with one group of each of the two major component acids, palmitic and oleic.

From inspection of the component fatty acids and glycerides of fraction L it is clear that incomplete separation of the glycerides has occurred, this fraction consisting of 35% of mono-unsaturated di-saturated and 65% of mono-saturated di-unsaturated glycerides. The greater amount of mono-saturated di-unsaturated glycerides (*i.e.*, palmitodistearins) in the hydrogenated material should be relatively easily separated from stearodipalmitins derived from oleodipalmitins. Further, from solubility considerations any symmetrical palmitodistearin should be concentrated in the most insoluble fraction. It is significant therefore that definite evidence of β-palmitodistearin was obtained, since the most insoluble fraction (LH1) melted at 66°. It appears that in this sub-fraction α-palmitodiolein and α-palmito-oleolinoleins occur in amounts approximating to those in which the β-isomer occurs. Little can be said definitely of the configuration of the mono-oleo-glycerides in this fraction except that from thermal evidence and solubility considerations of their hydrogenated derivatives they appear to consist entirely of α-oleo-glycerides.

Fraction M consists entirely of palmito-di-unsaturated glycerides. Exhaustive crystallisation of its hydrogenated derivatives indicated that it consists almost entirely of α-palmitodistearin, indicating the presence of α-palmitodiolein and α-palmito-oleolinolein in quantity in the parent fraction.

Fraction N contains 40% of tri-unsaturated glycerides. On crystallisation of the fully hydrogenated material no great difficulty was encountered in separating tristearin in quantity

TABLE II.

(a) *Transition and Melting Points of Fractions obtained from Fraction A.*

	G.	% of fraction.	Saponification equivalent.	Polymorphic forms. IV.	III.	II.	I.	M. p.*
A1	4·91	24·0	269·8	—	—	—	—	63—64°
A2	3·61	17·6	270·5	—	—	—	—	62—63
A3	6·05	29·5	269·6	—	—	—	—	64—65
A4	3·25	15·9	268·6	—	—	—	—	63—64
Tripalmitin †	—	—	268·7	45°	56°	—	65·5°	—
β-Stearodipalmitin ‡	—	—	278·0	49	59	65°	68	—
α-Stearodipalmitin §	—	—	278·0	46·5	55	59·5	62·5	—

(b) *Transition and Melting Points of Fractions obtained from Fractional Crystallisation of Hydrogenated Fractions, F, G, H, J, L, M, and N.*

	G.	% of fraction.	Polymorphic forms. IV.	III.	II.	I.	M. p.*
FH1	1·70	33·3	48°	59°	64°	67·0—67·5°	—
FH2	0·67	13·1	48	59—60	63·5—64·5	67—67·5	—
FH3	0·62	12·2	—	—	—	—	62—65°
FH4	0·67	13·1	—	—	—	—	61—62
GH1	10·28	55·6	49	58—59	64	67—68	—
GH2	0·89	4·8	48	58—59	63	67—67·5	—
GH3	1·06	5·7	—	—	—	—	64—65
GH4	0·50	2·7	—	—	—	—	62·5—64
GH5	1·63	8·8	45	53	58	62—64	—
HH1	3·67	28·2	49	58	64	67·5—68	—
HH2	0·19	1·5	47—48	57	63	66·5—67·5	—
HH3	1·15	9·1	—	—	—	—	63—64
HH4	1·40	10·8	45	53	57	61—62	—
HH5	1·45	11·1	46	55	59	62·5	—
HH6	2·02	15·5	—	—	—	—	60—62
JH	4·0	62·5	—	—	—	—	62—63
LH1	5·5	11·0	—	—	—	—	65—66
LH2	7·2	14·4	50	56	60	64—65	—
LH3	1·6	3·2	—	—	—	—	63—64
LH4	3·6	7·2	—	—	—	—	63—64
LH5	6·0	12·0	—	—	—	—	60—62·5
LH6	2·2	4·4	45	54	58	62—62·5	—
LH7	7·5	15·0	—	—	—	—	61—61·5
MH1	11·8	23·6	49	56	60	64·5—65	—
MH2	2·2	4·4	48	55	59	64—65	—
MH3	11·8	23·6	49	56	60	65—65·5	—
MH4	2·8	5·6	—	—	—	—	62·5—64
MH5	3·5	7·0	47	55	58	64—65	—
MH6	6·6	13·2	—	—	—	—	61—63
NH1	18·3	36·3	53	63	—	70—72	—
NH2	9·4	18·8	—	—	—	—	66·5—67
NH3	2·1	4·2	—	—	—	—	65—67
NH4	3·8	7·6	48	55	58—59	63·5—64·5	—
NH5	0·2	0·4	48	55	59	64—65	—
NH6	4·2	8·4	—	—	—	—	63·5—64
β-Stearodipalmitin ‡	—	—	49	59	65	68	—
α-Stearodipalmitin §	—	—	46·5	55	59·5	62·5	—
β-Palmitodistearin ‡	—	—	50	56	64	68	—
α-Palmitodistearin §	—	—	50	57	61	65	—
Tristearin †	—	—	54·5	65	—	71·5	—

* Detailed thermal data were not determined for fractions which were binary mixtures, the melting points only being recorded.

† Clarkson and Malkin, *J.*, 1934, 666.

‡ Malkin and Meara, *J.*, 1939, 103.

§ Carter and Malkin, *J.*, 1939, 577.

and in a moderate degree of purity. α-Palmitodistearin was also isolated, with intermediate fractions consisting of a mixture of these two glycerides; β-palmitodistearin was concluded to be absent from N since it was not observed in fraction M.

It was realised that the exhaustive crystallisation technique employed for the determination of the configuration of the major component glycerides is not conducive to an accurate quantitative determination of the component glycerides of an oil. Nevertheless, from the data recorded it is possible to make an estimate of the component glycerides of the palm oil investigated which is in tolerably good agreement with the computed values, based on the component fatty acids, according to the method devised by Hilditch and Meara (*J. Soc. Chem. Ind.*, 1942, **61**, 117).

TABLE III.

Observed and Computed Component Glycerides of the Palm Oil.

	Observed.	Computed.		Observed.	Computed.
Tripalmitin	5	5	Palmitodiolein	37	} 45
Stearodipalmitin	1	1	Palmito-oleolinolein	11	
Oleodipalmitin	} 38	36	Tri-olein	} 8	—
Oleopalmitostearin ...		7	Linoleodiolein		6

It is seen that the observed amount of mono-oleo-glycerides is lower, while the amounts of the di- and tri-unsaturated glycerides are higher, as compared with the computed values, this being largely due to the utilisation of 20 g. of material (4% of the whole oil, mainly mono-oleo-glycerides) for iodine value determinations during the numerous crystallisation processes required to produce the fractions F—K in particular.

Further, from Tables I and IIb it is possible to make an approximate estimation of the amount of α- and β-oleodipalmitins and α- and β-palmitodioleins in the oil, if the arbitrary assumption is made that fractions of intermediate melting point in Table IIb consist of a mixture of α- and β-glycerides in equal amounts.

TABLE IV.

Distribution of α- and β-Glycerides in Fractions F—N (Increments % mols.).

Fraction	F	G	H	J	K	L	M	N	Total.
β-Oleodipalmitin	3·2	9·7	3·0	—	—	—	—	—	15·9
α- ,, ...	1·1	1·2	3·7	5·7	0·8	8·3	—	—	20·8
β-Palmitodiolein *	—	—	—	0·3 †	0·4 †	2·0	—	—	2·7
α- ,, ...	—	—	—	0·3 †	0·4 †	13·7	18·5	12·2	45·1

* Including palmito-oleolinolein.

† Di-unsaturated glycerides taken arbitrarily as consisting of equal amounts of α- and β-palmito-glycerides respectively.

Thus approximately 45—50% of the palmitic acid in the mono-oleodipalmitins present in palm oil is attached at the α and α′ carbon atoms of the glycerol molecule, the remainder being present as the unsymmetrical α-isomer. β-Palmito-di-unsaturated glycerides, however, occur only to the extent of about 5—7% in the di-unsaturated glycerides, the bulk of the palmitic acid in this group being attached at the α-carbon atom. This is markedly different from the case of Piqui-a fruit-coat fat in which the di-unsaturated glycerides were shown to consist of both symmetrical and unsymmetrical palmitodioleins in approximately equal amounts.

It has been suggested (Banks, Dean, and Hilditch, *loc. cit.*) that, in naturally occurring mixed glycerides containing two different acids in combination, the symmetrical configuration is favoured so long as the acid which contributes two radicals to the mixed glyceride in the fat is in considerable excess of the other, the proportion of the unsymmetrical form increasing as the proportion of the less abundant acid increases. Increase in α-palmitodioleins occurred as the proportion of palmitic acid increased from 45% to 54% in the mixed acids of the two samples of palm oil investigated by these workers. That this generalisation is not rigidly true is indicated by the fact that Piqui-a fruit-coat fat containing 47% of palmitic and 51% of oleic acid contains a much smaller proportion of α-palmito-di-unsaturated glycerides than does palm oil.

It may equally well be that the increased amount of unsymmetrical mixed glycerides present in palm oil is connected with the fact that this oil does not follow the rule of even distribution as closely as most fats (Hilditch and Meara, *J. Soc. Chem. Ind.*, 1942, **59**, 117). Further, it may be significant that the only fats so far observed to contain unsymmetrical triglycerides in definite amounts are fruit-coat fats. Investigation of these problems is continuing.

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