267. *Thermal Interchange of Acyl Groups in Triglycerides.*

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β-Oleodistearin, when heated in an inert atmosphere at about 300°, is converted in about ten hours into a mixture of tristearin, oleodistearins, stearodioleins and triolein in proportions which are close to those deduced from probability considerations for a " randomly " distributed mixture of stearo- and oleo-glycerides. Acyl interchange is thus effected thermally and without catalyst at 300° in the same manner as it proceeds at lower temperatures in presence of catalysts such as sodium alkoxides or stannous and some other hydroxides. The thermally stimulated interchange of acyl groups is accompanied by a small but steady liberation of free fatty acids at the rate of about 1% per hour.

It has been recognised for many years that the acyl groups of a mixture of triglycerides may migrate, and a new mixture of mixed triglycerides be produced, at temperatures usually ranging from about 200° to 250° in presence of small proportions of a suitable catalyst (alkali alkoxides or hydroxide, certain compounds of tin, cadmium, or zinc, etc.). The same change proceeds, although relatively slowly, at 180° in presence of catalytic nickel during hydrogenation (Atherton and Hilditch, *J.*, 1941, 527). It is of some importance in connection with the thermal polymerisation (" heat-bodying ") of drying oils to know whether at the temperatures (290—300°) employed in this process acyl migration or interchange of this kind may take place amongst the glyceride molecules without the intervention of a specific catalyst. It has often been indicated (*e.g.*, Cowan, *J. Amer. Oil Chem. Soc.*, 1950, **27**, 493) that this is indeed already known to occur : but, apart from two instances of an early date cited by Cowan (*loc. cit.*, Table III), we have not been able to find unequivocal experimental evidence in the literature of acyl migration effected purely by thermal action. The instances mentioned were (*a*) that a mixture of ethyl benzoate and amyl acetate undergoes an appreciable amount of acyl interchange when heated at 300° for 3—5 hours without a catalyst, and (*b*) that a mixture of beef stearin and soya-bean oil, which melted at 42·5°, underwent a fall in m. p. to 36° after being heated (without catalyst) for 16 hours at 275°.

The *prima facie* possibility, or even likelihood, that such non-catalysed acyl interchange may occur at 300° in the case of glycerides may be considered a reasonable assumption from a comparison with the changes which occur in similar circumstances in the specific polyethenoid groups present in linoleo- or linoleno-glycerides. It is now well established (Steger and van Loon, *Fettchem. Umschau*, 1935, **42**, 217; Bradley and Richardson, *Ind. Eng. Chem.*, 1940, **32**, 963; Mitchell and Kraybill, *ibid.*, 1941, **33**, 764; Paschke and Wheeler, *J. Amer. Oil Chem. Soc.*, 1949, **26**, 278) that the primary change which sets in when such glycerides (in " drying " oils) are heated at 300° is a rearrangement of unconjugated pentadiene ($-CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH-$) systems to conjugated dienes. This change, brought about thermally at 300°, can be induced at lower temperatures by the intervention of specific catalysts [nickel (Waterman and van Vlodrop, *J. Soc. Chem. Ind.*, 1936, **55**, 320T; Radlove, Cowan, and Kass, *Ind. Eng. Chem.*, 1946, **38**, 997, 1002) or sulphur dioxide (Waterman and van Vlodrop, *J. Soc. Chem. Ind.*, 1936, **55**, 333T) at 200—220° or at 180° by the action of alkali hydroxide]. It was therefore considered of interest to ascertain definitely whether triglyceride " inter-esterification " or acyl interchange, which can be catalysed by the agents mentioned earlier at temperatures from about 220° downwards, may also proceed by thermal action alone in the neighbourhood of 300°.

Triglycerides containing a mixture of fatty acids (*e.g.*, for simplicity, a mixture of stearic and oleic acids), when prepared at comparatively high temperatures (150° or above), form a mixture the composition of which is not far from that indicated by the theory of probability (" random distribution " of acyl groups amongst the triglyceride molecules). Thus Bhattacharya and Hilditch (*Proc. Roy. Soc.*, 1930, *A*, **129**, 468) showed that the triglycerides produced at 145° by heating glycerol with a slight excess of binary mixtures of different saturated acids with oleic acid, in presence of traces of an aromatic sulphonic acid as catalyst, contained trisaturated glycerides in proportions which followed closely, but not quite identically with, the relation % trisaturated glycerides $\propto$ (% saturated acid)^3. With equimolecular mixtures of stearic and oleic acids, for example, the composition of the triglycerides was approximately 12·5% each of tristearin and triolein, with 37·5% each of oleodistearin and stearodiolein ; when saturated acids were in excess of unsaturated acids the observed percentage of trisaturated glycerides was somewhat greater than that calculated from probability, and conversely. It has since been proved that the mixtures of triglycerides present in natural fatty oils (which are *not* constituted on the lines of " random " or " probability " distribution), and also mixtures of simple triglycerides, when heated for some time at about 200° in presence of a suitable catalyst, undergo acyl rearrangement to a mixture of triglycerides which approaches in composition that calculable from probability considerations and that which is observed in glycerides synthesised from glycerol and fatty acids by esterification at comparable temperatures. Norris and Mattil (*Oil and Soap*, 1946, **23**, 289; *J. Amer. Oil Chem. Soc.*, 1947, **24**, 274) showed that, in presence of stannous hydroxide at 225°, the glycerides of soya-bean oil, of cottonseed oil, or of a mixture of tripalmitin and triolein underwent rearrangement of this nature. Naudet and Desnuelle (*Bull. Soc. chim.*, 1947, [v], **14**, 323) observed that an equimolecular mixture of tristearin and triolein, after being heated for some hours at 205° in presence of a small proportion of sodium methoxide, consisted of a mixture of tristearin 11·3%, oleodistearin 38·6%, stearodiolein 39·2%, and triolein 10·9%.

TABLE I.

Constitution of the (neutral) triglycerides obtained by heating β-oleodistearin at 300°.

	Tristearin, %.	Oleodistearin, %.	Stearodiolein, %.	Triolein, %.
Original oleodistearin	—	99·5	0·5	—
Calc. for " random distribution "	29·7	44·4	22·2	3·7
After 5 hours at 300° (in glass)	17·2	67·7	14·6	0·3
Calc.	(17·2)	67·8	12·9	2·1
After 5 hours at 300° (in silica)	19·9	61·8	18·1	0·2
Calc.	(19·9)	62·7	15·9	2·5
After 10 hours at 300° (in glass)	25·0	54·2	20·2	0·6
Calc.	(25·0)	53·2	18·7	3·1
After 10 hours at 300° (in silica)	27·5	48·1	24·2	0·2
Calc.	(27·5)	48·5	20·6	3·4
After 20 hours at 300° (in silica)	24·1	54·9	19·2	1·8
(Calc.	(24·1)	54·9	18·0	3·0
After 38 hours at 300° (in silica)	27·6	48·3	24·1	—
Calc.	(27·6)	48·4	20·6	3·4

For the purpose of the present work we have studied the behaviour of a single mixed glyceride, β-oleodistearin, when heated at 300° without catalyst under protection of an atmosphere of pure nitrogen. β-Oleodistearin is a natural glyceride present in quantity in a few specific seed fats, from one of which (that of *Garcinia morella*) it was readily isolated in an almost pure condition. The original material, and also the products obtained after heating it at 300°, were investigated by methods similar to those which have been recently described (*J.*, 1950, 3145). In the present instance, however, nearly all of any tristearin present was readily separated from the remaining constituents by reason of its very sparing solubility in ether at room temperature. The specimen of β-oleodistearin employed failed to yield any evidence of the presence of tristearin when submitted to this crystallisation procedure, the analysis indicating that it consisted of 99·5% of oleodistearin accompanied by 0·5% of stearodiolein. Its component fatty acids were stearic 66·5, oleic 33·4, and linoleic 0·1% (wt.). This composition corresponds with a " randomly distributed " glyceride structure (calculated according to probability) of tristearin 29·7, oleodistearin 44·4, stearodiolein 22·2, and triolein 3·7% (wt.).

The composition of the neutral glycerides left after the β-oleodistearin had been heated at 300° for varying periods in Wood's resistance glass or in silica vessels is shown in Table I. Appended to each experimental result is the composition of the oleodistearin, stearodiolein, and triolein proportions, calculated on the assumption that the observed percentage of tristearin had been produced by " random " rearrangement in the proportion of 29·7 parts of tristearin from 100 parts of oleodistearin, the other components having been correspondingly formed by operation of the same principle.

The results in Table I show unequivocally that acyl rearrangement in triglycerides proceeds steadily, if somewhat slowly, at 300° by thermal action alone, that equilibrium is reached in about 10 hours and that the composition of the equilibrium mixture approximates fairly closely to that calculated from probability considerations. Before discussing them in some further detail, however, attention may be directed to the steady but comparatively slow production of free fatty acids which also takes place. This is illustrated in Table II, and it should perhaps be pointed out that this is the only side reaction which could be detected. Much less discoloration of the glycerides was perceptible than might have been expected. The products after five and ten hours' treatment at 300° were still of only a very slightly darker cream colour than the original, and even after 38 hours at 300° the colour of the neutral glycerides left was not deeper than a clear yellow. Oleo-glycerides are thus of fairly high stability at 300° if contact with oxygen is avoided.

TABLE II.

Production of free fatty acids from β-oleodistearin at 300°.

	Neutral glycerides, %.	Free fatty acid, %.	Composition of free fatty acids,		
			stearic, %.	oleic, %.	linoleic, %.
After 5 hours at 300° (in glass)	96·3	3·7	65·7	34·3	—
,, 5 ,, 300° (in silica)	95·1	4·9	68·2	30·5	1·3
,, 10 ,, 300° (in glass)	91·6	8·4	57·6	42·4	—
,, 10 ,, 300° (in silica)	88·1	11·9	66·8	32·4	0·8
,, 20 ,, 300° (in silica)	82·9	17·1	67·7	31·4	0·9
,, 38 ,, 300° (in silica)	61·0	39·0	75·5	23·8	0·7

There is a comparatively steady production of free fatty acids at the rate of about 1% per hour at 300°. In four instances the composition of the liberated acids was indistinguishable from that of the original fat, in the remaining two it varied somewhat. The formation of free fatty acid is explicable in the following manner, on the assumption that the acyl interchange is effected by momentary severance of an ester-linkage (either as free radicals, or as a molecule of free acid and a free glyceryl hydroxyl group by the interaction of a molecule of water), followed by instantaneous recombination to the same or a different glyceride ester. At any one instant in any one triglyceride molecule it may be supposed that for the most part only one ester-linkage is concerned in this mechanism, but in a few instances two acyl groups might be simultaneously involved, and in a very few instances all three acyl radicals of one triglyceride molecule might be dissociated at once. In the last case if, as would be expected, the liberated molecule of glycerol (or the free glyceryl radical C_3H_5) were instantly thermally decomposed before it could be re-united with acyl groups, the elements of water necessary for the formation of free acid would arise from this source. This suggested explanation receives some confirmation from the fact that no distearin or monostearin was detectable in the fully-saturated glycerides precipitated from solutions of the products in ether at room temperature : these consisted wholly of tristearin, as indicated by their melting points alone and when mixed with an authentic specimen of tristearin (m. p. 71·3°) :

Fully-saturated glycerides isolated from β-oleodistearin after heating at 300°

	Melting point,	
	alone.	mixed.
After 5 hours at 300° (in glass)	71·6°	71·5°
,, 10 ,, 300° (in silica)	71·7	71·5
,, 20 ,, 300° (in silica)	71·4	71·4

The composition of the neutral glycerides after the heat-treatment presents several other features worthy of some comment. The use of a glass flask was replaced by that of a fused silica container in order to eliminate any possible catalytic effect of alkali in the glass. Actually it appeared that both the acyl interchange and the production of free fatty acid were slightly more pronounced in the fused silica than in the glass vessels.

The accordance between the calculated and the observed proportions of oleodistearin in the products is extremely close : that between corresponding values for stearodiolein and triolein is somewhat less so, the observed proportions of triolein being very small. This was not unexpected since triolein is rather different from other triunsaturated glycerides (such as oleolinoleins, linoleolinolenins, etc.) in that its solubility in acetone or ether is much less than that of those mentioned, and is more nearly comparable with that of dioleoglycerides such as palmito- or stearo-dioleins. Consequently efficient separation of small amounts of triolein from stearodioleins by crystallisation from solvents is a matter of great difficulty.

The maximum production of tristearin observed (27·5%) is some two units per cent. lower than that demanded by the application of the theory of probability : but it is identical with that shown by the graph (Bhattacharya and Hilditch, *loc. cit.*) connecting the observed proportions of trisaturated glycerides with the proportions of saturated acids in triglycerides prepared by high-temperature esterification of glycerol with saturated–oleic acid mixtures. It may well be that, just as most natural fats do not follow with complete rigidity the operation of " even " distribution indicated by mere arithmetical calculation, the " random " arrangement of mixed triglycerides produced at high temperatures does not wholly conform with that demanded by the purely algebraic application of the theory of probability.

It has been clearly demonstrated by this study, nevertheless, that acyl interchange in mixed triglycerides can be effected merely by heat at temperatures of 300° or thereabouts. In further illustration of this it may be noted that the present oleodistearin concentrates isolated from the products in the course of the crystallisation analyses (cf. Experimental, Table IV) melted indefinitely at various temperatures, all of which were considerably different from that (41·9°) of the original β-oleodistearin :

Oleodistearin concentrate from product after treatment at 300°.	Iodine value.	Component acids, stearic, %.	oleic, %.	M. p.
5 hours (in glass), crystallised fraction D	27·9	67·7	32·4	37—39°
5 ,, (in glass) ,, ,, E	28·8	66·6	33·4	32—36
5 ,, (in silica), ,, ,, C	28·1	67·4	32·6	41—44
5 ,, (in silica), ,, ,, D	28·8	66·6	33·4	38·5—40
10 ,, (in glass), ,, ,, D	29·0	66·4	33·6	25—31
10 ,, (in silica), ,, ,, D	27·9	67·6	32·4	35—39
20 ,, (in silica), ,, ,, C	29·0	66·4	33·6	31—37

These figures suggest that the mono-oleo-glycerides in the products are mixtures of both α- and β-oleodistearins. It is hoped that more detailed study of some of these fractions and their melting and transition points will be undertaken by Dr. M. L. Meara in this laboratory.

EXPERIMENTAL.

β-Oleodistearin was isolated in an almost pure condition by crystallisation of the fat from seeds of *Garcinia morella*, a supply of which was available. The component acids of this fat have been shown by Hilditch and Murti (*J. Soc. Chem. Ind.*, 1941, **60**, 16) to consist almost wholly of stearic and oleic acids, accompanied by small amounts (*ca.* 1% each) of linoleic and palmitic acids. The crude seed-fat (about 400 g.) was crystallised from acetone (4000 ml.) at 0°, and the deposited glycerides recrystallised again under the same conditions; about 120 g. of almost white fat (iodine value 28·9; calc. for oleodistearin 28·6; free fatty acid 0·1%) were obtained which melted sharply at 41·9°.

The component fatty acids of this specimen were determined by spectrophotometric analysis to be stearic 66·5, oleic 33·4, linoleic 0·1% (wt.). The component glycerides were determined by a further series of systematic crystallisations on the lines employed subsequently for the heat-treated products (see below). The oleodistearin (27·6 g.) was first crystallised from ether at 10—12°, and the deposited glycerides (13·0 g.) recrystallised under the same conditions, yielding fractions A and B. The material left in solution (14·6 g.) was crystallised three times from ether at 0°, leaving in solution fractions F, E, and D respectively, fraction C (12·8 g.) being deposited from the final crystallisation at 0°.

The component acids of each fraction were determined from the iodine values combined with spectrophotometric analysis (after alkali-isomerisation) for linoleic acid, which was only detectable in the most soluble fraction F. The consequent composition of the material is shown in Table III.

Thermal Treatment of the Oleodistearin.—The material was heated, either in a small round-bottomed flask of glass (Wood's resistance) or in a large test-tube made of fused silica. In either case an atmosphere of pure nitrogen was maintained over the surface of the melted glyceride and allowed to escape in a slow stream by a vent in the cork inserted in the neck of the apparatus, which was maintained at 300° (±3°)

TABLE III.

Component glycerides of the oleodistearin used.

	Fractions from ether.						
	A.	B.	C.	D.	E.	F.	Total.
Weight (g.)	1·4	11·6	12·8	0·3	0·3	1·2	27·6
Iodine value	29·1	28·6	28·7	32·4	33·0	30·0	28·9
Glycerides, % (wt.)	5·1	42·0	46·4	1·0	1·1	4·4	100·0
	Components acids (% wt.).						
Stearic	66·3	66·7	66·6	62·5	61·7	66·6	66·5
Oleic	33·7	33·3	33·4	37·5	38·3	32·1	33·4
Linoleic	—	—	—	—	—	1·3	0·1
	Component glycerides (increments, % wt.).						
" Oleo "-distearin	5·0	42·0	46·3	0·9	0·9	4·4	99·5
Stearo-di" olein "	0·1	—	0·1	0·1	0·2	—	0·5

TABLE IV.

Glyceride fractions separated by crystallisation after heating of oleodistearin at 300°

Fraction.	G.	%.	Iodine value.	Free fatty acid (%).	Component fatty acids present, %. stearic.	oleic.	linoleic.
			After 5 *hours' heating at* 300° (*in glass*).				
A	4·31	16·2	1·6	—	98·1	1·9	—
B	0·89	3·3	30·7	0·8 *	64·4	35·6	—
C	1·43	5·4	22·7	—	73·7	26·3	—
D	1·66	6·2	27·9	0·3 *	67·6	32·4	—
E	7·76	29·2	28·8	0·3 *	66·6	33·4	—
F	5·61	21·1	32·7	1·8 *	62·1	37·9	—
G	1·35	5·1	37·1	21·5	52·2 71·8	46·9 28·2	0·9 (neutral glycerides) — (free acids)
H	2·17	8·2	48·8	10·4	41·0 75·2	58·4 24·8	0·6 (neutral glycerides) — (free acids)
I	1·40	5·3	63·7	24·6	29·6 27·5	69·0 72·5	1·4 (neutral glycerides) — (free acids)
	26·58	100·0					
			After 5 *hours' heating at* 300° (*in silica*).				
A	1·64	17·2	2·4	—	97·2	2·8	—
B	0·64	6·7	16·2	0·6 *	81·2	18·8	—
C	1·16	12·2	28·1	—	67·4	32·6	—
D	2·82	29·7	28·8	0·2 *	66·6	33·4	—
FA	0·47	4·9	30·0	98·0	68·2	30·5	1·3 (free acids)
E	2·06	21·7	41·7	—	51·6	48·4	—
F	0·72	7·6	58·5	—	32·3	64·8	2·9
	9·51	100·0					
			After 10 *hours' heating at* 300° (*in glass*).				
A	6·84	21·7	1·3	—	98·5	1·5	—
B	5·58	17·7	25·2	0·4 *	70·8	29·2	—
C	2·39	7·6	32·4	1·2 *	62·4	37·6	—
FA	2·58	8·2	38·2	100·0	57·6	42·4	— (free acids)
D	5·99	19·0	29·0	—	66·4	33·6	—
E	3·19	10·1	37·0	—	57·1	42·9	—
F	1·60	5·0	53·7	—	37·7	62·3	—
G	3·37	10·7	59·3	—	31·6	66·9	1·5
	31·54	100·0					
			After 10 *hours' heating at* 300° (*in silica*).				
A	4·10	23·1	2·0	0·2 *	97·7	2·3	—
B	1·76	9·9	21·8	—	74·7	25·3	—
C	2·08	11·7	30·9	5·6 *	62·0	38·0	—
D	2·36	13·3	27·9	0·3 *	67·6	32·4	—
FA	1·99	11·2	30·6	100·0	66·8	32·4	0·8 (free acids)
E	2·04	11·5	35·0	—	59·4	40·6	—
F	1·74	9·8	53·2	—	38·3	61·7	—
G	1·15	6·5	58·3	—	35·4	63·2	1·4
H	0·53	3·0	61·8	—	30·9	65·9	3·2
	17·75	100·0					
			After 20 *hours' heating at* 300° (*in silica*).				
A	2·37	21·9	2·6	—	97·0	3·0	—
B	1·10	10·1	27·1	5·6 *	66·7	33·3	—
FA	1·79	16·5	29·9	100·0	67·7	31·4	0·9 (free acids)
C	2·51	23·1	29·0	—	66·4	33·6	—
D	0·95	8·8	42·7	—	50·5	49·5	—
E	1·35	12·4	43·1	—	51·1	48·2	0·7
F	0·78	7·2	64·8	—	26·5	71·9	1·6
	10·85	100·0					
			After 38 *hours' heating at* 300° (*in silica*).				
A	1·81	16·6	0·3	0·7 *	99·7	0·3	—
B	0·90	8·3	27·1	—	68·6	31·4	—
FA	4·26	39·3	22·0	97·0	75·5	23·8	0·7 (free acids)
C	3·88	35·8	39·5	2·1	53·1	43·8	3·1
	10·85	100·0					

* Small proportions of (saturated) acids deposited with fractions of the more sparingly soluble glycerides are calculated as stearic acid.

TABLE V.

Composition of glyceride fractions and, therefrom, of the glyceride mixtures produced at 300°.

Fraction.	Proportion, %.	Neutral glycerides present,				Free fatty acids,	
		tristearin.	oleodistearins.	stearodioleins.*	triolein.*	stearic.	oleic.*
		After 5 *hours' heating of β-oleodistearin at* 300° (*in glass*).					
A	16·2	15·3	0·9	—	—	—	—
B	3·3	—	3·1	0·2	—	Trace	—
C	5·4	1·1	4·3	—	—	—	—
D	6·2	0·2	6·0	—	—	Trace	—
E	29·2	—	29·1	—	—	0·1	—
F	21·1	—	17·8	2·9	—	0·4	—
G	5·1	—	2·3	1·7	—	1·0	0·1
H	8·2	—	1·7	5·7	—	0·6	0·2
I	5·3	—	—	3·5	0·5	0·4	0·9
Totals	100·0	16·6	65·2	14·0	0·5	2·5	1·2
		After 5 *hours' heating of β-oleodistearin at* 300° (*in silica*).					
A	17·2	15·7	1·5	—	—	—	—
B	6·7	2·9	3·8	—	—	Trace	—
C	12·2	0·3	11·9	—	—	—	—
D	29·7	—	29·6	—	—	0·1	—
FA	4·9	—	0·1	Trace	—	3·3	1·5
E	21·7	—	11·9	9·8	—	—	—
F	7·6	—	—	7·4	0·2	—	—
Totals	100·0	18·9	58·8	17·2	0·2	3·4	1·5
		After 10 *hours' heating of β-oleodistearin at* 300° (*in glass*).					
A	21·7	20·7	1·0	—	—	—	—
B	17·7	2·2	15·4	—	—	0·1	—
C	7·6	—	6·6	0·9	—	0·1	—
FA	8·2	—	—	—	—	4·7	3·5
D	19·0	—	18·8	0·2	—	—	—
E	10·1	—	7·2	2·9	—	—	—
F	5·0	—	0·7	4·3	—	—	—
G	10·7	—	—	10·2	0·5	—	—
Totals	100·0	22·9	49·7	18·5	0·5	4·9	3·5
		After 10 *hours' heating of β-oleodistearin at* 300° (*in silica*).					
A	23·1	21·5	1·6	—	—	*Trace*	—
B	9·9	2·4	7·5	—	—	—	—
C	11·7	—	9·5	1·6	—	0·6	—
D	13·3	0·3	12·9	—	—	0·1	—
FA	11·2	—	—	—	—	7·5	3·7
E	11·5	—	9·0	2·5	—	—	—
F	9·8	—	1·5	8·3	—	—	—
G	6·5	—	0·4	6·1	—	—	—
H	3·0	—	—	2·8	0·2	—	—
Totals	100·0	24·2	42·4	21·3	0·2	8·2	3·7
		After 20 *hours' heating of β-oleodistearin at* 300° (*in silica*).					
A	21·9	19·9	2·0	—	—	—	—
B	10·1	Trace	9·5	—	—	0·6	—
FA	16·5	—	—	—	—	11·2	5·3
C	23·1	—	22·9	0·2	—	—	—
D	8·8	—	4·5	4·3	—	—	—
E	12·4	—	6·6	5·8	—	—	—
F	7·2	—	—	5·7	1·5	—	—
Totals	100·0	19·9	45·5	16·0	1·5	11·8	5·3
		After 38 *hours' heating of β-oleodistearin at* 300° (*in silica*).					
A	16·6	16·3	0·2	—	—	0·1	—
B	8·3	0·5	7·8	—	—	—	—
FA	39·3	—	0·7	0·5	—	28·8	9·3
C	35·8	—	20·8	14·2	—	0·4	0·4
Totals	100·0	16·8	29·5	14·7	—	29·3	9·7

* Small amounts of linoleic acid or glycerides, when present, included with oleic.

in an aluminium air-bath which completely surrounded all except the top of the neck of the glass or silica vessel. Heating was applied in different experiments for 5, 10, 20, and 38 hours.

Examination of the Products.—These were first crystallised from 10% solution in ether at room temperature (usually 12—18°); insoluble matter (mainly tristearin) was at once deposited, and was recrystallised under the same conditions to give the two least soluble glyceride fractions A and B. The material left in solution in ether was then crystallised once or twice from acetone at room temperature, concentrates rich in oleodistearin being deposited. The acetone-soluble compounds were recovered and, at this stage, were in most instances dissolved in ether and neutralised by washing with dilute aqueous potassium hydroxide solution in order to remove the free fatty acid which had been produced (fractions lettered FA). Neutralisation of the total product was impracticable owing to the sparing solubility in ether of the tristearin present. [In one instance (5 hours at 300° in glass) this procedure was not followed, the free acidity being determined in each fraction, and the composition of the free acids being separately determined in each case.] Finally, in all cases, crystallisation of the more soluble remaining material (whether neutralised or otherwise) was continued from acetone at successively lower temperatures from 0° to —15° until as much resolution as possible of stearodioleins from oleodistearins or triolein had been accomplished. The crystallisation procedure varied in details according to the nature of the product, and Table IV gives a condensed summary of the proportions, characteristics, and composition of each of the glyceride fractions isolated from each of the heated products. The fatty acids in each fraction were determined from their iodine values in conjunction with spectrophotometric data for any linoleic or conjugated diene acid present. Diene acids were only evident in the most soluble or (at most) two most soluble glyceride fractions from each product. It was noticed in all cases that these acids were very largely in the conjugated form: thus, for instance, the acids from the most soluble fraction H of the product heated at 300° for 10 hours in a fused silica tube showed $E^{1\%}_{1\,\text{cm.}}$ (at 234 mμ.) 26 (unisomerised) and 34 (after alkali-isomerisation).

Occasionally, in some of the earlier crystallisations of a product, very small proportions of free saturated acid separated out with the oleodistearin and tristearin concentrates; these were calculated as free stearic acid (Table IV).

The deduced increments of tristearin, oleodistearins, stearodioleins, triolein, and free stearic or oleic acid in each glyceride fraction (and therefrom the proportion of each in the six products examined) are shown in Table V. For the purpose of the glyceride constitution the small amounts of linoleic acid, when present, have been included with the oleic acid in this table, which therefore, strictly speaking, shows the relative proportions of stearic and unsaturated (" oleo "-)glycerides of the different types The figures in Table V refer to compositions by weight, since in view of the small difference in molecular weights of stearic and oleic acids it is here unnecessary to consider separately the molecular proportions of the components of the mixtures.

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