370. *The Course of Hydrogenation in Mixtures of Mixed Glycerides.*

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When natural fats consisting largely of mixtures of palmito-di-unsaturated glycerides and tri-unsaturated glycerides (oleolinoleins, etc.), such as cottonseed oil or pig depot fat, are hydrogenated, the first-mentioned group pass into palmito-stearins to a very large degree before any tristearin is produced. In order to ascertain the cause of this apparent selective action, binary mixtures of suitable mixed tri-glycerides of known structure and configuration have been hydrogenated until approximately half of the products consisted of fully-saturated glycerides, the com-position (tristearin content) of the latter being then determined. It has been shown that the composition of the hydrogenated fats is the resultant of a number of factors, notably (i) the relative rates of the step-wise hydrogenation of tri-, di- and mono-unsaturated triglycerides and (ii) the proportion of each of these three types present in the original fat. The present results also show that the tentative hypothesis, previously put forward, that the observed preferential production of β-palmitodi-stearin during hydrogenation of a number of natural fats (including those mentioned above) may be due to relative difficulty of hydrogenation of β-oleoglycerides, is incorrect.

NATURAL fats are mixtures of mixed triglycerides, in which none, one, two or all of the acyl groups present may be unsaturated. Cottonseed oil, for instance, is made up ap-
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proximately of about 25% of tri-unsaturated glycerides (oleolinoleins) and nearly 75% of monopalmito-di-unsaturated glycerides, with very small amounts of dipalmito-glycerides. Having examined olive and cottonseed oils hydrogenated to varying extents, Hilditch and Jones (J., 1932, 805) showed that, after the initial selective conversion of linoleic into mono-ethenoid radicals, the action proceeds in the stages triolein —→ di-oleo-mono-saturated —→ mono-oleo-disaturated —→ trisaturated glycerides. The tri-unsaturated glycerides are attacked more rapidly than di-oleo-glycerides, and the latter somewhat more so than the mono-oleo-compounds. Hilditch and Jones also showed that, in both olive and cottonseed oils, the palmito-glycerides present were converted into the fully-saturated state before any appreciable quantity of tristearin was formed. Subsequently Hilditch and Stainsby (*Biochem. J.*, 1935, **29**, 90) observed similar marked preferential formation of palmito-distearin over tristearin during the progressive hydrogenation of pig depot fat, and also that the product was β-palmitodistearin. This led to the suggestion that the preferential production of fully-saturated (β-) palmito-glycerides might be due to relative ease of hydrogenation of oleic radicals attached to the α-glyceryl hydroxyl groups as compared with those attached in the β-position.

In order to test this hypothesis, a number of mono-oleo-disaturated glycerides have been prepared synthetically, or by separation from appropriate fats, and binary mixtures containing equal amounts of, for example, an oleodistearin and an oleodipalmitin have been hydrogenated half-way to complete saturation. Determination of the tristearin content of the product indicates the extent to which preferential formation of palmito-stearins occurred. Actually it has been found that the result is the same irrespective of whether the oleic group is attached to the α- or the β-glyceryl hydroxyl radical, and that, apart from a relatively slight tendency towards production of somewhat more palmito-stearin than tristearin, hydrogenation proceeds indiscriminately in all the instances studied. The idea that the position of the oleic group in the glyceride molecule affects the ease with which it undergoes hydrogenation was thus proved incorrect. Further attempts were therefore made to ascertain the reason for the marked preferential formation of fully-saturated palmito-glycerides during hydrogenation of the afore-mentioned natural fats. Instead of binary mixtures of equal amounts of two mono-oleo-glycerides, those in which the components were respectively mono- and di-oleo-, mono- and tri-oleo-, or di- and tri-oleo-glycerides were hydrogenated to a point at which the mixture should contain approximately 50% of fully-saturated and 50% of mono-oleo-glycerides. In these cases the originally less unsaturated component (*e.g.*, mono-oleo- in a mixture of mono-oleo-disaturated and di-oleo-monosaturated glycerides) consistently yielded the larger proportion of fully-saturated material, but there was usually 30—40% present of fully-saturated glycerides corresponding to the more unsaturated component. Results duplicating those obtained in the natural fats were, however, obtained when the proportion of the less-unsaturated component was increased to 75% of the binary mixture (the proportions of palmito-unsaturated glycerides in cottonseed oil and in pig fat are of the respective orders of 75% and 80%).

The preferential formation of fully-saturated palmito-glycerides over tristearin during hydrogenation of fats such as cottonseed oil or pig depot fat is therefore the resultant of several factors, the chief of which are the relative rates of step-wise hydrogenation of tri-, di- and mono-unsaturated triglycerides and the proportion of each of these three types present in the original fat. There is some evidence that, apart from these considerations, the presence of palmitic groups in the triglycerides favours in some slight measure hydro-genation of oleic groups; the possibility that chain-length of the saturated radicals in a mixed glyceride may have a subordinate effect on the hydrogenation of unsaturated groups also present remains to receive further investigation.

The method used was to hydrogenate each mixture of glycerides (using nickel–kieselguhr catalyst at 180° in an agitation apparatus) to approximately half-way between the stage of mono-oleo-disaturated glycerides and complete saturation (*i.e.*, to an iodine value of about 15). The products were oxidised with permanganate in acetone (Hilditch and Lea, J., 1927, 3106) in order to isolate the fully-saturated glycerides, which were then fractionally crystallised from ether in order to determine the amount of tristearin, etc., present

(Hilditch and Jones, *J. Soc. Chem. Ind.*, 1934, **53**, 13T). The minimum quantity of each binary mixture requisite for this sequence of operations was 50 g. It was clearly out of the question to prepare the large quantities of mixed glycerides necessary by the methods which have been employed by other investigators for the synthesis of individual mixed glycerides of known configuration. We have made use of the synthesis of α-monoglycerides (Hilditch and Rigg, J., 1935, 1774) whereby products containing about 90% of α-monoglyceride and 10% of αα'-diglyceride are obtained; further esterification of these compounds with a second fatty acid leads to the formation of triglycerides, about 93—95% of which consist of the α-mono-derivative of the first acid in combination with two radicals of the second acid. This order of purity was considered sufficient for the purpose of the present work. In one or two cases, mono-oleo-disaturated glycerides isolated from natural fats, or semi-hydrogenated products from synthesised palmitodiolein or stearo-diolein, were employed. Although simplified methods of synthesis were thus used, the preparation of the requisite materials for hydrogenation occupied a very large proportion of the time devoted to the whole investigation. The materials which finally served as components of the various binary mixtures are summarised below (for further details see Experimental) :—

	Approximate degree of purity, %.
Mono-oleo-disaturated glycerides.	
α-Oleodipalmitin (synthesised)	93
α-Oleodistearin (synthesised)	95
β-Oleodistearin (from *Allanblackia* fat)	96—97
β-Oleodistearin (from *Pentadesma* fat)	85 (15% oleopalmitostearin)
Oleodistearin (iod. val. 29·1, isolated from partly hydrogenated triolein, p. 1773)	91 (9% tristearin)
Di-oleo-monosaturated glycerides.	
α-Palmitodiolein (synthesised)	90—95
α-Stearodiolein (synthesised)	90
Tri-unsaturated glycerides.	
Triolein (synthesised)	100

Semi-hydrogenation of Mixtures of α- *and* β-*Mono-oleodisaturated Glycerides.*—α-Oleodipalmitin was mixed in equal proportions with each of four varieties of oleodistearin, and hydrogenated until the iodine value of the product was about 15, and the content of fully-saturated glycerides was in the region of 50%. The contents of tristearin in the fully-saturated glycerides were as follows, the figures in parentheses indicating the proportion of tristearin which would be expected if hydrogenation of α-oleo-glycerides were completely preferential :—

	% Tristearin in fully-saturated glycerides.
α-*Oleodipalmitin* + *equal weight of*	
α-oleodistearin (synthesised)	34 (50)
oleodistearin (iod. val. 29·1, isolated from partly-hydrogenated triolein, p. 1773)	37 (0)
β-oleodistearin (from *Allanblackia* fat)	69 (0)
β-oleodistearin (from *Pentadesma* fat)	43 (0)

With one exception, the percentage of tristearin is in the region of 40%, irrespective of the configuration of the oleodistearin in the mixtures. Other experiments were carried out with mixtures in which the palmitic derivative was, to a large extent, in the form of oleopalmitostearin. In one instance, a concentrate of oleopalmitostearin was prepared by crystallising pig depot fat from acetone, the material finally obtained containing about 63% of oleopalmitostearin together with 12% of fully-saturated palmitostearins and 25% of palmitodiolein. Semi-hydrogenation of a mixture of equal parts of this with β-oleodistearin (from *Allanblackia* fat) gave a product in which 47% of the fully-saturated glycerides consisted of tristearin. Palmitodiolein, hydrogenated to an iodine value corresponding with that of oleopalmitostearin, was similarly used as a source of the latter; but, as described later, the composition of the material was approximately 53% oleopalmitostearin, 24% palmitodiolein and 23% palmitostearins. Semi-hydrogenation of a mixture of equal parts of this material with β-oleodistearin (from *Allanblackia* fat) also gave a product, the fully-saturated components of which contained 47% of tristearin.

The above figures are in complete opposition to the view that glyceryl β-oleo-derivatives

are less readily hydrogenated than α-oleo-glycerides, and also display no marked evidence for the preferential formation of saturated palmito-glycerides.

Partial Hydrogenation of Triolein, α-Stearodiolein, and α-Palmitodiolein.—Further evidence that α- and β-oleo-glycerides are hydrogenated more or less indiscriminately, and that the hydrogenation in each of the three stages tri-oleo ——> di-oleo ——> mono-oleo ——> saturated glycerides is not wholly consecutive or "selective," was obtained by study of the partial hydrogenation of some individual unsaturated glycerides.

Triolein (synthesised) was hydrogenated to an iodine value of 32, *i.e.*, somewhat above that of oleodistearin (28·6); the composition of the product was found to be 15% tri-stearin, 57% oleodistearin and 28% dioleostearin. When hydrogenated further to iodine value 21, it still contained 5% dioleostearin, with 64% oleodistearin and 31% tristearin. Although, therefore, the amount of oleodistearin is substantial in the later stages of hydro-genation, some of it passes into tristearin concurrently with the completion of hydrogenation of dioleostearin to oleodistearin.

α-Stearodiolein (synthesised), hydrogenated to iodine value 13·5, contained 53% tri-stearin and 47% oleodistearin. The purest fractions of oleodistearin isolated from this product, and also from the above partly-hydrogenated trioleins, were each oxidised with potassium permanganate in acetone; the mono-azelaodistearin isolated from the acidic products of oxidation (Hilditch and Saletore, *J. Soc. Chem. Ind.*, 1933, **52**, 101T), after crystallisation from acetone and from light petroleum, melted finally in each case at 54—55°. β-Azelaodistearin, from the β-oleodistearin of *Allanblackia* fat, melts at 63° (Hilditch and Saletore, *loc. cit.*), whilst the azelaodistearin prepared from our synthesised α-oleo-distearin melted at 50·5°. The melting points (54—55°) of the azelaodistearins obtained from partly-hydrogenated triolein or stearodiolein thus point to a mixture of both α- and β-azelao-derivatives, *i.e.*, α- and β-oleo-groups are hydrogenated with more or less equal facility.

α-Palmitodiolein (synthesised), hydrogenated to an iodine value of 30·7 (oleopalmito-stearin, iod. val. 30·5), was similarly found to contain 23% of fully-saturated glycerides (palmitostearins), from which it follows that 53% of oleopalmitostearin and 24% of un-changed palmitodiolein were also present.

Partial Hydrogenation of Binary Mixtures of Glycerides containing Different Numbers of Unsaturated Acyl Groups.—Binary mixtures of equal quantities of mono-oleo- and di-oleo-, mono-oleo- and tri-oleo-, or di-oleo- and tri-oleo-glycerides were next studied, hydro-genation being, as before, continued until the iodine value of the product (*ca.* 15) indicated a stage midway between mono-oleo-disaturated glyceride and complete saturation. The approximate composition of the fully-saturated glycerides in the various hydrogenated products is given below, the *left-hand column* of figures referring in each case to the saturated product derived from the component of the original mixture which contained the *smaller* number of unsaturated acyl groups :—

	Fully-saturated components of hydrogenated product, %.	
50% of *Mono-oleo-* with 50% of *di-oleo-glycerides.*		
α-Oleodipalmitin and α-palmitodiolein	56 (stearodipalmitin)	44 (palmitodistearin)
α-Oleodipalmitin and α-stearodiolein	63 (stearodipalmitin)	37 (tristearin)
α-Oleodistearin and α-palmitodiolein	62 (tristearin)	38 (palmitodistearin)
Oleopalmitostearin * and α-stearodiolein	77 (palmitodistearin)	23 (tristearin)
50% of *Mono-oleo-glyceride with* 50% of *triolein.*		
α-Oleodipalmitin and triolein	61 (stearodipalmitin)	39 (tristearin)
50% of *Di-oleo-glyceride with* 50% of *triolein.*		
α-Palmitodiolein and triolein	59 (palmitodistearin)	41 (tristearin)

* Hydrogenated palmitodiolein (iod. val. 30·7).

These figures are much more consistent than those for the various mixtures of mono-oleo-glycerides (p. 1769), in that in each case the component which originally possessed a smaller number of unsaturated acyl groups has furnished the greater part of the completely saturated glycerides in the partly-hydrogenated products. We may, indeed, say that, in the main, the more unsaturated component of the mixture is attacked first, and is hydro-genated until both the components reach the same degree of unsaturation, after which hydrogenation of each proceeds simultaneously and indiscriminately. This is, however,

only a partial statement of what occurs, and must be supplemented by the following : hydrogenation of a less unsaturated (*e.g.*, mono-oleo-) component proceeds to some extent whilst the more unsaturated components (*i.e.*, tri- or di-oleo-) are still being reduced to that stage.

That this is the case is shown by separate experiments in which we hydrogenated equimolecular mixtures of (*a*) α-oleodipalmitin and triolein and (*b*) α-palmitodiolein and triolein to iodine values of 25 and 29 respectively (*i.e.*, degrees of unsaturation corresponding approximately with that of mono-oleo-disaturated glycerides alone). The fully-saturated glyceride contents of the products were respectively 17% and 14%, but no tristearin was present in either. This implies that, by the time the average unsaturation of the mixture was reduced to that of mono-oleo-disaturated glycerides, 25—30% of the less saturated components of the original mixture (but none of the triolein) had been transformed into completely saturated glycerides.

Put in other words, all unsaturated components in a mixture of glycerides are attacked concurrently during hydrogenation, but reduction of the more unsaturated components is relatively more rapid; this holds until the unsaturation of the mixture has become uniform, after which there is little difference in the rate of hydrogenation of the remaining unsaturated components. (Some of our data suggest that, to a minor degree, palmito-glycerides may be slightly more readily saturated than tri-C_{18}-glycerides. The possible influence of chain-length in this respect is being further investigated in this laboratory.)

The above conclusions, however, still leave unexplained the extreme degree of apparent selectivity shown in the production of saturated palmito-glycerides during the hydro-genation of natural fats such as cottonseed oil and pig depot fat (cf. p. 1768). Nothing approaching this degree of preferential formation of these glycerides was observed in any of the foregoing results with mixtures of equal quantities of palmito-oleo-glycerides and triolein. The proportion of palmito-oleo-glycerides in these two fats is, however, much greater than 50%, namely, about 75% and 80% respectively. We have proved that this effect is merely the result of the relative concentration of the palmito-oleo-glycerides, superimposed on the other influences which have been discussed above; for, on altering the proportions of the components, in mixtures of α-oleodipalmitin or α-palmitodiolein with triolein, we obtained the results shown below, which resemble exactly the behaviour which has been observed in the hydrogenation of cottonseed oil or pig depot fat :

		Hydrogenated product.			
			Fully-saturated	Tristearin, %,	
Mixture and proportion of glycerides.		Iod. val.	glycerides, %.	in fully saturated glycerides.	in whole fat.
50% α-Oleodipalmitin + 50% triolein		15·8	52	39	20
75% ,, + 25% ,, ...		16·5	44	Trace	Trace
50% α-Palmitodiolein + 50% triolein		14·5	53	41	22
75% ,, + 25% ,, ...		17·4	39	5	2

EXPERIMENTAL.

Preparation of Mixed Triglycerides.—The fatty acids required were prepared as follows :

Oleic acid was obtained from the mixed acids of olive oil, the lead salts of which were crystallised from alcohol (cf. Twitchell, *J. Ind. Eng. Chem.*, 1921, **13**, 806) to remove palmitic acid as far as possible. In some of the earlier preparations the acids from the soluble lead salts were converted into lithium salts, and the latter crystallised from 80% alcohol (Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320T), the separated lithium oleate being thus purified to a large extent from accompanying linoleic acid. In later preparations the separation of linoleic acid was omitted, the time occupied and the concurrent loss of oleic acid both appearing unnecessarily wasteful, since it is well established that linoleic glycerides pass almost completely into oleic (or *iso*oleic) glycerides (under the conditions of hydrogenation used in this work) before any hydrogenation of the latter sets in. In all cases, the purified oleic acid was converted into methyl esters and fractionally distilled in a vacuum, when any palmitic ester remaining was eliminated in the portions of lower boiling point. The main fractions of ester, on hydrolysis, furnished the oleic acid used in the glyceride syntheses. When the lithium salt purification

had been employed, the oleic acid thus finally obtained had iodine value 89·2—90·6; when this was omitted, the iodine value of the oleic acid was 98—99 (*i.e.*, a mixture of about 90% oleic and 10% linoleic acid).

Attempts to utilise good specimens of commercial (distilled) oleic acid as the starting material were failures, the purification required being much more than in the case of the acids prepared from olive oil and the yield of purified oleic acid much less. The processes employed in the manufacture of commercial oleic acid (" oleine ") involve the formation of a good deal of isomeric oleic acids and also, to some extent, hydroxylated acids. For scientific investigation it is recommended that suitable natural fats such as olive or groundnut oil are the best source of pure oleic acid, in spite of the somewhat lengthy procedure involved in separation of the latter from palmitic and other accompanying acids.

Palmitic acid was obtained from stocks of crude methyl palmitate accumulated in the laboratory in the course of ester-fractionation analyses of different fats. The crude palmitic acid was subjected to lead salt–alcohol separation to remove small proportions of oleic acid, and the recovered " solid " acids re-methylated and fractionally distilled in a vacuum to eliminate minor amounts of myristate and stearate. Hydrolysis of the main fractions of ester gave pure palmitic acid.

Stearic acid was prepared by completely hydrogenating mixed methyl oleate–linoleate esters (a stock of which had been similarly accumulated from fractionation analyses of various vegetable fats), hydrolysing the product, and crystallising the acid obtained from 80% alcohol (10 c.c. alcohol per g. acid); pure stearic acid was then readily obtained.

Preparation of α-Monoglycerides.—The fatty acid was heated at 160° for 4 hours, and subsequently at 180° for 2 hours, with an equal weight of glycerol and of phenol in presence of 0·1% of camphor-β-sulphonic acid, and the monoglycerides isolated, according to the method of Hilditch and Rigg (*loc. cit.*). Quantities of 50—80 g. of acid were used at a time, the yield of monoglyceride being approximately equal to the weight of acid taken.

By this means the following monoglycerides were obtained : mono-olein, sap. equiv. 353·5—354, iod. val. 73—74 (calc. : sap. equiv. 356, iod. val. 71·6), containing 95—96% α-mono-olein; monopalmitin, sap. equiv. 325—326 (calc., 330), containing 92—93% α-monopalmitin; monostearin, sap. equiv. 353—354 (calc., 358), containing 91—92% α-monostearin.

Conversion of α-Mono- into Mixed Tri-glycerides.—The monoglyceride was heated (without solvent) with slightly more than the amount of fatty acid necessary to convert it into triglyceride, in presence of 0·3% of camphor-β-sulphonic acid, at 160—180° in a vacuum for about 6 hours, At first, the amount of fatty acid employed was 15—20% more than the theoretical weight required, but it was observed that, to a certain extent, interchange of acyl groups took place (*v. infra*), and that this was lessened by using a smaller excess of acid, namely, 5%. This smaller excess was found sufficient to ensure complete conversion into triglycerides. The following products were obtained :

α-Oleodipalmitin, from α-mono-olein and palmitic acid, sap. equiv. 279—280, iod. val. 34·5—36·0 (calc. : sap. equiv. 277·3, iod. val. 30·5). From the analytical figures, the product contains about 93% of α-oleodipalmitin. It was employed without further purification.

α-Oleodistearin, from α-mono-olein and stearic acid. When 15% excess of stearic acid was used, the product contained appreciable amounts of tristearin. It was therefore crystallised several times from ether (10 c.c. per g.) at 0°; nearly 15% of tristearin (m. p. 70·5—71°) then separated. The ether-soluble material, after crystallisation from acetone at 0°, melted at 45—47°. The amount of tristearin produced was much less when only 5% excess of stearic acid was used in the esterification. The α-oleodistearin (*ca.* 95% pure) used in the hydrogenation experiments was purified as described from tristearin by removing the latter by crystallisation from ether.

α-Palmitodiolein, from α-monopalmitin and oleic acid, sap. equiv. 285, iod. val. 58·4 (calc. : sap. equiv. 286, iod. val. 59·2). The small excess of unesterified acids recovered from the preparation had an iodine value (83) lower than that of oleic acid (90), indicating as usual a small amount of interchange of acyl groups. The product, however, from the analytical data, contained at least 90%, and possibly as much as 95%, of palmitodiolein.

α-Stearodiolein, from α-monostearin and oleic acid. Here, again, using 15% excess of oleic acid, some interchange of acyl groups occurred and some tristearin and oleodistearin were observed in the final product. These were removed by crystallisation of the latter from acetone at 0°. The most soluble portion (sap. equiv. 296, iod. val. 66·5) was used in the hydrogenation experiments; it was now free from oleodistearin and tristearin, but evidently contained about 10% of triolein.

Triolein (sap. equiv. 295, iod. val. 87·0; calc. : sap. equiv. 295, iod. val. 86·2) was prepared by direct esterification, at 160° in a vacuum, of glycerol with excess of oleic acid in presence of 0·2% of camphor-β-sulphonic acid.

Preparation of β-Oleodistearin from Natural Sources.—The synthetical preparation of β-oleodistearin in quantity is difficult and, since it has been shown (Hilditch and Saletore, *J. Soc. Chem. Ind.*, 1931, **50**, 468T; 1933, **52**, 101T) to occur in quantity in the seed-fats of *Allanblackia Stuhlmannii* and *Pentadesma butyracea*, it was obtained from these.

β-Oleodistearin was prepared from *Allanblackia* fat by repeated crystallisation of the latter from acetone and, subsequently, from ether. The material finally obtained (60% of the weight of the original seed-fat) had sap. equiv. 294, iod. val. 30 (calc. : sap. equiv. 296, iod. val. 28·6).

β-Oleodistearin from *Pentadesma* fat was less pure, because this fat also contains a certain proportion of oleopalmitostearin. By repeated crystallisation a specimen of crude β-oleodistearin (sap. equiv. 291·3, iod. val. 29·9) was finally obtained. The component acids present in this (determined by ester-fractionation) were palmitic 5, stearic 61, oleic 34% (mol.), so that its glycerides consisted approximately of 85% β-oleodistearin and 15% oleopalmitostearin.

A product containing about 63% of oleopalmitostearin was prepared by crystallisation of pig depot fat (1500 g.) from acetone, a sparingly soluble fraction (sap. equiv. 283, iod. val. 41·5) being finally obtained. The component acids of this material, determined by ester-fractionation, were palmitic 38·2, stearic 23·9, oleic 29·4, and linoleic 8·5% (mol.), whilst oxidation with permanganate in acetone showed that it contained 12% of fully-saturated glycerides [the acids in which were palmitic 48, and stearic 52% (mol.)]. These figures correspond with the following component glycerides in the whole fat : oleopalmitostearin 63%, palmitodiolein 25%, palmitostearins 12%.

Partial Hydrogenation of Triolein, Stearodiolein, and Palmitodiolein.—*Triolein hydrogenated to iodine value* 32·2 (cf. p. 1770). The hydrogenated product (99 g.), crystallised from 500 c.c. of acetone at 0°, deposited 75 g. of solid (iod. val. 25·8) and left in solution 24 g. (iod. val. 52). The solid fraction (75 g.) was systematically crystallised three times from ether at room temperature and finally gave 16 g. (iod. val. 3·8) of a least soluble fraction and 59 g. (iod. val. 31·1) of ether-soluble glycerides. From the iodine values of these fractions it follows that the composition of the hydrogenated product, iod. val. 32·2, was approximately 15% tristearin, 57% oleodistearin, and 28% dioleostearin.

Triolein hydrogenated to iodine value 21·2 (cf. p. 1770). Systematic crystallisation from ether gave a least soluble fraction (27 g., iod. val. 3·5) and ether-soluble fractions amounting in all to 50 g. (iod. val. 29·1). The composition of the hydrogenated material of iodine value 21·2 was therefore approximately 31% tristearin, 64% oleodistearin, and 5% dioleostearin.

α-Stearodiolein hydrogenated to iodine value 13·5 (cf. p. 1770). Crystallisation from ether yielded 25 g. of sparingly soluble material (iod. val. 1·7) and 36 g. of more soluble products (iod. val. 25·9), leading to an estimated composition of 53% tristearin and 47% oleodistearin.

The ether-soluble products isolated from the above three products of partial hydrogenation were recrystallised from ether and then possessed the following melting points : (*a*) from triolein hydrogenated to iod. val. 32·2, 51—53°, (*b*) from triolein hydrogenated to iod. val. 21·2, 49—51°, (*c*) from partly-hydrogenated stearodiolein (iod. val. 13·5), 48—50°. These melting points, however, are of little significance as a guide to whether α-oleodistearin (m. p. 45—47°) or β-oleodistearin (m. p. 43—44°) is present, because during hydrogenation both oleo- and "*iso*oleo-" (mainly elaido-)glycerides are produced. The presence of unsaturation in the α- or β-positions of the glycerides in the hydrogenated products must therefore be examined by reference to the corresponding azelao-glycerides produced when the materials are oxidised by potassium permanganate in acetone (cf. p. 1770). Each product was oxidised by this method, and the greater part of the mono-azelao-disaturated glycerides recovered by separation of their sodium or potassium salts from solution in ether as described by Hilditch and Saletore (*loc. cit.*). The melting points of the azelao-glycerides thus obtained, after successive crystallisations from acetone or light petroleum, are given in the table which follows :

	Azelao-glycerides, g.	M. p. after successive crystallisations.				
		1st acetone.	2nd acetone.	1st petrol.	2nd petrol.	3rd petrol.
Triolein hydrogenated to iod. val. 32·2 (5·1 g.)	2·2	47—48°	48—49°	51—52°	52—54°	54°
Triolein hydrogenated to iod. val. 21·2 (6·7 g.)	2·4	50—51	50—51	50—52	52—53	54
α-Stearodiolein hydrogenated to iod. val. 13·5 (5·3 g.)	1·5	47—49	48—49	52—52·5	53—54	55

α-*Palmitodiolein hydrogenated to iodine value* 30·7 (p. 1770). The product (22·9 g.) was oxidised with potassium permanganate in acetone, and yielded 5·3 g. of fully-saturated glycerides, the proportion of which was thus 23%. It follows that the hydrogenated product was composed of about 53% oleopalmitostearin, 24% unchanged palmitodiolein, and 23% palmitostearins.

Hydrogenation of Mixtures of Mixed Triglycerides.—The relevant data for the hydrogenations referred to in the course of this paper are tabulated below :

Mixture.		Hydrogenated product.		
			Fully-saturated glyceride present.	
	Iod. val.		% (mol.).	Tristearin content, % (mol.).
50% α-Oleodistearin + 50% α-oleodipalmitin	16·0		51	34
50% Oleodistearin [1] + 50% ,,	14·0		51	37
50% β-Oleodistearin (*Allanblackia*) + 50% oleodipalmitin	15·5		54	69
50% ,, (*Pentadesma*) + 50% oleodipalmitin	13·7		59	43
50% ,, (*Allanblackia*) + 50% oleopalmitostearin [2]	15·⸱		47	47
50% ,, (*Allanblackia*) + 50% oleopalmitostearin [3]	13·6		58	47
50% α-Palmitodiolein + 50% α-oleodipalmitin	15·3		55	*
50% α-Stearodiolein + 50% ,,	13·9		55	37
50% α-Oleodistearin + 50% α-palmitodiolein	16·1		51	62
50% α-Stearodiolein + 50% oleopalmitostearin [3]	15·9		51	23
50% Triolein + 50% α-oleodipalmitin	25·0		17	Nil
50% ,, + 50% ,,	15·8		52	39
25% ,, + 75% ,,	16·5		44	Nil
50% ,, + 50% α-palmitodiolein	29·0		14	Nil
50% ,, + 50% ,,	14·5		53	41
25% ,, + 75% ,,	17·4		39	5

* 44% Palmitodistearin and 56% dipalmitostearin.

[1] Partly-hydrogenated triolein (ether-soluble fraction, iod. val. 29·1, p. 1773).

[2] Isolated from pig depot fat (63% oleopalmitostearin, 25% palmitodiolein, 12% palmitostearins).

[3] Semi-hydrogenated α-palmitodiolein (53% oleopalmitostearin, 24% palmitodiolein, 23% palmitostearins).

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