271. *The Configuration of Naturally Occurring Mixed Glycerides. Part VI. The Component Fatty Acids and Glycerides of Stillingia Tallows.*

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The component acids of two specimens of the tallow encasing the seeds of *Sapium sebiferum* (one from Hong Kong, the other from South Texas), and also the component acids of a specimen of tallow from *Sapium discolor* have been found to be, respectively: lauric, —, 1·5, —; myristic, 0·5, 3·4, 1·7; palmitic, 63·2, 72·1, 46·8; stearic, 7·6, 1·6, 2·0; oleic, 27·1, 20·4, 46·4; linoleic, 1·6, 1·0, 3·1% (by weight).

The chief component glycerides occurring in the Hong Kong specimens of *Sapium sebiferum* and *Sapium discolor* are respectively: *S. sebiferum*, oleodipalmitin, 64, stearodipalmitin 13, tripalmitin 8, and oleopalmitostearin 8%, with very small amounts of oleomyristopalmitin, linoleodipalmitin, and palmito-oleolinolein; *S. discolor*, oleodipalmitin 51, palmitodiolein 29, palmito-oleolinolein 6, oleomyristopalmitin 5, oleopalmitostearin 5%, with very small proportions of oleomyristostearin, linoleomyristopalmitin, linoleodiolein, and traces of triolein.

The stearodipalmitin and the oleodipalmitin occurring in *Sapium sebiferum* have been shown to occur exclusively as the symmetrical isomers.

Computation of the component glycerides from the component fatty acids by application of the rule of even distribution gives values in tolerable accordance with the observed values.

CHINESE vegetable tallow or Stillingia tallow is a hard fat, coating the seeds of the Chinese tallow tree [*Stillingia sebifera*, Willd. syn. *Sapium sebiferum* Roxb. (Euphorbiaceæ)], indigenous to China but also grown in India, Japan, and other subtropical countries. The tree has been exploited for the leaves, from which was obtained colouring matter for dyeing silk, and for the seed oil, the separation of the tallow representing a secondary product. The tree grows to a height of about 40 feet, commences to bear fruit at 4—5 years and when fully grown produces 25—30 kg. of seed per annum.

The fruit consists of a 3-lobed capsule, each lobe containing an oval seed, average weight 0·125 g., which is surrounded by a thick (white) tallow-like mass filling the space in each cavity. The seeds consist of 70% of shell and 30% of kernel, the shell being coated with up to 30% of tallow and the kernels containing about 60% of a drying oil of entirely different constitution from that of the vegetable tallow (Hilditch, *J. Oil Col. Chem. Assoc.*, 1949, **32**, 5).

Two samples of tallow from *Sapium sebiferum* were used in the present investigation. The first was obtained from fruit, from trees growing in Hong Kong, which had been placed at our disposal by Dr. G. A. C. Herklots and Mr. I. P. Tamworth of the Development Secretariat, Hong Kong, and the second from trees growing in South Texas and placed at our disposal by Mr. J. Q. Wood of Oklahoma, U.S.A. The surface of the tallow coating of the latter specimen was black, apparently owing to a mould growth but this blackening did not penetrate below the surface layers.

The Hong Kong authorities also made available to us a specimen of the fruit of *Sapium discolor*, a closely related species. The fruit and seeds of this species are very similar in general appearance to those of *Sapium sebiferum* except that the capsule is somewhat thicker, the seeds are smaller (average weight 0·042 g.), and the surface of the tallow layer encasing the kernel shell is greenish white.

Discussion.

A survey of the literature reveals that Stillingia tallow is of relatively simple composition, the only major component fatty acids being palmitic and oleic. Somewhat wide divergence in the proportions of these acids has been reported, as is indicated by the observed range in iodine value (10—36) of the fat. This range may in some cases (especially in commercial samples) be due to incomplete extraction of the fat, or to the extraction of a small amount of the kernel oil. Potts and Bolley (*Oil and Soap*, 1946, **23**, 316) have recorded data for uncontaminated samples of the tallow from *Sapium sebiferum* grown in Texas, the iodine values of which range from 10·5 to 25·0. This observation, taken in conjunction with the data obtained by Hilditch and Priestman (*J. Soc. Chem. Ind.*, 1930, **49**, 397T), and with results obtained in the present investigation (Table I), indicates that the tree appears to be able to produce tallow of somewhat variable composition. The tallow from *Sapium discolor* has a considerably higher oleic acid content that that from *Sapium sebiferum* (see Table I).

Table I.

Component fatty acids of Stillingia tallows.

	Sapium sebiferum.						*Sapium discolor.*
	U.S.A.,*		Chinese,*		Hong Kong,†	South Texas,†	Hong Kong,†
	crude.	neutralised.	crude.	neutralised.	neutral.	crude.	neutralised.
Lauric	1·9	1·2	0·8	2·5	—	1·5	—
Myristic	3·7	2·9	5·8	3·6	0·5	3·4	1·7
Palmitic	66·3	63·1	69·6	57·6	63·2	72·1	46·8
Stearic	1·2	3·2	3·1	1·8	7·6	1·6	2·0
Oleic	26·9	29·6	20·7	34·5	27·1	20·4	46·4
Linoleic	—	—	—	—	1·6	1·0	3·1

* Hilditch and Priestman (*loc. cit.*). † Present investigation.

It is evident from Table I that the unsaturation of *Sapium discolor* tallow is considerably greater than that of the *Sapium sebiferum* fruit-coat fat, and that the increased unsaturation is due almost entirely to an increase in the oleic acid content of the tallow at the expense of palmitic acid, and (in the Hong Kong specimen) of stearic acid. The linoleic acid content rises only from 1·5 to 3·0%. It may be noted, however, that the stearic acid content of the Hong Kong specimen of *Sapium sebiferum* fruit-coat fat is distinctly higher than that recorded for other samples of this species by Hilditch and Priestman, and that the use of low-temperature crystallisation and spectrophotometry has indicated the presence of a small but significant linoleic acid content.

TABLE II.

Component fatty acids and glycerides of Sapium sebiferum *fruit-coat fat.*
Fractions obtained by crystallisation of fat.

	A.	*B.*	*C.*	*D.*	Total.	
Wt. (g.)	21·82	8·92	60·01	9·85	100·6	
I.V.	1·6	28·4	31·3	44·4	26·0	
Sap. equiv.	274·5	281·7	279·3	278·7	278·3	
Glycerides, % (wt.)	21·7	8·9	59·6	9·8	100·0	
,, % (mol.)	22·0	8·8	59·4	9·8	100·0	
Component acids (increments, mol.-%) :					% (mol.).	% (wt.).
Myristic	—	—	0·6	—	0·6	0·5
Palmitic	17·4	5·2	36·8	6·0	65·4	63·2
Stearic	4·2	0·8	2·1	—	7·1	7·6
Oleic	0·4	2·8	19·4	2·9	25·5	27·1
Linoleic	—	—	0·5	0·9	1·4	1·6
Component glyceride categories (increments, mol.-%) :						
(i) Fully saturated	20·8	0·5	—	—	21·3	
Disatd. mono-unsatd.	1·2	8·3	59·1	8·0	76·6	
Monosatd. di-unsatd.	—	—	0·3	1·8	2·1	
Tri-unsaturated	—	—	—	—	—	
(ii) Monopalmito-	—	1·8	8·4	1·8	12·0	
Dipalmito-	13·8	7·0	51·0	8·0	79·8	
Tripalmitin	8·2	—	—	—	8·2	
(iii) No oleo-	20·8	0·5	1·3	1·0	23·6	
Mono-oleo-	1·2	8·3	58·1	8·8	76·4	
Dioleo-	—	—	—	—	—	
Triolein	—	—	—	—	—	
Possible component glycerides (increments, mol.-%) :						
Fully saturated (21·3%)						
Tripalmitin	8·2	—	—	—	8·2	
Stearodipalmitin	12·6	0·5	—	—	13·1	
Mono-" oleo " glycerides (76·6%)						
Oleomyristopalmitin	—	—	1·8	—	1·8	
Oleodipalmitin	1·2	6·5	49·7	7·0	64·4	
Linoleodipalmitin	—	—	1·3	1·0	2·3	
Oleopalmitostearin	—	1·8	6·3	—	8·1	
Di-" oleo " glycerides (2·1%)						
Palmito-oleolinolein	—	—	0·3	1·8	2·1	

Component Glycerides of Stillingia tallow.—(a) Sapium sebiferum *seed from Hong Kong.* In computing the glycerides present in fractions *A* and *B* (the fractions containing the bulk of the fully saturated glycerides, and the residual fully-saturated glycerides together with mono-oleo-glycerides, respectively, cf. Experimental) the unsaturation is considered to be present only in the form of mono-unsaturated disaturated glycerides, this being a necessary consequence of the fractional crystallisation. Similarly, fully saturated glycerides are assumed to be absent from fractions *C* and *D* (cf. Experimental) the components consisting of mono-" oleo " and di-" oleo " glycerides.

It is possible in most cases to consider the component glyceride categories present in an oil or fat in a number of ways. Taking into account component glyceride categories with respect to (i) unsaturation, (ii) palmitic acid distribution, (iii) oleic acid distribution, and considering these simultaneously and in conjunction with the component fatty acids of each fraction it is possible in this case to arrive at an accurate estimate of the probable component glycerides of the stillingia tallow.

This specimen of *S. sebiferum* tallow is thus a remarkably simple fat, two glycerides alone, namely stearodipalmitin and oleodipalmitin together constituting about 77% of the whole fat, and no other glyceride present occurring to the extent of more than 8%.

Sufficient material was available from fractions *A* and *C*, respectively, to permit investigation of the configuration of the mixed triglycerides occurring in these fractions. Crystallisation of a portion of fraction *A* from ether at high dilution gave rise to a fraction (60% of the whole) melting at 66·5—67°, this being a fairly pure specimen of β-stearo-αα'-dipalmitin (m. p. 68°), 16% of a mixture of β-stearo-αα'-dipalmitin and tripalmitin (m. p. 65—66°), and 20% of fairly pure tripalmitin (m. p. 64·5—65°) (65·5°, literature). There appears to be no evidence of the unsymmetrical α-stearo-α'β-dipalmitin (m. p. 63°) occurring in this fat.

TABLE III.

Component fatty acids and glycerides of Sapium discolor *fruit-coat fat.*
Fractions obtained by crystallisation of neutral fat.

	A.	*B.*	*C.*	*D.*	Total.	
Wt. (g.)	25·31	32·61	31·08	8·52	97·52	
I.V.	31·4	32·3	61·4	83·6	45·8	
Sap. equiv.	278·0	277·6	286·1	315·5	283·3	
Glycerides, % (wt.)	25·9	33·5	31·9	8·7	100·0	
Glycerides, % (mol.)	26·5	34·1	31·6	7·8	100·0	
Component acids (increments, mol.-%):					% (mol.).	% (wt.).
Myristic	—	1·3	0·7	—	2·0	1·7
Palmitic	17·1	20·1	10·3	1·5	49·0	46·8
Stearic	0·4	1·0	0·5	—	1·9	2·0
Oleic	8·9	11·3	18·5	5·4	44·1	46·4
Linoleic	0·1	0·4	1·6	0·9	3·0	3·1
Component glyceride categories (increments, mol.-%):						
(i) Disatd. mono-unsatd.	26·0	33·3	2·6	—	61·9	
Monosatd. di-unsatd.	0·5	0·8	29·0	4·5	34·8	
Tri-unsaturated	—	—	—	3·3	3·3	
(ii) Monopalmito-	1·8	7·7	30·8	4·5	44·8	
Dipalmito-	24·7	26·4	—	—	51·1	
(iii) Mono-oleo-	26·2	33·8	7·7	—	67·7	
Dioleo-	0·3	—	23·9	7·1	31·3	
Triolein	—	—	—	0·7	0·7	
Probable component glycerides (increments, mol.-%):						
Mono-"oleo" glycerides (61·9%)						
Oleomyristopalmitin	—	3·7	1·2	—	4·9	
Oleomyristostearin	—	—	0·8	—	0·8	
Oleopalmitostearin	1·2	3·0	0·7	—	4·9	
Oleodipalmitin	24·7	26·3	—	—	51·0	
Linoleomyristopalmitin	—	0·3	—	—	0·3	
Di-"oleo" glycerides (34·8%)						
Palmito-oleolinolein	0·2	0·9	5·0	—	6·1	
Palmitodiolein	0·3	—	23·9	4·5	28·7	
Tri-unsaturated glycerides (3·3%)						
Linoleodiolein	—	—	—	2·6	2·6	
Triolein	—	—	—	0·7	0·7	

A portion of fraction *C* on hydrogenation, followed by similar crystallisation from ether at high dilution, gave a practically quantitative yield of β-stearo-αα′-dipalmitin (m. p. 68—68·5°), indicating the presence of β-oleo-αα′-dipalmitin in this fraction, and again giving no evidence of the occurrence of the unsymmetrical isomer.

These findings are in general agreement with those of earlier work in that when one component acid in a relatively simple fat is greatly in excess of the other the resulting glycerides tend to assume the symmetrical configuration.

(b) Sapium discolor *seed from Hong Kong.* The considerable difference in the proportions of palmitic and oleic acid in this tallow as compared with that from *Sapium sebiferum* seed is reflected in the component glycerides.

Table III shows that the fat still remains remarkably simple in composition in that two major component glycerides, oleodipalmitin and palmitodiolein, between them constitute approximately 80% of the whole fat, no other component occurring to the extent of over 6%.

In *Sapium discolor* fruit-coat fat there is no evidence of the occurrence of fully saturated glycerides; no fraction of iodine value substantially lower than 31·4 (oleodipalmitin I.V. 30·5) was obtained, and it is known (Meara, *J.*, 1947, 773; 1948, 722) that it is relatively easy to separate fully saturated glycerides from dioleo-glycerides by crystallisation.

More than half of the fat is seen to consist of oleodipalmitin. Moreover, all the stearic acid occurs in mono-unsaturated glycerides (therefore as oleopalmitostearin or oleomyristostearin), none occurring in the di-unsaturated glyceride fractions, as is indicated by the absence of stearic acid from fraction *D* which contains only di- and tri-unsaturated glycerides.

Table IV compares the experimentally found component glycerides of these fats with those which can be computed from their component fatty acids by the application of the rule of even distribution, as most completely enunciated by Hilditch (*J. Amer. Oil Chem. Soc.*, 1949, **26**, 41), and by random distribution.

TABLE IV.

Observed and computed values of the component glycerides of Sapium sebiferum *and* Sapium discolor *fruit-coat fats.*

	Sapium sebiferum,			*Sapium discolor,*		
		computed,			computed,	
	observed.	even.	random.	observed.	even.	random.
Tripalmitin	8·2	13·9	28·0	—	—	11·8
Stearodipalmitin	13·1	6·3	9·1	—	—	1·4
Oleomyristopalmitin	1·8	1·8	—	4·9	6·0	2·6
Oleomyristostearin	—	—	trace	0·8	—	trace
Oleopalmitostearin	8·1	15·0	7·2	4·9	5·7	2·5
Oleodipalmitin	64·4	58·5	32·7	51·0	46·9	31·8
Linoleomyristopalmitin	—	—	trace	0·3	—	trace
Linoleodipalmitin	2·3	3·3	1·9	—	—	2·2
Palmito-oleolinolein	2·1	1·2	1·4	6·1	9·0	3·9
Palmitodiolein	—	—	12·9	28·7	32·4	28·6
Linoleodiolein	—	—	trace	2·6	—	1·7
Triolein	—	—	1·6	1·7	—	8·6
Other theoretically possible glycerides	—	—	5·2	—	—	4·9

It is seen that even with such simple fats as the *S. sebiferum* and the *S. discolor* tallow, although the component glycerides cannot be computed with as high a degree of accuracy as can be obtained in the case of some seed fats, notably *Allanblackia* fats, the maximum difference in the case of either fat is of the order of 7 units % between the observed values and those computed on the basis of even distribution. This in no way invalidates the general rule of even distribution since accordance with mathematical precision between experimental and computed values is not to be expected, the rule predicting to a greater or lesser degree of conformity the order of the amounts of the component glycerides to be expected in any given fat.

Much less accordance between observed and computed values is obtained when the latter are derived by the theory of random distribution, this being further strong support for the belief that random distribution of the fatty acids amongst the glycerol molecules plays little if any part in the synthesis of naturally occurring mixed triglycerides.

EXPERIMENTAL.

The seeds were extracted with acetone, by Mr. A. Crossley, B.Sc., to remove the hard coating of tallow in which the shells are enclosed, it being found (Crossley, private communication) that only after prolonged extraction does this solvent penetrate the shell and begin to extract the kernel oil.

Component Fatty Acids of Stillingia Tallows.—(a) Sapium sebiferum *seed from Hong Kong.* The fat (approximately 100 g.) was resolved by crystallisation, until 4 fractions (*A*—*D*) were obtained. Fraction *A* contained the bulk of the fully saturated glycerides, fraction *B* the residual amounts of fully saturated glycerides together with some mono-" oleo " glycerides, fraction *C* mainly mono-" oleo " glycerides, and fraction *D* mono-" oleo " and di-" oleo " glycerides, as adjudged from their respective iodine values.

The component fatty acids of each fraction were determined by the usual procedure adopted in these laboratories, spectrophotometric determinations being applied to fractions *C* and *D*, unsaturation in fractions *A* and *B* being taken as monoethenoid. From the data so obtained the component fatty acids of the tallow are deduced and are given in Table II.

(b) Sapium sebiferum *seed from South Texas, U.S.A.* The tallow obtained from the seeds of this specimen was saponified directly, on account of its high free acidity, and the component fatty acids determined (see Table I) after resolution of the mixed fatty acids into 2 fractions by crystallisation from ether at $-30°$.

TABLE V.

Extraction of Stillingia tallow.

	Wt. of seeds (g.).	Extraction.	Wt. of tallow.	%, Tallow.	Sap. equiv.	I.V.	Free acidity, %, as oleic.
Hong Kong *Sapium sebiferum*	657	1	109·1	16·6	272·2	25·1	0·8
		2	1·0	—	—	78·1	—
South Texas, U.S.A. *Sapium sebiferum*	854	1	151·0	17·9	269·5	18·6	48·8
		2	2·2	—	—	84·2	—
Hong Kong *Sapium discolor* ...	900	1	163·9	18·8	278·7	47·1	5·5
		2	21·3	—	—	120·0	—

(c) Sapium discolor *seed from Hong Kong.* The component acids of this tallow were determined after resolution of the fat into 4 fractions as in the case of Hong Kong *Sapium sebiferum*, the values obtained appearing in Table III and, together with those of various specimens of *Sapium sebiferum*, in Table I.

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